ENVIRONMENTALLY INDUCED PHYSICAL CHANGES IN ANCIENT KAURI (*AGATHIS AUSTRALIS*) WOOD

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ABSTRACT

The physical properties of 30,000-year-old and modern kauri (*Agathis australis*) were explored. The acidic burial environment had modified the ancient wood cell-wall structure, affecting strength properties. Degradation of labile cell-wall polysaccharides resulted in strength differences in the ancient kauri both below and above the proportional limit (PL) of the wood. Significantly lower modulus of elasticity (MOE) and work to proportional limit (WPL) values, as compared with modern kauri, indicated that the ancient material was more readily deformed. Above the PL, the modulus of rupture (MOR) of the ancient wood was significantly lower and the work to maximum load (WML) significantly higher than the corresponding values for recently felled kauri, suggesting that the ancient material did not resist stress; rather, the structure gradually "gave way" under imposed stress. Scanning electron micrographs (SEM) of the fractured ancient kauri surfaces reveal degradation of the woody cell wall.

Keywords: *Agathis australis,* ancient wood, buried wood, carbohydrates, lignin, scanning electron microscopy (SEM), strength.

INTRODUCTION

Ancient wood, recovered in a variety of degradational states, serves as a unique research material. Wood is chemically and structurally complex, and this complexity is compounded by the diverse ways in which ancient wood can be changed by its environment over time. Chemical and physical changes in ancient wood have been explored (Waksman and Stevens 1929; Mitchell and Ritter 1934; Gortner 1938; Varossieau and Breger 1952; Kohara 1953, 1954, 1956; Wayman et al. 1971; Winandy 1984; Hedges et al. 1985; Jagels et al. 1988). One way to quantify physical changes in wood

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is through standardized mechanical strength tests. Unfortunately, there is great difficulty in assessing the strength properties of ancient wood. Because ancient wood is rarely found in either large quantities or in sound shape, structural studies of ancient material are often restricted to micrographs of selected cells (Blanchette et al. 1990). If mechanical tests are conducted, both test specimens and sample population sizes are usually small (Winandy 1984; Jagels et al. 1988).

The comparison of the mechanical properties of ancient wood to the same species, recently felled counterpart can provide a picture of environmentally induced structural changes that have occurred over time. Severe alteration of wood structure by decay fungi will drastically alter mechanical strength (USDA Forest Service, Forest Products Laboratory 1987). However, bacterial degradation will not always result in decreased strength properties (Winandy 1984). Therefore, to elicit meaningful mechanical test results from scarce ancient wood samples, it is essential to initially choose an informative testing method. Previous work with ancient wood has shown static bending tests to be a good overall test of strength changes over time (Jagels et al. 1988).

The behavior of ancient degraded wood under load cannot be easily categorized, as the type and extent of degradation will influence mechanical strength. Values for the modulus of elasticity (MOE), a measure of a material's ability to withstand deformation under load, typify such variation in ancient material. Jagels and others (1988) noted a loss of stiffness, or increased plasticity, in their wet and highly degraded wood. Kohara's (1954) study of 1,300-year-old cypress (*Chamaecyparis obtusa*) samples indicated that the MOE was higher for the ancient samples, as compared with modern cypress. Rather than becoming more plastic over time, the ancient cypress was hard, strong, and brittle. Winandy (1984) noted that 50-year-old live oak (*Quercus virginiana*) samples, previously submerged and infected by bacteria, exhibited equivalent MOE values as compared to newer live oak. Behavior of wood above the proportional limit (PL) has yielded more predictable results. Degraded ancient wood will often show lowered strength properties, translating to lowered MOR and work to proportional limit (WPL) values (Winandy 1984; Jagels et al. 1988).

Mechanical tests alone give an incomplete picture of the extent of wood alteration over time. Changes in the chemical bonding characteristics of wood are intricately linked to physical disruption of cellular structure. Cellular structure, in turn, influences the ability for the composite to effectively transfer stresses under load. Therefore, alteration of the chemical and physical properties of wood will affect the strength properties of the composite. Strength is provided by the basic structural units of the cell wall, the microfibrils. Losses of hemicelluloses, which are thought to act as packing material in the cell wall, are associated with losses in strength (Schniewind 1964). The lignin-rich middle lamella serves as the cellular glue, binding adjacent tracheids together. Degradation of lignin would result in loss of cellular organization and decreased structural rigidity.

Density measurements can also be used as a predictor of wood strength. Increasing specific gravity values correlate with increased strength properties (Winandy and Rowell 1984), and a more dense material will be expected to show the property of increased stiffness. For example, Kohara (1954) found that ancient cypress wood possessed a higher specific gravity than the modern same-species counterpart, and subsequent strength tests revealed that the ancient material was indeed stiffer than recently felled cypress. With deterioration of wood structure, the density and strength properties of wood should correspondingly decrease. However, strength losses are not always mirrored by density changes (Schniewind 1990). If enzymatic attack resulted in depolymerization of cellulose, the ensuing strength loss might not be detected by density changes. Seifert and Jagels (1985) found specific gravity to be a poor predictor of waterlogged ancient wood strength due to wide density fluctuations.

To explore the interaction of the chemical and physical changes in wood over time, 30,000-year-old and recently felled kauri wood (*Agathis australis*) from New Zealand were used in this study as test specimens. Preserved forests of ancient kauri have been recovered from acidic swamp environments in North Island, New Zealand. Modern kauri forests can be found in the same ecological space as the ancient material. Chemical and mechanical testing was facilitated by the availability of large quantities of both the ancient and recently felled kauri. Using recently felled kauri as a basis for comparison, changes in the chemical composition of the ancient kauri were characterized through extensive chemical analyses (Freedland et al. in press). Through static bending tests and spectroscopic studies of cut and fractured cell surfaces, the interaction of chemical change and structural alteration over time could be elucidated.

MATERIALS AND METHODS

Samples of recently felled kauri (*Agathis australis*) and 30,000-year-old kauri were obtained from swampy regions around Kaitaia and Herekino, North Island by the New Zealand Forest Research Institute, Rotorua, New Zealand. Determination of ash content, pH, acetyl content, monosaccharides after acid hydrolysis, acid soluble lignin, and Klason lignin were conducted according to the established Forest Products Laboratory procedures (Effland 1977; Pettersen and Schwandt 1991). The molecular weight of the derivatized cellulose fraction was analyzed using the procedure of Wood et al. (1986). Analysis of molecular weight was conducted on a Spectra-Physics SP8100 liquid chromatograph. Shodex KF803 and KF805 SEC columns were connected in series. The THF eluent flow rate was 1 ml/min. A UV spectrophotometer (Spectra-Physics SP8400) was used at 235 nm. Molecular weight and retention volume correlation for the carbanilate was based on calibration using a narrow molecular weight distribution of polystyrene standards. The Mark-Houwink coefficients were $K = 0.0053$, $a = 0.84$. The methoxyl content of isolated Klason lignin was determined by Galbraith Laboratories, Knoxville, Tennessee.

One hundred precut samples (2.5 cm × 2.5 cm × 30.5 cm) of both ancient and recently felled kauri (*Agathis australis*) were received at the Forest Products Laboratory in an air-dried state. Visible collapse of the tangential surfaces of the ancient samples indicated that the material had been wet at the time of cutting. All samples were acclimated under the identical environmental conditions (73 C, 50% RH) at the Forest Products Laboratory. The samples were rotated regularly to promote even conditioning. After 90 days, the samples showed little loss in weight, and were determined to be stable. The moisture content of each sample was calculated using the conditioned weight at test and the oven-dry weight after test.

For density measurements, the wood was cut into small samples and the volume measured before and after drying according to ASTM D2395-83 (American Society for Testing and Materials 1986). Density measurements were calculated on an oven-dried basis, following two days of oven-drying at 103 C.

Clear samples of ancient and recently felled kauri wood were subjected to a center-point load static bending test as defined by ASTM D-143 (American Society for Testing and Materials 1986). The specimens, 71 ancient kauri and 61 recently felled kauri samples, were cut to 1.3 cm by 1.3 cm by 22.9 cm and tested on an Instron Universal Mechanical Testing Machine. Each sample was tested on the radial face with a head load speed of 0.13 cm/min. A load cell with a 453 kilogram capacity was utilized, and the deflection of the wood was measured with an LVDT to ±1% accuracy.

Cellular structure of gold-coated ancient and recently felled kauri samples (air-dried) was studied with a JEOL JSM-840 scanning electron microscope (SEM). Two sample preparations were examined: razor-planed sample surfaces, as well as fracture surfaces following

TABLE 1. *Chemical composition of ancient and modern kauri (*Agathis australis*) wood.*

Sample	Acetyl (%)	Glucose (%)	Xylose (%)	Galactose (%)	Mannose (%)	Arabinose (%)	Acid-soluble lignin (%)	Klason lignin (%)	Methoxyl on Klason lignin (%)	Total[1] (%)
Ancient	0.1	50.1	2.0	1.2	8.1	0.2	0.4	40.4	14.7	102.6
Modern	0.7	45.6	4.9	4.5	11.8	1.4	0.5	33.5	15.3	102.6
% Diff[2]	−85.7	9.9	−59.2	−73.3	−31.4	−85.7	−20.0	20.6	−3.9	0.0

[1] Sum of glucose, xylose, galactose, mannose, arabinose, lignin and ash.
[2] % Difference = [(% ancient/% modern) − 1] × 100.

bending tests. To detect mineral components in the wood, carbon-coated sections were subjected to X-ray analysis by a Tracor Northern TN-5500 energy dispersive spectrometer (EDS).

RESULTS

Chemical studies

The ancient kauri had been buried in an acidic swamp environment for thousands of years. Results of pH determinations revealed that the ancient kauri was more acidic (pH = 3.7) than the modern wood (pH = 4.4), suggesting that the acidic swamp environment had facilitated degradation of the waterlogged kauri. Chemical analyses (Table 1) indicated losses of labile carbohydrates (arabinose and galactose) normally existing as susceptible branching units on hemicellulose chains (Freedland et al. in press). Deacetylation was also evident, as well as degradation of the hemicellulosic backbone units (mannose, xylose). In addition, molecular weight studies of isolated α-cellulose revealed depolymerization of cellulose chains (Table 2). By contrast, the chemical change in ancient kauri lignin appeared to be restricted to cleavage of side chains and some demethoxylation. The acid-hydrolyzing effects of the burial environment could account for these changes.

Anatomical studies

Kauri has a very simple anatomical structure. The wood is composed of rounded to irregularly polygonal tracheids bordered by large intercellular spaces (Fig. 1), some axial parenchyma, and rays (Butterfield and Meylan 1980; Garratt 1924). There are no resin canals (Meylan and Butterfield 1978). Growth rings are delineated by a gradual transition of narrow thickened bands of cells at the end of the latewood tissue (Garratt 1924). Micrographs of cut surfaces demonstrate the remarkable preservation of ancient kauri fibers. In cross-sectional views, both the recently felled and ancient kauri show a large amount of earlywood (Fig. 2).

The tracheids and ray cells have a varied pitting structure. In radial longitudinal sections, the intertracheary pits of the kauri should be bordered by circular pit apertures (Meylan and Butterfield 1978). However, the tori and

TABLE 2. *Mechanical test results and molecular weight determinations for modern (n = 61) and ancient (n = 71) kauri (*Agathis australis*) wood.*

Sample	Moisture content (%)	MOE (× 10⁶ psi)	WPL (in.-lb/cu in.)	MOR (psi)	WML (in.-lb/cu in.)	Number avg. molecular weight	Weight avg. molecular weight
Ancient	9.9[1]	0.9[1]	1.3[1]	9,547[1]	16.1[1]	96,514[2]	380,728[2]
	(0.04)	(0.1)	(0.1)	(218)	(0.9)	(186)	(734)
Modern	10.5	1.4	2.7	13,469	13.5	104,531	418,347
	(0.1)	(0.1)	(0.1)	(229)	(0.7)	(201)	(806)
% Diff[3]	−5.8	−32.8	−51.3	−29.1	18.8	−7.7	−9.0

[1] Average (standard error).
[2] (Degree of polymerization).
[3] % Difference = [(% ancient/% modern) 1] × 100.

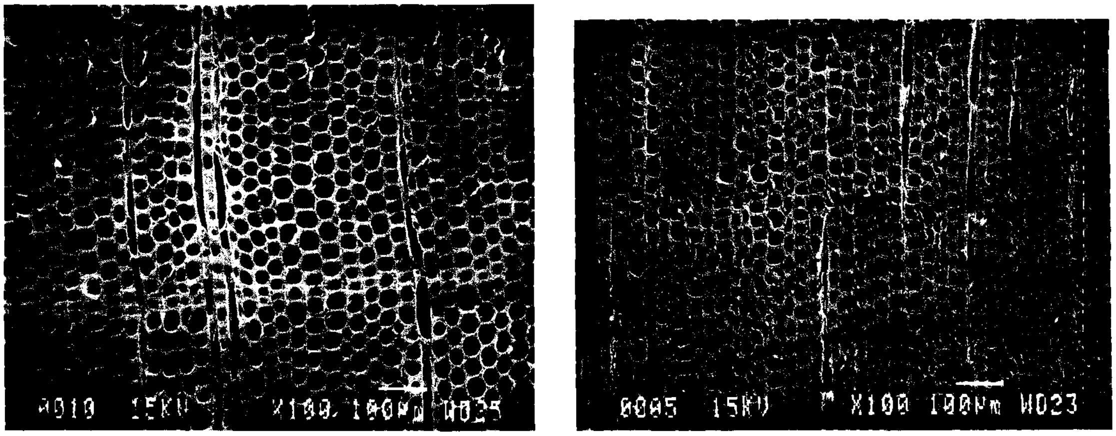

FIG. 1. Transverse face of modern (A) and ancient (B) kauri (*Agathis australis*). Growth rings, formed by narrow thickened cells at the latewood boundary, are difficult to detect in both the modern and ancient wood. Band = 100 μm.

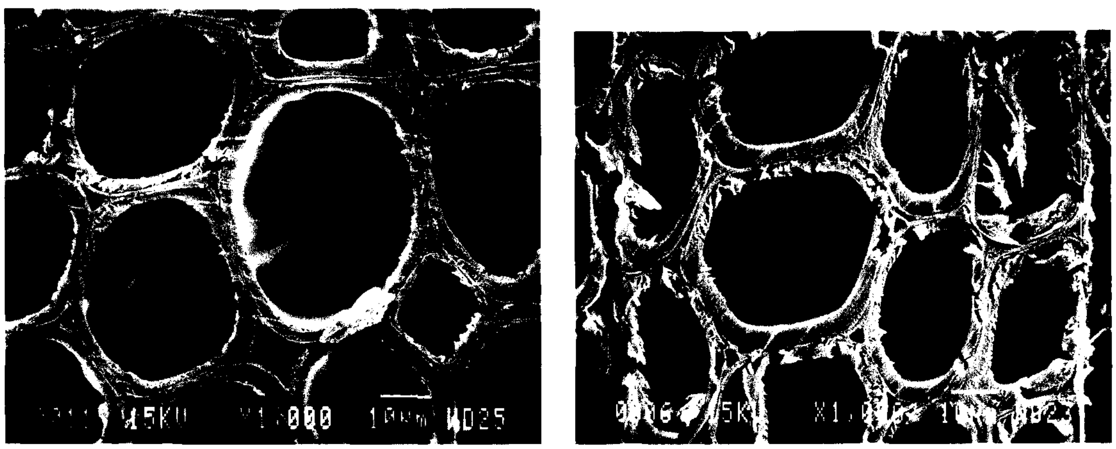

FIG. 2. Transverse face of modern (A) and ancient (B) kauri (*Agathis australis*), showing the rounded to irregularly polygonal tracheids of the earlywood bordered by large intercellular spaces. Band = 10 μm.

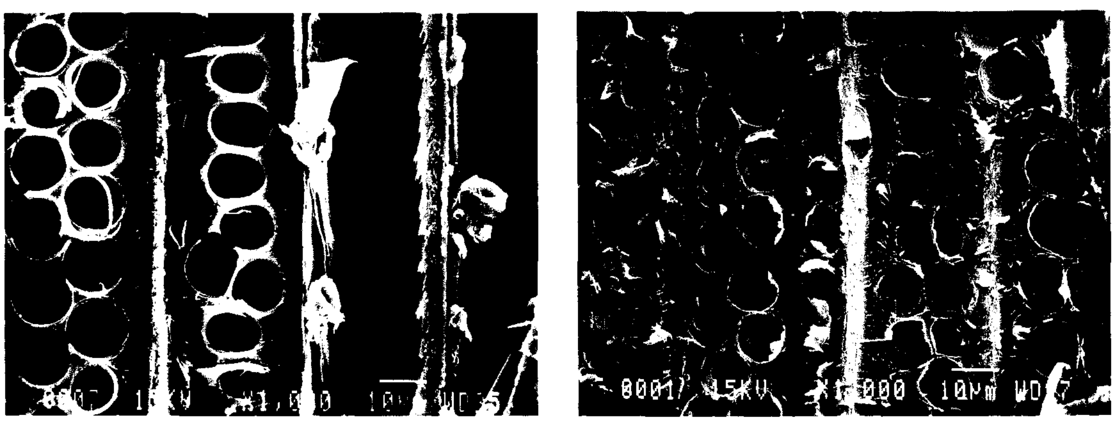

FIG. 3. Radial longitudinal face of modern (A) and ancient (B) kauri (*Agathis australis*). Tori, absent on the intertracheary pits of the modern wood, are visible in the ancient wood. Band = 10 μm.

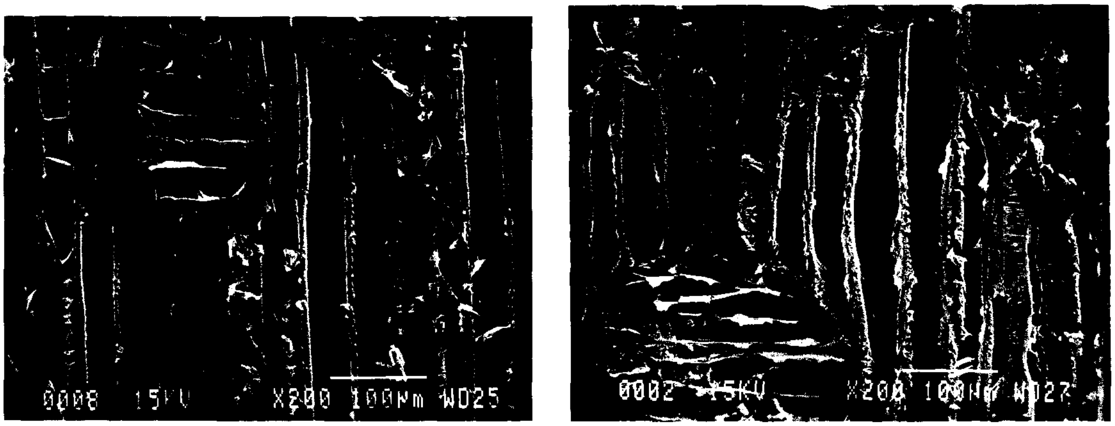

FIG. 4. Radial longitudinal face of modern (A) and ancient (B) kauri (*Agathis australis*). Cupressoid pits between tracheids and rays are collapsed in both the modern and ancient samples. Small tears in the cell walls of the ancient kauri could be the result of drying stresses. Band = 100 μm.

surrounding tissue of both the modern and ancient kauri are in poor condition. While the tori are absent in the recently felled kauri sections, intact tori are visible in the ancient wood sections (see Fig. 3). Tracheid to ray pits are collapsed into angular slit-like openings in both recently felled and ancient samples (Fig. 4). Small tears in the cell walls of the ancient kauri extend through the tracheid to ray pits, possibly the result of drying stresses following sample preparation. In addition, the rays of the ancient wood (Fig. 5) are filled with sulfur-rich particles (Freedland et al. in press). In the tangential longitudinal section, cell-wall material is peeling away from the tracheids of the ancient wood (Fig. 6).

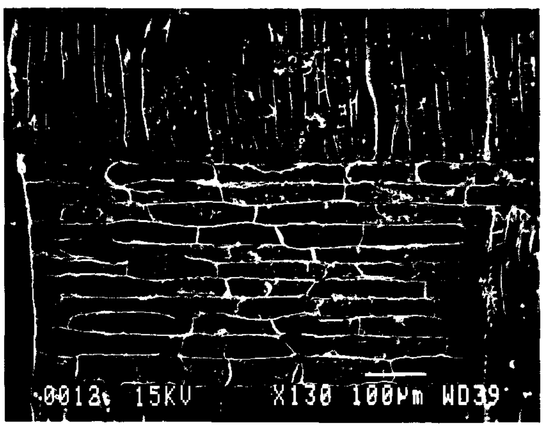

FIG. 5. Radial longitudinal face of carbon-coated ancient kauri (*Agathis australis*). EDS scans of the particles within the rays indicated a sulfur-rich material. These particles were absent in the modern kauri wood. Sulfur compounds are abundant in swamp environments. Band = 100 μm.

Micrographs of ancient and modern kauri fracture surfaces illustrated the relationship between chemical changes and cell-wall strength (Fig. 7). Using the recently felled kauri as the basis for comparison, it can be seen that the S_2 layer of this recently felled material has fractured cleanly. The cell has separated at the S_1-S_2 interface, causing the middle lamella to become structurally distorted. By contrast, the middle lamella-S_1 area of the ancient kauri is intact, while the carbohydrate-deficient S_2 layer is structurally distorted and porous. In some cells, individual lamellar sheets can be differentiated, and pinholes within the S_2 layer represent areas where bundles of microfibrillar strands have been pulled from the surrounding matrix.

Mechanical studies

The results of all mechanical tests are tabulated in Table 2. The ancient material, which was initially cut in New Zealand while still wet, showed some collapse and warping along the radial and tangential faces. As determined by

FIG. 6. Tangential longitudinal face of modern (A) and ancient (B) kauri (*Agathis australis*). Cell wall material is peeling from the ancient wood tracheids. Band = 100 μm.

oven-drying, the ancient material had a higher specific gravity (0.51) than the recently felled kauri (0.47).

Ideally, the wood should be tested when it has been conditioned down to a 12% moisture content. The ancient kauri was conditioned to an average of 9.9% moisture content [Standard Error (SE) = 0.04], while the recently felled wood exhibited an average moisture content of 10.5% (SE = 0.1). A statistical comparison between these two groups was significant [$t(130) = 6.61$, $P < 0.001$], indicating that the moisture content of the ancient kauri was reliably less than the moisture content of the recently felled kauri.

The mean MOE value for the ancient wood (0.9×10^6 psi; SE = 0.1×10^6) was contrasted against the mean MOE value for the recently felled wood (1.4×10^6 psi; SE = 0.1×10^6). The ancient kauri MOE was significantly less than the recently felled kauri MOE [$t(130) = 6.51$, $P < 0.001$]. The results would support the conclusion that the ancient wood had a lower resistance to deformation. The mean

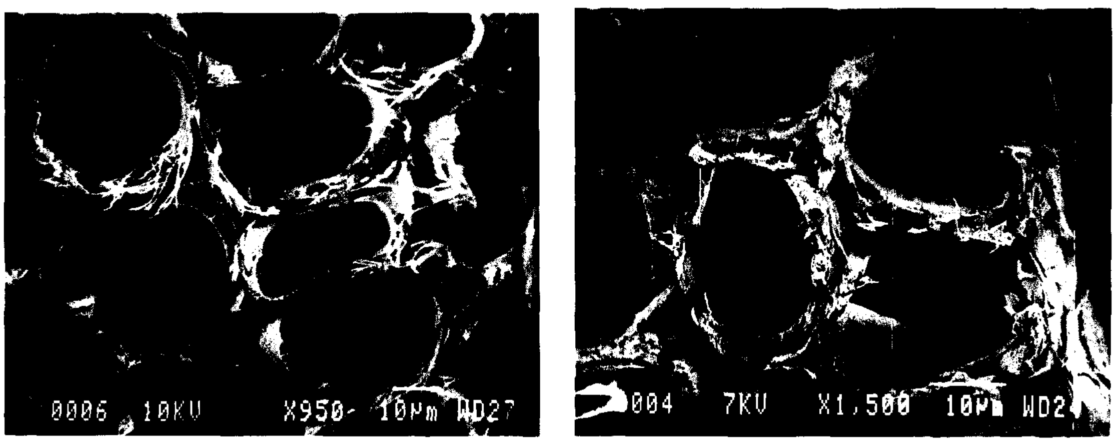

FIG. 7. Transverse fracture surface of the modern (A) and ancient (B) kauri (*Agathis australis*). The S_2 layer of the modern material fractured cleanly, in contrast to the ragged fracture surface of the ancient wood. Loss of carbohydrates within the wood cell wall has altered the strength properties of the ancient kauri. Band = 10 μm.

WPL value for ancient wood was 1.3 in.-lb/cu. in. (SE = 0.1), while the mean WPL value for the recently felled wood was 2.7 in.-lb/cu. in. (SE = 0.1). The ancient kauri WPL was significantly less than the recently felled kauri WPL [$t(130) = 13.06$, $P < 0.001$], meaning that it would take less work to move the ancient wood from the unloaded to the elastic limit of the material.

The ancient kauri MOR (9547 psi; SE = 218) was significantly less than the recently felled kauri MOR (13469 psi; SE = 229); $t(130) = 12.38$, $P < 0.001$). The results substantiate that ancient wood had a lower ultimate strength. The work to maximum load (WML) mean value for the ancient wood was 16.1 in.-lb/cu. in. (SE = 0.9), while the WML mean value for the recently felled wood was 13.5 in.-lb/cu. in. (SE = 0.7). Again, the ancient kauri WML value was significantly greater than the recently felled kauri WML value ($t(130) = 2.22$, $P < 0.029$). The findings suggest that more work was required to ultimately cause failure in the ancient wood.

DISCUSSION

The mechanical behavior of nondegraded wood can exhibit several predictable trends. For instance, below the fiber saturation point (FSP), increasing moisture content will result in decreased stiffness. The stiffness of wood is controlled by interatomic bonds, such as hydrogen bonding between cellulose chains in microfibrils. As water enters the cell wall and pushes tightly packed cellulose chains apart, swelling occurs perpendicular to the microfibrillar axis. The decrease in the degree of cell-wall packing results in the property of decreased stiffness, as evidenced by the extreme flexibility of wet ancient wood at test (Jagels et al. 1988).

By contrast, dry degraded wood exhibits variable behavior under load. Generally, drying stresses can cause the hemicelluloses in the cell wall to collapse structurally, thereby imparting increased strength properties. Degradation of cell-wall components, a common feature of ancient wood samples, can facilitate this collapse. In fact, air-dry moisture contents of ancient wood are often lower than for modern material (Kohara 1956). In the case of the ancient kauri, however, the combination of low moisture content and hemicellulose degradation imparted lowered strength properties.

Results of static bending tests indicated that the ancient and recently felled kauri exhibited differences in mechanical behavior both below and above the PL of the static bending curve. Below the elastic limit, MOE and WPL values for the ancient kauri were significantly lower than the recently felled kauri values. Not only was the ancient kauri more readily deformed, but not as much energy was needed to reach the proportional limit of the wood. At the molecular level, movement of the polymers within the cell wall is controlled by steric hindrance and bonding characteristics. For the ancient kauri, degradation of carbohydrates had likely altered the tightly bonded network of hydrogen and covalent bonds within the cell wall. Not only had cellulose depolymerization reduced the number of covalent bonds within the microfibrillar structure, but removal of hemicelluloses probably resulted in the cleavage of lignin-hemicellulose bonds. These structural changes could have facilitated the rotation and twisting of molecular components within the cell wall, resulting in plastic deformation of the ancient kauri wood.

Beyond the PL, MOR and WML values indicated that the cell walls of the ancient material were less brittle than the cell walls of the recently felled kauri. Because the flexible cells of the ancient kauri had a lower ultimate strength (MOR), more work (WML) had to be done to actually fracture the material. SEM of the fracture surfaces revealed that cell-wall fracturing behavior differed between the ancient and recently felled samples. Under load, stress is elastically transferred along the tracheids and cell-wall material until a discontinuity is reached. At the site of the discontinuity, stress will build and cracks eventually develop (Winandy and Rowell 1984). At a cell-wall level, the fracturing of wood can take several forms. Schniewind (1964) described the cell-wall structure as a less rigid S_2 layer bounded by more rigid S_1 and S_3 layers. Lignin, highly concentrated in the middle lamella, effectively holds the cells together under load. Due to the strength of the lignin matrix, failure will occur in the carbohydrate fraction of the wood (Winandy and Rowell 1984). For this reason, failures usually occur within the cell wall, rather than the lignin-rich region between cells.

This fracture behavior was noted in the recently felled kauri samples. The secondary cell-wall fracture surface was cleanly broken, with cellular distortion at the S_1-S_2 interface. Therefore, stress was distributed within the cellular matrix up to a critical point, at which time the stress was rapidly released through a clean fracture of the cell wall. By contrast, SEM of the fractured ancient kauri surfaces vividly revealed degradation of the woody cell wall within the S_2 layer. Because of carbohydrate degradation in the ancient kauri, as noted in chemical analyses, the cell walls could not evenly distribute stresses. Degradation of packing material (hemicelluloses) from around the cellulose microfibrils loosened the cell-wall structure. Note that some ancient kauri secondary cell walls are divided into lamellae-like structures, indicating that cellular components have been removed from between the microfibrillar sheets (Fig. 7).

This structural disorganization resulted in stresses building up at voids and discontinuities within the cell wall, causing cellular distortion. With applied load, the microfibrils could shift in orientation and lose the ability to effectively transfer and resist stress. Stress was incrementally relieved by gradual tearing of this secondary cell-wall material, giving the fractured surfaces of the degraded ancient kauri a very porous, rough appearance. Pinholes in the S_2 layer are evidence of microfibrillar strands being pulled from the surrounding matrix, a feature that was not evident at the recently felled kauri fracture surface.

In addition to the losses of hemicellulosic material, chemical analyses revealed a decrease in the degree of cellulose polymerization. Since the microfibrils serve as the strength component of the cell wall, the effect of this depolymerization would be manifested in lowered strength properties. The MOE and MOR values for the ancient kauri wood were significantly lower than the corresponding recently felled wood strength values.

By contrast, the ancient kauri lignin remained essentially unaltered in structure or chemistry. Serving as the stiffening material of the cell, the lignin continued to hold adjacent cells together under load. However, the degradation of the other cellular components had offset any advantages that the stiffening properties of lignin could provide.

Ancient kauri wood did not follow the specific gravity-stiffness trend. Despite a higher specific gravity value than the recently felled material, the significantly lower MOE values for the ancient kauri revealed a loss of stiffness over time. This variation in the specific gravity-stiffness trend may be explained by the natural variation of wood structure within species. In this manner, even with degradation of cellular components, the density of ancient wood may still be higher than the same-species modern material (Schniewind 1990).

CONCLUSIONS

Chemical and physical tests revealed that the structure of the ancient kauri cell wall had been modified. Because of carbohydrate degradation, structural disorganization prevailed in the ancient material. Rather than the bonds within the composite material imparting strength properties, the ancient wood had a decreased ability to withstand deformation. This increased plasticity is reflected in the significantly lower MOE and WPL values of the ancient as compared to recently felled kauri wood. The amount of work needed to reach the PL is lowered, because the material is more readily deformed.

Since depolymerization of the carbohydrates had already been chemically initiated in the acidic swamp, the cell wall fractured more readily under load. The MOR of the ancient wood was significantly lower than the

MOR value for the recently felled kauri, indicating that flexible cells had a lower ultimate strength. However, because of this plasticity, more work must be done to actually fracture the material. The significantly higher WML value for the ancient wood indicated that the ancient material did not resist stress; rather, the structure gradually "gave way" under imposed stress.

Scanning electron microscopy of the fractured ancient kauri surfaces shows this loss of cellular organization. Whereas the secondary cell wall fracture surface within the recently felled kauri wood was cleanly broken, the fractured surface of the degraded ancient kauri exhibited a very porous appearance. Because the ancient kauri S_2 layer was weaker than the recently felled kauri S_2 layer, the stress was incrementally relieved by gradual tearing of this secondary cell-wall material. However, serving as the stiffening material of the cell, the essentially unaltered lignin continued to hold adjacent cells together at the middle lamella.

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