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Academy Lecture

Aging and fossilization of wood and its components*

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Summary. Aging of wood begins with the cutting of a tree. The subsequent changes of the wood substance proceed very slowly and depend on environmental conditions. In a hot, dry desert climate wooden objects and cellulose textiles are preserved for several millenia, whereas their degradation is accelerated by conditions which favor the attack of microorganisms.

Two conditions under which aging processes take place can be distinguished: a) aerobic conditions as prevailing in wooden buildings, sculptures etc.; b) anaerobic conditions valid for wooden items buried in the ground or submerged in water such as foundation pillars, ships etc. Submersion and underground embedding initiate the very slow process of fossilization in which the cell wall substance is transformed into highly condensed compounds (coalification) or is substituted by minerals (silicification).

The various wood components are subjected to different kinds of degradation and conversion. The polysaccharides disappear with aging and seem to be more sensitive than lignin. Although more resistant, the lignin is converted chemically and its structure differs increasingly from its original state. Even extractives may survive millions of years.

Introduction

The processes of aging and fossilization are generally considered to be exceptions in the natural cycle. The bulk of organic matter usually disappears in the course of time as solid matter is transformed back into the compounds from which it had originally been synthesized, namely carbon dioxide, water and ammonia. In this cyclic process organic compounds are synthesized, combined and organized to form organisms, to initiate and maintain life processes. With its death an organism has accomplished its

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function and now serves as life source for microorganisms which decompose the organic matter. Microorganisms have become highly specialized for the attack on specific kinds of compounds. Under favorable conditions the various compounds forming the wood structure resist degradation in different ways, and this resistance in turn affects the processes of aging and fossilization.

The remains of these processes bear witness to former cultures and vegetations on earth. With each discovery further advances into the history of mankind and into that of living beings on earth are made. Thus we are able to move back in time in the range of hundreds, thousands and even millions of years.

It can be seen from the geological time scale (Fig. 1) that residues or conversion products of wood can be expected – at the earliest – in the carboniferous era, deriving from fern trees. Within a time span of about 300 million years the wood substance was converted into coal.

At the opposite end of this scale we find Man who has been populating this earth for less than 1 million years and has since been using wood as a material for requisites and buildings.

Relics of worked wood from the dawn of the human era are very rare. The oldest findings from the paleolithic period are a wooden spear head found near Clacton on

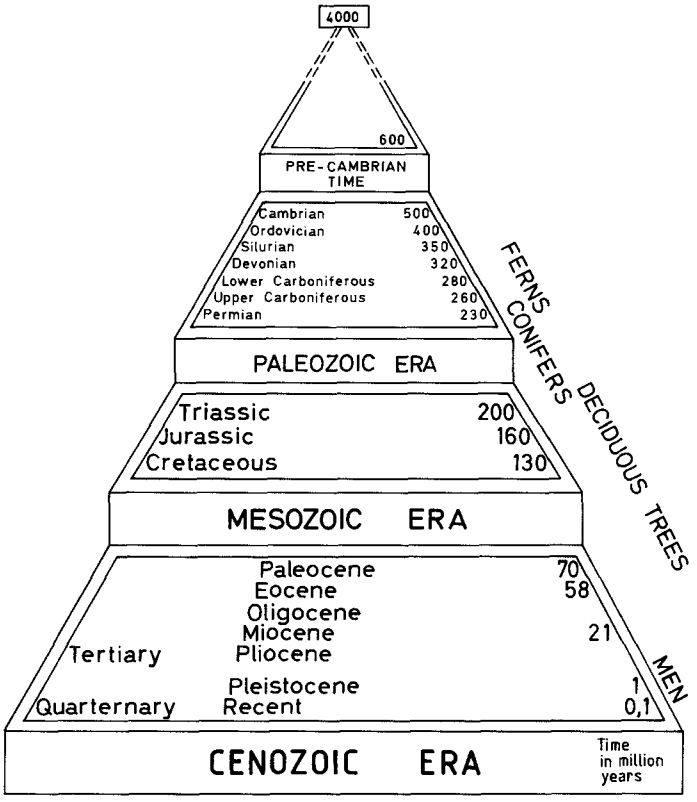


Fig. 1. Geological time scale

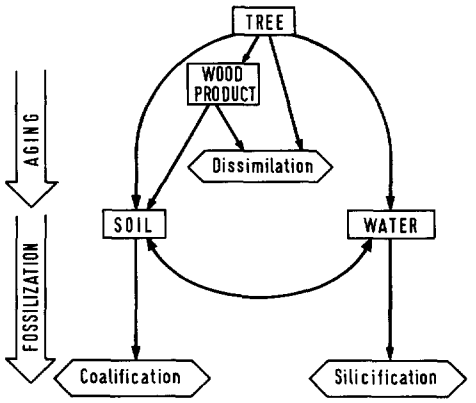


Fig. 2. Scheme of aging and fossilization

Sea in Southern England which is approximately 290,000 years old and a spear of yew wood found near Verden on the river Aller in West-Germany, which is said to be 150,000 years old (Sandermann 1967).

Looking at the entire time scale within which we can expect to find residues of wood or conversion products the range of 300 million years is the maximum. Within this time span aging occupies only a very short period of several thousand years whereas fossilization takes millions to hundreds of millions of years (Fig. 2).

Fossilization can be subdivided into the process of coalification during which the cell wall substance is transformed into highly condensed compounds and into the process of silicification during which the cell wall substance is substituted by minerals.

Historical and archaeological wood

Objects stored under atmospheric conditions

Studies on wood aged under aerobic conditions are not very numerous but range from the wood of freshly cut trees to samples from Egyptian pharaonic times.

Whichever way aging may be defined, alterations of the wood substance begin shortly after a tree has been cut. Reduction in the water content and the access of oxygen on the one hand and the residual activity of enzymes present in wood plus the settlement of microorganisms on the other cause chemical variations, beginning, in the first instance, with the composition of the minor constituents. Reactions which take place during the seasoning of pulp wood have been studied in the sixties by Assarsson and Croon. They found a reduction in fats, waxes and resins and an increase in fatty acids during the first 3 to 4 months. Later the amounts of fatty acids as well as of higher alcohols, resin acids and hydrocarbons decrease by oxidative and enzymatic reactions (Assarsson, Croon 1963; Assarsson et al. 1963; Croon 1965). An accelerating influence of temperature on the rate and the kind of reactions was shown by Donetzhuber and Swan (1965).

Tracing the contents of the main extractives in broad-leaved trees and conifers (*Cercidiphyllum japonicum* Sieb. et Zucc. and *Cryptomeria japonica* D. Don) for 150 to 180 days after cutting Ohashi et al. (1988) found that sugars were metabolized mainly in the outer sapwood, whereas phenols and their glycosides were synthesized in the inner sapwood. The process is comparable to the heartwood formation in intermediate wood.

The comparison of milled wood lignin from fresh pine wood and pine wood logs seasoned for 15 years showed an increase in the degree of oxidation both in sapwood and heartwood during the aging process (Fengel, Stöcklhuber 1985). Fischer and Schmidt (1983) found oxidative changes of beechwood lignin even after few days' storage.

In sprucewood and pinewood from roof constructions 290 and 365 years old a certain decrease in polyoses content was found while the cellulose percentage did not differ from that of new dry wood (Fengel 1989). The content of acid insoluble lignin was nearly the same as in recent wood although a slight tendency towards a lower value is indicated particularly when also considering the about 20 to 30% higher organic-solvent extract. According to these results there were no variations in the micro-structure of the cell walls which could be attributed to aging.

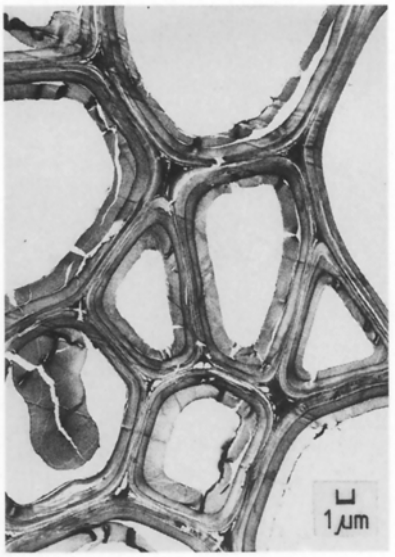
A reduction of 2 to 3% in the cellulose and lignin contents of a teak wood (*Tectona grandis*) from a Buddhist temple in India 1,800 years old was found by Narayanamurti et al. (1958). The ethanol-benzene extract amounted to 14 times the value of recent teak wood.

Samples of *Pinus pinea, Juniperus phoenica* and *Acacia nilotica* from Egypt stored under dry and dark conditions for over 4,000 years were sensitive to mechanical treatment as found by Borgin et al. (1975a). Although the cell walls were well preserved and did not show any degradation some parts exhibited fissures, cracks and loss of adhesion mainly caused by the electron microscopic preparation. Similar observations were made by Nilsson and Daniel (1990) who studied some hardwood samples (*Acacia* sp., *Tamarix* spec.) from Egypt and Jordan with ages between 2,000 and 4,000 years and Douglas fir samples (*Pseudotsuga* spec.), 750 and 1,130 years old, from New Mexico. Despite of a dry storage some of the samples were affected by soft-rot fungi.

The percentages of acid insoluble lignin of the samples of Borgin et al. (1975b) were lower compared to corresponding recent wood species. Infrared spectroscopic studies indicated oxidative changes of the lignin structure which are probably responsible for a higher acid solubility of these samples.

Recently wood samples taken from the inner panelling of an Egyptian tomb chamber were studied (Fengel 1989). The shape of the planks, however, suggested that they might originally have belonged to a boat. Parts of this boat were reconstructed at the museum (State Collection of Egyptian Arts, Munich). The age of this wood is estimated to be more than 5,000 years, which means to be the oldest wood sample ever found in Egypt.

The wood of the planks was from *Acacia nilotica* and *Tamarix* spec.; the planks were in different states of preservation. The wood structure of one of the well-preserved planks shows some mechanically caused fissures and cracks as described by Borgin et al. (1975a). Holes in the intercellulars and a loosening of the compound middle lamella and the S 1 layer are also visible (Fig. 3).



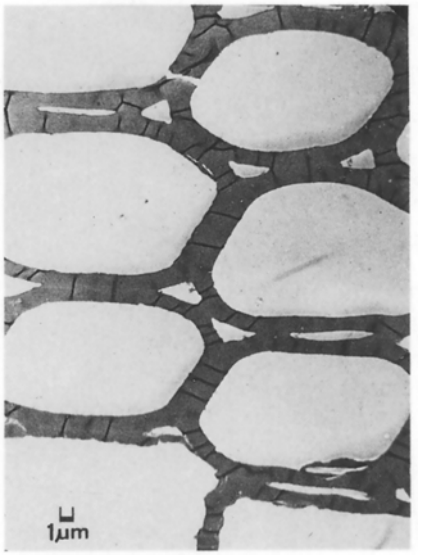


Fig. 3 Fig. 4

Fig. 3. Archaeological wood (*Acacia nilotica*) from an Egyptian tomb chamber, about 5,000 years old. TEM micrograph

Fig. 4. Archaeological wood (*Juniperus drupacea*) from Chattussa, about 3,500 years old. TEM micrograph

The chemical analysis of this wood revealed that it contains 55.2% cellulose. The amount of polyoses is drastically reduced with only 5.2% remaining. The calculated lignin content was 39.6%. The ultimate analysis indicates a relatively high amount of protein (7%) which obviously derives from microorganisms. After subtracting the CHO values of the polysaccharides and the CHON values of protein from the CHON values of the total wood the residual values correspond in their H/C ratio to lignin (1.2) but the O/C ratio is higher. This means that the lignin of the wood has been altered chemically and has, in particular, been oxidized during aging. The wall substance has become dark and conversion progresses from the lumen side towards the middle lamella. A conversion can also be observed in the compound middle lamella.

Another kind of conversion was found to have taken place in residues of wood from Chattuscha, the capital of the Hittite Kingdom in Asia Minor (1900–1200 BC). The sample (*Juniperus drupacea*) was found non-buried and in dry condition. It is very brittle and brown and looks brown-rotted. In the electron microscope the wood structure is well preserved and no deterioration of the cell walls can be seen (Grosser et al. 1974; Fig. 4). Also, details such as bordered pits are well preserved.

The contrast within the cell walls, however, is reduced and it is hard to differentiate between the wall layers. The protein content, usually indicative of the presence of microorganisms, is low (1.8%), and indeed no microorganisms were found in the electron microscope. The carbohydrates content is very low, namely 5.1%, of which

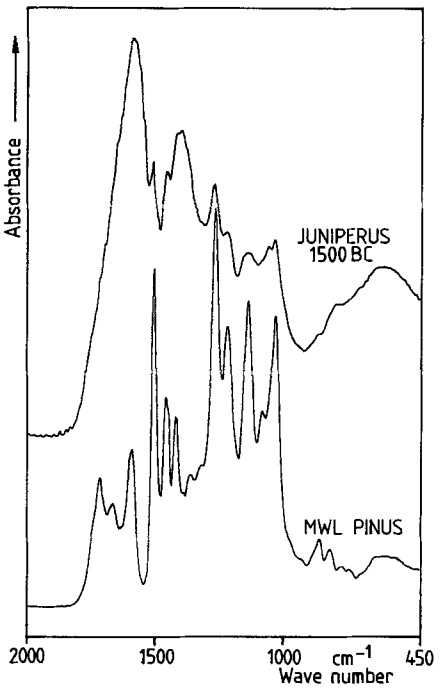


Fig. 5. FT-IR spectra of milled wood lignin from pine (MWL Pinus) and of archaeological juniper from Chattussa (Juniperus 1,500 BC)

4.7% represent cellulose. The elemental composition of the substance remaining after subtraction of carbohydrates and proteins corresponds in its H/C and O/C ratios to lignin. The infrared spectrum, however, is quite different from the spectra of softwood lignins. (Fig. 5). The maximum absorption at 1,590 cm^{-1} in combination with the band at 1,270 cm^{-1} can be attributed to condensed guaiacyl units. Compared to softwood lignin the vibration peaks of syringyl units (1,220 and 1,320 cm^{-1}) and the phenolic OH groups (1,365 cm^{-1}) are missing. Thus in this case the polysaccharides have been largely degraded and lignin has been condensed without oxidation taking place (Fengel 1989).

The only component of the plant cell wall which occurs in nature by itself and not necessarily in conjunction with others is cellulose. Several plant fibres consist of rather pure cellulose. One of these fibres is flax which has been used for textiles for several millenia. Linen textures have been preserved in the hot desert climate of Egypt for over 4,000 years.

In a study of ancient Egyptian linen more than 50 samples covering a period of about 2,000 years were investigated (Stoll, Fengel 1988). These textures varied greatly and ranged from extremely fine and delicate fabrics to rough cloths.

The state of preservation of the samples differed greatly and seemed to be independent of their age. The degree of preservation of the textures was reflected in the structure of the fibres (Figs. 6 and 7).

The degree of polymerization ranged from 1,500 to 200; both extremes were obtained from samples dating from roughly the same time, 5th–6th dynasty. This result indicates that there was no direct correlation between the variation of DP with

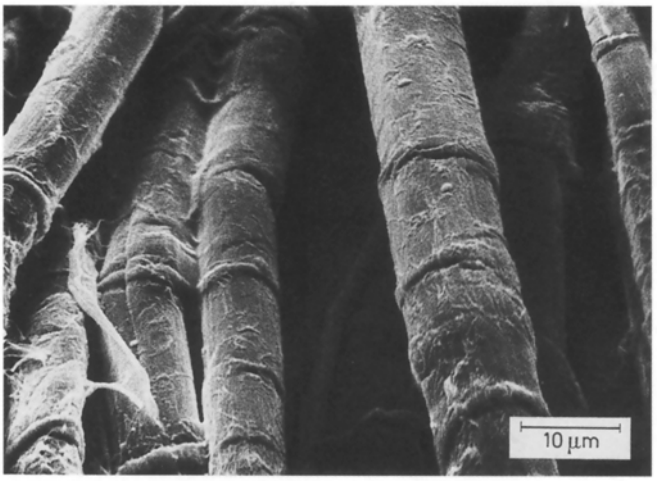


Fig. 6. Linen fibres in good condition from Egyptian cloth, 23rd dynasty, about 2,800 years old. SEM micrograph

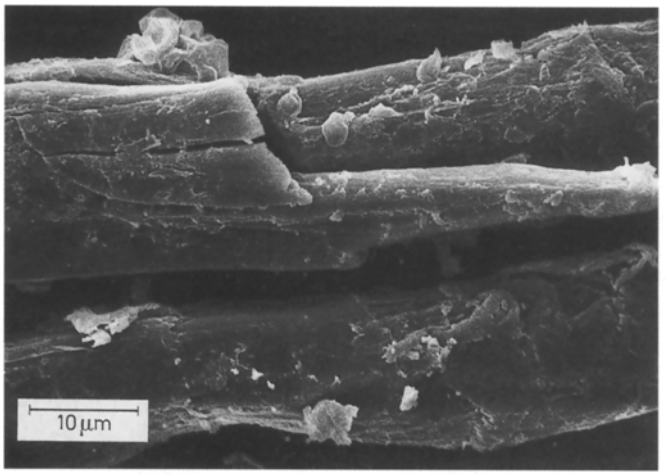


Fig. 7. Linen fibres in bad condition from Egyptian cloth, 6th dynasty, about 4,200 years old. SEM micrograph

either time or age. But there was a correlation between the change of DP with time versus age. But an equation for the DP was developed by which mechanisms with different degradation velocities were proved to exist (Fig. 8).

The main variation during the aging of cellulose is the decrease in chain length but there are also various other influences beginning with the method according to which the fibres had been isolated and bleached and ending with how they were stored after excavation.

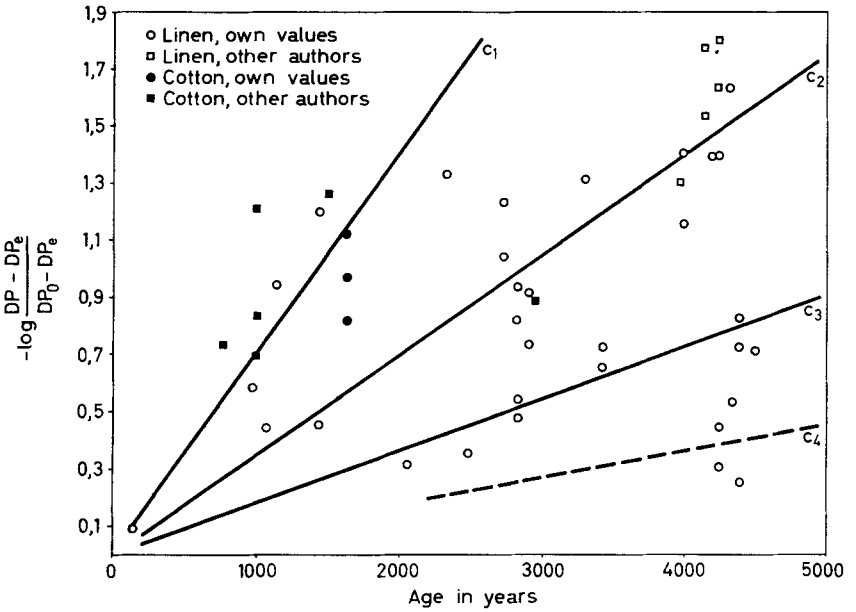


Fig. 8. Dependence of the DP on the age of Egyptian linen. Straight lines represent degradation mechanisms with different reaction constants ($c_1 - c_4$)

Objects stored in water and soil

Either by intent or by chance wooden objects have often been stored or lodged in water and soil. To this day logs are still being stored under water to prevent fungal attack, poles were once used for foundations in muddy ground, wooden ships have sunk in rivers and oceans. Samples of these objects are interesting specimens for the investigation of the variation in structure and composition under wet conditions.

The study of the extractives of softwood and hardwood logs after 12 months' storage under water revealed a hydrolysis of the glycerides but no change in the resin content (Assarsson, Akerlund 1967). In sprucewood which was stored under water for 17 years a slight decrease in the content of extractives and acid insoluble lignin was found (Fengel, Wegener 1988). Although there was no measureable change in content and composition of the polysaccharides an attack of bacteria was assumed since the permeability of the wood was increased due to the perforation of the pit membranes (Bues 1986).

Objects which were predestined for submersion in water so to speak were the wooden ships of former times. Many of them were found, salvaged and conserved, such as the Swedish warship Wasa, sunk in Stockholm harbour, the Hanse-Cog of Bremen, the Mary Rose, flagship of Henry VIII, found near Portsmouth, the Ronson ship, excavated in Manhattan, the over 700 years old Chinese junk raised off the south western Korean coast and the Roman riverships of Mayence and Cologne.

In most cases the wood used was oakwood but other wood species such as pine, ash, elm and poplar were also used. The longterm action of water changes the physical

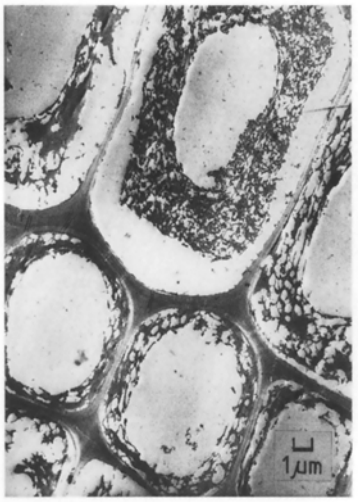


Fig. 9. Ancient pinewood (*Pinus massoniana*) from a submerged Chinese junk, 700 years old. TEM micrograph

and chemical properties of wood substance. A swelling of the secondary walls causes a loosening of the fibrillar texture. This process initiates the accessibility of the cell wall components particularly of the carbohydrates which are slowly hydrolyzed (Hoffmann, Parameswaran 1982; Hoffmann, Jones 1990). The degradation begins at the lumenside and proceeds towards the compound middle lamella. As the water substitutes the carbohydrates the lignin sceleton remains in a highly swollen condition (Fig. 9).

According to this substitution process the maximum water content of the wood increases and the density decreases. In the case of the pinewood from the Chinese junk the water content had risen to over 450% while density had been reduced to values of 0.19–0.25 g/cm^3 (Kim 1987). Water contents of more than 1,000% and densities between 0.08 and 0.09 g/cm^3 were found in highly deteriorated alder and poplar wood by Barbour (1984) and Hoffmann and Jones (1990).

Various parts of the excavated ships show different degrees of degradation. If various species of timber had been used for interior fittings, oakwood was generally the best preserved one (Squirrell, Clarke 1987). The samples of beams and planks are relatively well preserved in the core whereas the outer parts have deteriorated to a greater or lesser extent (Hoffmann, Jones 1990; Hoffmann et al. 1986; Kim 1987).

The chemical composition of the inner part of the planks of the Chinese junk is only slightly changed compared to the recent wood of Chinese red pine whereas the content of polysaccharides is strongly reduced in the outer part (Kim 1987, 1990). The percentage of soluble substances increases in the same direction. This is also true for oakwood as shown by Hoffmann and Jones (1990).

In most cases there is a sharp border line between the more and the less degraded part. The degradation of waterlogged wood depends on the conditions, and a change of environment may e.g. initiate the settlement of microorganisms. Thus Ruetze and Peek (1987) found a secondary fungal invasion in the oakwood coping of an excavated well.

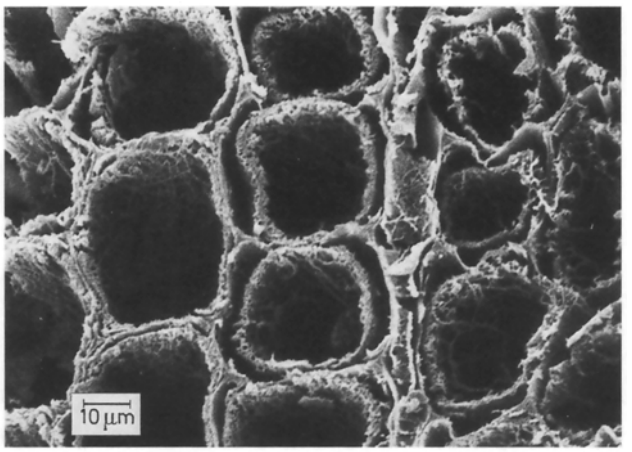


Fig. 10. Waterlogged pinewood (*Pinus* spec.), 1st century AD. SEM micrograph

A secondary invasion was obviously also the reason for the dense settlement by fungal hyphae on a pinewood sample stored under water since the 1st century AD (Fig. 10; Tomellini, Fengel 1987).

A special position is occupied by the Ronson ship as it was used as a landfill repository in the harbour of Manhattan (Jagels et al. 1988). It was not only stored in wet ground but also filled with trash and all the iron of the ship had disintegrated. Thus in several parts the iron content of the wood was very high with a maximum of 9.5%. The degradation and conversion of the wood components was about the same as for waterlogged objects.

Formerly oakwood was not only used in ship-building, but also for houses, foundations, bulwarks, streets etc. Therefore it was mainly oakwood which was found in many excavations. Also many oaktrees were submerged in swamps and were thus preserved for millenia.

The oldest and also relatively well preserved samples in this series are 8,500 and 8,100 years old and were found in Großenzersdorf, Austria, and in Gabcikovo-Nagymaros, Czechoslovakia (Bednar, Fengel 1974; Solár et al. 1987). Another sample, 25,000 years old, found off the coast of Louisiana, USA, was severely degraded (Hedges et al. 1985). The structure of the Großenzersdorf sample cannot be macroscopically differentiated from that of recent oakwood except for the color. At higher magnification deformations of the cell wall and fissures in the compound middle lamella and in the S1 layer are visible (Fig. 11).

This deformation is due to the drying of the log which was buried in wet gravel before its excavation. Furthermore the lumenside of many cells is covered with a layer of dark substance. These layers vary in thickness and many of them also fill the chambers of bordered pits.

In both oakwood samples which are over 8,000 years old the content of lignin as well as of cellulose is increased compared to recent oakwood. The increase in cellulose is related to the reduced amount of polyoses. A certain degradation of cellulose is obviously restricted to the less ordered regions as the degree of polymerization and the degree of crystallinity was somewhat higher than in recent oakwood (Bednar,

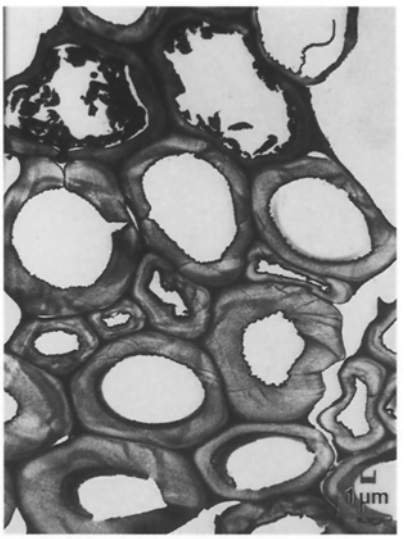


Fig. 11. Ancient oakwood (*Quercus* spec.) from Großenzersdorf, Austria, about 8,500 years old. TEM micrograph

Fengel 1974; Solár et al. 1987). According to Solár et al. (1987) mainly xylan is degraded. The increase in phenolic OH and α- and β-carbonyl groups indicates a polymerization of lignin.

A comparison of these results with a study of a 2,500 years old oakwood pole by Wazny (1976) makes the influence of environment evident. Two distinct zones of degradation were identified. In the badly degraded outer zone the cellulose content was drastically reduced and amounted to only 2.5%; also the lignin content was lower than that in recent wood. In the less degraded inner zone the cellulose content was reduced by only 7%, and the lignin content was slightly higher as compared to recent oakwood. Surprisingly the percentage of polyoses remained relatively high and there were no differences between the two zones.

Further studies concerning buried ancient and subfossil oakwood with ages between 300 and 5,000 years confirm this kind of degradation although with varying intensity (Greczynski, Surmanski 1962; Dzbenski 1970; Kommert, Wiehaus 1970; Scheiber, Wagenführ 1976; Pecina, Kommert 1985; Reinprecht et al. 1988). Despite great variations in the data for cell wall components of ancient and subfossil oakwood from various sites a general trend in the correlation with the age of wood can be deduced. Fig. 12 shows a graph of all values for various oakwood samples including those for waterlogged wood compiled from existing literature.

The content of acid insoluble lignin or non-hydrolyzable residue increases continuously with age whereas the content of polyoses decreases at the same time. The relative percentage of cellulose increases slightly reaching a maximum between 1,000 and 10,000 years; subsequently it decreases rapidly. According to Nakao et al. (1989) the crystallinity of softwood cellulose increases during the first 500 years and then remains approximately constant for about 2,000 years whereas the crystallinity of hardwood cellulose decreases continuously from the very beginning of the aging process. Apart from a 25,000 years old oak sample Hedges et al. (1985) compared ancient alder and spruce wood of the same age (2,500 years old) and from the same

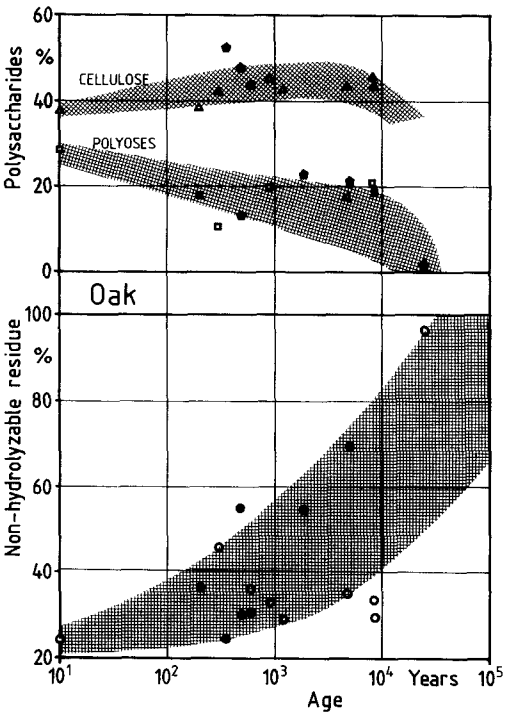
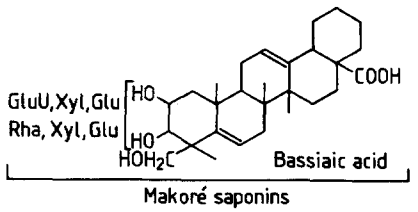


Fig. 12. Percentages of cellulose, polyoses and non-hydrolyzable residue versus age of the oakwood samples as compiled from literature

site (bank of the Hoko river, Washington State, USA). In contrast to both hardwoods the sprucewood showed only minimal changes. The carbohydrate content was slightly reduced and the lignin composition as determined by CuO oxidation was the same as for lignin from fresh sprucewood. The carbohydrates of alder and of the much older oak were strongly reduced and part of the syringyl lignin was degraded.

Alkaline nitrobenzene oxidation of buried ash (*Fraxinus* spec., 12,000 years old) and chestnut (*Castanea* spec., 6,000 years old) resulted in a lower syringaldehyde yield compared to recent wood. The yield of vanillin was only slightly reduced so that the ratio of syringaldehyde to vanillin was lower in the ancient wood (Tiyama et al. 1988). The yield of vanillin from the softwood torreya (*Torreya* spec., 6,000 years old) was approximately the same as that from recent wood. These findings coincide with the IR spectroscopic studies of Borgin et al. (1975) who obtained identical spectra for lignin of recent pine and of pine wood 2,000 years old.

From these results it can be concluded that in the aging process guaiacyl lignin is more stable than syringyl lignin. This may be the reason for the higher resistance of softwood fibres and of hardwood vessels compared to hardwood fibres (Fujii et al. 1988). By contrast, in a 6,600 years old log of *Bischofia polycarpa* from the river-bed of the Yangtze river Pan et al. (1990) found the same guaiacyl-syringyl ratio as in recent wood of the same species. The methoxyl content, however, was lower, while both the content of phenolic and aliphatic hydroxyl groups as well as the degree of condensation were higher. Therefore the authors concluded that during aging a slow O-demethylation and an in-situ acid-catalyzed hydrolysis of α-aryl bonds and condensation of aromatic rings take place.



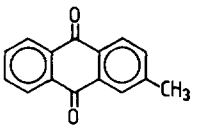


Fig. 13. Formulas of saponins and of tectoquinone

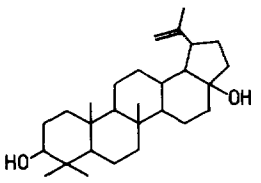


Fig. 14. Formula of betulin

Apart from the main components of the wood substance the minor components may also play more or less important role during aging of wood. The extractives of several wood species are known to act as insecticides and fungicides. They are responsible for the durability of wooden objects under unfavourable climatic conditions. Thus relatively well preserved wood carvings of Maya temples were detected in the termite contaminated jungles of Central America (Sandermann, Funke 1970). Relatively well preserved wood samples of Pterocarpus, Shorea and Tectona with ages between 500 and 2,000 years were also found in India (Narayanamurty et al. 1958, 1961; Chowdhury et al. 1967). Tests with termites and fungi using the ancient wood samples and their isolated extractives proved that the compounds had retained their effectiveness (Sandermann et al. 1958; Narayanamurty et al. 1961). Among the effective compounds are the saponines of zapote wood (*Manilkara zaota* L.) from Central America and tectoquinone of the Indian teak wood (*Tectona grandis*) (Fig. 13).

According to Narayanamurty et al. (1958) the extractives in teakwood survive although parts of the cell wall substance are degraded. The durability of components of wood extractives was also shown by the analysis of ancient and archaeological tars. Tar in barrels from a Russian shipwreck of 1790 had nearly the same composition as freshly prepared pine tar and compounds such as mono- and sesquiterpenoids and diterpenoid resin acids were identified (Reunanen et al. 1989).

A tar from the early Iron Age (approx. 700 BC) excavated in Austria contained betulin, a triterpenoid deriving from birch bark (Sauter et al. 1987) (Fig. 14).

During aging the mineral content of wood increases. Amount and composition depend on the kind and composition of the environment. Thus the variation of values

can be very great. Very high ash contents between 15 and 19% have been found in 3,000 years old wood residues from caves of worship (Kommert, Wienhaus 1970). The incorporated minerals such as silica, calcite or hematite may crystallize within the cell lumina. Krutil and Kokon (1982) found a relation between the colour of subfossil oakwood and its iron content.

Pellets of metallic copper were detected in a pine wood sample (*Pinus halepensis*) from a Phoenician copper mine in Cyprus (Parameswaran, Borgin 1980). The additional impregnation of the total wood tissue with copper preserved it for more than 2,500 years.

A strongly degraded pinewood sample with a cellulose content of 6.6%, about 32,000 years old, contained pyrite and alkaline earth silicates within the cell walls only (Staccioli, Tamburini 1988).

Fossilized wood

Silicified wood and the process of silicification

The deposition of silica within the cell lumina may be the first stage of silicification of wood. Although silicified woods are the most frequently occurring fossils there are also samples impregnated with other minerals. Buurman (1970) distinguishes between silicification, phosphatization, carbonization and accumulation of sulphides and iron oxides (Table 1).

According to Buurman (1970) silicification of wood is mainly a terrestrial process although it may occur in marine environment. Carbonization can occur under both marine and terrestrial conditions. Phosphatized wood is known to come from marine sediments exclusively but it could also form under very special terrestrial circumstances. Impregnation with iron oxides and hydroxides will occur in terrestrial environment while accumulation of sulphides is influenced by pH conditions exclusively. Furuno et al. (1986b) proposed a model of the process of silification of wood tissue in four distinct phases (Fig. 15).

Table 1. Mineralization of wood

Kind of mineralization	Deposited minerals	Formula
Silicification	quartz, tridymite, chalcedony	SiO_2
Phosphatization	phosphorite, francolite	$Ca_5(PO_4)CO_3(OH \cdot F)$
Carbonization	calcite	$CaCO_3$
	dolomite	$CaCO_3 \cdot MgCO_3$
Accumulation of sulphides	pyrite, marcasite	FeS_2
	sphalerite	ZnS
Accumulation of iron oxides	siderite	$FeCO_3$
	hematite	Fe_2O_3
	goethite, lepidocrocite	$FeO \cdot OH$

In the first phase the lumina are filled with silica, in the second one deposition of silica in the lumina continues and degradation of the cell wall substance begins; during the third phase the cell wall substance is partially replaced by silica; finally most or all of the cell wall is replaced by silica and in some cases the intercellular substance disappears.

In many cases anatomical details are well preserved and ground sections were used for identification of genus and species of the specimens (e.g. Grosser et al. 1974; Selmeier 1990; Hoshiron, Suzuki 1987; Furuno et al. 1986a).

During the deposition of silica its crystalline form changes and various kind of crystals such as opal, chalcedony, tridymite, crystobalite were identified in silicified woods (Mitra, Sen 1956; Buurman 1970; Scurfield et al. 1974; Furuno et al. 1986b). Recrystallization often destroys structural details of the cell wall. The structure of the cell wall is well preserved in wood-opals (Fig. 16) but disappears with increasing amounts of quartz (Fig. 17) (Buurman 1970). By tridymite silicification the cellulose is obviously replaced as the optical orientation of silica corresponds to that of cellulose in fresh wood.

Silicified woods contain mostly organic carbon even if only in percentages of less than 0.01% (Furuno et al. 1986b). Furuno et al. (1986a, 1988) also found well preserved contents of the resinous material in resin canals and parenchyma cells. Carboxylic, hydroxylic and alkyl groups remained.

Samples in the process of coalification

Regarding the process of coalification its beginnings have been mentioned earlier when discussing archaeological wood samples. The group of the subfossil wood with ages of several tens of thousands to several hundreds of thousands of years have to be dated between these and the real fossil woods. There are several wood findings which are well preserved particularly when they had been buried in frozen sediments or enclosed in glaciers for a long time. The pressure of glacier and/or hundreds of

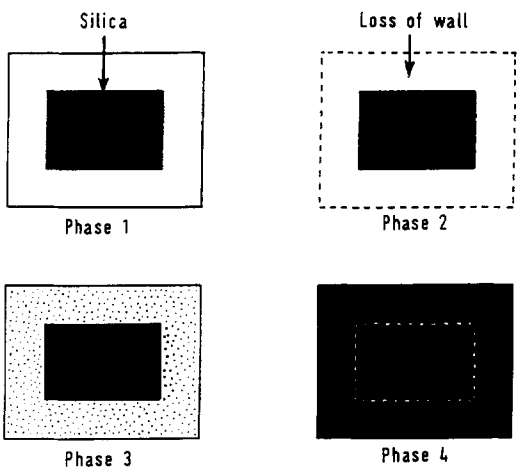


Fig. 15. Model for the silicification of wood cells (Furuno et al. 1986b)

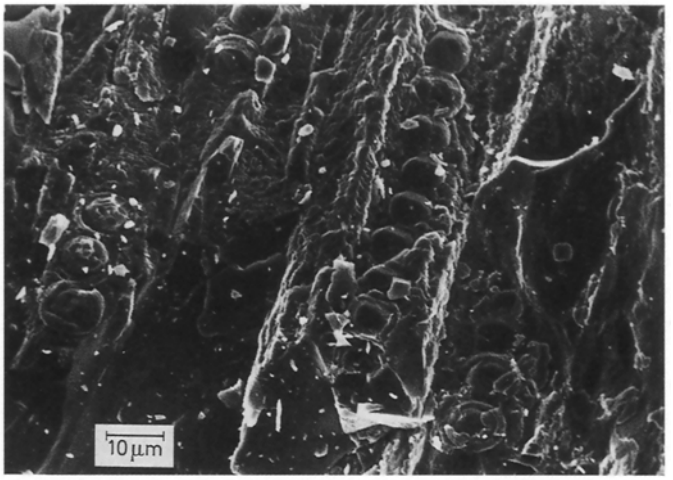


Fig. 16. Silicified wood, cell walls with pit rows. Sample collected near Moab, Utah, USA. SEM micrograph

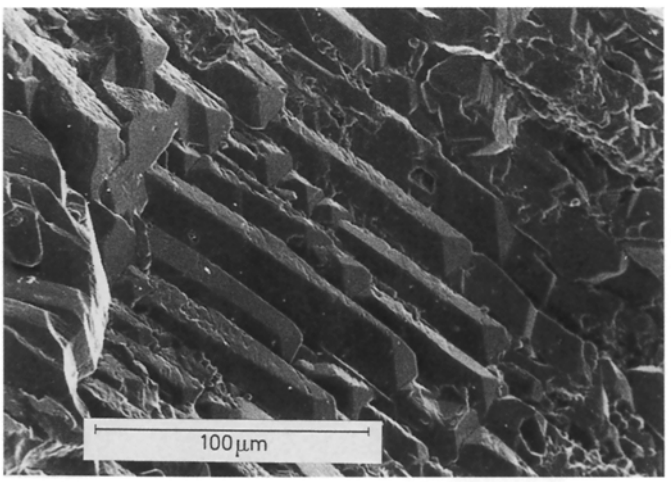


Fig. 17. Silicified wood, quartz crystals. Sample collected near Moab, Utah, USA. SEM micrograph

meters of sediments have deformed round logs into logs whose cross sections look like oval lenses.

In a subfossil spruce log (*Picea abies*) with an age of about 100,000 years the deterioration of the wood was in an advanced stage although there were various degrees of degradation across the transverse plane (Fengel 1971). The content of polysaccharides was strongly reduced compared to recent wood. The cellulose content was only 12%, the polyoses content 4.5%. The percentage of non-hydrolyzable

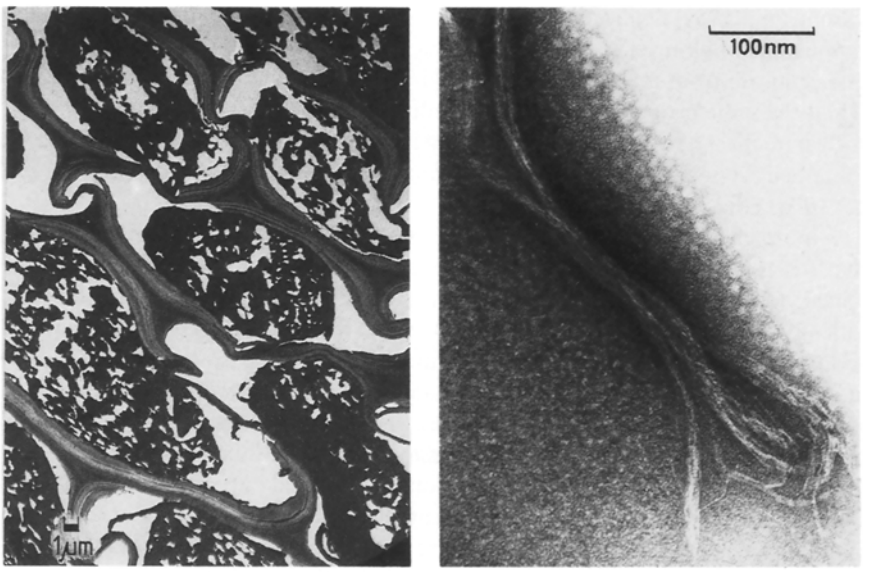


Fig. 18. Subfossil spruce, found in Zeifen, Bavaria, about 100,000 years old. TEM micrograph

Fig. 19. Cellulose fibres isolated from a fossil redwood (*Taxodioxylon gypsaceum*), 20 million years old. TEM micrograph

residue had increased to 75%. Similar data were obtained with a 30,000 years old sample of Acacia by Narayanamurty et al. (1960).

The transformation of the cell wall substance is visible in the accumulation of dark material within the lumina (Fig. 18). Along with the formation of dark substance the cell walls are reduced in thickness. The cell walls of the latewood are particularly resistant; they are often well preserved whereas the adjacent earlywood cell walls are strongly degraded.

The process of conversion of the cell wall substance proceeds very slowly. If we compare wood samples tens or hundreds of thousands of years old with those several millions of years old only slight differences or none at all can be observed. In 1985 a large area with buried forests from the miocene to the paleocene was detected in the arctic part of Canada about 1,000 km north of the Arctic Cirle. There were several places with many horizons of fossil forests one stacked upon the other, at one site 20 forests were found in this way (Obst et al. 1989).

The wood logs which were completely buried were well preserved in the frozen ground. The good state of preservation of the wood samples with ages between 20 and 65 million years can also been seen from the content of polysaccharides: the amount of glucose in the hydrolysates ranges from 37 to 10% (Obst et al. 1989). Also, in other sites, mostly lignite or ore mines in Canada and Europe, fossil wood samples of comparable ages were found with cellulose contents of over 10% (Brasch, Jones 1959; Crook et al. 1965; Wayman et al. 1971; Fengel et al. 1973).

Brasch et al. (1959) determined the DP of cellulose from a Cedrus species (*Cedrus phenhallowii*) 20 million years old. The DP_n was 800, the DP_w 1,600. A paper test-sheet made of cellulose from a 30 million years old selery top pine (*Phyllocladus asplenii-folius*) had the same properties as that of cellulose from recent softwood (Crook et al. 1965). Despite the aggressive treatment during isolation well preserved cellulose fibrils were obtained from a fossil redwood (*Taxodioxylon gypsaceum*) 20 million years old (Fengel 1974) (Fig. 19).

Even in much older fern samples fibrillar cell wall structures have been observed (Purelis 1962). However, whether the cellulose itself is preserved in this case cannot be decided. In fossil woods older than 100 million years the polysaccharide content is drastically reduced. Thus Brasch and Joes (1959) found only 1.1% carbohydrates in wood, 140 million years old while we determined the carbohydrate content of a 180 million years old Protopinaceae to be less than 0.1% (Fengel 1976). The presence of glucose, mannose and xylose units was proved. The disapperance of polysaccharides is combined with an increase in dark conversion material in the cell lumina.

The specimen in Fig. 20 derives from a strongly degraded part of a 20 million years old redwood with a residual cellulose content of about 15%. Only residues of the compound middle lamella and the S1 layer are present, and even the substance of the intercellular spaces is partially converted. In this area the tissue structure has mostly disappeared. In some other parts the cell walls are better preserved.

STEM studies show that there are two zones of conversion with different electron absorption within the cell walls (Obst et al. 1989).

Surprisingly in the oldest wood investigated to date the wall structure with the various layers can be recognized although the polysaccharides have been almost completely degraded (Fengel 1976) (Fig. 21).

The IR spectrum (Fig. 22) indicates the predominant aromatic character of the Protopinaceae substance (maxima at 1,600 and 1,500 cm^{-1}; guaiacyl units 1,225 cm^{-1}, aryl ketones: 1,650 cm^{-1}). There are furthermore vibrations of carbonyl groups (1,700, 1,715, cm^{-1}) (Fengel 1989). The increase in C=O vibrations as a consequence of oxidation is also described by other authors (Crook et al. 1965; Wayman et al. 1971).

Further studies deal with the methoxyl content. The series of samples studied by Obst et al. (1989) shows methoxyl contents between 14 and 9.6%, the lowest value belonging to the oldest sample from the paleocene. Using solid state ^{13}C-NMR spectroscopy Hatcher (1988; Hatcher et al. 1982) sees the conversion of lignin (1) in the loss of methoxyl carbons from the guaiacyl units with replacement by hydroxyls and increased condensation, (2) in the loss of hydroxyls or aryl ethers with replacement by hydrogen, and (3) in the loss of alkyl groups with continued replacement by hydrogen.

A sample of coniferous wood which had been buried in an oil shale deposit for 50 million years contained lignin which was obviously changed only to a small extent. Alkaline degradation resulted in a similar relative ratio of degradation products as known for spruce lignin (Habermehl, Hundrieser 1983).

Obst et al. (1989) analyzed the extractives of two fossil wood samples. The content of organic solubles was lower than that of recent softwoods. In the extracts saturated fatty acids, C-16, -18, -22, -24 as well as deterpenoid acids such as isopimaric, abietic, dehydroabietic and neoabietic acid were identified. The persistance of

Fig. 20

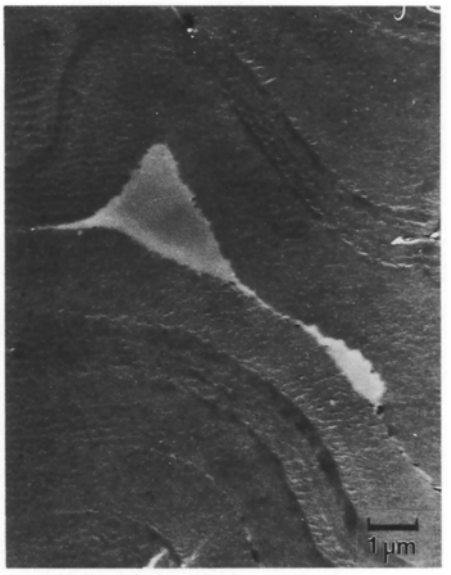


Fig. 21

Fig. 20. Fossil redwood (*Taxodioxylon gypsaceum*) excavated in Wackersdorf, Bavaria, 20 million years old. TEM micrograph

Fig. 21. Fossil softwood (Protopinacea), excavated near Schnaittach, Bavaria, 180 million years old (Jurassic). TEM micrograph

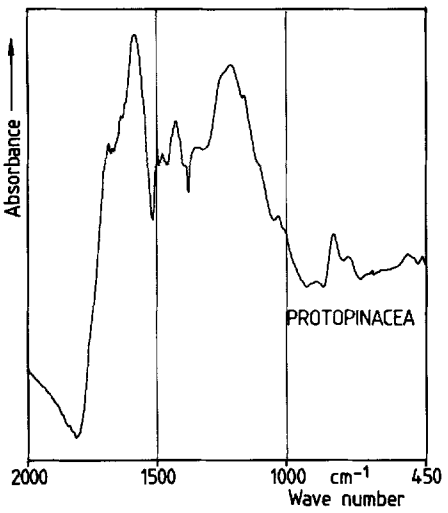


Fig. 22. FT-IR spectrum of the Protopinacea, 180 million years old (Jurassic)

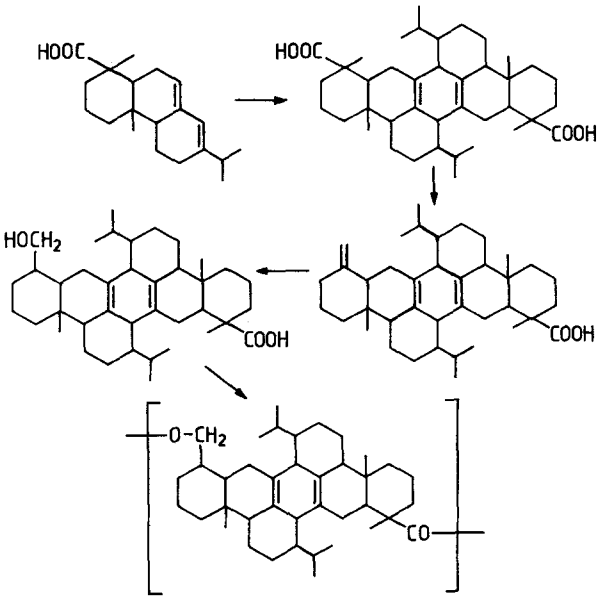


Fig. 23. Formation of condensed abietic-acid structures

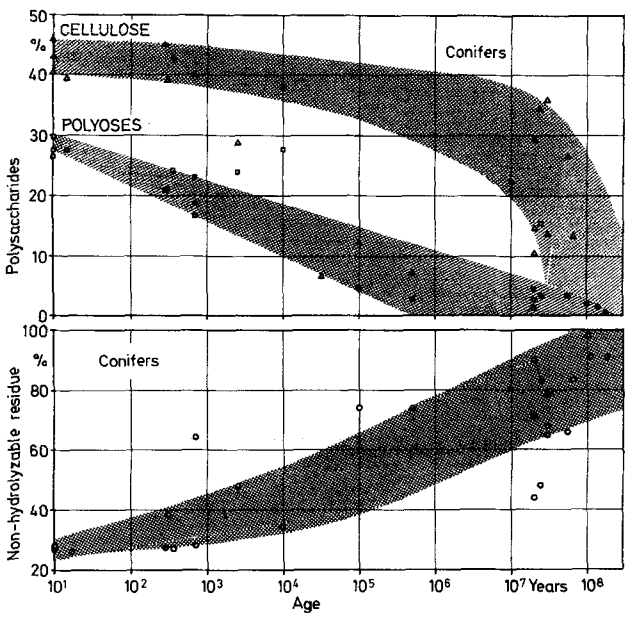


Fig. 24. Percentages of cellulose, polyoses and non-hydrolyzable residue versus age of coniferous wood samples as compiled from literature

extractives was also shown by Ekman and Fagernäs (1983; Fagernäs, Ekman 1985). They detected wax and resin components in the organic solvent extracts of peat such as C-12 to C-32 alkanes, aliphatic alcohols and acids as well as sterols and triterpenoids.

Highly polymeric aliphathic compounds deriving from plant cuticles have been found in plant residues from a permian sediment (280–240 million years old) (Nip et al. 1986). Pyrolysates consisted of straight-chain alkanes, alk-1-enes and α-ω-alkadienes ranging from C-6 to C-29. Kotra and Hatcher (1988), however, attribute the aliphatic biopolymers more to an algal origin.

Another material deriving from tree exudates is amber. Amber is the conversion product of the terpenoid components of coniferous resins. It can be described as a mixture of oxidized and polymerized resin acids and resin alcohols (Langenheim 1969; Beck 1972). Its chemical composition varies with geographic origin. The formation of condensed structures as found in amber starting with abietic acid according to Rottländer (Beck 1972) is shown in Fig. 23.

Conclusions

Provided there is no microbial influence wood is changed very slowly in its chemical composition, the process beginning with the cutting of the tree. The conversion of the wood components is strongly influenced by environmental conditions. A complete absence of microorganisms during the aging and fossilization of wood may be an exception if it is possible at all. In general the conversion and degradation mechanisms of the wood substance seem to be the same in soil and water, while the rate of degradation may vary.

The percentages of polysaccharides decrease with the age of wood samples. Despite large variations in data reported in literature a specific tendency for the degradation of polyoses and for that of cellulose can be demonstrated (Fig. 24). The polyoses are continuously degraded as acidic groups splitt off and cause an in-situ acid hydrolysis. The cellulose resists hydrolysis for a long time because of its crystalline order system. Degeneration observed in samples with ages up to 1 million years progresses only slowly and is followed by a rapid drop after 10 million years.

With the decrease in polysaccharides the percentage of the remaining residue, whose bulk derives from lignin, increases (Fig. 24). The changes taking place in the lignin molecules are very complex: Oxidation, demethylation, loss of hydroxyl groups and condensation are interdependent reactions which lead to more and more condensed structures and a progressive loss in lignin character with the passage of time.

The most resistant wood components seem to be those parts of the extractive which are found more or less unchanged even in silicified samples.

Regarding the graphs (Fig. 24) another phenomenon can be seen: There are two blanks, one between ten and 300 years and another between thousand and ten million years. For these periods only few samples or none were studied. Samples from the first period, in particular, should be interesting as to reactions taking place at the beginning of the aging process, all the more so as samples should be available whose past can still be traced.

Several steps in the processes which take place during the aging and fossilization of wood have been studied in excavated and otherwise conserved samples. Many questions, however, still remain. Therefore this field of research will be of great interest also in the future.

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