CHAPTER 9. ANATOMICAL, PHYSICAL AND CHEMICAL DETERIORATION OF WOODY MATERIALS IN ARTIFACTS

9.1. Introduction: What is deterioration? Figs.9.1 a-d

We often say that a material that looks deteriorated and fragile is old. The changes we observe have happened because of the intensity of manufacturing processes, usage, environment, and biological activity, and in most cases a combination of them—not just age. It can happen in a day or in years depending on the type and intensity of the damaging activity. Deterioration of wood is not caused by time alone.

The causes of deterioration of woody materials are many. Beside the alteration due to plant cell death, the plant materials may be altered through cultural methods of preparation, environmental history, usage, and even conservation treatments.

Deterioration may have occurred before the use of the material. Bast fibers used for textiles may have been retted in stagnate ponds full of bacteria and fungi that may have already deteriorate some of the fibers used in artifact materials.

What we consider deterioration may be just natural, inherent, characteristics. An example is the brown colored spots on a natural cotton textile. These are commonly, just the remnants of the cotton boll shell to which the cotton fibers are still attached, that were not removed during cotton ginning. You can even see them on cotton Q-tips. They are inherent to the textile thus not a conservation concern. Raw linen commonly has light brown spots which are colored fungal tangles that have grown adhered on the flax plant and can no longer grow on the textile.

Brown streaks in wood may not be stains but simply the response of a tree against fungal attack. The tree produces an anti-fungal polyphenolic compound in cells to compartmentalize them, preventing further growth of the fungus.

During use of objects deteriorating influences may occur. For example spruce root baskets were used for boiling food in water over a fire. The basket in the museum is dry and the delicate spongy roots have shrunk and are brittle from heat damaged and are easily fractured. Just handling it, easily causes some fractures. Knowing that it is spruce root alerts the conservator to these physical problems.

During wet burial, archaeological wood material, dependent on the environment and time, will have some physical changes. The wood may separate into layers. This occurs where the thin walled early wood and thick walled late wood are adjacent. Thus it is due to its anatomy and wet environment. In removing a waterlogged wood, it is of utmost importance to realize that this material is in equilibrium with its burial environment and when excavated it is placed in a whole new set of environmental parameters that may enhance deterioration. Usually it is stored wet.

Exfoliation, separation, of wood layers, can also be caused on dry wood by mechanical pounding causing separation again on growth rings. An example is seen commonly in train wooden ties. These separations are due to inherent weaknesses but caused by external impacts.
Good deterioration? Weathering of wood surfaces is caused by natural weathering cycles of light, water, and fungi. Sun light deteriorates the brown cell lignin. Rain washes it off leaving just the cellulose walls of the cells. The presence of the fungal biofilm glues together the weathered cellulose shells of wood fibers leaving a silver grey surface. This cellulose film reflects the light and prevents further environmental damage. It stops, or at least slows down the natural cycling. Beneath it the wood has retained its normal brown lignin color and cell structure.

Dry bark or branch materials used for basketry may be tightly pressed in the weaving process. Just cleaning with water may swell these materials and they lose their pressed state- they have no elastic memory and cannot return to their original pressed form. On some species, an unaltered branch bark has a surface waterproofing layer of wax which can be easily removed by surfactants, soapy water, polar chemicals and just physical rubbing. These are deteriorating treatments. The knowledge of the structure, chemical nature, and deterioration of material of artifacts is essential information required to determine logical conservation stabilization.

There are many deteriorating processes of wood. Figs 9.1a-d, are examples of normal and deteriorated spruce wood and root tissue.

Fig.9.1a shows a photomicrograph of normal undeteriorated 2nd xylem-the wood- of spruce. Fig.9.1b shows water logged spruce wood deteriorated by soft rot fungal infestation. The swelling of the cell walls has been caused by being waterlogged and the degradation of the central inner part of the cell walls has been removed by fungal activity. It is an example of both biodeterioration and environmental deterioration. Fig.9.1c shows spruce wood from the Franklin arctic expedition, deteriorated by the extreme environment. It was exposed for years in the fluctuation of extreme temperatures and low humidity of the arctic environment causing the fracturing of the cell walls and loss of tissue integrity. The cell walls have fractured along the direction of the natural coil of the cellulose microfibrils in the cell walls giving it the curled look. Cell chemicals have been removed. The middle lamella joining the cells together into a tissue has been removed by water leaching and or bacterial hydrolysis or both. It is probably the result of a combination of several deterioration processes.
Fig.9.1a - Cross section of normal spruce wood (2nd xylem), but slightly dehydrated by histological preparation. It shows a growth ring with compact thick walled late cells and large thin walled early wood. PhotoML Florian

Fig.9.1b - Cross section of waterlogged spruce wood infested with soft rot fungi. It restricts its activity to the S2 layer (see Fig. 9.4) of the cell wall. PhotoML Florian

Fig.9.1c - Scanning electron microscopic image of a fragment of spruce wood from the Franklin arctic expedition, 1845, showing physical and chemical deterioration due to the extremes in an environment. PhotoML Florian

Fig.9.1d spruce root Tlingit basket (Alaska State Museum 2008-18-1) showing heat damage to the rim from usage. With kind permission from Alaska State Museum.

Fig. 9.1d shows deterioration in a Tlingit basket made solely of spruce root. Usage has caused the deterioration. Woven spruce root baskets were used for heating water for cooking. The root tissue was used because it is very adsorptive and swells with water to seal the surface and make it waterproof. On continuous usage the heat from the open fire has damaged the spruce root warps and wefts at the rim causing them, when dry, to become extremely brittle and thus fracture easily at the top edge of a basket.
9.2. Deterioration caused by wood anatomy inherent weakness

9.2.1 Drying effects Figs. 9.2a-A and B, Fig.9.2b

Wood refers to 2nd xylem heartwood, the structural component of a tree. It was dead tissue when harvested. Its pits have been closed and resin is present that both make it water and biodeterioration resistant.

Normal anatomical structure of wood may have inherent weaknesses. For example, as a log of wood dries it commonly splits along the radial surface. This is due to the anatomy of the wood. On drying, the thick radial walls of 2nd xylem cells shrink causing a decrease in the circumference of the wood log. The xylem tissue has ray parenchyma bands, shown in Fig. 9.2a, that run in the log radially from the outer surface to the center of the tree trunk. As the xylem dries, the walls shrinks tangentially it pulls away and fractures the thin walled ray parenchyma bands, causing radial cracks. This is an inherent weakness of wood due to anatomy. Commercial kiln dried wood is a slow drying process that prevents this splitting.

The cellular structure of wood is complex thus the shrinkage and swelling is also complex. Inherent swelling and shrinking occurs differently depending on the anatomy of the cell walls on the exposed surface. A general ratio for the differences of shrinkage is, 10-tangential: 5- radially: 0.1-1 longitudinally. Because of these shrinkage differences, a cut of a piece of wood according to its surface grain, tangential, radial, or longitudinal surface, warping on drying, may occur.

The grain of wood is the result of the growth rings shown in Fig. 9.2a, In Fig.9.2a- B, the surface is tangential – expose outer surface- and shows several growth rings, in Fig.9.2a-A, is a cut radially through the center of the wood log, showing no growth rings just the radial surface of the ray parenchyma bands., This is the choice cut for wood panel paintings because there is no stress causing warping or splitting of the wood on drying.
Fig. 9.2a, A-radial and B- tangential illustrates the grain of the wood according to their cut location on the log. Wiki public domain

In Fig.9.2a, board A, shows the grain on the radial surface of a middle radial cut showing the radial surface of the ray parenchyma bands. The central line represents the very center of the heartwood where there may be some crushed remnants of primary xylem and pith cells. Board B, shows many growth rings cut through giving the grain, on the outer tangential cut surface. The grain is the result of growth rings, some have thick walled, and some thin walled cells.
Wood warping is a change in flatness of cut wood due to shrinkage because of differential drying of the exposed cells. True radial cuts do not experience warping but tangential cuts near the surface of the log show dramatic warping.

Fig. 9.2b shows the results of warping due to the anatomy of exposed cells on the surfaces. Bow, occurs when one surface shrinks more longitudinally than the other does. Crook, occurs when one edge shrinks more longitudinally than the other edge. Kink, is due to a growth anomaly, probably due to growth response to physical movement of the position of the tree. Cup, is warp across the width of the surface face of a piece of wood. It occurs when one face shrinks more in width than the opposite face. The end becomes cup shaped. Twist, is also due to anatomy, some trees have normal spiral growth tree trunks.

9.2.2 Anatomical inherent weakness Fig.9.3

Anatomical variations, that influence drying dimensional changes, vary greatly with wood species. There are many variations, such as: the wood fibers (xylem tracheids) length; width and size of the lumen; the presence and size of vessels in hardwoods; and wood rays amounts; height; width; contents, etc. An example of inherent weakness is the anatomy of the hardwood black ash tree vessels that give the basket makers an advantage in preparing black ash splits. In the anatomy of all hardwoods there are different sizes, density, and positions of the vessels. Vessels transport water throughout the sapwood. In black ash (Fig.9.3) wood, there is a concentration of very large vessel along the growth ring. Pounding of this wood on the tangential surface causes fracturing of these vessels and the wood separates at the growth rings forming what basket makers call splits. The splits are then easily separated. These are thin sheets of one or a few growth rings. In making black ash splits for basketry a mallet or some type of heavy tool is used.
Fig.9.3 photomicrograph of the cross section of black ash wood showing the large vessels along a growth ring. photomflorian

Fig.9.3 shows the concentration of large vessels along the growth ring. These easily fracture under pounding allowing tangential splitting of the wood at growth rings into splits for weaving split ash baskets.

Another example of anatomy inherent weakness is reaction wood. Reaction wood are wood growth pattern changes that develop when a tree has bent by some accident and are not vertical or branches are under pressure by their weigh. The tree responds to maintain a balance by forming special tissue called reaction wood. Both softwood coniferous gymnosperms and hardwoods dicotyledonous trees and branches produce reaction wood but use it in different ways. In dicots branches the reaction wood is produced on its upper side and is called tension wood. In conifers it is on the lower side of the branch and is called compression wood.

Hardwood tension wood forms on the upper side of the branch and it contains a higher content of cellulose than normal wood. High cellulose content is especially strong in tension and can prevent the branch from bending downward. The cells have distorted shapes and gelatinous lumens. Coniferous compression wood forms on the underside of branches and the cells contain more lignin than normal wood. Wood with high lignin content is especially strong against compression. The cells are more round as compared to their rectangular normal cells and have higher lignin content.

The physical condition of reaction wood is different from normal cells. It dries abnormally, the cut surface dries with a fuzzy surface, and the strength of cells differs. In both groups the cross section of a branch, reaction wood characteristically has its pith off center.

The presence of extractives, tree age, and juvenile, sapwood and heartwood (see chapter 2), may influence the physical change in wood on drying. Heartwood is dry dead 2nd xylem, sapwood is living embryonic, and metabolic tissue thus has higher moisture content than heartwood. Because of this it is vulnerable to fungal attack and thus is cut off during lumber manufacturing and ethnographic use such as in carving totem poles.

9.3 Biodeterioration

9.3.1 The vulnerability of the different layers of the wood xylem cell Fig.9.4
Fig. 9.4 is an illustration of the microstructure of a wood cell wall. The cellulose molecules (lines) show the specific direction they take in the different growth stages. P- refers to the early primary growth and S- to the following secondary growth: ML-middle lamella, P-primary wall, S1- first 2nd wall, S2 –second 2nd wall, S3- tertiary cell wall. With permission @ James Deacon

Plant cells have primary thin walls and secondary thick walls. A primary wall is thin and composed of a single layer of cellulose. They are present in parenchyma cells. 2nd xylem wood cells have secondary walls that are made up of a number of layers (Fig. 9.4) with different ratios and orientation of chemicals. The layers are commonly named from outside inward. The middle lamella (ML) joins the adjacent cells together in a tissue. The primary cell wall (P), the first formed wall followed by the secondary layers that are made up of the three layers S1, S2, and innermost S3. This combination is designed for strength and resistance.

The secondary layers are made up of bundles of polymers of cellulose fibrils in a matrix of pectin, hemicellulose, proteins and lignin and some with phenolics. Each layer in the cell wall contains different amounts of chemicals.

Cellulose gives the structure, hemicellulose binds the cellulose molecules, pectin acts as glue and controls water, and pH in the cell wall and lignin strengthens the cell wall and acts as a biocide as well as the phenolics. The S2 layer has the most cellulose, and the primary wall and middle lamella complex, the most lignin. The middle lamella also has large amount pectin that glues the cells together to make a tissue. In very old archaeological samples of wood, from wet sites, the lignin remains. It makes the skeleton of the primary wall and also holds the cells.
together in the tissue in the middle lamella. Lignin is a complex chemical that has many forms. The strongest form in the archaeological is more condensed (the arrangement of phenolic groups) and is not water soluble or commonly hydrolyses by bacteria or fungi.

### 9.3.2 Fungal activity Figs.9.5a-c. Table 9.1

There are several groups of wood destroying fungi: blue staining and white soft rot ascomycetes; dry rot and brown rot basidiomycetes. The fungi grow in specific outdoor natural environments. Each group utilizes one specific polymer in the wood structure.

Blue stain fungi cause surface losses and a blue staining of the cells of sap wood in damp lumber. They utilize the most soluble part of the cells, the protoplasm and readily soluble hemicellulose.

Soft rot fungi hyphae move in the coil direction of the cellulose microfibrils in the S2 layer. Digestion occurs only at a hyphal tip and hydrolyses only the cellulose. The hypha, like a worm, digests its way along this layer of the cell wall and leaving a distinctive pattern of lytic troughs (tunnels) inside the cell wall, Fig. 9.5a, shows the soft rot pattern under polarizing light as crossing coils –lower right –over the crozier cross of bordered pits of the xylem tracheid. Both soft wood fungi and bacteria are active in anaerobic environments such as wet burial sites deeper than 18 inches that is without oxygen. The soft rot fungi are Ascomycetes of the species Chaetomium and Ceratocystis in terrestrial environments and the species *Lulworthia, Halosphaeria,* and *Pleospora* in salt water sites.

Brown-rot utilizes the polymeric cellulose, leaving behind the brown lignin. White rot fungi utilize the brown lignin leaving behind white cellulose. Fungal deterioration observed in wooden artifacts would have occurred in the natural environment before being placed in the museum, or before it was used to make the artefact.

Fig. 9.5b shows the characteristic cuboidal patter of brown rot fungal decay of wood. The common brown rot species are the Basidiomycetes *Schizophyllum commune* and *Fomes fomentarius*.

Fig. 9.5c shows the characteristic of white rot decay of wood. White rot fungi are two common Ascomycete white rot fungi species, *Xylaria hypoxylon* and *Xylaria polymorpha*. They do the opposite of the brown rot. They utilize the brown lignin leaving the white cellulose wood fibers.

Dry rot fungi are a special group of brown rot fungi (*Serpula and Meruliporia*) that decay wood at a distance. They are commonly found in old building or wooden structures. They have their main colony in one environment, usually calcium rich soil that is moist, and from there they send out rhizomorph- hyphal cords to the wood decay site. In buildings the calcium rich soil may include gypsum (hydrated calcium sulfate (CaSO$_4$.2H$_2$O) from cement, plaster, mineral wool insulation or Gyprock –board. The dry rot fungus in contact with gypsum produced calcium oxalate crystal and transport calcium into the wood.
Fig. 9.5a - photomicrograph of soft rot fungi in infested wood tracheids of archaeological wood from a terrestrial wet site. It shows the crosier cross, caused by polarizing light, of the bordered pits of the xylem tracheid. The tracheid is surrounded by the black lines caused by the removal of cellulose microfibrils by the soft rot fungus. The single tracheid is approximately 40µm in width. photomflorian

Fig. 9.5b- characteristic cuboidal fracturing of brown rot fungi decayed. (kind permission © Jim Deacon)

Fig. 9.5c- showing characteristic cell fragments of white cellulose. The brown lignin has been utilized by white rot fungi. Sten Porse Wiki creative commons
Table 9.1 A summary of the actions and salient features of groups of wood destroying fungi. (after Florian 2002)

### 9.3.3 Bacterial degradation Fig.9.6

There are bacteria that can live in both an oxygenated and anoxic environments but are limited by moisture. They require at least fiber saturation of the wood. This is the point at which liquid water is free in the tracheid or vessel tubes over 50µm in diameter. Submerged in water, the rate of bacterial decay is slower than at just fiber saturation point, because it may have less oxygen.

Archaeological wood buried in ocean anoxic sediments have survived thousands of years. The rate and extent of wood deterioration varies because of the different environments, microorganism, wood species, and usage and to the manufacturing process it was exposed to prior to burial. The deterioration process in archaeological wood in terrestrial and marine environments differs, but the bacterial deterioration patterns are similar. Marine bacterial activity is restricted below approx 25 inches.

The presence of 3.5% sodium chloride in the ocean restricts swelling of cellulosic materials. If an object from this environment is placed in fresh water it will swell which will weakens its mechanical strength and increases solubility of its chemicals. The anaerobic
bacteria causing the deterioration are called according to the patterns they create on hydrolysis of the substrate. i.e., erosion bacteria, tunneling bacteria, cavitation bacteria, pit degrading bacteria and scavenger bacteria (see Salient references in Appendix II for excellent references). The distinct patterns are a result of the utilization of the bacteria hydrolyzing different regions of the cell walls of the wood.

Fig. 9.6

**Fig. 9.6- Photomicrograph under polarizing light of wood tracheids of an archaeological sample from a marine site.** Cellulose under the polarizing light appears blue. The black lines in the tracheid indicate loss of cellulose by tunnelling bacteria. In the bottom blue tracheid the voids are caused by hydrolysis of cavitation bacteria. Fibers approximately 40µm. photo mflorian.

Fig. 9.6-shows the activity of bacterial degradation from an archaeological marine site. The xylem tracheids have large voids and linear lines, and cell wall disruptions. The characteristics of the damage can be attributed to groups of specific bacteria.

Erosion bacteria enter from the lumen into the S1 layer. The deterioration pattern starts with a cone shape which enlarges into a diffuse bacterial colony. They can tolerate a near anoxic conditions on sediment covered waterlogged wood.

Tunneling bacteria enter the cell through the lumen or the chamber of the bordered pits on the longitudinal surface of the xylem cell wall. The deterioration pattern is narrow worm like tunnels in the S2 layer. Inside the tunnel, remnants of the exocellular film form characteristic concentric bands.

Cavitation bacteria are associated with bordered pits in soft wood tracheids and utilize the cellulose in the thin wall of the cavity pits. They commonly utilize the complete cell wall leaving voids and some diamond shape cell fragment, shown in Fig.9.6. They commonly penetrate the ray parenchyma and thin walled ray tracheid walls.
Pit degrading bacteria deteriorates the bordered pits membranes. Scavenging bacteria are the most prolific and often mask the activities of the others. They are cleaning up the debris. They appear to tolerate near anoxic conditions.

Bacterial degradation is not simply secretion of enzymes and adsorption of the products. Bacteria have a cellulosome that is a multiprotein complex that carries the enzymes required for digesting cellulose. The cellulosome is attached to the substrate, by a calcium mediated cell protein to a substrate protein interaction; the closeness of the two allows efficient recovery of hydrolytic products, overcoming diffusion losses. The cellulosome may also be involved in hydrolysis of other polysaccharides besides cellulose. This specific approach for hydrolyzing specific molecules is much more logical than just excreting extracellular enzymes into the substrate and hopefully adsorbing monomers.

The cellulosic structures used in heritage objects are extremely variable in plants. Because each structure varies in chemistry and anatomy, it has a specific response to the bacterial attach. For example, cotton and kapok are single celled seed hair and are mainly cellulose, linen is a phloem fiber rich in cellulose with little lignin, hemp has much more lignin and hemicellulose than linen. Wood and bark are complex cellular tissues that have beside cellulose, up to 35% lignin, depending on species. In archaeological wood, because cellulose is easily leached or biodegraded, the reaming structure structures contains up to 75% amorphous lignin.

Archaeological wood also may show biodeterioration from terrestrial surfaces, such as wooden object excavated from earth surfaces. An example is wooden boxes which have been in contact with soil for years, and bases of wooden structures are partially eroded. The cellulose is digested by both fungi and bacteria. The fungal activity will not continue once removed from the natural environment. Fungal structures on these objects will not infect wooden objects in the museum environment.

9.3.4 Insect damage Figs.9.7a-d

The insects that damage wood are the termites, ants, and beetles. The beetles are the ones that may cause most damage to artifact woody materials because they eat it. It is the wood beetle’s larval stage that causes the damage and they require a relatively high humidity or moisture content of the wood material. In museums if there is a beetle problem with wood furniture, the insects came with the artifact. Insect infested artifacts that were from an outdoor environment, when placed in an museum environment the insects rarely can live.

In nature, wood on the forest floor is doomed to become a part of the forest floor with the help of a regiment of beetles, fungi and others. A cedar bent wood storage box in a museum showed a sandwich type of deterioration. The surface of the boards was intact except with many beetle holes. This damage would have occurred in nature over a long period of time in a damp condition. The boards are virtually a sandwich with paper-thin outer surfaces between which the wood was completely riddled with lyctid beetle galleries and tunnels filled with frass.
There are many species of the Lyctid power post beetles (Fig. 9.7a). They can infest many hardwood species i.e., ash, hickory, oak, mahogany, and maple. In homes it may infest hardwood flooring and structural timbers, furniture, picture frames, and baskets if environmental conditions are met. Lumber can be infested in one location, transported away long distances, and spread the infestation to new areas.

There are also the common Anobiid (Fig.9.7b), death watch, wood worm beetles that infests wood in homes and in forest areas depending on species. They infest softwood as well as hardwoods with similar damage as by the Lyctid beetles. In softwood they usually are located in areas of sapwood that has remained as part of lumber. The beetles lay eggs in entrance holes on the wood that has a high moisture content. The hatched larvae tunnel into the interior of the wood (Fig.9.7c). The surface has two types of holes of different size, the entrance for egg laying and hatching larvae, and the exit for the metamorphosed pupa adult.

**Fig.9.7a** *Lyctus* - powder post beetle. Wiki public domain

**Fig.9.7b** Anobiid - death watch, wood worm beetle. Wiki public domain

**Fig.9.7c**
Bamboo stalks (culms, branches) are reported to have a problem with the powder post beetle (*Dinoderus minutum*) whose larvae eat the starch and sugar in the branch. Heartwood, branch sapwood and root wood, have variable insect vulnerability. The heartwood is the most resistant because it has been dried while on the tree and commonly contains biocidal polyphenolic and does not contain protoplasm or stored starch. Whereas sapwood in branch and tree trunks and roots are vulnerable because they are filled with protoplasm, stored starch, oils, and have high moisture adsorption. The branch has a waxy waterproof membrane on the outer epidermal cells that prevent water or humidity entering but the beetles bore through it easily so as to deposit their eggs. In common preparation of branches for weaving, the branch is split and the outer epidermis and cortex and central pith is removed. It may be stored and dried. The dried strips are then soaked to make it flexible for weaving. It readily adsorbs water and if left damp in a natural environment, it would be vulnerable to both insect and fungal infestation.

The root structure varies with families of plants. In trees, fine roots store starch in late fall. In the spring—as in the maple tree— it is converted to sugar for the sap flow. Whole spruce roots and western red cedar roots used for basket making may have some starch in the phloem and cortex and radial rays of the 2nd xylem and in 2nd xylem strips alone also contains sugars, starch and proteins.

Some species of monocot and dicot trees have fine roots with an endodermis, (Fig. 9.7d). It is a narrow layer of thick walled, dark brown to red colored, cells that encircles the vascular tissue in the center of the fine roots. In the plant root, the endodermis controls, water movement, and prevents fungal and beetle activity. The endodermis is dark red colored when dry due to the presence of specific polyphenolics. In the monocot Yucca, the endodermis is collected ethnographically for its coloration in making coiled basketry.
Fig. 9.7d cross section of Yucca rootlet. The central vascular tissue is surrounded by a thin layer of cells called the endodermis. For ethnographic use, the outer tissue of the cortex is removed down to the endodermis. The endodermis and central core is used as cordage and weaving. Originally published in Florian, Mary Lou, Dale Paul Kronkright, and Ruth E. Norton, The Conservation of Artifacts Made from Plant Materials (Los Angeles: The Getty Conservation Institute, 1990) p 62 fig.2-27. Getty Trust. Reprinted by permission of the publisher.

9.4 Environmental deterioration impacts

9.4.1 Water leaching over years Figs.9.8a and b

To summarize, the analytical information of archaeological or ancient wood shows variability in chemical changes and losses that may result from the wet burial environment, the wood species, sapwood or heartwood, outer or inner wood, anomalies in growth. The solubility of wood biopolymers varies. The most insoluble is lignin, and the solubility increases with pectin, then cellulose, and the most soluble with hemicellulose. As a rule, increase in moisture content indicates increase in degradation.

Archaeological wood can be solely cellulosic or lignitic, or anything in-between. The organic chemicals may be replaced by inorganic chemicals, and the wood may be mineralized.

Examples of wood species differences were shown with hardwood alder and soft wood spruce that were excavated from a deposit contemporaneous with a 2500-year-old archaeological site on the Hoko River bank on the Olympic Peninsula of Washington State. This wood, even though not artifact material, illustrated the changes that would affect archaeological wood of this age in this environment. The spruce showed no significant losses or degradation of biopolymers. The alder, taken from the same excavation horizon as the spruce, was significantly altered. Alder
has a significant amount of open vessels that allow water entry. Hardwoods that have vessels filled with tyloses prevents water entering, such as in white oak.

Fig. 9.8a - photomicrograph of ash wood from the 6000 + years old Sweet Trackway. photo mflorian

Fig. 9.8b Reconstruction of ancient Sweet Trackway at Peat Moors Visitors Centre, Somerset Levels, in Sweet, Westhay. Geof Shedard Creative commons wiki

The acidity or alkalinity may make a difference in wet environments. The Sweet Trackway (Figs 9.8a and b) is one of several trackways built during the Neolithic and Iron Age that are preserved in the boggy bottoms of the peat marsh called Somerset Levels near Glastonbury. Excavations in 1970s in the Somerset Levels were conducted by John Coles of Cambridge University.

Such a bog has a pH around 5, thus slightly acidic. The depth of the find, type of wood, etc. must contribute to its physical state. The fenn water, that would be fresh water, leached all chemicals leaving only lignin shells of the wood.

Sap wood and heart wood have different vulnerability to water leaching because of the chemicals present and the cellular structure. Sapwood has embryonic tissue and metabolic tissue that are filled with soluble protoplasm and stored starch. Heartwood is devoid of protoplasm, has been sealed from water by water insoluble phenolic chemicals.

Deterioration varies in its anatomy because of species, age, and part i.e., root, branch, sapwood and heartwood. It varies also in deterioration patterns because of the activity of microorganisms and the environment(s), and the time(s) it was buried. It also varies in changes due to human activity. In all there are some general patterns.

Analyses of chemical and physical changes in archaeological wood were used to determine the degree of deterioration in wood of ash (Fraxinus) and oak (Quercus sp.) of two different ages, 5200 and 4500 years soil buried archaeological wood. It was determined that oak
Heartwood was generally better preserved than ash. Ash because of its anatomical structure is more water permeable than oak which is a major influence in deterioration. Also younger samples appeared generally better than the older samples.

In specific physical changes as compared to normal hard wood, it was found in deteriorated ash, that the wood tracheids and vessel walls were physically thinner than the normal-ash normal - 3 µm, 5200- 1 µm, and 4500 - 2 µm; with the oak; normal -4 µm and the older wood below 1 µm and the younger near normal wood.

It was determined that there was delignification in all 2nd walls and that the lignin in the middle lamella was intact. It was observed that in the younger oak normal size wood tracheid, that they had lost their birefringence due to the loss of crystallinity of the cellulose. In the younger wood, the deterioration was confined to their inner surface and was granular whereas in older wood the whole cell contained granular material in a shell of the middle lamella. In all the wood samples it was considered that the deterioration was abiotic. The results are generic- in many analyses of different archaeological wood similar results have been observed. Every piece of archaeological wood is different.

9.4.2 Sunlight Figs.9.9a-c

Weathered wood surface is the result of a sequence of environmental processes, i.e., wet/dry cycles, hot/cold cycles and ultraviolet (UV) radiation from sunlight. The UV breaks down the surface lignin in the first few layers of the surface wood cells. It is washed away by rain leaving the silver grey cellulose surface of wood cells, shown in Fig.9.9a. The remaining surface cellulose cells (Fig 9.9b) reflect UV preventing further deterioration of the lignin. Lignin acts as a biocide protecting wood from insects and wood destroying fungi. This weathering of wood is not considered biodeterioration even though a black yeast-like fungus, Aureobasidium pullulans is always associated with these silver grey surfaces, This yeast utilizes small molecules such as sugars and proteins and forms a slimy biofilm made up of, mainly a common sugar polymer, beta-glucans, which holds the surface cellulose cells together, This is one place that the fungal biofilm is welcomed.
Fig. 9.9a. Australian aboriginal carved Eucalyptus pole in an outdoor light exposed environment showing the white surface of cellulose cells. photoMLFlorian.

Fig. 9.9b. A thin section, under scanning electron microscopy, of an Eucalyptus wood from an Australian aboriginal carved tree from an outdoor dry, light exposed, weathered surface. The bottom margin shows the surface birefringent cellulose cells. photoMLFlorian.

Fig. 9.9c shows the guided tourists at S’ Gang Gwaay (Ninstints) on Haida Gwaii (Queen Charlotte Islands) in 1996. The poles show their weathered wood surface. PhotoMLFlorian.
9.4.3 Deterioration by vegetation Fig.9.10

Fig. 9.10 shows the changes of the vegetation and alteration of the totem poles over the years of 1901-1957 on the vacated village of S’ Gang Gwaay (Ninstints) on Haida Gwaii (Queen Charlotte Islands). (From Florian, M.-L. E. and R. Hebda. 1981. "The totem poles and the vegetation at Ninstints Village, Anthony Island. DATUM. Heritage Conservation Branch, B.C. Newsletter. Vol. 6, No. 3, p. 10-16.)

The village of S’Gang Gwaay (Skungwai, Ninstints) is on a small island on the southwestern coast, tip of Haida Gwaii (Queen Charlotte Islands). It is a UNESCO World Heritage Site and Canadian National Park Reserve. Fig.9.9, shows photos the totem poles of the village over the years 1901-1957 prior to it becoming a world heritage site, Before the village was vacated the there was a longhouse a few yards behind them with no vegetation around or close to them.

Photo 1901 shows low shrubs at the foot of the poles and a mature forest away back from them. There was no apparent vegetation on the poles. Some of the poles were leaning slightly most probably due to normal settling in the post hole.

Photo 1913 shows the loss of shrubs and only beach grass. The shrub loss suggests salt water flooding killing the previous shrubs, and a comeback of the beach grass. There is a
suggestion of forest encroachment. The blackening of the surfaces of the poles are a result of algal and fungal growth that occurred prior to 1913, when heavily shaded and surrounded by shrub vegetation. It was not caused by fire because it was reported to have occurred in the late 1800’s and the photos of the poles in 1901 do not show blackening.

Photo 1935 shows the low salal shrubs surrounding the base of the poles and the encroaching spruce forest and some vegetative growth on the poles. These poles are mortuary pole and are tree trunks that have been erected with its top set in the ground. It is characteristic of western red cedar to have what is called a skirt at its base. It is several feet out around the tree trunk and has a large empty hole in the centre. It is in this hole, as it now was at the top, that burial boxes were placed. Humus built up in the top hole and has supported the vegetation.

On 1957, the frontal poles, the tall heavily carved surfaces seen in photo 1913, were removed and were placed in several museums. The striking change is vegetation is the growth of the now surrounding spruce forest.

In the 1970s, the Royal British Columbia Museum had undertaken with the Haida First Nations Band to reduce the vegetation close to the base and on the poles. In September 1979, Royal BC Museum, Conservation Scientist, M-L Florian, after undertaking an environmental assessment of the area around the poles, reported that to allow the poles to gain longevity and save the poles the vegetation and spruce forest must be removed at least 100 ft from the poles. The purpose of this was to allow sunlight in so the natural weathering process on the surface of the poles would then form and slow down dramatically further deterioration. Fig. 9.8c shows the stable weathered surface of the poles. Archaeological excavation was done around the poles to remove the soil and replace it with beach gravel for water drainage.

The work was undertaken by Richard Wilson of Haida First Nations Band and Richard Beauchamp of Chief Conservator at the Royal BC Museum. The vegetation on the poles was continuously clipped, which over the years killed its growth. No chemicals or physical force was used. A few spruce trees were left to maintain a park like feel, Florian disagreed with this. These trees over the years have caused problems. The rising of the ground due to the growth of the spruce roots caused adjacent poles to slant. Most recently the First Nations have removed some of the slanting totem poles and righted them.
9.4.4 Anatomical changes due to heat Figs.9.a-c

Fig. 9.11a, and b. show the damage caused by the intense heat from the eruption of Mt.St. Helens. Fig.9.11a shows a cross section of the spruce heartwood cells. The outstanding feature is the uniform color probably from the heating of the lignin in the cell walls. The lumen shows that there is a little irregularity in the inner cell surface but it is not in all cells and considering the uniformly in all cells of cellulose spiral voids in Fig. 9.11b, it is not soft wood fungal deterioration. Fig.9.11b, is a tangential surface, and shows the length of the xylem tracheids with spirals. These spirals are voids and are the positions of the cellulose microfibrils that would have vaporized by pyrolysis into a gas leaving the voids. The wood would be mainly lignin.
Fig. 9.11c

Fig. 9.11c is an example of observable change to charcoal to a brown color of Sitka spruce 2nd xylem tracheids and radial ray cell walls. (Burnt wood 1325T31 F8:1 wood chip 10,000 year old).

Fig 9.11c shows the dark brown color in charcoal due to heating of lignin in the cell walls. The wood is carbonized and brittle.

9.5. Archaeological Wood- Chemical Changes

9.5.1 Introduction-variations

Various chemical changes have occurred in archaeological wood. Such wood may be normal chemically, that is, contain the same ratios and amounts of the basic chemicals, the biopolymers lignin, cellulose, hemicellulose, and pectin, and the extractives and inorganic chemicals, or it may have altered amounts of the chemicals. The organic chemicals may be replaced by inorganic chemicals, and the wood may be mineralized.

These variations in chemical changes and losses are the result of the type of burial site, i.e., terrestrial or marine, anoxic or aerobic, etc. It also varies because of the wood species and the type of wood- sapwood or heartwood, anomalies in growth. Also there may be variation due to biodeterioration of the material during fabrication or usage prior to burial. As a rule, increase in moisture content indicates increase in degradation.

The chemical losses and changes are reflected on the cellular and tissue level. On the cellular level, changes in thickness of specific layers of the cell walls, fungal lytic troughs, bacteria pitting, and inorganic precipitates are observed. On the tissue level, selective losses such
as parenchyma cells of the longitudinal and radial wood rays, separation of growth rings, and tracheids are observed.

Cell types may show variable resistance to degradation. For example, a piece of oak from a Late Middle Ages marine wreck in the Netherlands was completely waterlogged. Histological examination using polarized light shows that very little crystalline cellulose is present. The remaining crystalline cellulose is associated with the middle lamella-primary cell wall complex and the tyloses of the large vessels. The tyloses of the vessels are intact show no changes, and even have air that was trapped there during the wood's growth hundreds of years ago. Adjacent to these cells are fiber cells with only amorphous chemicals. These fiber cells are hydrated and swollen to the extent that there is no longer a cell lumen. On drying, the vessels do not collapse or shrink, like those of the adjacent fibers.

9.5.2 The polymers

9.5.2.1 Introduction

The chemical stability of wood biopolymers has been found to be (in decreasing order): lignin, pectin, cellulose, and hemicellulose. The polymers may have undergone some chemical deterioration such as depolymerization into single units; or the crosslinks between molecules if present may have been severed; or the number of crosslinks may even have been increased or the stability of the organic colloid may have been disrupted by the excess of water or the ionic balance of the solution. The nature of these polymers is important to know.

9.5.2.2 Cellulose

Cellulose is an organic compound with the formula \((\text{C}_6\text{H}_{10}\text{O}_5)_n\), a polysaccharide consisting of a linear chain of several hundreds to thousands of \(\beta(1\rightarrow4)\)-linked D-glucose units. It is a straight chain molecule with no branching. The units are strongly bonded and hard to break giving it its low solubility. It has crystalline and amorphous regions. The crystalline region contains the normal linkage of the glucose molecules. If the linkage is broken it is said to be amorphous. These amorphous regions are easily accessible for enzymes and solvents. Brown rot fungi alter the crystalline cellulose to amorphous state that they then can easily hydrolyze.

Hydrated cellulose has water molecules held by secondary force but most abundantly by chain segments in amorphous regions causing swelling. When swelling is extreme, the micellar structure is destroyed, and the cellulose is no longer crystalline. The change of crystallinity to amorphous state can be observed by polarized light. Crystalline regions have positive birefringence and amorphous regions have negative birefringence. Archaeological wood will show a decrease in crystallinity and polymerization.

Dry cellulose is inflexible or brittle but cellulose with 12% MC at 60-80% RH. is quite flexible. Water therefore acts as a plasticizer for cellulose. In most organic colloids after dehydration, rehydration is possible. But with waterlogged cellulose during dehydration, the strong inter-cellulose bonds bring the molecules tightly together, eliminating moisture and
causing extreme shrinkage, making it impossible to rehydrate. This is one of the greatest problems with conservation of cellulosic materials - how to retain sufficient moisture between the cellulose molecules to retain flexibility and prevent extreme shrinkage.

Enzymatic degradation does occur readily with cellulytic bacteria and fungi. Bacterial degradation of cellulosic material can occur in sea water and in sediment less than 24.5", the maximum depth for bacterial activity. Prior to burial of marine fungi, biodegradation could have occurred under aerobic conditions and thus would be limited to the sediment water interface.

The effects of the chemical change in cellulose due to biodeterioration of both marine fungi and bacteria is expressed in the physical changes such as digestive troughs in wood cell walls aligned along the angle of deposition of the cellulose macrofibrils and in bordered pits. These changes will cause local physical weakening of the cell wall.

Archaeological wood from a marine environment, may have been preserved because of the restriction of swelling due to the presence (high concentration - 3.5%) of sodium chloride normally in sea water. If such materials are placed in deionized or fresh water to remove sodium chloride or for storage, excessive swelling may occur. Such swelling may cause irreversible bond breakage and deformation of the cellulose fibers, giving them weaker mechanical strength and greater chemical solubility.

Enzymatic degradation does occur readily with cellulytic bacteria and fungi. Bacterial degradation of cellulosic material can occur in sea water and in sediment less than 24.5", the maximum depth for bacterial activity. Prior to burial, biodegradation by marine fungi could have occurred in aerobic conditions up to the sediment water interface.

9.5.2.3 Lignin

Lignin cell walls vary in amounts depending on the cell or tissue type and species origin. For example, 19-25% is present in hardwood fibers and 25-30% in soft wood fibers, Lignin along with hemicelluloses and pectin fill the interstices between cellulose microfibrils. It is suggested that because of the insolubility of lignin that it is chemically bound to the hemicelluloses, Lignin and carbohydrate polymers in the cell wall protect each other by preventing solvents or at least retarding their entrance, In woods with hemicellulose loss, the lignin is exposed to chemical change. Analysis of waterlogged woods usually shows a loss in hemicelluloses. Lignin is extremely persistent; near normal amounts have been reported in 100 million year old wood from terrestrial burial. It is also the precursor of coal.

9.5.2.4 Hemicellulose

Hemicellulose association with cellulose is not completely clear, but it is considered to be found in cell walls in more or less intimate association with cellulose and lignin, It is thought to have a major role in the integrity of the cell wall. Lignin bonds chemically to hemicellulose but not to cellulose, It is suggested that hemicellulose is a protective colloid acting as a hydrated amorphous matrix surrounding cellulose fibrils, preventing aggregation, hydrogen bonding and co-crystallization of the cellulose fibers.
Hemicelluloses are amorphous carbohydrate polymers. They are short chains, usually branched structures, usually with no microfibrillar structure. They are made up of a mixture of several different monomers [residues] (the pentose sugars, D-xylose, D-mannose, D-glucose, d-galactose, L-arabinosa) and uronic acids (40-methyl-D-glucuronic acid, D-glucuronic acid + D-galacturonic acid). The amounts and selection of the residues vary with plant species. The characteristic feature of all hemicelluloses is the presence of the acidic D-glucuronic + D-galacturonic acid residues. The uronic acids allow large amounts of water to be absorbed during hydration.

**9.5.2.5 Pectin**

Pectin substances are located mainly in the middle lamellae and primary wall. The amounts of the pectic substance vary greatly with cell types e.g., wood (xylem) 0.5-1.5% (of dry weight), bark 7-30%, cotton (primary wall) 9%, and collenchyma (supporting cells in stems and leaves) 45%. Pectic substances are hydrophilic substances and act as a molecular colloid in cell walls. They can form gels, the rigidity of the gel depends on the length of the polymer. They form a part of the continuous amorphous matrix between cellulose microfibrils in primary walls. They give rigidity to cell walls and act as cement, cementing the amorphous cuticle to the surface of epidermal cells and as intercellular cement. In terms of plant parts used for artifact material such as leaves, the intercellular cementing feature of the pectic substances is of utmost importance. Loss of the pectic substances may cause loss of tissue integrity. The pectic substances may also play an important role in permeability of the cell wall to ions. In vivo studies show that Na, K, Ca, Fe, PO₄ are absorbed in the pectin like substance of the cuticle wax. The pectic substances can be readily hydrolysed by acids and enzymes. Many bacteria and fungi are capable of utilizing them for nutrients. The retting of flax, hemp, and jute to make free fibers and the ponding of logs to make them more permeable to impregnation treatments depend on bacterial hydrolyses of the pectic substances.

**9.5.3 An example of chemical alteration of polymers due to burial, age, and species.**

This is a review of comparative analysis of the same wood species of contemporaneous wood and 2500 year old buried wood from the same site.

The alder and spruce were excavated from a deposit contemporaneous with a 2500-year-old archaeological site on the Hoko River bank on the Olympic Peninsula of Washington State. This wood, even though not artifact material, illustrates the changes that would affect archaeological wood of this age in this environment.

Remarkably, the spruce showed no significant losses or degradation of biopolymers. The alder, taken from the same excavation horizon as the spruce, was significantly altered was the oak. The simple phenols of lignin and the neutral sugar products of carbohydrates were quantified by capillary gas chromatography. The results from the buried wood were compared to those of their modern counterparts. The sugar and phenol analyses showed that there were
chemical degradation and losses. In the alder and oak, respectively, 90 and 98% of the polysaccharides and 15 and 25% of the lignin was lost or degraded. Approximately 75% of the degraded biopolymers had been lost from the two samples. The analyses showed that the vanillyl and p-hydroxyl lignin units were the most stable, followed by the syringyl lignin groups. Of the neutral sugars analyzed, arabinose, galactose, fucose, and rhamnose are least degraded, followed by glucose, mannose, xylose, and ribose, the most degraded. The biopolymers in decreasing order of stability are lignin, pectin, α-cellulose, and hemicellulose.