EVALUATING THE WOODEN REMNANTS OF THE *TEKTAŞ BURNU* SHIPWRECK

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ABSTRACT

A small vessel thought to be a Greek merchant ship sank to the floor of the Aegean Sea near Tektaş Burnu, Turkey between 440-425 B.C., or shortly thereafter. Scattered among the many remaining artifacts were a few small wooden remnants of the ship's hull and equipment. These remains were investigated to determine the type of wood used in the construction of the ship and to obtain information on the degradation processes that have occurred in the wood over the past millennia. Several small segments of wood were all that remained of the ship, and twelve of these woods have been identified as *Pinus* (5 samples), *Quercus* (3 samples), *Ulmus* (3 samples) and one very small sample remains unidentified. Micromorphological studies indicated the woods were severely degraded and lacked structural integrity. In all samples examined, the secondary wall layers of the wood cells were extensively degraded with minute holes and tunnels present among disrupted cell wall material. The middle lamella between cells remained and was not eroded. The deterioration in the secondary wall layers has characteristics indicating that bacterial degradation was the major type of microbial decay. The advanced stage of decay and changes that have occurred from environmental influences and secondary scavenging bacteria were found to often mask the decay of the primary bacteria that

attacked the wood. Erosion and tunneling bacteria followed by secondary scavenging bacteria most likely were involved with the deterioration observed. Decay by erosion bacteria is characterized by depletion of cellulose and hemicelluloses in the secondary wall, leaving only a lignin-rich framework of the middle lamella. Tunneling bacteria attack the secondary wall producing small tunnels and may penetrate and degrade the middle lamella to a limited extent. In sediment covered, waterlogged woods where oxygen is restricted both erosion and tunneling forms of bacterial degradation may be found. The ship's wood that remained was infiltrated with copper and other metal corrosion products that apparently helped to inhibit microbial degradation and aid in the woods preservation. Identification of the wood species found in the shipwreck has provided information on the types of woods used for building this ship and the characterization of decay has documented the current condition of the wood and elucidated the type of microbial degradation occurring in this waterlogged environment.

INTRODUCTION

Wood provides a wealth of information when it is found at an archeological site. Wooden artifacts can give great insight into past civilizations, cultures, technology and environmental conditions (Blanchette, 1995). However, wood is often lost to microbial decay processes in terrestrial and marine environments, unless conditions that suppress these organisms prevail. All wood degrading microorganisms have general requirements for survival that include: moisture, oxygen, nutrients, favorable temperature, suitable pH and a non-toxic substrate (Blanchette and Hoffman, 1994; Eaton and Hale, 1993). If any of these requirements are not provided their development is greatly reduced or nonexistent. In terrestrial conditions where these requirements are met, brown and white rot fungi are typically responsible for rapid degradation of wood (Blanchette and Hoffman, 1994). However, in marine environments where oxygen is often limited, soft rot fungi and bacteria are the dominant organisms that attack wood, causing a relatively slow decay (Daniel and Nilsson, 1997; Singh and Butcher, 1991). It is also very important to understand the degradation and chemical properties of archaeological woods if conservation and preservation procedures are to be successful (Blanchette, 2000). This paper reviews the current understanding of microbial decay of archeological wood from marine environments and investigates the wooden remnants of the Tektaş Burnu shipwreck.

Fungi that cause soft rot decay in wood belong to the *Ascomycota* and *Deuteromycota* phyla. They can not compete with the brown and white rot fungi and are typically found in woods that have limited access to oxygen, or are found in an environment of moisture extremes that will not support the basidiomycetous decay fungi. Soft rot fungi are capable of two forms of decay: type 1 or cavity formation and type 2, a cell wall erosion type of attack. Bacteria need high moisture contents and are most common in waterlogged environments even when oxygen is limited. Wood degrading bacteria are often divided into three major groups: Erosion bacteria, tunneling bacteria and cavitation bacteria, based on the type of attack within the various cell wall layers. Pit degrading and scavenging bacteria are two other groups that degrade wood or wood residues, but have not been studied extensively. The pit degrading bacteria concentrate their attack on bordered pits and related structures and scavenging bacteria are considered secondary degraders that gain their required resources from residual material generated by primary degraders. These organisms may work individually or together to slowly degrade historically important woods in marine environments.

WOOD DEGRADING ORGANISMS FROM MARINE ENVIRONMENTS

Erosion bacteria

In marine environments one of the most predominant types of wood degradation appears to be caused by erosion bacteria (Singh and Kim, 1997). This type of cell wall attack starts as conical troughs that initiate from the cell lumen and move toward the middle lamellae. The bacteria appear to preferentially degrade cell wall layers that have a considerable amount of cellulose and hemicellulose and avoid regions of the cell with high lignin contents. The secondary cell wall, consisting of the S_1, S_2 and S_3 layers, is the largest region of the cell wall and the layer most degraded [FIG. 1]. Erosion bacteria appear to enter the cell through the lumen by penetrating the S_3 layer to access the remaining layers of the secondary wall. Although the bacteria penetrate localized areas of the S3 they do not fully degrade this layer. The S_3 layer is often absent in areas of the wood cell wall where extensive degradation of the S_2 layer has occurred and erosion troughs have coalesced into larger voids. It is not apparent, however, whether this is caused by direct bacterial degradation or a loss of structural support from the underlying S_2 layer after it has been degraded (Daniel and Nilsson, 1997). Within the secondary wall, the bacteria tend to follow the cellulose microfibrill orientation. After advanced decay by erosion bacteria, the secondary wall is riddled with holes, but the middle lamella remains unaltered. Wood decay by bacteria requires some oxygen for degradation to progress, but erosion bacteria apparently can tolerate near anaerobic conditions since they can be found in sediment covered, waterlogged woods (Daniel and Nilsson, 1997).

Tunneling bacteria

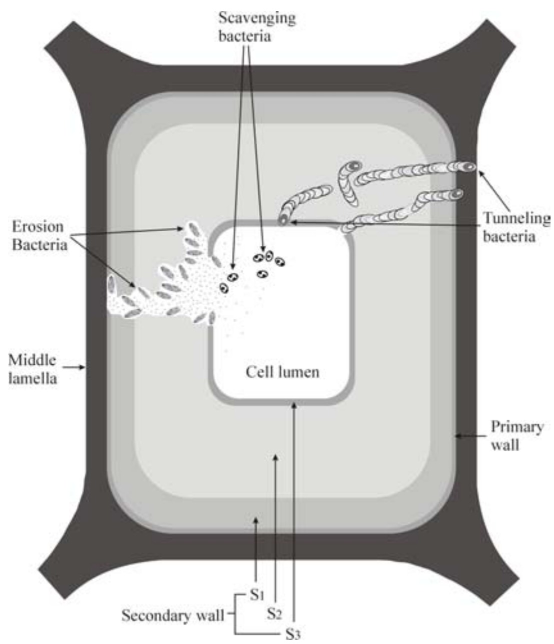
Unlike erosion bacteria, tunneling bacteria do have the ability to degrade lignin and the middle lamella region of the cell wall. They enter wood cells through the lumen, and also have been observed entering the secondary wall via the chambers of bordered pits when the lumen is full of extractives (Singh and Butcher, 1991). Once the cell wall has been penetrated, the bacteria readily degrade all layers of the secondary wall and often do not follow the orientation of cellulose microfibrills in the S_2 layer. In the secondary wall, the bacteria produce small tunnels that are similar in diameter to the bacterium. As they degrade the cell wall, concentric bands of residual materials from degradation and extracellular slime are left behind [FIG. 1]. If conditions remain favorable, decay progresses and the small tunnels eventually coalesce forming larger areas of degradation. Secondary bacterial scavengers often grow and utilize the residual cell wall components left by the tunneling bacteria. One of the few areas of the wood cell that appears to be immune to degradation by tunneling bacteria is the corner regions of the middle lamellae (Singh and Butcher, 1991). Although evidence of tunneling and erosion bacteria can often be found within the same cell wall, tunneling bacteria seem to require greater oxygen concentrations than erosion bacteria (Björdal, 2000).

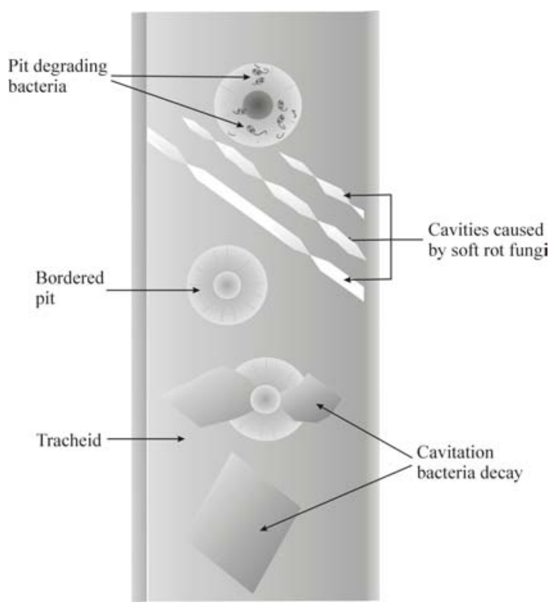
Cavitation Bacteria

As the name implies this type of bacterial attack produces cavities primarily in the S_2 layer. Similar to the erosion and tunneling bacteria, cavitation bacteria appear to enter the cell wall by boring a small hole in the S_3 layer, but do not degrade large areas of this layer. After removing the cellulose and hemicellulose in the S_2 layer, the thin S_3 appears to collapse because of reduced support. Studies have also shown that the cavities created by these bacteria are not limited to the S_2 and can extend in to the S_1 layer (Singh and Butcher, 1991). The cavities are often associated with bordered pits, implying that the bacteria gain entry to the cell through the pit chamber. Cavities have also been observed in areas adjacent to the bordered pits suggesting direct penetration of the cell wall is also possible (Singh and Butcher, 1991). The cavities are generally angular and often diamond shaped with the long axis of these cavities running either parallel to or perpendicular to the long axis of the cell [FIG. 2]. This type of wood degrading bacteria does not appear to have the ability to degrade the middle lamellae. The oxygen requirement for cavitation bacteria is not yet known, but they do not appear to be common in extremely oxygen depleted environments.

Pit degrading bacteria

Although cavitation bacteria appear to gain entrance into the wood cell though bordered pit chambers and tunneling bacteria are able to degrade pit membranes, there is a type of bacteria that seem to selectively degrade only the pit membrane and not the cell wall (Burnes *et al.*2000; Singh, 1997). They appear to preferentially degrade the nonlignified, pectin-rich region of the pit membrane





[FIGURE 1] Diagrammatic representation of a transverse view of a wood cell and cell wall layers with several types of wood degrading bacteria. [FIGURE 2] Longitudinal view of a wood cell, with degradation caused by cavitation and pit degrading bacteria and soft rot fungi.

including the margo and torus, which are primarily composed of cellulose. These pit-degrading bacteria accumulate in the pit chamber and attach to the microfibrils of the margo [FIG. 2]. They have the ability to completely destroy the margo leaving the torus partially intact, or may cause a complete dissolution of both structures.

Scavenging bacteria and environmental influences

Scavenging bacteria and environmental influences often mask degradation patterns created by wood degrading bacteria (Blanchette, 1995). Scavenging or secondary bacteria degrade the residual materials left after degradation by tunneling and erosion bacteria [FIG. 1]. They are not found in areas were primary bacterial degradation is occurring and appear to rely on degraded wall components and not intact cell wall material (Singh and Butcher, 1991). These organisms and the influence of environmental factors on woods that have been exposed to marine environments for long periods often remove or alter residual material, creating large voids in the wood cell making positive identification of primary degraders difficult. Scavenging bacteria appear to tolerate near anaerobic conditions, similar to that of erosion bacteria.

Soft rot fungi

Soft rot decay by fungi can be divided into two different categories: type 1 or cavity formation and type 2 or erosion attack, both of which can be observed in hardwoods and softwoods. The type 1 form of decay is characterized by angular cavities in the S_2 layer that follow the cellulose microfibril orientation when viewed longitudinally [FIG. 2]. These chains of cavities with conical ends are often seen as round holes or voids when viewed in transverse sections. The fungus enters the wood cell wall through the lumen by creating a small-bore hole in the S_3 layer. Once the hyphae are aligned with microfibrils, growth stops and cavity formation is initiated. The cavities expand for a period and hyphal growth begins again with the production of a proboscis hypha, which may extend from one or both ends of the cavity. As hyphal growth stops a new cavity begins, creating a chain of cavities that are connected by angular ends. This type of decay primarily affects the S_2 and S_1 layers, with minimal or no damage to the S_3 (Eaton and Hale, 1993; Khalili *et al.* 2001). Soft rot fungi do not degrade the middle lamella.

A complete erosion of the secondary wall and a slight modification of the middle lamella in advanced stages of degradation characterize the type 2 form of soft rot decay (Daniel and Nilsson, 1997). There are differences between the erosion of secondary wall layers of hardwoods and softwoods (Eaton and Hale, 1993). The erosion process in hardwoods often consists of troughs of different sizes, giving the degraded wood a striped appearance. The decay involves a degradation of all secondary cell wall layers, starting at the lumen and moving toward the middle lamellae. In softwoods the fungus enters the wood cell through

Sample #	Description	Identification	Comments
Tektaş Lot 389 Hull remains (?)	Softwood	*Pinus sp.* (Pine)	Bacterial degradation
Tektaş Lot 394 Hull remains (?)	Hardwood	*Quercus sp.* (Oak) (White oak group)	Bacterial degradation
Tektaş Lot 831.01 Peg	Softwood	*Pinus sp.* (Pine)	Bacterial degradation
Tektaş Lot 867.01 One of 11 fragments from atop lead anchor stock core 867	Hardwood	*Ulmus sp*. (elm)	Bacterial degradation
Tektaş Lot 868.01/TK 252 Wood from anchor stock core 868	Hardwood	*Ulmus sp*. (elm)	Bacterial degradation
Tektaş Lot 902/TK 251 Wood from anchor casting bolt 867	Hardwood	*Ulmus sp*. (elm)	Bacterial degradation
Tektaş Lot 912/TK 270 Found with lead casting bolt, thought to be part of either anchor shaft or anchor tine	Softwood	*Pinus sp.* (Pine)	Bacterial degradation
Tektaş Lot 989.01	Softwood	*Pinus sp.* (Pine)	Bacterial degradation
Tektaş Lot 1025 Damaged fragment has nail hole and copper corrosion products	Softwood	*Pinus sp.* (Pine)	Bacterial degradation and copper oxidation products
Tektaş Lot 1032 Thought to be dunnage or wickerwork found intermingled with small fish bones	Hardwood	Unknown, very small diameter, odd hardwood stem, very decayed	Appears to be dunnage, not a structural component
Tektaş Lot 1166 One of four small fragments from beneath lead anchor stock core 1152	Hardwood	*Quercus sp.* (Oak)	Bacterial degradation
Tektaş Lot 1168/TK 303 Wood beneath anchor stock core 1151	Hardwood	*Quercus sp.* (Oak) (White oak group)	Bacterial degradation

[Table 1] Wood sample identification from the *Tektaş Burnu* shipwreck with comments on sample location and type of degradation found.

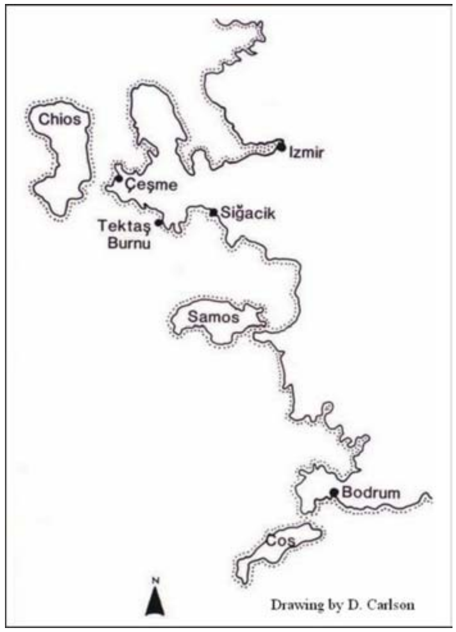
the S_3 layer, but does not appear to degrade it. The decay progresses into the cellulose rich S_2 layer, but only has a minimal effect on the S_1 and no effect on the middle lamellae. Soft rot fungi appear to have a limited tolerance to low oxygen. However, when diffusible oxygen is readily available in marine environments, soft rot is often the dominant wood degrading microorganism (Daniel and Nilsson, 1997). Some soft rot fungi and most of the above-mentioned wood degrading bacteria do have the ability to degrade wood treated with preservatives (CCA, CCB, etc.) in wet environments (Daniel and Nilsson, 1997; Singh and Butcher, 1991). The degree to which these organisms tolerate inhibitory chemicals varies, with tunneling bacteria having the greatest tolerance and soft rot fungi being the least tolerant of microorganisms tested (Daniel and Nilsson 1997; Eaton *et al*. 1989). Rarely does a single type of wood degrading microorganism colonize and decay wood in marine environments, rather a combination of attacks affects the wood. This can often make identification of degrading organisms difficult and mask previous decay patterns.

Marine crustaceans and borers

The deterioration of wood in marine environments is often greatly influenced by marine crustaceans and borers (Cragg *et al.*, 1999). In aquatic systems that support their existence, they may cause severe damage to wood in a short period of time. Water temperature, salinity and oxygen availability are some of the most important factors controlling the distribution of these invertebrates, and if any of these requirements drops too low their activities are inhibited (Cragg *et al*., 1999). The high salinity and relative warmth of the Aegean Sea supports large populations of wood borers that often preferentially attack woods that have been degraded by marine fungi and bacteria (Eaton and Hale 1993; Cragg *et al*., 1999).

TEKTAŞ BURNU SHIPWRECK

In September of 1996 the Institute of Nautical Archaeology research vessel, *Virazon*, discovered a shipwreck about 40 meters below the surface of the Aegean Sea, while doing an annual survey for wrecks off the Turkish coast. The site is located on the southwest shore of Turkey, at Tektaş Burnu, or the “One Rock Cape” [FIG. 3]. Shortly after its discovery three amphoras were recovered, identified and subsequently dated to between 440 and 425 BC (Carlson, 1999). Excavation of the Classical Greek ship was not initiated until the summer of 1999 and was complete in the summer of 2001 [FIG. 4]. The vast majority of artifacts were amphoras, with more than 250 recovered from the site. However, many cups, bowls, oil lamps, cooking pots and other ceramic items were found mixed amongst the amphoras (Carlson, 2001). Two of the most interesting and historically important finds at the wreck were associated with rectangular lead bars and cooper nails. The lead bars



[FIGURE 3] The shipwreck site is located on the southwest coast of Turkey, at *Tektaş Burnu,* or "one Rock Cape". [FIGURE 4] Underwater excavation of the Classical Greek ship.

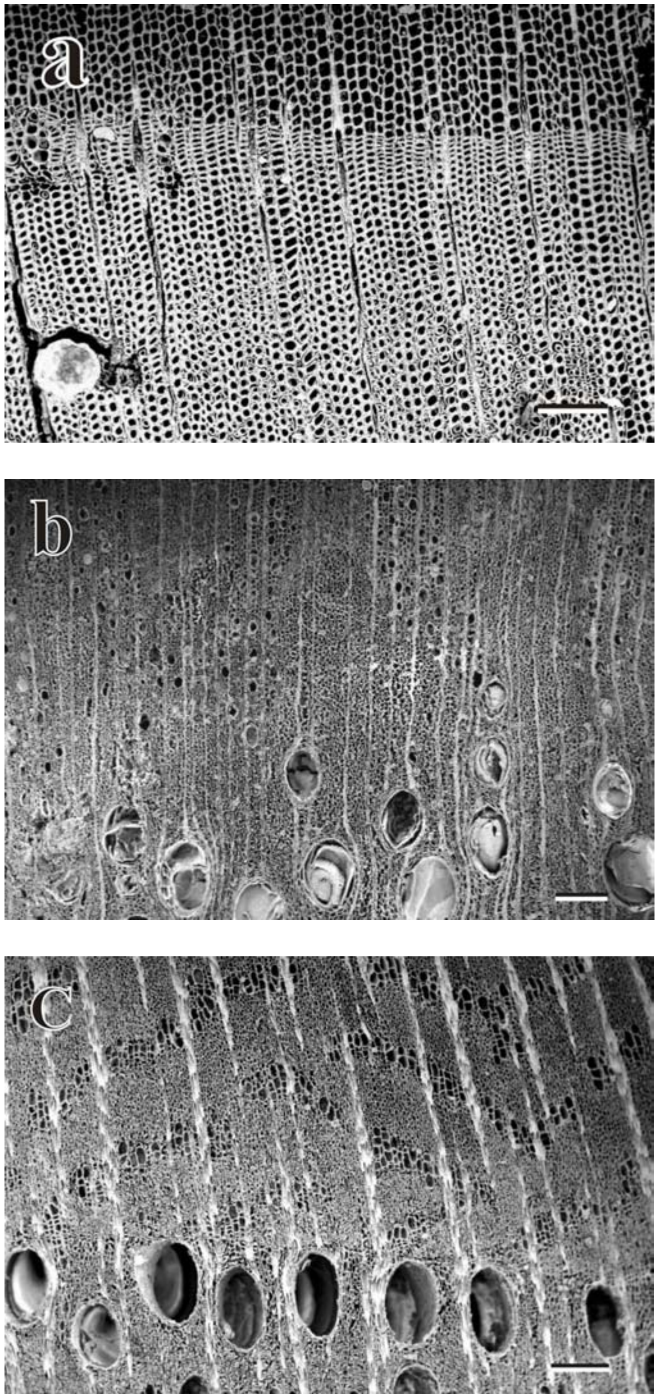
were cores from wooden anchor stocks and represent the earliest example of what is referred to as a Type IIa anchor (Trethewey, 2001). The cooper nail size and clenched shape provided evidence that the ships wooden hull was nailed to its internal frame, which again represented the earliest documented used of this type of construction (Bass and Platt, 2002).

Materials and Methods

Wood samples were obtained from the Institute of Nautical Archeology, College Station, Texas. All samples went through a gradual desalination process shortly after their removal from the shipwreck site and were transported in fresh water to the University of Minnesota. Small segments of the original samples were prepared for scanning electron microscopy by the following procedure. Segments were cleaned in deionized water, infiltrated with O. C. T. (Tissue Tek®) embedding medium under vacuum, frozen to -20°C and sectioned with a Cryo-cut freezing microtome. All sections were then washed in water and dehydrated through an ethanol series and critical point dried. Small segments of the historic woods were also taken for elemental analysis. These consisted of representative samples from the three different woods identified and a piece of modern pine and oak analyzed for comparison. The analysis was carried out by multielemental inductively coupled plasma atomic emission spectroscopy as described by Blanchette *et al*. (2002).

Wood identification of the Tektaş Burnu *Shipwreck*

Although the ships hull, internal frame, anchors and undoubtedly portions of its cargo were made from wood, only small remnants of wood remain. The ship is thought to have come to rest between two large rocks, keeping it above the sea floor and away from sediments. If the ship had been covered in sediments, oxygen would have been limited and more of the hull would most likely have remained. Samples of the wood were identified to their genus and are listed in Table 1 along with additional comments provided by the divers who recovered them. [TABLE 1] Five of the samples are pine (*Pinus sp.*) [FIG. 5a], three are oak (*Quercus sp.*) [FIG. 5b], three are elm (*Ulmus sp.*) [FIG. 5c] and one very small piece remains unidentified. The oak and pine appear to have been used in the hull construction and the elm may have been used as the anchor stock. Most of the woods were associated with either the lead cores from the anchor or the copper hull nails, and were dark in color or had obvious metal corrosion products on their surface. In the preparation of samples for both microscopy and elemental analysis it became apparent that the woods were not just affected by metals on the surface, but that corrosion products had infiltrated the wood. The samples found near the lead cores had black streaks or were black throughout the entire piece, and wood found near



[FIGURE 5] Transverse sections of *Pinus sp.* [**a**], *Quercus sp.* [**b**] and *Ulmus sp.* [**c**] recovered from the *Tektaş Burnu* shipwreck. Bars = 200 µm.

copper nails or with nail holes in them were green, similar to the color of oxidize copper.

Wood decay in the Tektaş Burnu *Shipwreck*

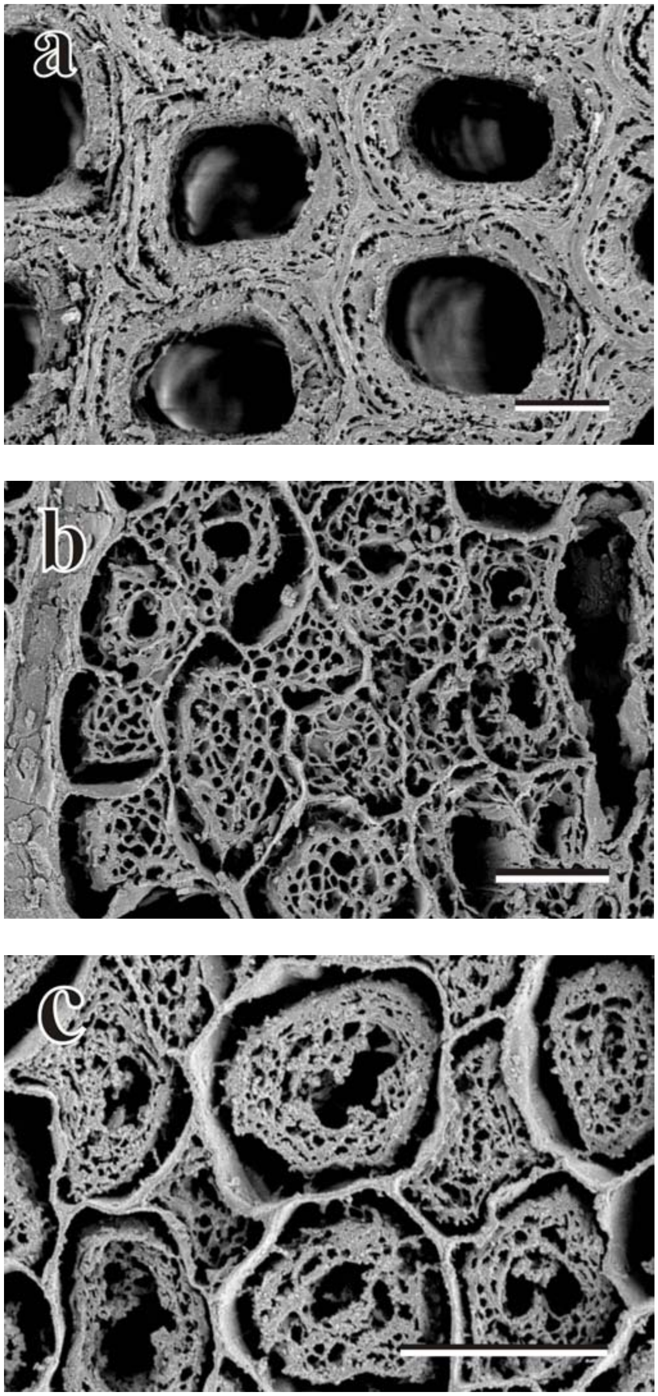
Evidence of marine borers and extensive decay was present in all samples, with oak exhibiting the greatest alteration to its anatomy, and the pine showing the least. Figure 6b is a transverse section of oak displaying a honeycombed appearance common to highly degraded woods found in marine environments. [FIG. 6b] The secondary wall of the fiber cells has large voids that appear to have been caused by a coalescing of cavities caused by erosion bacteria. Holes in the middle lamellae also indicate tunneling bacteria caused the decay. Little evidence of residual material generated by these primary degrades is evident in the wood cell walls, suggesting scavenging bacteria and environmental influences have affected the degraded cells. The S_3 layer has also been altered and appears to have collapsed into the cell lumen, probably because the underlying S_2, which provides structural support to the very thin S_3 layer, was severely degraded. The only layer that has remained relatively intact is the highly lignified middle lamellae.

Degradation in fiber cells from the elm wood sample is very similar in appearance to that of the oak. [FIG. 6c] The degradation patterns indicate that erosion bacteria caused the holes and they often coalesced in the secondary wall creating large voids. Small diameter holes in the middle lamellae and vessel walls verify that tunneling bacteria were also present in these cells. The concentric bands and extracellular slime produced by tunneling bacteria and the granular matrix created by erosion bacteria during their decay processes are also absent in the elm sample, and scavenging bacteria and environmental influences were most likely responsible for degrading this material.

The pine wood exhibited the least amount of decay, when compared to the other woods. [FIG. 6a] The wood does not have the large voids caused by extensive erosion or tunneling bacteria decay. The small diameter holes in the secondary wall and middle lamellae suggest tunneling bacteria were present and the existence of larger diameter holes in the secondary wall and characteristics of the degradation indicates that erosion bacteria were responsible for some of the degradation in this wood as well.

Element analysis of Tektaş Burnu *Shipwreck wood*

Although the wood of the *Tektaş Burnu* shipwreck suffered extensive degradation, a few remnants survived not only microbial decay, but attack by wood boring marine invertebrates. It is possible that sediments gradually covered the woods eliminating oxygen needed for the wood degrading organisms to persist. However, the large concentrations of metal ions [Table 2] present in the woods most likely had an inhibitory effect on microbial growth. Since decay was found in



[FIGURE 6] Transverse sections of degraded *Pinus sp.* [a], *Quercus sp.* [b] and *Ulmus sp.* [c] recovered from the *Tektaş Burnu* shipwreck. All wood samples show degradation caused by erosion, tunneling and scavenging bacteria and environmental influences. Bars = 10 µm.

the wood cell walls of the samples, degradation had occurred before the infiltration of metals into the wood. The decay likely made the wood more permeable, allowing the metal corrosion products to easily penetrate the wood. Microbial degradation likely occurred for many years after the ship had sunk and once metal ion concentrations increased the decay stopped and the woods were protected from further attack. Wood without metals apparently continued to decay and was completely degraded.

The importance of analyzing element concentrations in archaeological woods taken from marine environments has recently gained importance with the discovery of high acidity in woods recovered from the Swedish warship, *Vasa* (Sandström *et al*., 2002). The ship was removed from Stockholm harbor, where it had rested for 333 years and place in a museum after extensive treatment of its waterlogged timbers. In recent years the pH of some of the timbers had values below 2 and acid hydrolysis of the wood has become a major concern. It was determined that sulfur products, produced by sulfate-reducing bacteria, reacted with corroded iron bolts used to hold the ship together had generated sulfuric acid. The authors stress the importance of removing metal ions such as iron and copper to inactivate the reaction and make conservation of the wooden artifacts successful.

CONCLUSIONS

Wood degrading organisms in marine environments are often responsible for the loss of archaeological wood. However, when requirements for their existence are not met, degradation stops. The woods recovered from the *Tektaş Burnu* shipwreck exhibited extensive degradation caused by erosion, tunneling and scavenging bacteria as well as marine borer activity, but they did persist when essentially all other woods were lost. The presence of heavy metals and toxic elements found in the woods appear to be responsible for the preservation of these few remaining wood remnants. An understanding of the decay and elements present within archaeological woods is required if conservation methods are to be successful on these important wooden cultural properties.

[TABLE 2] Elemental analysis of woods from the *Tektaş Burnu* shipwreck and two modern woods used for comparison. Elements in ppm.

Element	*Ulmus sp.* (Tektaş Lot 867.01) [a]	*Pinus sp.* (Tektaş Lot 1025) [a]	*Quercus sp.* (Tektaş Lot 1166) [a]	Modern Modern *Pinus sp.*	Modern Modern *Quercus sp.*
Aluminum (Al)	471	95	4048	5	6
Arsenic (As)	108	98	72	[b]	[b]
Boron (B)	77	69	525	2	34
Cobalt (Co)	10	414	31	0	[b]
Copper (Cu)	800	90647	46	1	8
Iron (Fe)	2397	9406	4039	10	45
Magnesium (Mg)	4636	2360	6934	133	34
Manganese (Mn)	11	18	6	51	28
Sodium (Na)	2514	8432	10275	7	32
Nickel (Ni)	109	1597	110	0	0
Lead (Pb)	7980	1896	22324	1	1
Vanadium (V)	925	534	130	0	[b]
Zinc (Zn)	156	237	74	2	6

[a] Numbers assigned to the samples when collected.
[b] Element not measured.

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