Water in archaeological wood : a critical appraisal of some diagnostic tools for degradation assessment.

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Water in Archaeological Wood:

A Critical Appraisal of Some Diagnostic Tools for Degradation Assessment

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Abstract

Waterlogged wood conservation is ultimately directed towards effective drying of artefacts, since through this procedure is the best hope for their stabilisation. This is a much more risky activity for the conservator than it is for the modern timber technologist, because of the extreme chemical and physical changes the material has undergone during its burial. Nevertheless, we already have a number of adequately successful methods for the conservation of archaeological wood. What we don't have is all the information we might want for the modification of these techniques to provide fully predictable results for the widely variable material which comes in for treatment, or for the economical treatment of large structures and bulk assemblages. The conservator's primary concerns are with permeability, diffusion rates, drying behaviour, and internal surface calculation, all of which depend on the wood's chemical preservation, and are mirrored in its sorption characteristics.

Wood-water relations of archaeological material have not as yet received much attention from researchers, and the chemistry of this material only slightly more. The findings of wood science can not be assumed to apply to archaeological material where radical chemical change has significantly changed its properties. This thesis addresses this problem by providing a comprehensive and critical synthesis of past and current research from the fields of waterlogged wood conservation, wood technology, chemistry, and microbiology, wood degradation, and wood-water relations. One of the outcomes of this work was the bringing to light of evidence for a much greater role for anaerobic decay vectors than has up to now been acknowledged. This only serves to emphasise the very real need for more research in the water relations and degradation chemistry of archaeological waterlogged wood, and perhaps even more for research into the development of assessment techniques specifically designed for this material, and easy and inexpensive to apply for the practising conservator. This thesis investigates the development of such techniques and compiles a critical review of a number of the techniques already in common use by conservators and wood scientists. The designs for a simple, accurate sorption measuring apparatus are given, and the results from a large group of archaeological wood samples reported. From these results it is determined that the controlling factor in the water relations of this material appears to be bulk mass losses rather than changes to chemical constituent ratios.

Alternative diagnostic tools which have the potential of obtaining indirect information about wood-water relations indirectly are also critically appraised. The results from bulk chemical analyses are compared to those from physical tests of density, moisture content, and strength measurements. Results from Sibert resistance drill trials and polarising microscopy are appraised. Certain findings from these contradict some of the assumptions which underpin our models for calculating internal void space in archaeological waterlogged wood which are used in defining our conservation treatment approaches. Three techniques of instrumental analysis are also examined. The results from FTIR, Py-GC/MS, and elemental analysis reveal a number of useful and easily-recognisable markers for degradation. A series of important new markers for syringyl lignin degradation arise from this study. In the final appraisal, preference lies with these latter diagnostic tools, and arguments are provided for their greater accessibility to the conservator.

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The only portion of this research published prior to completion of this thesis is the co-authored work reported in Chapter 8, section 8.4.4.5, identifying new degradation markers (methoxy catechols) from Py-GC/MS studies of degraded woods (van Bergen *et al*, 2000). In this work, the larger proportion of the analyses were carried out by Ogilvie, while the major proportion of the interpretation was the work of van Bergen.

Introduction

The basic question underlying this research project is whether it is possible to devise a method that is both non-technical and inexpensive (in terms of time, equipment, and materials) for the working archaeological conservator to utilise to find out what he needs to know about a piece of deteriorated wood in order to assess how to treat it.

Like many other archaeological materials, waterlogged wood is no longer the same substance that the materials scientist would call wood. Both physically and chemically, the material has undergone a number of significant changes. For this reason, it lies with archaeological and conservation scientists to, in a sense, re-define this material so that improvements in the field of waterlogged wood conservation can go ahead.

Up to this point, conservation treatments have largely centred themselves around bulking out cell walls in order to provide a support for them once the water which had become their support in lieu of the cell wall chemicals lost through degradation, has evaporated during drying. New understanding about chemical changes to this material may change this so that treatments become more specifically aimed at treating only those chemical and structural elements which are left. But in the meantime, the conservator is in need of new ways of understanding how to get bulking chemicals into wood and water out of it, quicker, less expensively, and with more predictable success.

Wood-water relations are thus at the centre of our understanding of these processes. Permeability, diffusion rates, drying behaviour, and internal surface calculation all depend on the sorption characteristics of the wood. The initial brief of this thesis work was to investigate the designing of a simple sorption apparatus, accessible as far as materials to most conservators, and able to produce data of good quality, either for artefact appraisal or for conservation research. This is the subject of Chapter 5.

As researched progressed, it became more and more apparent that sorption analysis of wood is fraught with logistical and theoretical difficulties. There is therefore an urgent need for alternative diagnostic tools which the practising conservator can use to obtain information about wood-water relations indirectly--without the problems associated with lengthy sorption analysis, and more accurate and reliable in their results. An array of such diagnostic tools already exists and is investigated in this thesis. Critical appraisal is given to their ability to fit these needs. Tests of physical characteristics are discussed in Chapter 6, techniques of bulk constituent analysis in Chapter 7, and the results from instrumental analyses in Chapter 8.

Chapters 1 through 4 contain a detailed synthesis of past and current research from the fields of wood technology, wood degradation, wood-water relations, and waterlogged wood conservation, because little effort yet has gone into bringing together the aspects of each of these disciplines salient to the concerns of archaeological wood conservation.

1 Wood as Material: Structure and Properties

1.1 Introduction

We need to understand the structure of wood before we can understand its characteristic and non-characteristic degradation paths, its complex relations with water, and the reasons for success or failure of the conservation treatments given to it. The discussion which follows is drawn largely from the following standard texts of wood science and technology: Desch (1981); Fengel and Wegener (1988); Hoadley (1980, 1990); Kollman and Côté (1968); Stamm (1964).

Wood is still one of our most strong engineering materials. Its ability to accommodate use stresses and to resist the biological, physical and chemical affects of ageing are extraordinary and built into the organisation and structure of the material while still part of the biological unit-- the tree. The tree is composed of root system, trunk and crown. Most wooden artefacts we recognise as archaeological wood have been fabricated from trunk or *hole* wood. *Branch wood* may turn up as part of wattle construction, and *root wood* as bindings, but as these materials can have quite significant differences in structure and composition, discussion in this thesis will centre around trunk wood.

Trunk wood is built up in layers. (Figure 1.1) Bark, phloem (inner living bark), cambium, and xylem are all designed to protect the wood material from degradation. The xylem, is composed of a particularly efficient combination of vertically- and radially-oriented arrangements of differentiated tissues that, although dead, take care of the load-supporting and liquid-conducting needs of the tree. It is also the broadest region of tissues in the tree. It is this region of the tree, the xylem, whose physical structures and chemical composition yield the requisite density, strength, flexibility and distinctive appearance to make a particularly suitable material for artefact construction. The other layers are usually removed before construction takes place and therefore are not generally included under the term *wood*.

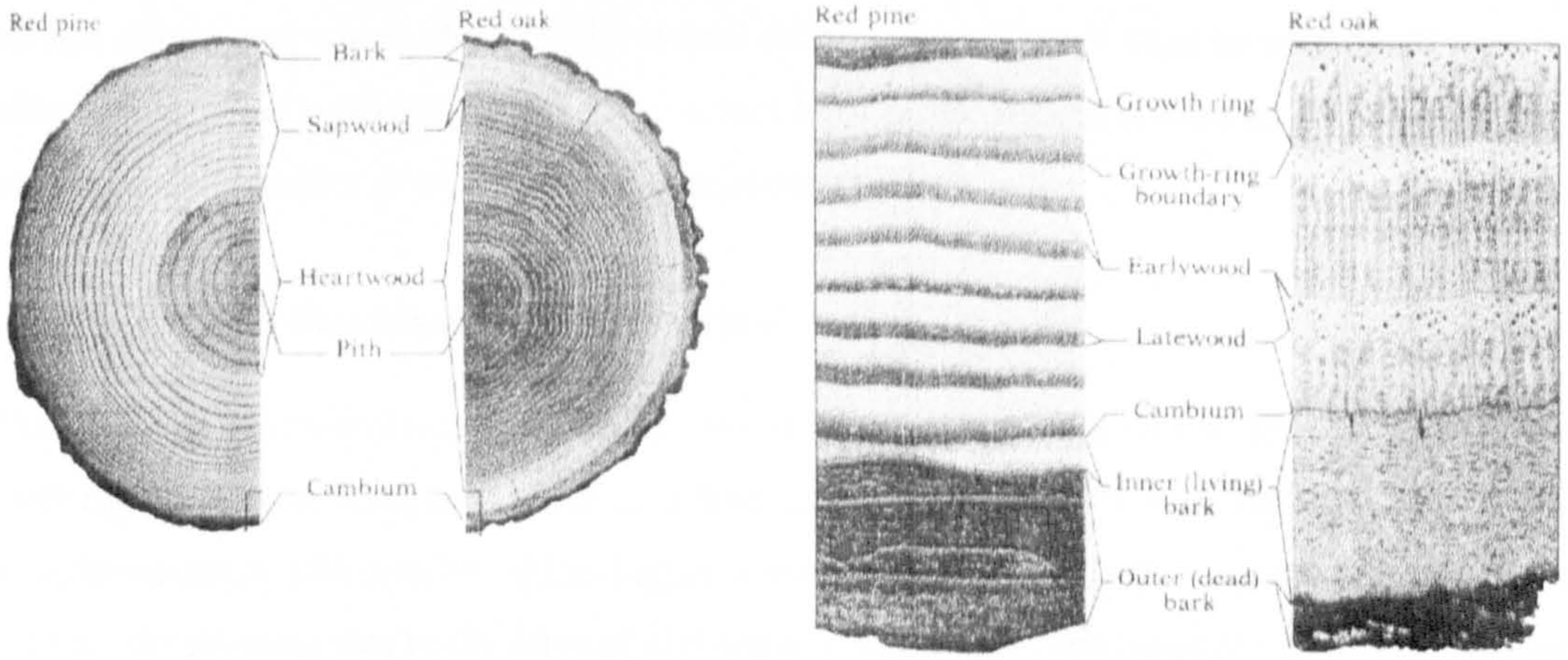


Figure 1.1 **Tree cross-section** **(Hoadley, 1980)**

Different species of trees yield wood with different tissue arrangements and small, though nevertheless significant, variations in chemical composition. Wood chosen for artefact manufacture reflects the workman's understanding of these structural differences, both in terms of mechanical aspects such as workability, durability and flexibility, and in aesthetic characteristics such as grain. Possibly the most common species of wood to turn up in archaeological material from sites in Northern Europe, partly because of its natural inherent working qualities, and partly because of its native high durability, is oak wood (*Quercus robur*). Because of its chemical and structural properties it is also one of the more problematic of woods for the conservator to treat. This chapter investigates the subject of structure in oak wood more deeply (Figure 1.2), in order to provide a basis for explaining deterioration phenomena and problems in our approach to the conservation of archaeological wood.

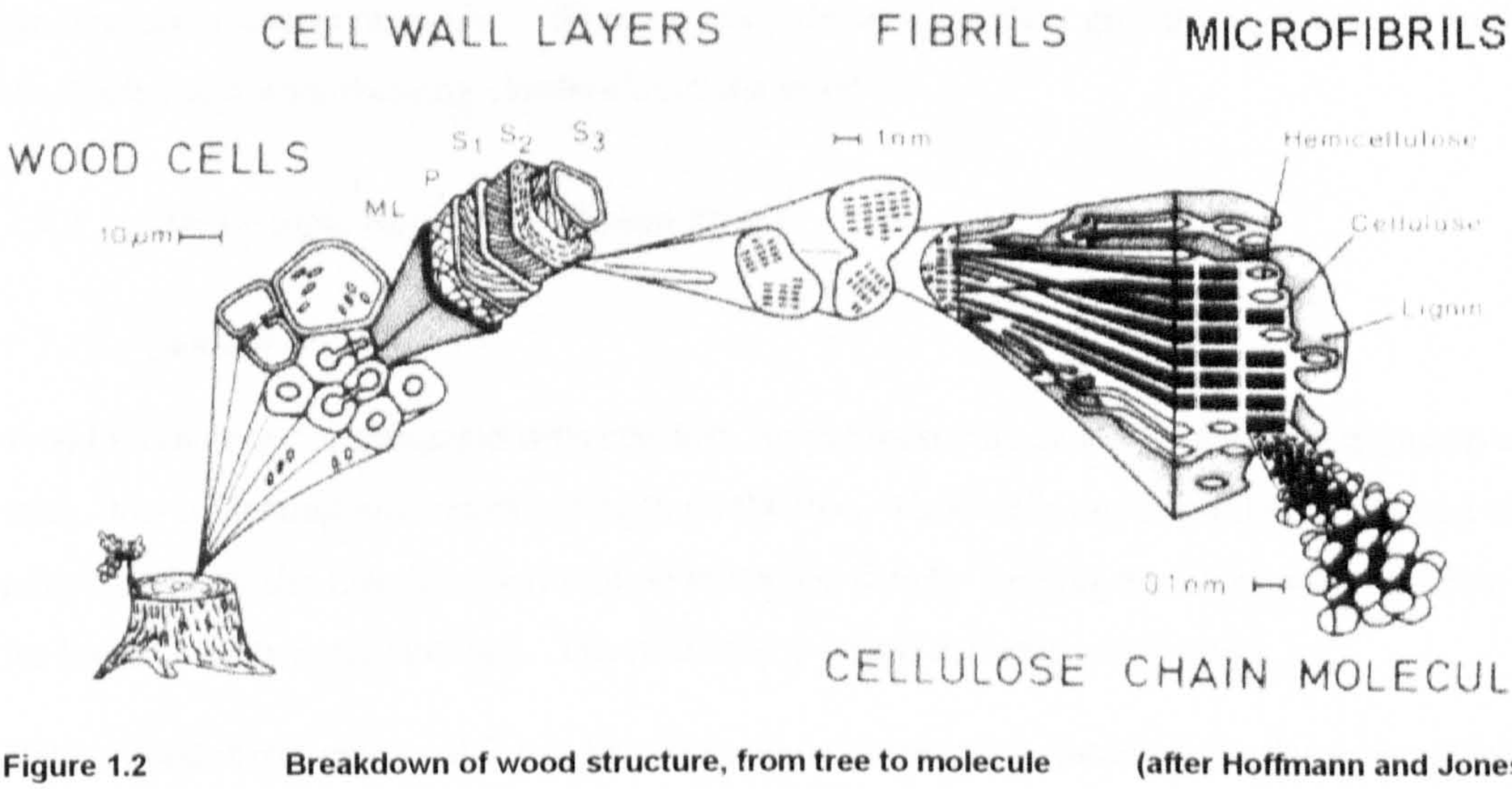


Figure 1.2 **Breakdown of wood structure, from tree to molecule** **(after Hoffmann and Jones, 1990)**

1.2 The Physical Organisation of Wood

Perhaps encouraged by the relative bulk uniformity of its chemical makeup, we often discuss wood as though it were a single, uniform material,. In physical terms, however, there are structures in wood that are specialised for different functions in the living organism, some of which are specific to certain species of tree, and whose effect on the overall deterioration of wood must be considered separately. In other words, wood's physical or *macro*-structure must be considered at least as important to the properties and stability of wood as its chemical construction.

1.2.1 Physical Organisation in Xylem Wood

The xylem layer in wood is divided up into two distinct regions with very different characteristics. The outer region of cells, lying next to the cambium, and lighter in colour, form the *sapwood*. Sapwood may be made up partly of live cells. It has higher water content than the other layers of the tree and stores food for the growing tree in the form of carbohydrates (starch). The inner or central layers of the xylem are called the *heartwood*; this region often appears darker in colour than the external wood, the result of the deposition of extractives in its cells. Extractives serve as waterproofing and help resist decay. Both

sapwood and heartwood act to give structural support to the tree, but it is the heartwood, with its load-supporting fibres and water-conducting vessels, that makes up the composite material we most often meet in artefacts. Sapwood is usually removed along with the other outer layers (bark and phloem) before construction of the artefact takes place. Rougher structural timbers may be found to have undergone less working and be left with their sapwood still in place.

Xylem cells, while participating in the living functions of the whole system, are for the most part *dead* in biological terms (i.e., are without cell contents). The cells that were laid down earlier in a growing season (*earlywood*) tend to be larger and thinner-walled than those laid down later on (*latewood*), so that there are inequalities of density throughout this layer. Because these inequalities are regular in occurrence, they appear as concentric or *growth rings*. Since trees growing under differing environmental conditions grow at differing rates, the width of their growth rings varies as well, effecting the density and water-bearing capabilities of the wood.

1.2.2 Macroscopic Structure of Xylem Wood

1.2.2.1 General

Wood is composed of elongated cells oriented, for the most part, in the longitudinal direction of the stem, thus conferring mechanical strength on the tree. These cells are connected end-to-end via *sieve plates*, and laterally through a series of pit openings, thereby forming a continuous conduction system for liquids—both water and food. The cells vary in shape according to function.

Xylem wood is common to all trees, but distinctions in botanical classification, for example softwoods (*Gymnosperms*) and hardwoods (*Angiosperms*) (Figure 1.3), reflect a certain amount of significant difference in the tissue arrangements within xylem wood.

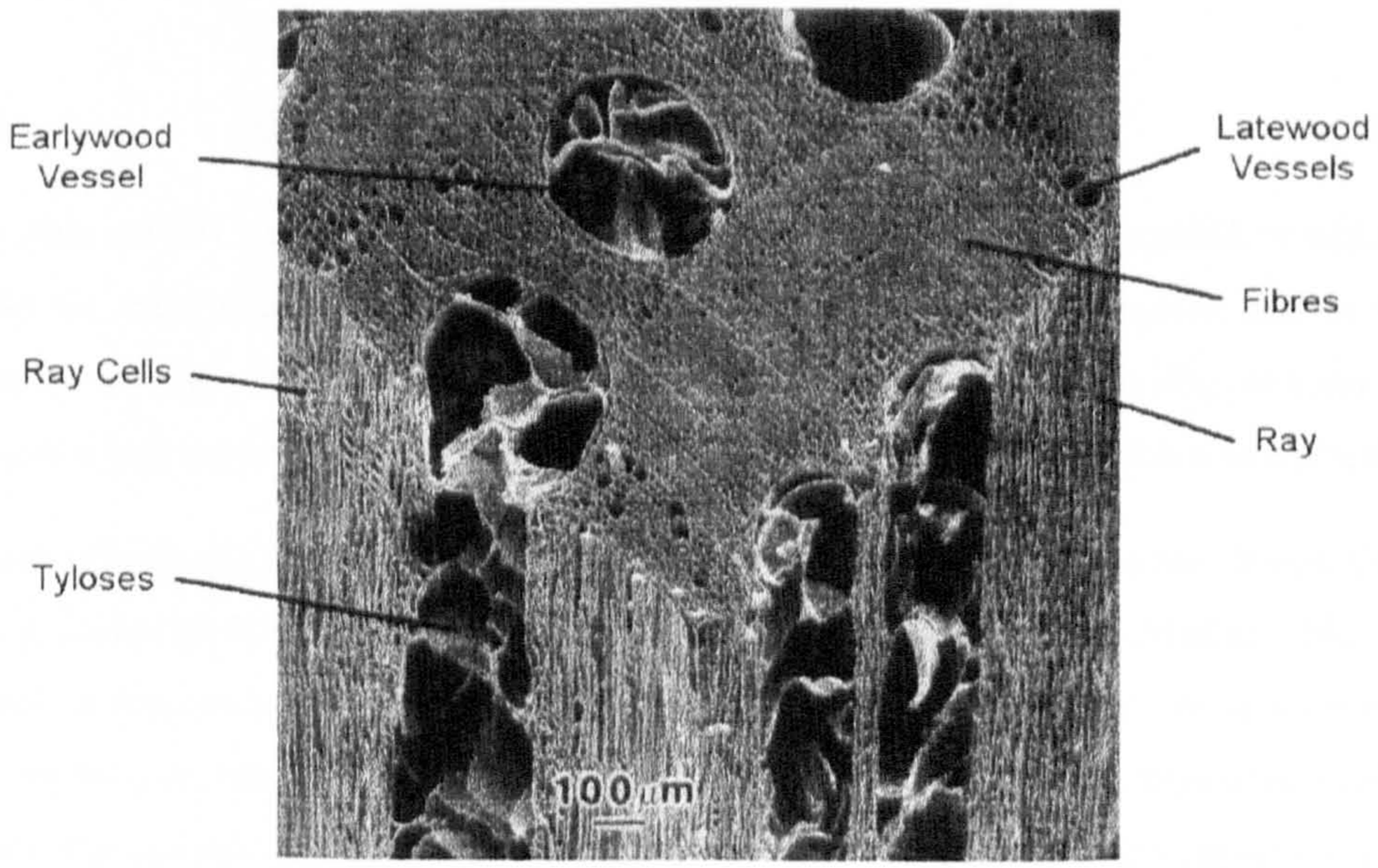


Figure 1.3 **3-D sectional view of *Quercus rubra* xylem showing main structural features (after Zabel and Morrell, 1992)**

The conservator of wooden artefacts is concerned to maintain or augment the *supporting* ability of what has become a rather deteriorated macrostructure, and attempts to take advantage of the *conducting* abilities of wood tissues to achieve this.

1.2.2.2 Tissue arrangements/cell types

There are three main cell types in the xylem wood of hardwoods such as oak:

1. the water-conducting tracheary elements, *vessels*;
2. the supporting *fibres*; and
3. the metabolic or storage tissues called *ray parenchyma*.

The characteristic morphology of these is displayed in Figure 1.4 below.

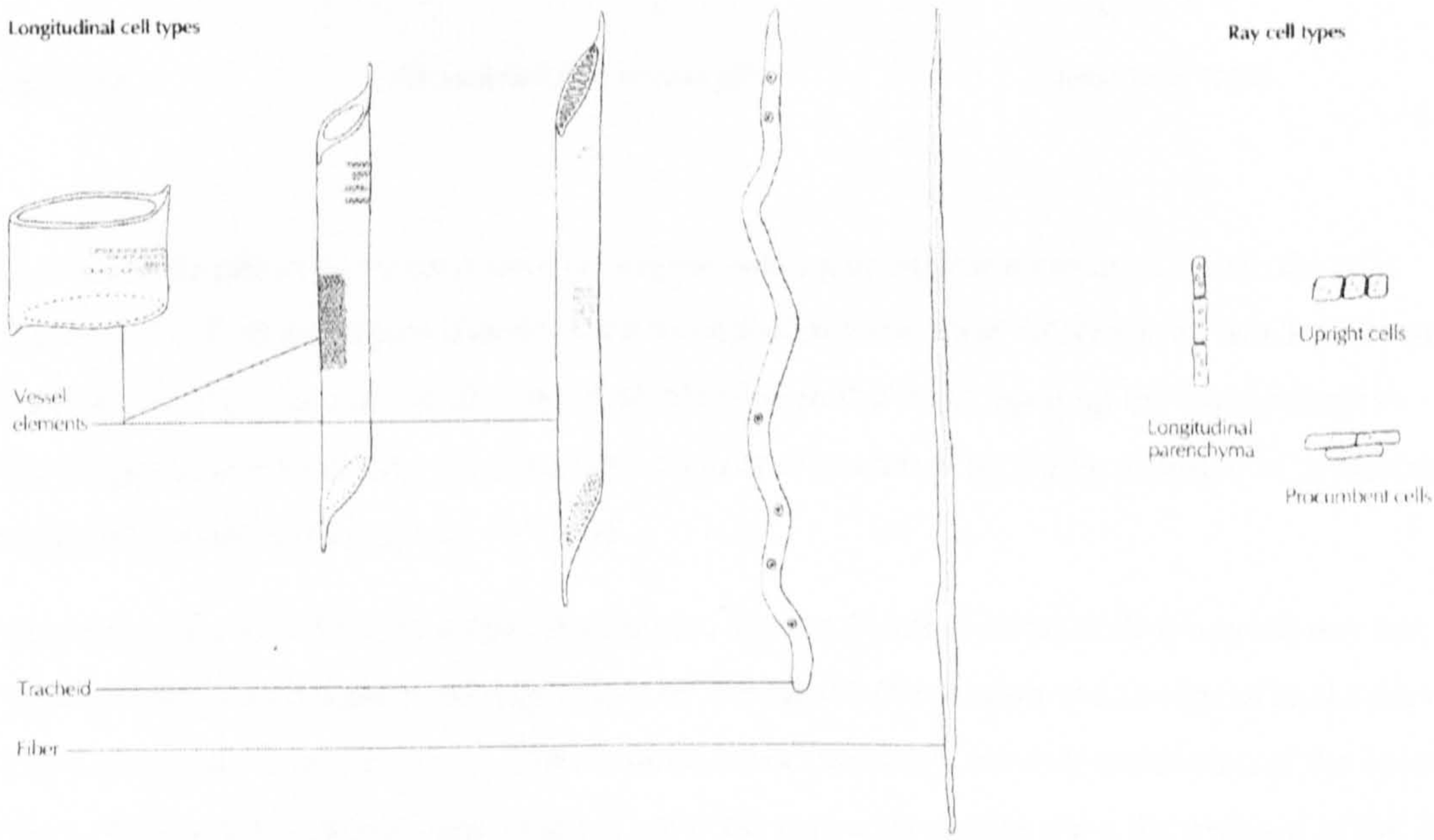


Figure 1.4 Morphology of the three main types of cell in hardwoods (after Hoadley, 1990)

The fibre cells of hardwood tissues are short, narrow and tubular, with pointed, closed ends and thick walls; for these reasons they are well-adapted to physically support the vessels and the wood in general. They have simple, narrow pits and their walls may be lignified (which is why, in some cases, the fibres of hardwoods may remain after deterioration of the rest of the structure has taken place).

Vessel cells are generally shorter,broader and thinner walled than fibre cells, though they can differ in size in early and latewood (as in *ring porous* woods such as oak) with a resultant effect on the overall density and porosity of the wood. Vessel cells (*members*) are laid end-to-end to make up the long conductance vessels of hardwoods, and their open ends are separated by membranes called *perforation plates* that can take various forms depending on species. These plates are important to the condition of the wood, since their breakdown can allow uninhibited access to the vessel system for solvents and for bacterial and fungal byproducts. The open ends of vessels in cross section are referred to as *pores*.

The walls of vessels contain many *simple pits*. Pits are an important feature of all cells in wood. The flow of water from one cell to the next is controlled by these structures. When wood is under stress these pits will tend to *aspirate* or close off the conducting tissue so that uncontrolled moisture loss or ingress is prevented. The relatively small size of pits has an indirect effect on the distribution of oxygen throughout wood, which means that any deteriorative mechanism that relies on oxygen (e.g., microorganism decay, photo-oxidation) is likely to be reduced in its effect as it gradually works its way inward (Grattan 1987).

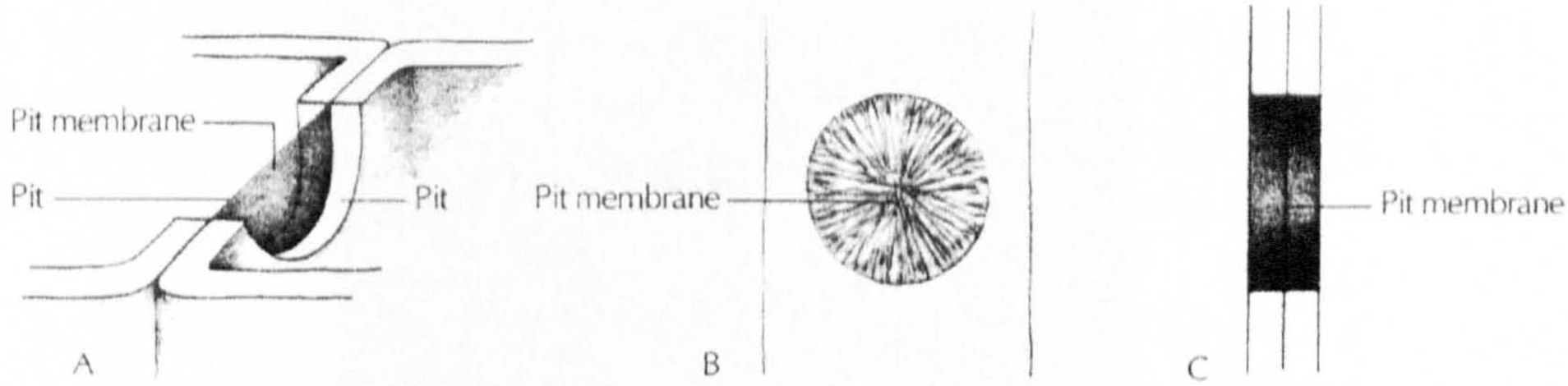


Figure 1.5 **Pit aspiration in simple pits** **(Hoadley, 1990)**

In general the pits in *heartwood* have undergone sealing or *aspiration* so as to isolate the cells (Figure 1.5). This undergoes change when biological and chemical deterioration attack pit margins, and the effect of this is to increase the rate of degradation in the wood, open up the wood system to waterlogging, and indirectly, improve the prospects of treatment by aiding diffusion of conservation treatment chemicals throughout the wood.

Extending into the xylem from the cambium are distinct bands of living cells (*parenchyma)* one or more cell wide, that are thought to be responsible for the lateral distribution and storage of food reserves and waste materials. These are *rays*. The combination of the *axial* (vertical) orientation of the vessels and fibres of the *xylem* with the radial orientation of the rays cells confers upon the material of this layer a great deal of additional strength, as well as some of the complications inherent to the anisotropism thereby produced.

Ray cells are thin walled and heterogeneous in size and shape in hardwoods such as oak. They radiate out from the central pith of the tree to its outside and provide pathways for liquid flow at right angles to the longitudinal vessel/tracheid systems

They are connected to the longitudinally-oriented cells by pits. However, since the ray cells contain food reserves that can attract bacteria and fungi, these pits can also permit free access of these organisms and their byproducts (e.g., enzymes) throughout much of the system of the wood tissues. Thus the destruction of pit membranes is often the cause of much of the increased permeability of degraded archaeological wood. The deposition of calcareous material or iron compounds, however, may have the opposite effect—i.e., to cause the blocking of pores and the reduction of permeability (Grattan 1987). In hardwoods, especially in *Quercus* spp., the commonest cause of impermeability are *tyloses* (Figure 1.6),

tissue outgrowths that enter vessels from neighbouring ray cells (Sjöström 1981), obstructing the passage of liquids (including treatment solutions applied by conservators) to the interior of the wood.

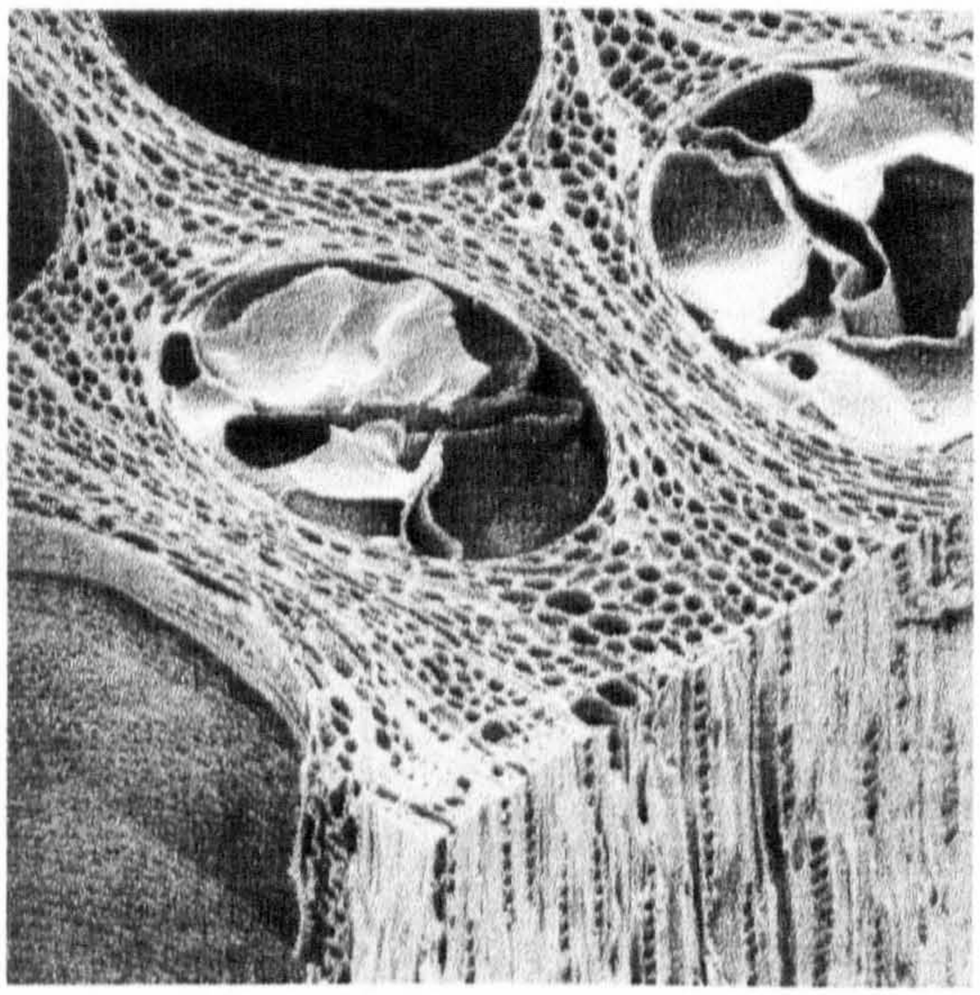


Figure 1.6 **Tyloses in oak wood** **(Core *et al.*, 1979 in Hoadley, 1980)**

1.2.3 Cell Wall Organisation

The cell walls of both tracheids and vessels are laid down in two distinct phases: first, or outermost, the *primary cell wall*, with a random orientation of fibrils that allows the wall to change shape, and then three layers of *inner secondary thickening* that give structure and strength to the cell wall by the opposite orientation of their fibrils and their differing angular directions (Figure 1.7).

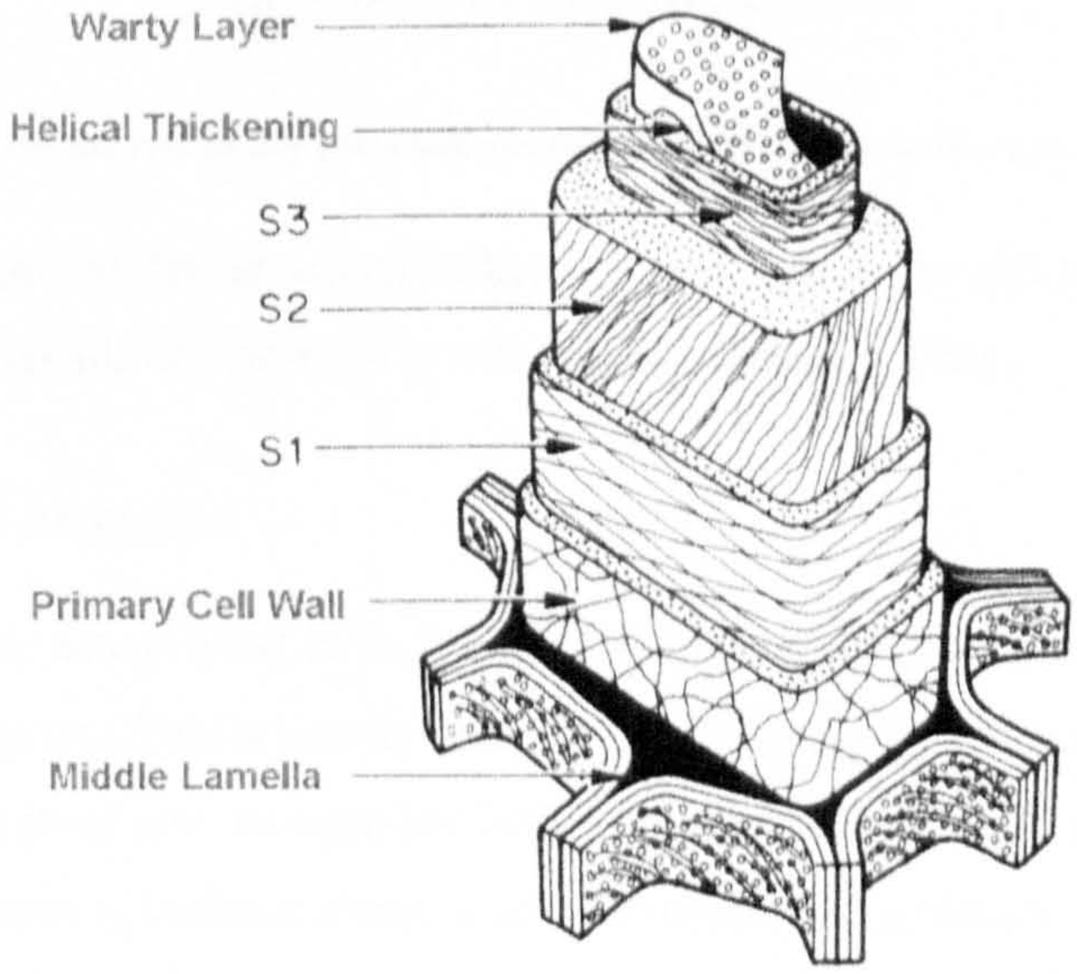


Figure 1.7 **Layers and fibre orientations in the cell wall** **(after Côté, W.A., 1965)**

The primary wall is the thinnest of the layers, 0.1-0.2µm thick. Between the primary walls of adjacent cells lies the cementing layer of the *middle lamella*, a mixture of resilient and protective lignin and hemicellulose. These two layers, primary cell wall and middle lamella, are lumped under the term *compound middle lamella*. This layer is 0.2-1.0µm thick. The three secondary cell walls, known as S1,

S2 and S3 lie just inside the primary cell wall. The S1 (0.1 μm thick) and S3 layers (0.2-0.3 μm thick) are thin, and the S2 layer much thicker (1-5μm thick). The layers differ from one another, not just in thickness and fibre orientation but, more significantly (as can be seen in Figure 1.8 below) in their chemical composition.

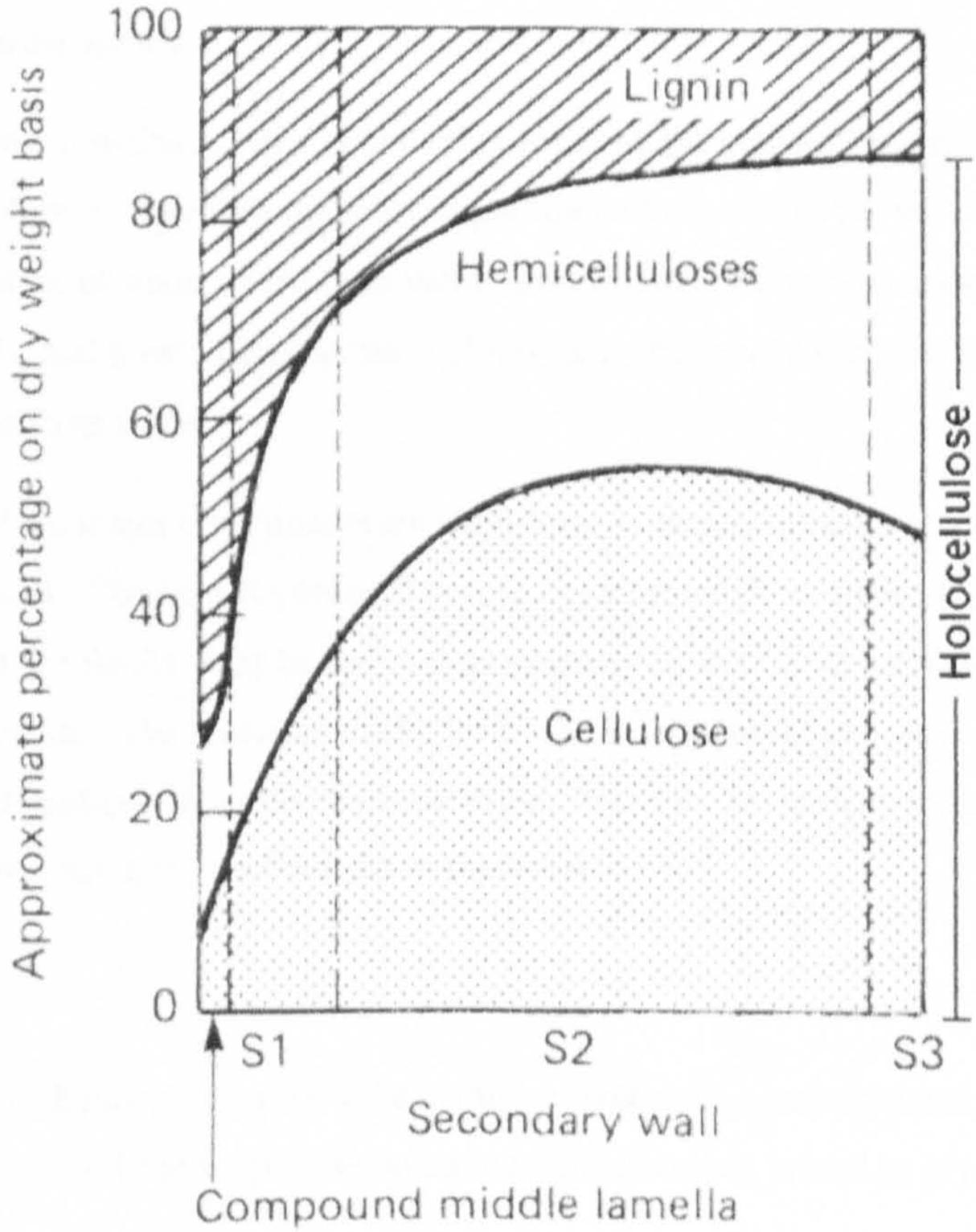


Figure 1.8 Distribution of the principal chemical components in the cell wall layers (Grattan, 1987)

Innermost of the cell-wall layers, which makes up the surface of the cell *lumen*, is the very thin, *warty layer*, whose function and composition is still unclear (Sjöström 1981).

1.2.4 Structural Anomalies

It is possible to come across wood in archaeological artefacts or structural timbers that is atypical in structure and properties. This is usually *reaction wood*, formed by special tissue grown as a tree attempts to reorient itself after its stem has been displaced. In hardwood species, it forms as *tension wood* on the upper side of inclined stems, leading to contracted structure. Reaction wood tends to be slightly heavier, harder, and denser than normal wood, since its cells have shorter lengths, increased wall thickness, and differences in the relative thickness of cell-wall layers (e.g., S1 is thicker than normal, S3 absent, and S2 contains deep helical cavities). The cellulose content of this wood is slightly higher, and its lignin content lower than normal wood. Despite its increased density, reaction wood is much weaker, chemically and physically, than normal wood and has a greater tendency towards

dimensional change. Its presence can be recognised by radial checks occurring in the transverse section of fibre walls (Côté and Day 1965).

1.3 The Chemical Organisation of Wood

1.3.1 Wood Ultrastructure

There are three main constituents or fractions that make up the cell-wall matrix in wood: cellulose, hemicellulose and lignin. They are the most important contributors to the structural properties and chemical deterioration of wood. Further to these, however, are the extraneous substances: pectins, tannins, resins, oils, and a varying proportion of inorganic material called *ash* as a result of its usual method of isolation from wood.

The proportions of the major constituents are significant to the monitoring of level and cause of deterioration in wood. Their exact chemical nature has a lot to tell us about the role they play in the wood as a material, a role that may be lost and properties that may have been altered after the wood undergoes deterioration. The building blocks from which these wood polymers are constructed are also useful in analytical studies, where they provide the evidence for identification, understanding, and quantification of deterioration mechanisms in the wood.

1.3.1.1 Cellulose

The basic structural chemical of wood is the cellulose molecule, a carbohydrate polymer and polysaccharide, made up from ß -glucose monomers (aldohexose), joined by glycosidic linkages (Figure 1.9).

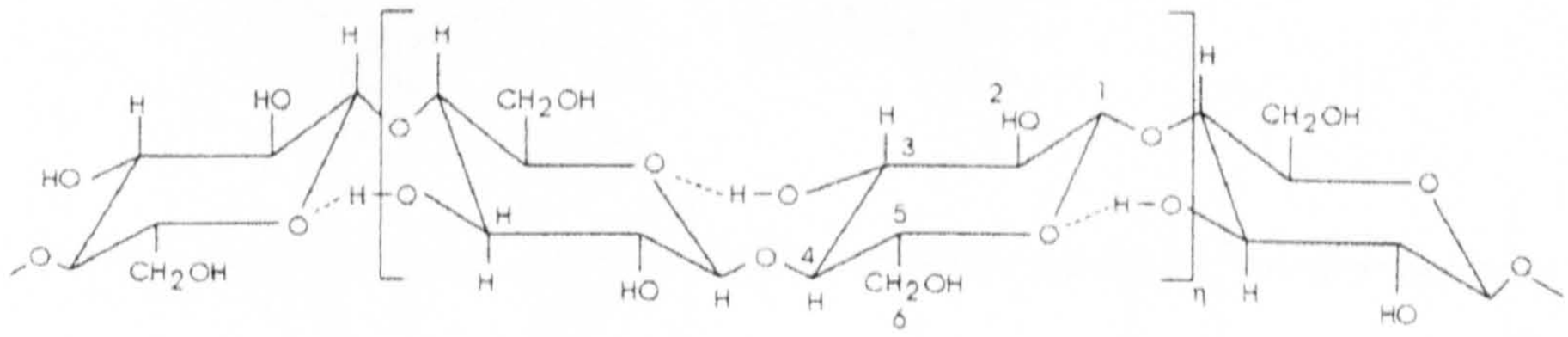


Figure 1.9 **Linking of glucose monomers** **(Kronkright, 1990)**

Because of the particular form of structural isomerism that they take, these monomers tend to form very strong linear chain polymers. The two stereoisomeric forms of glucose enantiomers, produce the characteristic birefringence cellulose exhibits under polarised light (Sjöström 1981).

Cellulose makes up 40-45 wt% of the cell-wall matrix (Hedges 1990), the majority of it located in the secondary cell wall.

Though the chemical structure of cellulose has been understood in detail for a long time, its grosser organisation (such as its crystalline and fibrillar structure) is still under debate (Sjöström 1981). Research organised around such analytical techniques as gas-liquid-chromatography/mass spectrometry

and ^{13}C nuclear magnetic resonance have been instrumental in clarifying some of these issues, though problems such as the exact size of the molecule, possible polydispersity between cell wall layers, and dimensions of microfibrils still remain unresolved (Tekely and Vignon 1987; Newman and Hemmingson 1990).

1.3.1.2 Hemicelluloses

Hemicelluloses are amorphous, short-chain carbohydrates, located throughout the structure of the cell walls of wood in mixtures with both lignin and cellulose and, as well, between the cells themselves. They differ from cellulose in having molecular chains that are branched and much shorter in length. Also, they are heteropolysaccharides, meaning that they may be polymerised from different proportions of their component monomers, unlike the homopolysaccharide cellulose. These constituent monomers are: D-glucose, D-mannose, D-xylose, L-arabinose; and in much smaller quantities, L-rhamnose, and D-glucuronic acid, 4-O-methyl-D-glucuronic acid, and D-galacturonic acid. Most of these average a degree of polymerisation of only 200 (Sjöström 1981). The principle hemicellulose in hardwood species is glucuronoxylan (15-30 wt%) (Figure 1.10), whose base hydrolysis is one of the primary reasons for the excess of acetic acid in hardwood species such as oak (Hedges 1990). The other hemicellulose present in hardwoods is glucomannan (2-5 wt%).

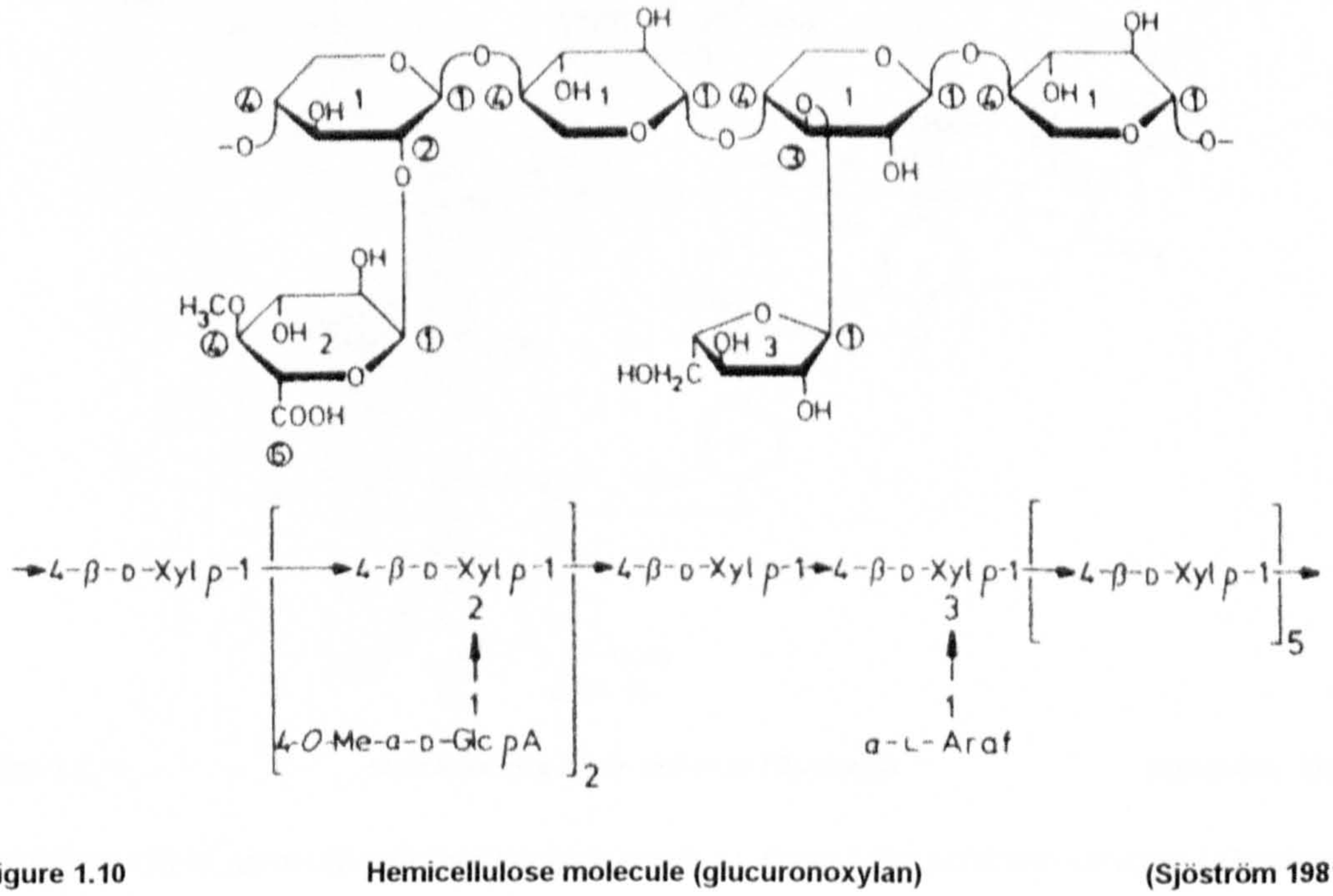


Figure 1.10 **Hemicellulose molecule (glucuronoxylan)** **(Sjöström 1981)**

In hardwood, they make up 20-30 wt% of the cell-wall matrix. Considerable variations also exist in their distribution and proportionation within different structures of the wood and layers of the cell wall. In hardwood xylans occur in in larger quantities in the S2 layer, explaining the greater susceptibility of this layer to degradation.

The hemicelluloses are thought to act as a protective hydrated coating that surrounds the cellulose fibrils and keeps them from undergoing too much crosslinking (Koshijima *et al.* 1989). Yet it is not thought that there is any chemical bond existing between cellulose and hemicelluloses, just a mutual adhesion provided by hydrogen bonds and van der Waals forces. True chemical bonding does, however, exist between hemicelluloses and lignin (Newman 1992), thus the separating of these components for chemical analysis can lead to errors in quantification.

1.3.1.3 Lignins

Lignins are polymers based on phenylpropane units, present in varying quantities in different types of wood—proportionally larger quantities found in softwoods than in hardwoods, and more in certain types of wood cell than in others, but in general something in the range of 20-30 wt% of cell-wall constituents. They are very large, aromatic polymers, amorphous in form, and highly insoluble in water (Figure 1.11).

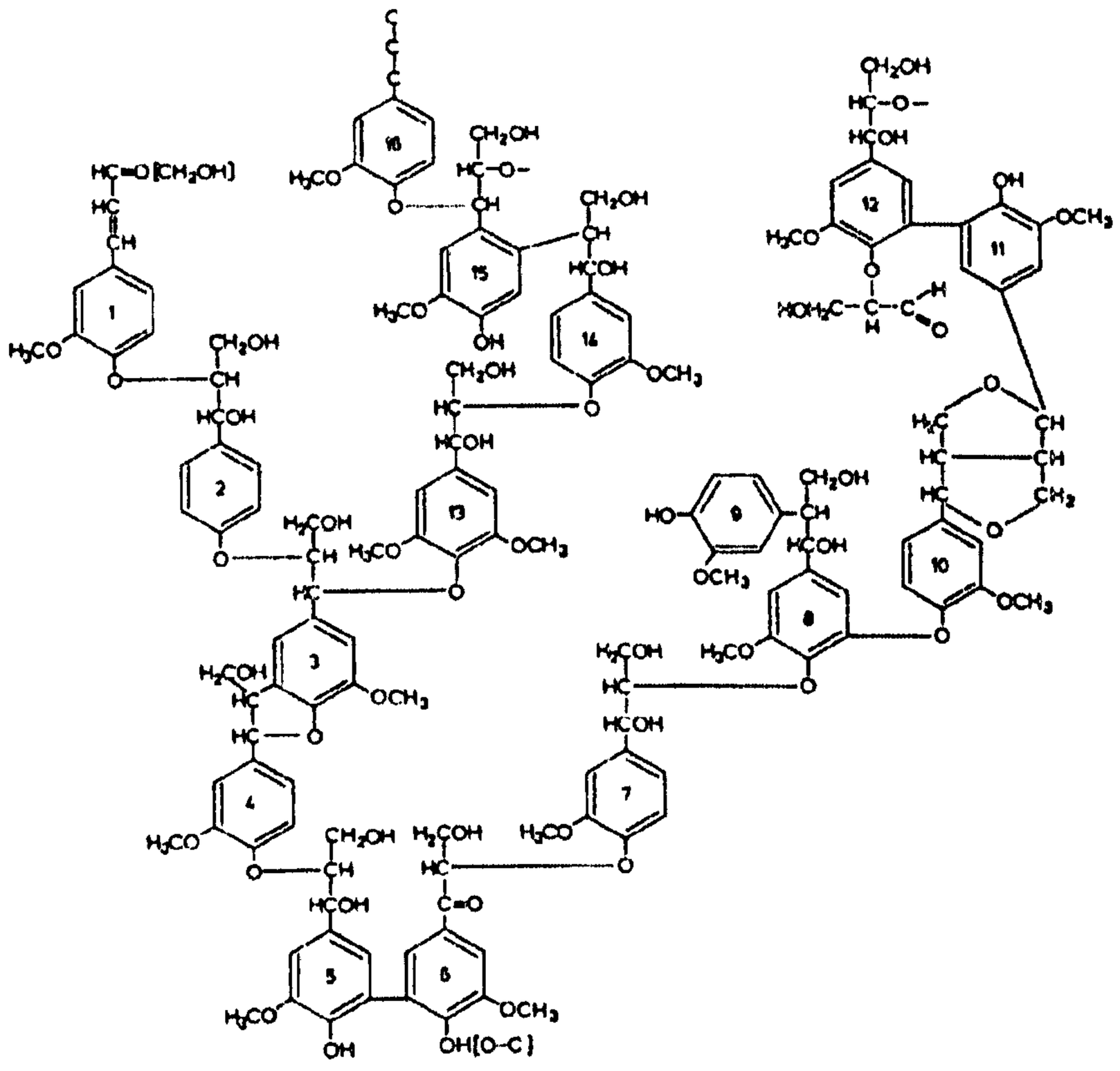


Figure 1.11 **Structure of a lignin polymer (Guaiacyl)** **(Sjöström, 1981)**

Many aspects of lignin chemistry remain unresolved, though the principal structural elements have been clarified within the last few decades. Work on lignin structure and polydispersity continues as the major field of current investigation in wood chemistry. Techniques such as ^{13}C NMR (Ede *et al.* 1990) and pyrolysis gas chromatography mass spectroscopy (Galletti and Bocchini 1995), as well as computer-aided molecular modelling (Faulon and Hatcher 1994) are gradually clarifying the more complex structural relations within lignin.

Lignins are produced from coniferyl, *p*-coumaryl, and sinapyl alcohols— three cynnamyl alcohols that differ only in the number of methoxy groups (-OCH_3) substituted on the benzene ring (Figure 1.12). They are joined by ether linkages in the majority and by carbon-to-carbon bonds to a lesser extent, in endwise polymerisation, resulting in a polymer with a low number of unsaturated side chains.

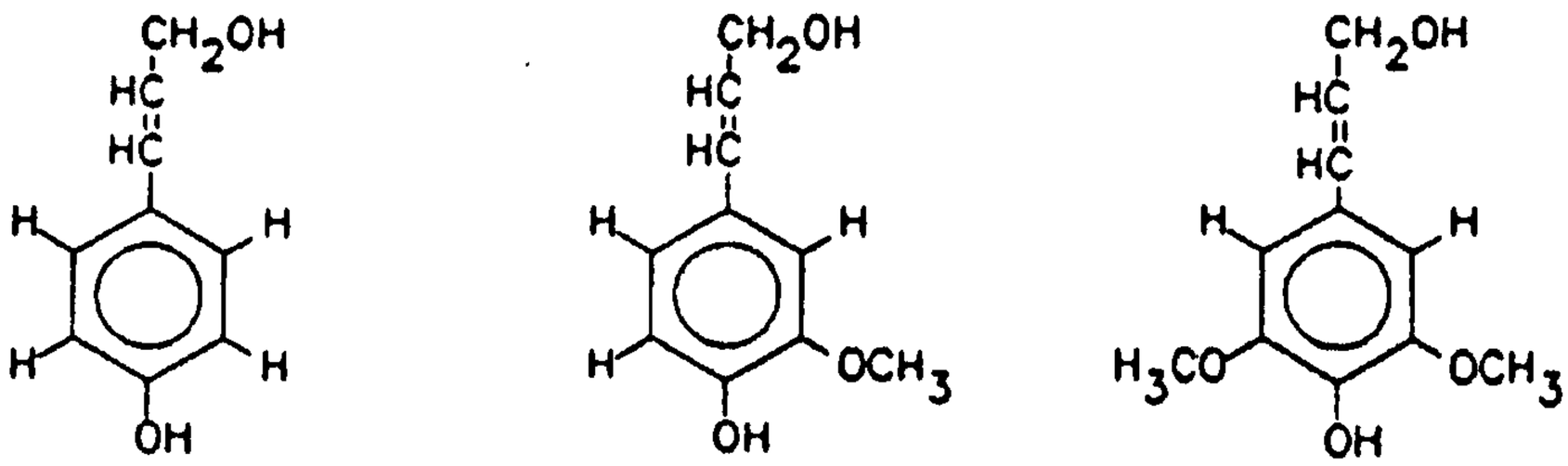


Figure 1.12 **Lignin precursors** **(Zabel & Morrell, 1992)**

The weight-average molecular weight of certain lignins appears to be slightly less than 20,000 for hardwoods.

Goring's model of lignin in its super-molecular state delineates it as a "random three-dimensional network polymer composed of phenylpropane monomers linked together in different ways" (Goring 1989), and distinguishes between middle lamellar lignin and secondary cell-wall lignin, the latter of which is a non-random two-dimensional network polymer. This view is contradicted by Faulon and Hatcher (1994) who propose a purely three-dimensional helical structure, interlinked by intermolecular hydrogen bonds, a model energetically favoured over random structures (Figure 1.13).

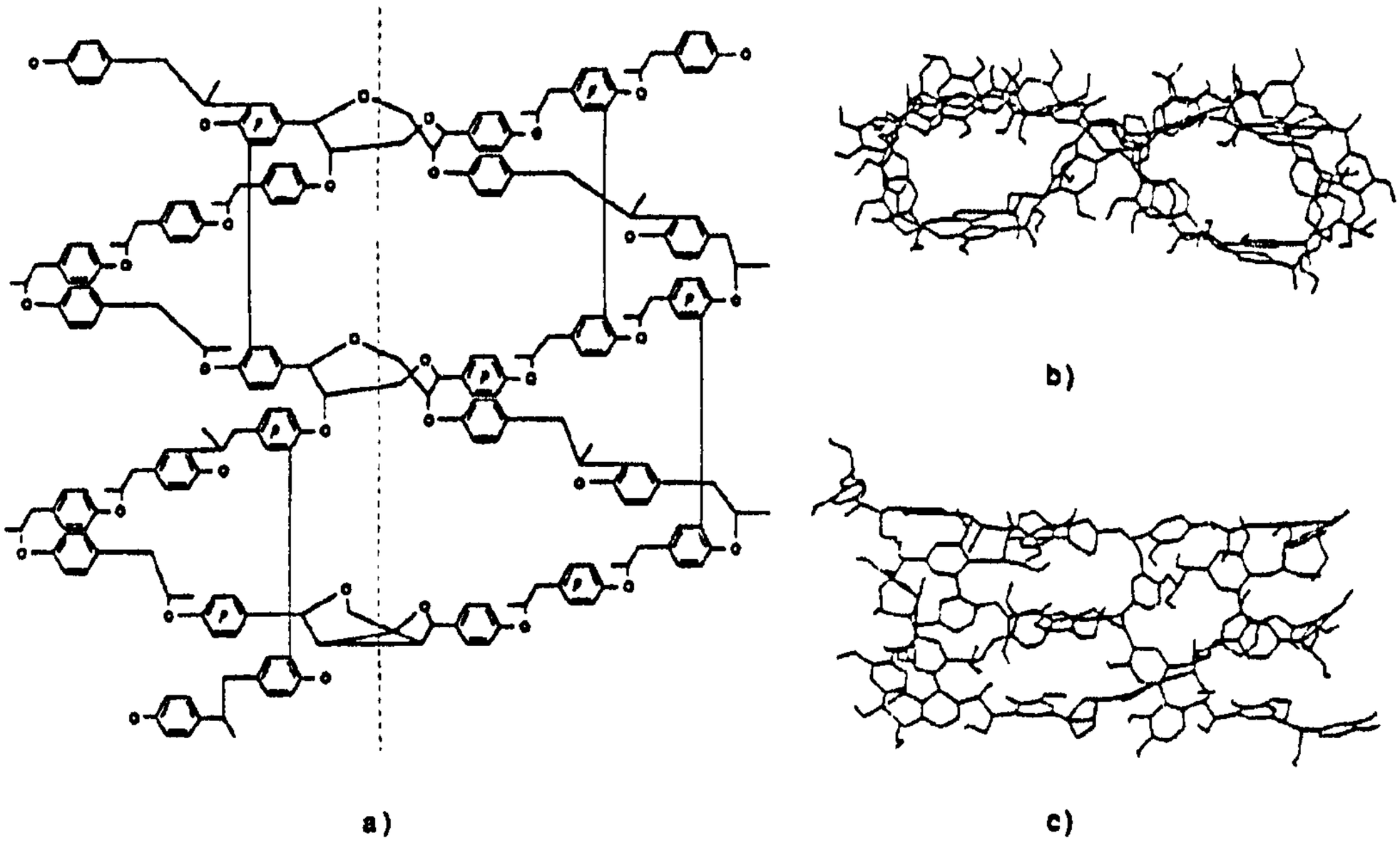


Figure 1.13 **Proposed Helical structure of Lignin** **(Faulon and Hatcher,1994)**

Further information on the macromolecular chemistry of lignin (such as molecular weight and polydispersity, as well as gravimetric studies) have been hampered by difficulties in isolating lignin from

wood without degrading it. Because lignin is highly insoluble, very strong acids and alkalis must be used to separate it. Few of these methods are entirely successful in producing a completely pure product, and most lead to a partially-depolymerised structure (Sjöström 1981). More recently computer-aided structure elucidation and molecular simulation techniques have proved useful (Faulon and Hatcher 1994). The main advantage Faulon and Hatcher's new model is that it can explain lignin's affinity for the organised polysaccharide ultrastructure of the cell wall.

Lignins are generally divided into three classes in terms of the type of glyceryl methoxyphenol units that predominate: *guaiacyls*, *syringyls*, and *p-hydroxyphenyls*. Softwoods contain guaiacyls and *p*-hydroxyl units while hardwoods contain both guaiacyl and syringyl lignins. The former combination yields more cross-linking than the latter, which explains why the lignin of hardwoods is more readily degraded than softwood lignin (Hedges 1990).

Lignin's presence in the interstices between cellulose microfibrils provides much of the rigidity that holds the fibres upright in wood. Its highest concentration is in the middle lamella, with lesser amounts, proportional to polysaccharides, in the secondary cell wall. However, as much as 70% of the total lignin content may be located in the secondary cell wall. (Sjöström 1981). Latest studies indicate that lignin located in the secondary wall has larger amounts of syringyl units, while that in the middle lamella has more guaiacyl (Sjöström 1981), explaining the preferential preservation of the latter

In conjunction with hemicellulose, lignin plays a major role in blocking the access of solvents and other chemical agents to the cellulose of the cell walls. Studies have shown indications that there are covalent linkages between lignin and hemicelluloses. The linear, gel configuration of cellulose contrasts sharply with the much more compact configuration of lignin, which explains why water interactions are favoured so much more with cellulose than with lignin.

1.3.1.4 Other wood constituents

Unlike the major constituents just discussed, the extraneous materials are not structural components of wood. and thus play lesser roles in influencing the structural properties of wood. They are both organic and inorganic in type.

The organic component contributes to properties such as colour, odour, taste, decay resistance, density, hygroscopicity and flammability. It includes tannins and other polyphenolics, colouring matter, essential oils, fats, resins, waxes, gums, starch and simple metabolic intermediates. Its proportions in wood range from 5-30 wt%, depending on external factors. Organic extractives are of minor interest to the study of archaeological wood because they have undergone almost total dissolution through water-solvent action, enzymic hydrolysis, oxidation by air, etc. (Sjöström 1981). The role of tannins however, in complexing iron salts during burial has particular significance in the deterioration of archaeological wood (Chapter 4). Oak wood is known for its high tannin content (2.7% to 7.9%) (Hagglund 1951). However, it is usually the inorganic iron content rather than the tannin content that is measured as an indicator of degradation of the material.

The inorganic component (ash) of extractives generally comprises 0.2-1.0 wt% of the wood substance. Calcium, potassium and magnesium are the more abundant elemental constituents, with only trace amounts (<100ppm) of phosphorus, sodium, iron, silicon, manganese, copper and zinc (Ellis 1965; U.S Forest Products Laboratory 1989). Ash content in heartwood appears to be much higher than in sapwood (Hagglund 1951). Ellis (1965) points out the significance of certain minerals such as silicon as contributors to decay resistance. Kim (1990) studied the differences between ash constituents in waterlogged archaeological and recent pine woods (Figure 1.14).

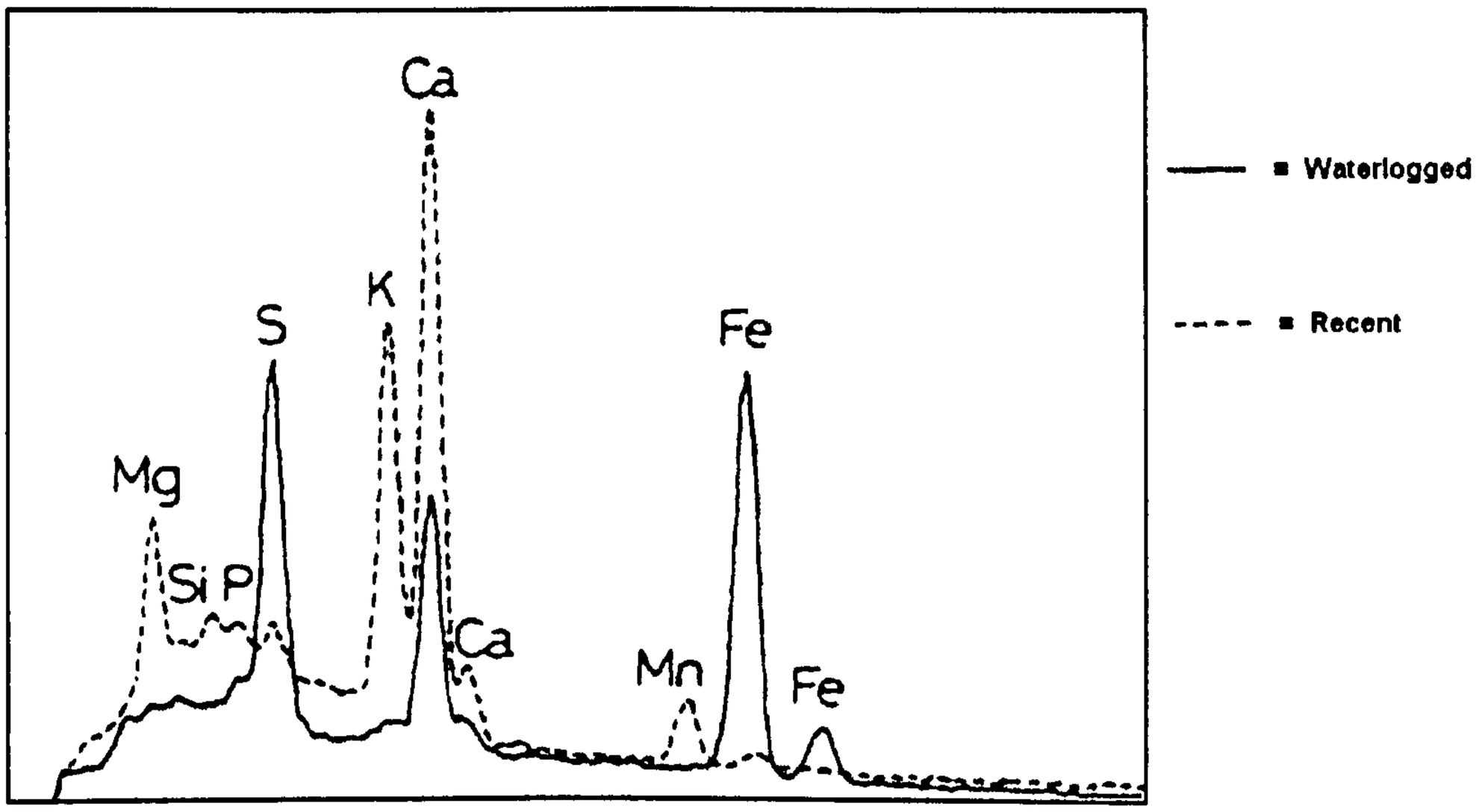


Figure 1.14 EDXA spectra comparing ash constituents of waterlogged and recent pine (Kim, 1990)

Grignon and Scallan (1980) have investigated the swelling effect these metallic elements in salt form have upon the cell-wall matrix.

1.3.2 Construction of Microfibrils and Macrofibrils from Cellulose

The simplified picture of fibril and fibre formation shows cellulose forming a fibril skeleton that is then surrounded by hemicellulose as a matrix and lignins as encrusting materials. The smallest building element of this skeleton is considered to be the *elementary fibril* (microfibril), though there is still some discussion over this point (Sjöström 1981). The elementary fibril is made up of a bundle of 36 parallel cellulose molecules held together by hydrogen bonding. It is now generally accepted that all chains in the elementary fibril are oriented parallel to one another.

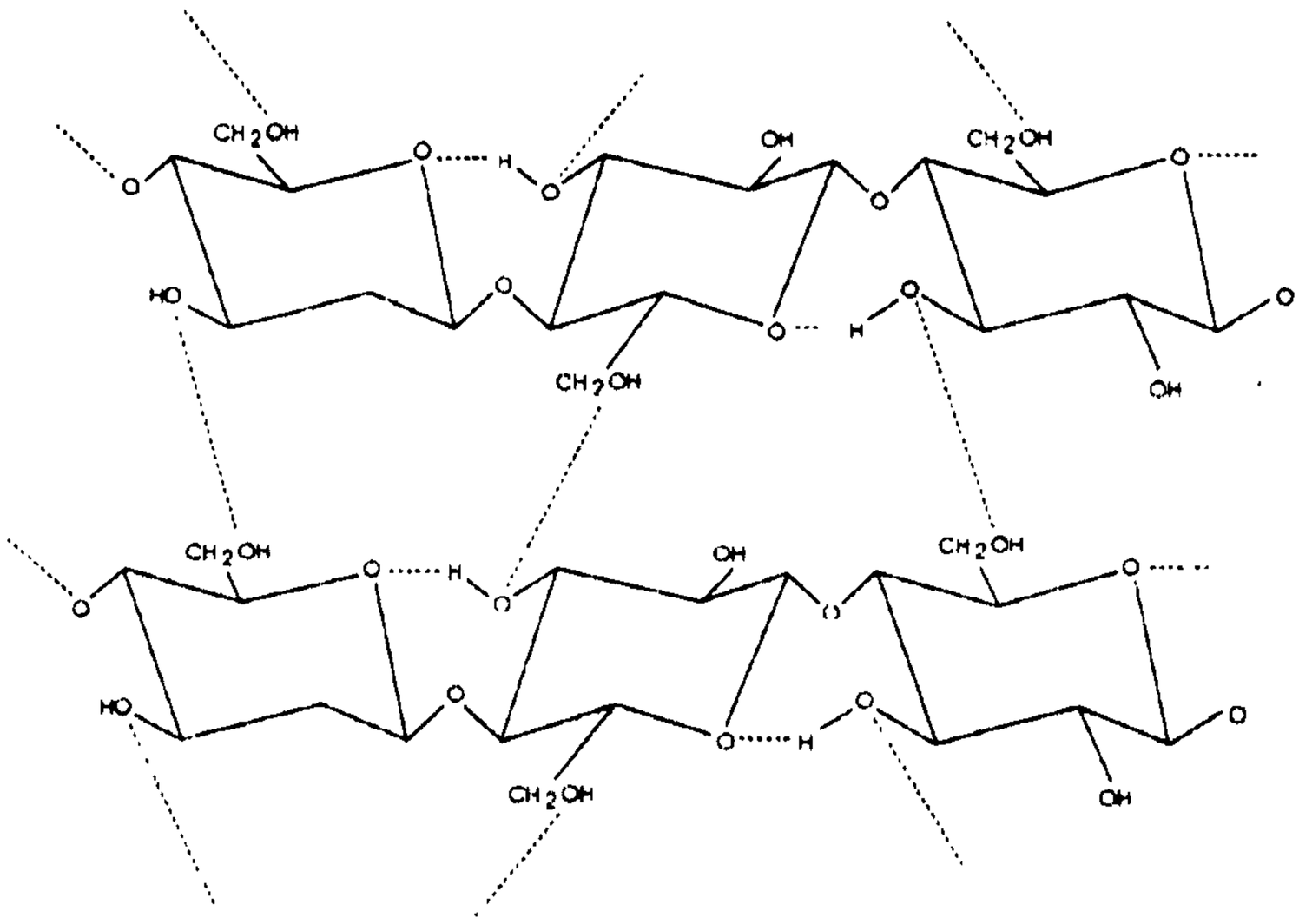


Figure 1.15 **Hydrogen bonding between cellulose chains** **(Kronkright, 1990)**

Hydrogen-bonding between the oxygen molecule of one monomer and the hydroxyl (-OH) group of the next results both in the bonding of these units in long chains, and in the crosslinking that occurs between aligned neighbouring cellulose chains, leading to the formation of microfibrils (Figure 1.16). This crosslinking results in the glucose monomers in the cellulose chain forming a linear and highly polar molecule. This polarity plays a role in the bonding together of microfibrils into the macrofibrils and fibres that make up the cell walls in wood tissues. Microfibrils become aligned and held together in some places by the strong intermolecular covalent bonds produced by this polarity (Figure 1.15), and at other places they are held together in less well-aligned configurations by molecular bridges composed of water (*structural water*).

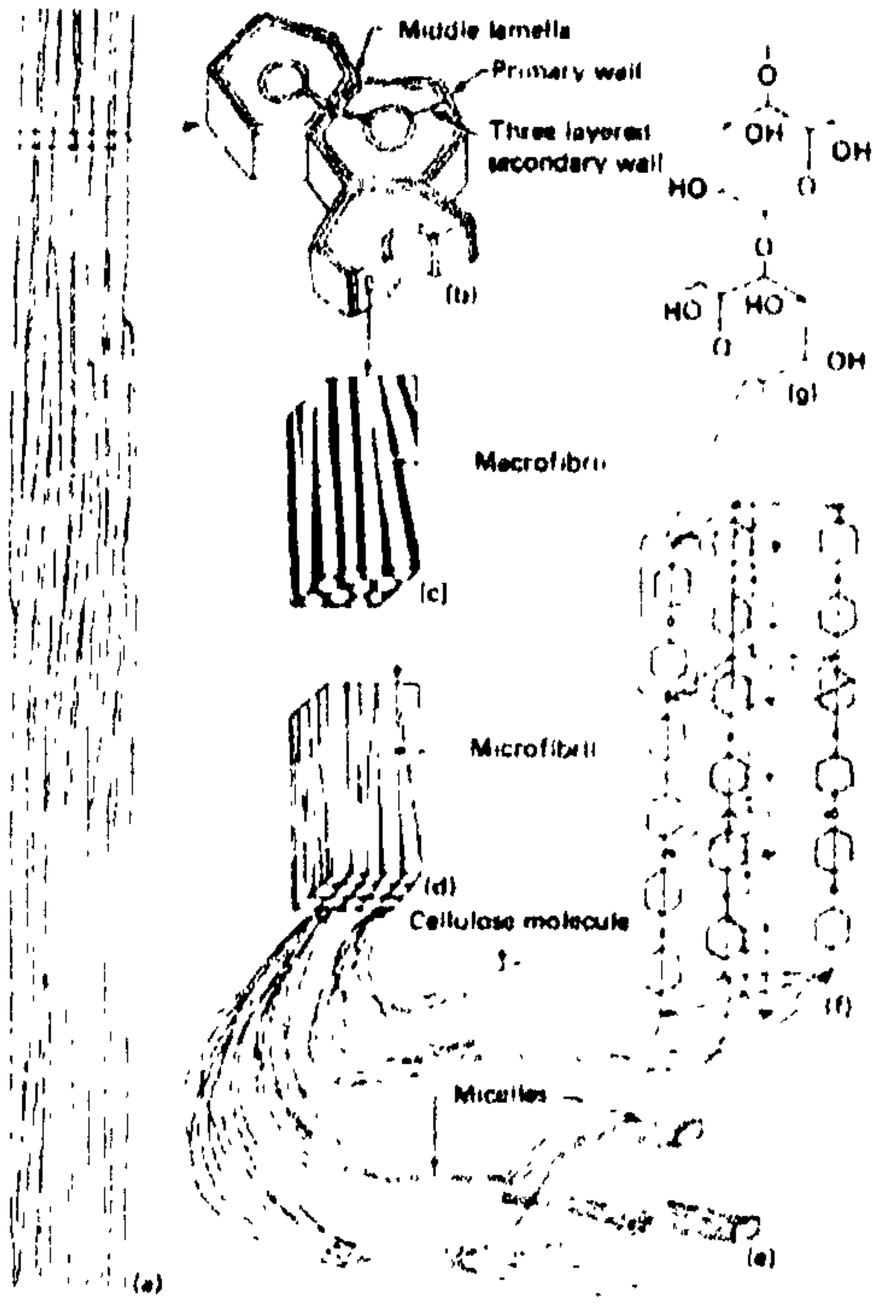


Figure 1.16 **Organisation of polymers to form cell wall fibre matrix** **(Florian, 1987 after Esau 1953)**

The first type of bonding together of microfibrils results in the formation of areas of *crystallinity* along the macrofibril; the second type of bridging results in *amorphous* areas being formed. Amorphous areas are more flexible than the brittle crystalline areas, and thus in some ways more resistant to physical stresses. Yet the main consequence of cellulose's fibrous structure and strong hydrogen bonding in its crystalline regions is to produce a material with high tensile strength and insolubility in most solvents. Amorphous areas of the cellulose fibre are more vulnerable to chemical attack and penetration by solvents such as water.

Wood microfibrils are not, however, just composed of crosslinked and intertwined cellulose polymers. A more complete view of them, which takes into account the other chemical substances associated with woody material, describes them as essentially bundles of cellulose molecules embedded in an amorphous matrix of hemicelluloses and a small amount of lignin that fills the spaces between the microfibrils. This has been termed the *reinforced-matrix concept* (Figure 1.17), and is believed to account for the high strength and resistance of wood to deterioration (Koshijima *et al.* 1989).

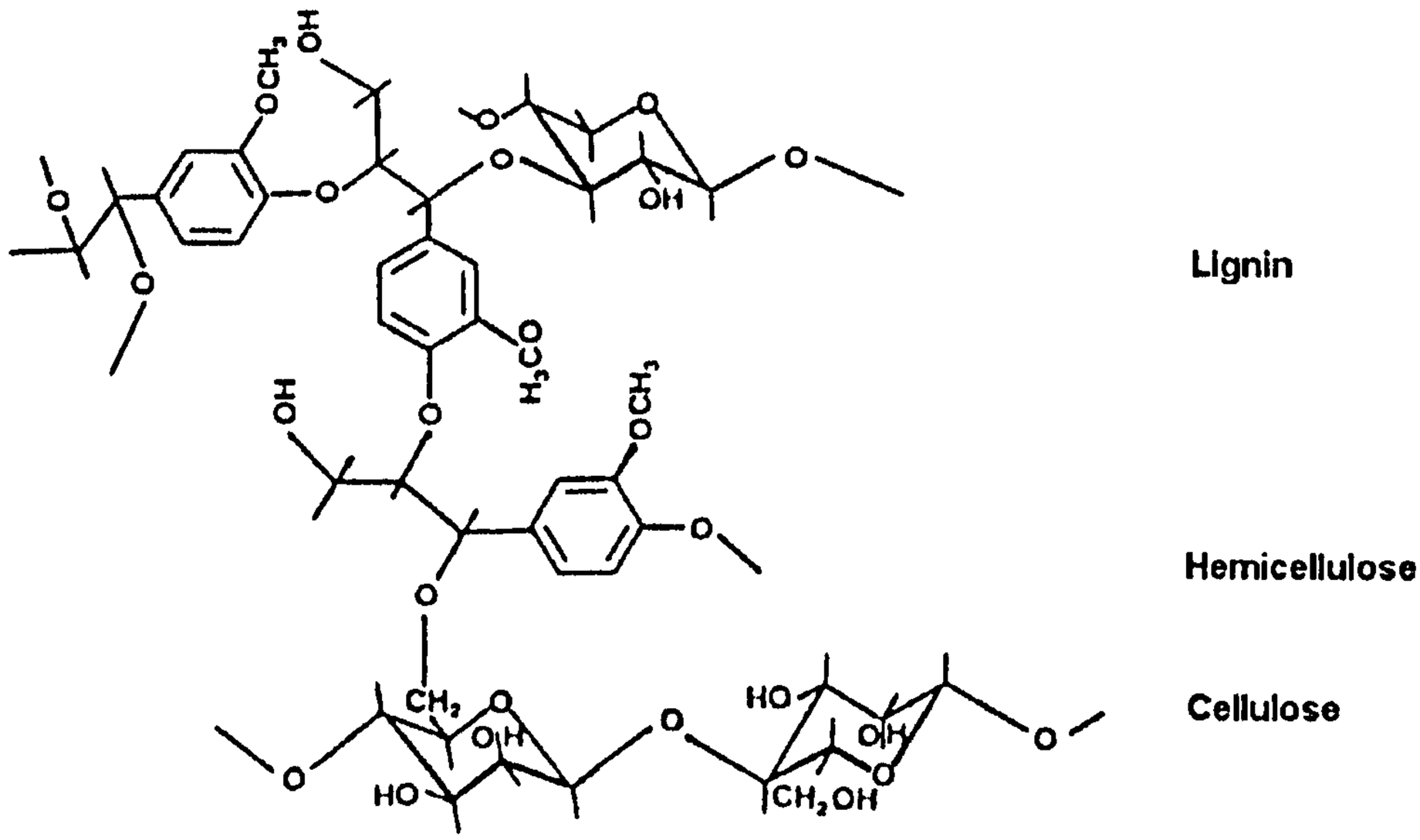


Figure 1.17 **Linkages between lignin and carbohydrates in the re-inforced matrix (Koshijima *et al.*, 1989)**

1.3.3 Cell Wall Construction

Cellulose macrofibrils and their reinforced matrix are organised into sheets of *lamellae*—fibres interwoven into a felt-like material—that make up various layers of the cell walls of wood cells. Each layer of the cell wall is composed of lamellae with a different angle of weave, spirally oriented around the longitudinal axis of the cell (Ruel *et al.* 1978). This lends to the layers different properties of strength, flexibility, and durability, and to the whole the properties of strength associated with any strong laminated material.

The distinctive properties of each of the layers in the two cell walls that form each wood cell has already been discussed in more detail in the earlier section dealing with the physical structures of wood.

1.3.4 Microcapillary System and Second-Order Space

Within the reinforced matrix of fibrils are spaces up to 10nm in diameter, as well as systems of *microcapillaries* or *second-order space* that tend to run parallel to the orientation of the microfibrils in the cell wall (Grattan 1987). These areas are particularly important for the moisture-holding capabilities of the cell wall and thus both to its strength and vulnerability to chemical and biological attack.

1.4 Physical Properties of Wood

1.4.1 Water and the Physical Properties of Wood

Water is as much a part of the composite that makes up wood as are its polymeric constituents. When wood, a complex organic colloidal solid, is appraised, its moisture content must always be taken into account. This is particularly so with its physical properties, as will become apparent in this section, and in much more detail in Chapter 3.

Regardless of external variations, the overall structure of wood, chemical and physical, makes up a system of interconnecting capillaries of various sizes, created from cells with their long axes organised longitudinally, and operating as a vast network for water transport. Capillary diameters within wood are highly variable and depend on species, season and function (Grattan 1987). Outside these capillary systems there is a complex interrelationship of different cells, pore systems that link them to each other, and more subtle, largely chemically-activated systems existing as microcapillaries in the intrafibrillary spaces existing within and between the cell walls of wood. It is in the context of a capillary system that wood properties and deterioration are best understood.

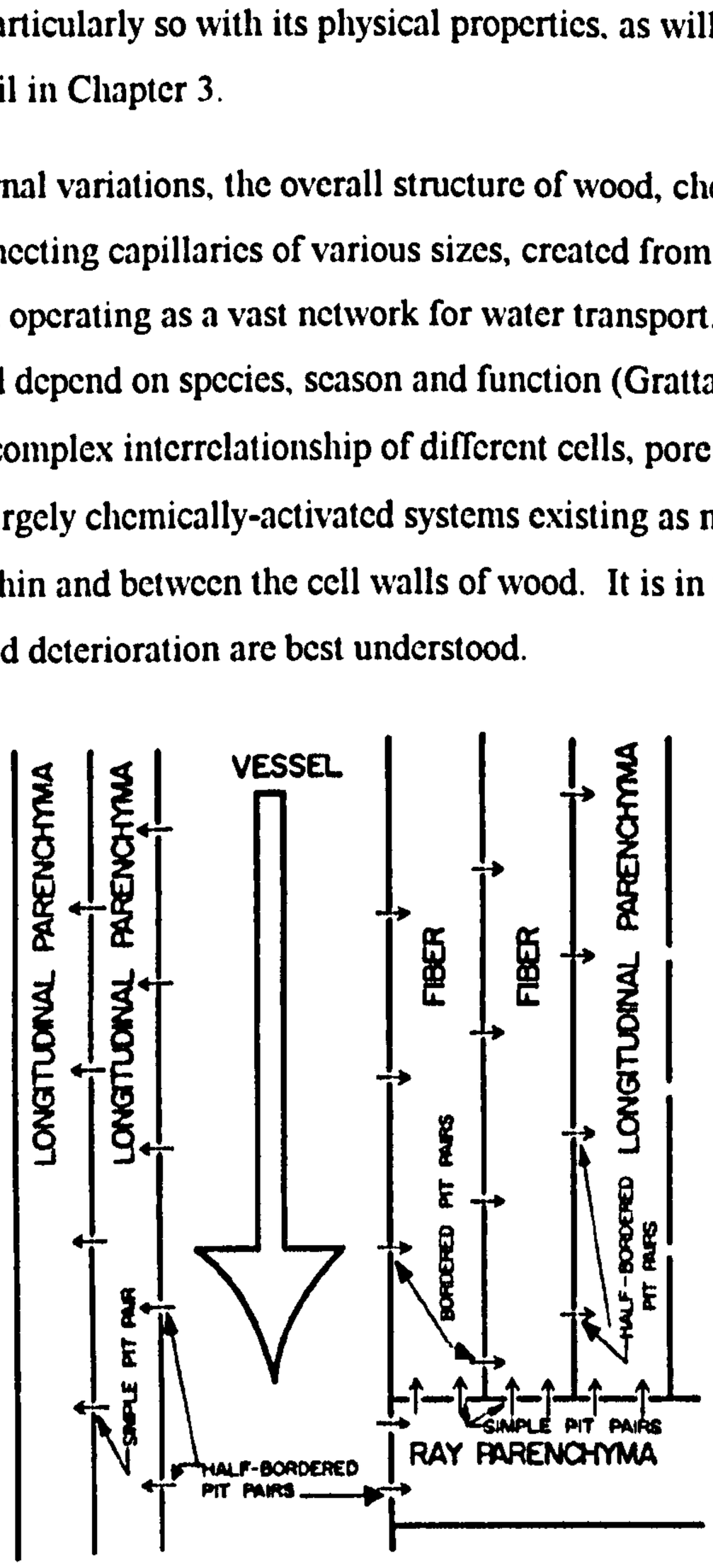


Figure 1.18 **Generalised flow model for hardwoods** **(Siau, 1984)**

As wood dries the water in it is released in patterns that reflect the varying strength of bonding of the water to the wood substance (Figure 1.18). These patterns are replicated with some important

differences when moisture is re-introduced into wood. A measure exists for the point at which these moisture movements begin to have a serious effect on wood properties, the *fibre saturation point* (FSP). A low moisture content at FSP is an indication of natural durability and inherent dimensional stability (Rijsdijk and Laming 1994). At and above FSP, wood registers relatively weak strength values. This is particularly noticeable for an over-saturated material such as waterlogged archaeological wood. It is only when wood dries below its fibre saturation point, indeed when the associated dimensional changes have already begun to occur, that wood begins to increase in strength. For both the conservator and the wood technologist, the prime aim is to bring wood to or below this point without any sudden change to dimensions. The technologist has to bring fresh oak down from a saturated or 'green' moisture content of approximately 64% to somewhere between 20-30% (Hoadley 1980), while the conservator will be starting from somewhere between 100% and 1000% moisture content in the saturated state (Figure 1.19).

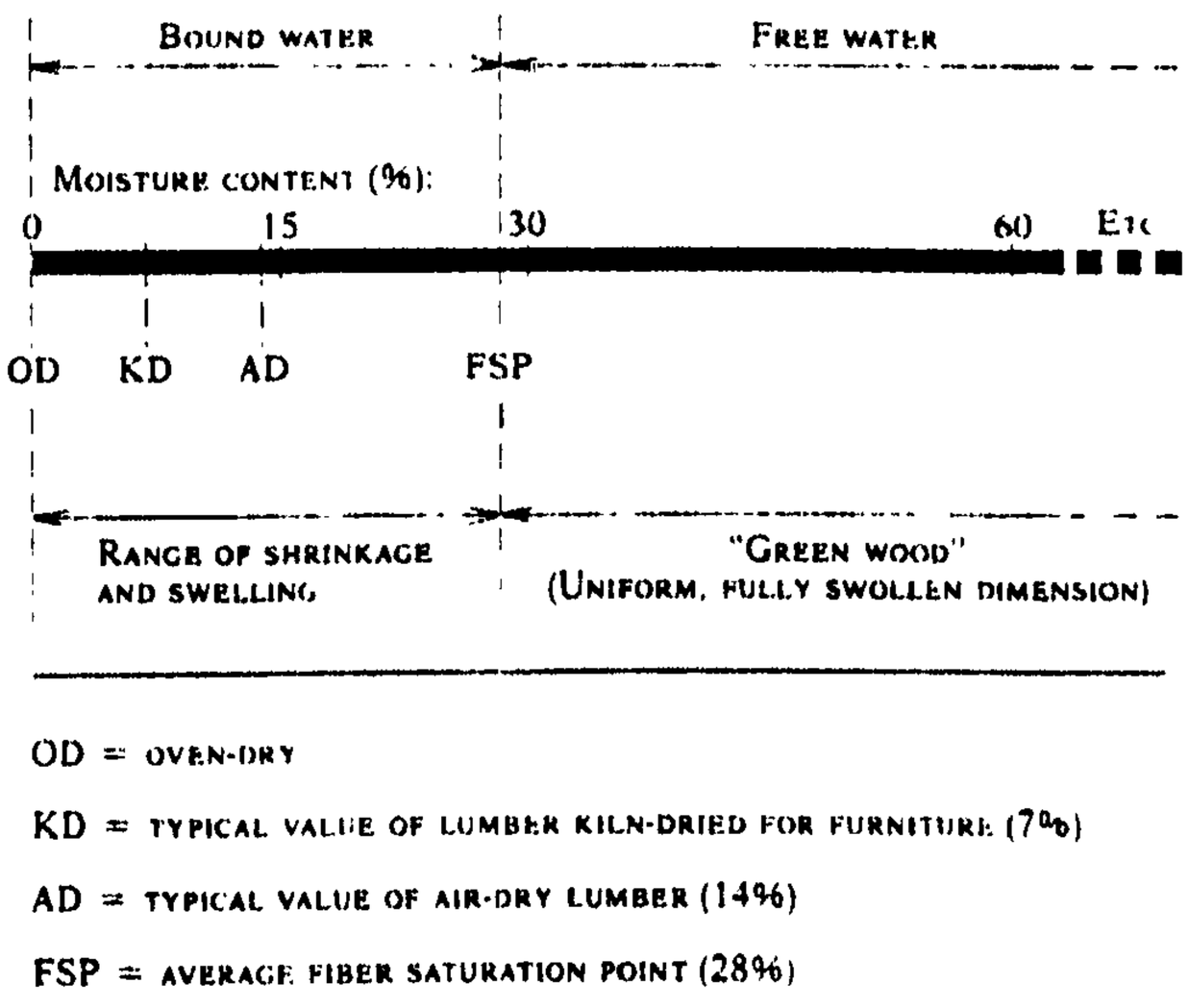


Figure 1.19 **Types of water involved in drying of wood** **(Hoadley, 1980)**

Both macroscopic and ultrastructural variations in wood affect the behaviour of wood on drying. With archaeological wood, controlling this behaviour is much more complex and problematic because of the unknown changes that have occurred to archaeological wood during burial. Identifying methods that can be easily applied to appraising these changes in waterlogged artefactual material will help improve conservation treatments.

1.4.2 Measures of Physical Properties of Wood

Some of these methods involve standard physical measurements of wood. Density is considered the single most important indicator of stability in wood (Desch 1981), since it predicts such characteristics as strength (dense woods are mostly stronger), resistance to movement under changing moisture conditions (dense woods exhibit higher movement), and changes to chemical constituent levels (degradation is linked to losses in density). Density will obviously vary greatly between species as a

result of differences in structural organisation. The density of most species falls between 400-800 kg/m³ (at 15% m.c.). That of *Quercus* spp. is in the region of 640-720 kg/m³ (Rijsdijk and Laming 1994).

Strength measurements will also yield information on changes to wood caused by degradation. The assessment of strength or the mechanical properties of wood is complicated by the fact that wood is an anisotropic heterogeneous material—a uniphase organic composite exhibiting much higher strength values than those of its individual constituents (Hoadley 1980)—that varies with structural differences and changes to chemical composition as well as with the design of the artefact. Wood-water relations are particularly critical (Figure 1.20). The relationship between all of these and degradation in wood is investigated in Chapters 2 and 6.

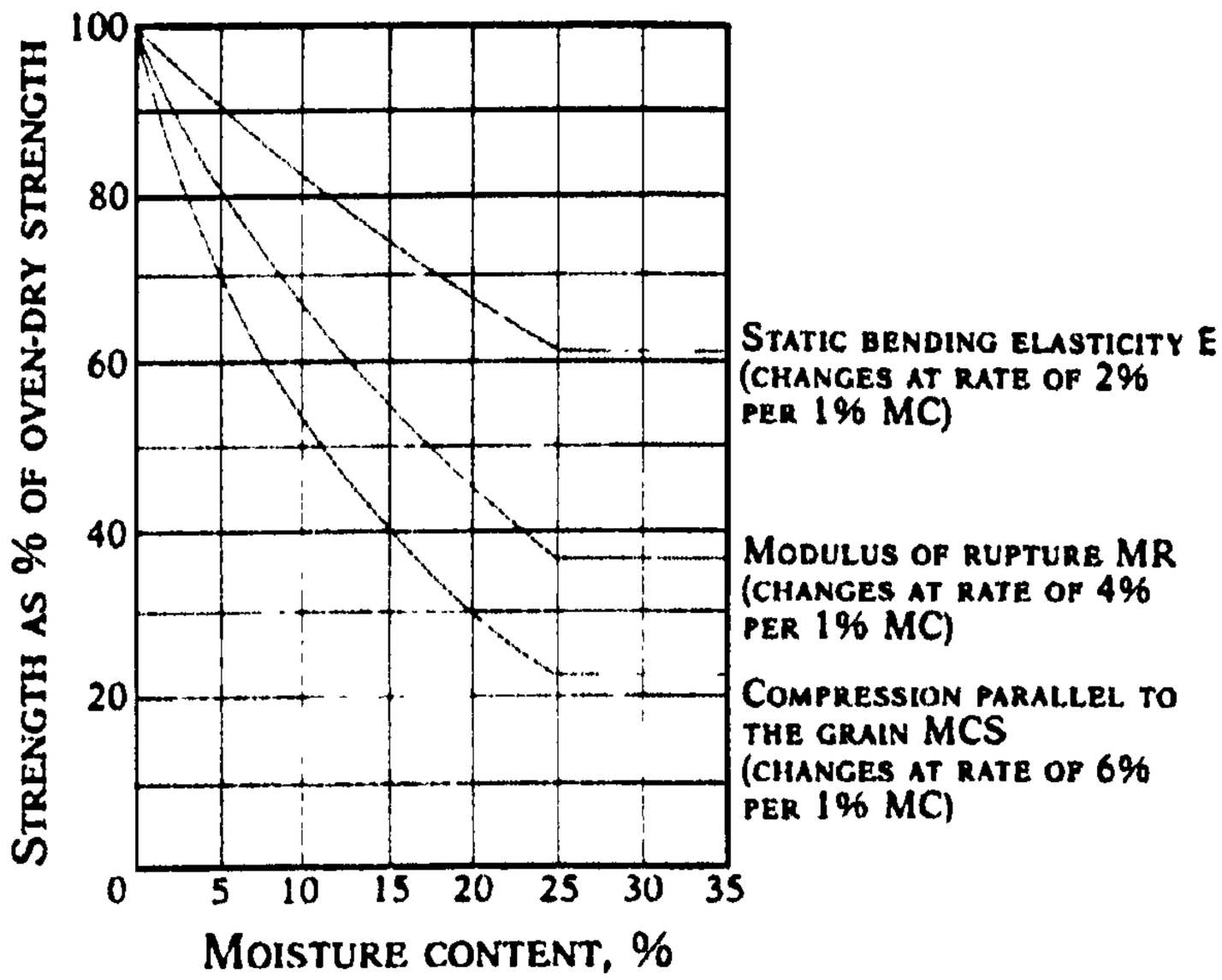


Figure 1.20 **Changes in strength properties with moisture content** **(Hoadley,1980)**

The table below summarises some of the main physical and chemical properties of oak wood (*Quercus robur*). The type of chemical solubility analysis used to produce the data below is the cause of constituent totals not adding up to 100% (discussed further in Chapter 7; also Hoffmann 1982).

Chemical Composition [1]						
Total Holocellulose	Cellulose	Hemicellulose	Lignin	Other Polysaccharides	Organic Extractives	Ash
73.2 wt%	41.1 wt%	23.3 wt%	29.6 wt%	12.2 wt%	0.4 wt%	0.3 wt%
Physical Properties [2]						
Green Moisture Content	Moisture Content at FSP	Bulk Density	Specific Gravity	Shrinkage [3]		
64 %	30 %	0.666 g/cm^3	0.572	Tangential	Radial	Volumetric
				9.5 %	6.6 %	14.7 %
Mechanical Properties [4]						
Compression Parallel to Grain			Static Bending (Modulus of Rupture)			
62.6 MPa			71.1 MPa			

Sources:
[1] Fengel & Wegener, 1984
[2] Rijsdijk and Laming, 1994
[3] Kollman and Côté, 1968
[4] Schniewind, 1990

Table 1.1 Properties of *Quercus* spp. (U.S. Forest Products Laboratory, 1989)

1.5 Summary

This chapter has laid the groundwork for an understanding of wood as a material. The inherent chemical, physical and mechanical properties of wood contribute to the understanding of deterioration processes undergone by wooden artefacts as they move toward the waterlogged state, the water relations controlling this, and the conservation treatments that aim to take advantage of all of these properties to stabilise the material successfully. The immense inconsistency of wood's properties, predicted by the extent of the variation that exists within the material, explains why consistently-successful stabilisation of waterlogged wooden artefacts is still a concern for conservators.

The interrelationship between the physical and structural characteristics of archaeological waterlogged wood (specifically *Quercus robur*), its changed chemistry, its water relations and their control is the subject of this thesis. *Quercus robur* was chosen because of its relative common preservation in archaeological sites of Northern Europe, and because of the particular challenges it produces for the conservator, which are the result of a combination between its inherent chemical and physical structure and the characteristic degradation paths it follows under burial conditions—the subject of the next chapter.

2 Degradation of Archaeological Waterlogged Wood

2.1 Introduction

It is only under conditions of extreme cold, wet, desiccation, or anoxism that wooden objects are preserved over the long term. It is the preservation condition of wooden artefacts buried in wet environments that is the focus of the current study.

Diffusion of water from a wet burial environment gradually fills wood cell-wall microcapillaries, causing their expansion. The term that refers to the complete filling with water of all pore spaces in wood is *waterlogging*. This complete saturation of the fibre matrix means that the oxygen necessary for oxidative degradation and biodeterioration is largely absent. However, the swelling process itself encourages some breakdown of the ligno-cellulose matrix of the cell wall. Outside materials that penetrate the swollen matrix—salts, acids, alkalis, metal cations—all promote this swelling among the fibrils, in addition to causing dimensional change, breakdown of cell-wall carbohydrates through hydrolysis and oxidation, and the production of degradation by-products that provide nutrient for bio-deteriorants.

The main factors determining the degree of wood preservation in wet soils are oxygen levels, pH, presence of salts (such as sulphates and nitrates), presence of polyvalent anionic metals (in particular iron), and the influence of all these on the activities of microorganisms present in the burial environment. Depth of burial is extremely significant, as are drainage conditions and external pollution of the soil with salts from land activities or associated metallic artefacts. The possible combinations are many, and calculating the resulting effects is extremely complex and difficult to do. Painter (1995) stresses the need for much more research in this area. The complexity of these interrelationships is what leads to the high unpredictability of preservation conditions for wood. We can state with some certainty, however, that wood in saturated conditions and with undisturbed stable chemistry will have a high likelihood of good preservation, as oxidative processes are restricted and the activity of microorganisms slowed down. These complexities will be discussed in later sections of this chapter.

The extent of waterlogging in wood tissues is dependent, to a large extent, on the condition of those tissues before they enter the burial soil—species, inherent permeability, and degradative changes already produced by deteriorative processes active during the artefact's use-life and before its burial. In considering the degradation of archaeological materials, we tend to overlook the fact that wooden objects deteriorate considerably during their use-life. Most archaeological objects will have been buried as a result of discard, often because they have become too degraded to carry out their original purposes. The sort of deterioration that a wooden artefact will have undergone before burial follows the pattern of dry wood deterioration, a subject comprehensively discussed in wood technology literature. We need to

bring elements of this discussion into our own models for the degradation particular to waterlogged wood.

All wood exposed to the external environment will have undergone significant modification to its chemical and physical structure and to its properties as a material. Wood structure's characteristic anisotropism will mean that such deteriorations manifest themselves in different areas and concentrations throughout the wood's tissues, adding further complexities to the process. Moreover, only some of the degradative changes manifest themselves visibly—in changes to colour, texture, strength, and shape. The swollen condition produced by the waterlogging process may hide the true condition of the wood, because the excess water lends support to cell walls, causing the artefact to appear much stronger and more cohesive than it is. However, it also may cause the conservator to judge a treatment a failure undeservedly when hidden deterioration is exposed after drying.

Changes to the chemical structure of wood are much less observable, and it is these, viewed in conjunction with physical structural changes, that can provide us with a more complete picture of the processes involved in deterioration. The conservator needs to know what these changes are, so as to aim the right preservation chemicals at the wood, and use the right processes to do so, in order to stabilise the wood against further decay.

Deterioration after excavation has recently become of concern as well, because reduced conservation funding leaves much archaeological wood untreated for many years, and storage for this sheer bulk of objects will be required for long periods of time.

Most of the information available on wood degradation mechanisms and changes to chemistry comes from research on unworked wood, on fossil or subfossil remains, and from wood technology studies. Very little, as yet, has been published on archaeological material. Some researchers claim waterlogged wood to be similar to fossil remains, inasmuch as they have undergone similar ageing and deterioration processes, differing only in the effects of cultural activity and the extension of the ageing process (Schniewind 1990a; Hedges 1990). Since the waterlogging process is a distinctive one, this assumption bears investigation.

This chapter will outline the larger details of the degradative processes that affect archaeological waterlogged wooden artefacts. In general, biological, chemical and physical factors act together in processes of deterioration; here, however, they will be discussed in turn, with some effort expended to show their comparative importance and how they influence one another other.

2.2 Natural Decay Resistance

Natural durability makes the difference between a few months of use-life for some species to forty or fifty years for others, such as oak (Zabel and Morrell 1992). It has long been recognised that ancient technologists chose woods for their natural durability or decay resistance (Munby 1991; Goodburn 1993). Choosing particular species and discarding sapwood in favour of heartwood resulted from some understanding of the nature of wood decay and from knowledge of the distribution and properties of naturally toxic compounds to be found in the heartwood of certain species.

There is variability in natural decay resistance, both between species and between individual trees of the same species. It is a factor not only of inherent wood structure but of local environment, and much of it has to do with extractive content and the extent of lignification.

The primary factor in decay resistance is the presence of toxic extractives formed and deposited in the heartwood tissues of the wood from carbohydrates present in parenchyma tissues near the heartwood-sapwood transition zone. Outer layers of sapwood have little or no extractive content. Zabel and Morrell (1992) provide a table summarising the four major chemical groups of heartwood extractives. These are: *terpenoids* (mostly in coniferous species) that confer upon wood considerable natural durability; *tropolones*, produced from terpenoid precursors and the most toxic of the wood extractives; *polyphenols*, toxic to bacteria, fungi and insects in varying amounts; and *tannins*, compounds that are water soluble, relatively low in toxicity, and especially responsible for the durability of oak.

Lignin type, content and pattern of deposition appear to play critical roles in wood's resistance to biodeterioration, and relatively minor differences can produce large changes in resistance. Where it varies between species and within individual parts of the same tree (e.g., the primary cell wall and middle lamella), it confers greater resistance to microbial attack. Oak is significantly more lignified than most other hardwoods of northern European origin (Chapter 1).

Growth characteristics are significant too in that old growth trees will tend to be more durable than second-growth trees of the same species because of their higher extractive content (Zabel and Morrell 1992). Elevated soil nitrogen contents are found to reduce durability by providing bacterial nutrients and increasing relative proportion of early to late wood (Merrill and Cowling 1965; Painter 1995). Archaeological wood will most likely have come primarily from old growth trees (Goodburn 1993), grown in soils as yet unpolluted by the residues of intensive agriculture, and for this reason caution must be used when applying the data from modern timber physical analysis to archaeological wood.

Other criteria significant to wood decay resistance are the location from which the wood was taken within the tree and the technological processes applied to the wood in forming objects from it.

Heartwood will be more durable than sapwood and base wood rather than crown wood because of variations in relative constituent ratios and permeability. This means that archaeological structural timbers of oak species in roundwood form (including bark and sapwood) may have no more inherent durability than a much less durable species. Heat treatments used for drying or bending of wood cause volatilisation, leaching, and denaturing of the extractives important for decay resistance (Scheffer and Eslyn 1961).

Understanding the natural decay resistance of the wood under analysis or conservation can contribute important information about the probable susceptibility to degradation during the use-life of an artefact; and that, in turn, can explain some of the differences we see between the condition of an artefact and its response to treatment.

2.3 Preburial Degradation

Preburial degradation comes from physical, chemical and biological sources. It is rare that these work in isolation from one another.

2.3.1 Physical

Physical sources of preburial degradation include preferential erosion and mechanical wear. Prolonged exposure to the abrasive effects of running water or wave action and wind- or water-driven sand will result in the erosion of wood surfaces along the grain lines. Dense areas in the wood tissues (e.g., rays and the denser late wood in the growth ring) will tend to be left standing preferentially to softer, more easily eroded tissue areas, giving a corrugated appearance to the surface of the wood. In comparison, mechanical wear, involving abrasion, rupturing and surface losses due to handling and loading, is only a minor source of wood degradation. Fibrous surfaces typically result from long term mechanical degradation mechanisms.

2.3.2 Chemical

Preburial degradation from chemical sources is largely restricted to weathering processes, though may incorporate charring.

Weathering results from a mixture of chemical and physical processes, and affects all externally exposed wood that is unprotected by coatings. It is often claimed that the damage caused by weathering is largely superficial, leaving the surface grey and somewhat cross-checked, but having no appreciable effect on strength. The primary cause of weathering is photochemical damage to wood cell-wall constituents, oxidation of breakdown products, leaching of soluble decomposition products and, finally, mechanical damage to surface elements as a result of fluctuating swelling and shrinkage cycles from

surface wetting. It can be seen, then, that weathering takes place in stages. Initially, there is a darkening of colour. This colour then turns to grey and develops a rough texture. This rough outer shell will tend to protect both surface and inner wood from further damage, until continued wetting and drying cycles produce surface checking, eventually leading to exfoliation of the surface and exposure of the inner surface to future cycles of weathering. Losses from weathering are negligible over the service life of larger wooden objects, with estimates of 6-7 mm of outerwood removed each century (Feist 1977). though the strength of smaller artefacts may be affected, surface detail lost, and fastenings loosened.

Some sources suggest that weathering processes are more significant in their degradation effect than is usually implied (Feist 1982). The photchemical decomposition of lignin and extractives reported by Feist may lead to free radical catalysed decomposition of structural carbohydrates (Hon *et al.* 1980). It is probably weathering as much as the natural progression of bacterial and chemical degradation from outer surface to inner which causes the outer zones of archaeological oakwood to be so much more severely degraded than inner.

Charred wood occasionally comes into the conservation laboratory for treatment. This material has decomposed at temperatures above 200°C, is largely pure carbon, and no longer shares wood's ultrastructural characteristics (Caple and Murray 1994). Wood constituents each have a characteristic decomposition temperature with hemicelluloses the lowest and lignins as high as 500°C. Charring may however be incomplete leaving some wood constituents intact, but still resulting in colour change, surface embrittlement, reduction in hygroscopicity and strength loss.

2.3.3 Biological

Biological decay agents are the primary source for degradation in archaeological waterlogged wood, both before and after burial, as they are for sound wood (Kim 1990).

2.3.3.1 Insects

Insects are as major an agent of deterioration of wood as microorganisms. They use wood for habitation and as a food source. In both cases they chew it into frass, leaving holes of various sizes and orientations, often the best diagnostic to which insect is active. Insects are vectors of microorganism decay, and insect and fungal damage often develop under the same conditions (Pinniger 1994). Insects may damage wood when living, when freshly cut, in storage as timber, during service, or after discard if not immediately buried. Many descriptions of insect damage exist in the wood technology and conservation literature (Coggins 1980; Pinniger 1994; Zabel and Morrell 1992) but are outside the range of the current study.

2.3.3.2 Decay fungi

There are four different broad classes of wood-destroying microorganisms—white-rot fungi, brown-rot fungi, soft-rot fungi, and bacteria—each of which is a specialist in the breakdown of one of more of wood's polymer components, and each reflecting very different chemical processes in the decay of wood (Hedges 1990).

In the discussion of degradative processes in the conservation literature, emphasis has been placed largely on the soil chemistry of the burial environment. It has not included the fact that the hydrolytic and oxidative processes involved in the degradation of artefactual wood, while fundamentally chemical processes, are initiated by microorganisms in the soil that in turn are either encouraged or discouraged by the chemistry of the burial environment. Moreover, little attention has been given to the contribution of pre-depositional decay by agents such as white- and brown-rots in preparing the wood for post-depositional microbial actions. Schniewind, in fact, entirely discounts the significance of decay fungi in the deterioration of archaeological wood, stressing the lack of availability of oxygen in waterlogged wood (Schniewind 1990a). But waterlogged artefacts will not always have been waterlogged, even after deposition, and thus considerable damage to cell-wall constituents by decay fungi must be considered to have taken place before the actions of anaerobic micro-fauna, even if evidence of their actions has been lost through subsequent phases of deterioration.

Numerous reviews of the biological aspects of decomposition exist (Kommert 1977; Zabel and Morrell 1992; Blanchette *et al.* 1990). These paragraphs will give only an outline of the major selective alterations to cell-wall compounds characteristic of pre-burial decay by *Basidiomycetes* species (white rot and brown rot fungi).

Fungi have three major effects on wood: mould action, staining, and decay. Only a limited group of fungi possess the enzymes capable of the digestion of wood polymers that cause decay (though Blanchette (1991) describes certain sequences of decays that suggest that some non-enzymatic events occur). Non-artefactual wood (waterlogged or fossilised *in situ*) and untreated wood in contact with the ground see a progression of decay from soft-rot bacteria to decay fungi (usually brown-rot first), with sapwood decays extending into heartwood decays. Zabel and Morrell (1992) stress that the decay of wood by microorganisms probably occurs in a "cascade of simultaneous and interactive reactions" with varying species in competition with one another.

They get into wood either adventitiously, through natural openings such as pits and perforation plates between vessel elements, or they penetrate the cell wall directly. Cells with the highest food reserves (parenchymatous cells) tend to be colonised first (Blanchette *et al.* 1990). The fungi have two major and closely interlinked effects on the physical structure of wood: chemical dissolution of cell-wall

constituents leading to material loss, and increases in the permeability of the cell wall. Destruction of pit membranes tends to contribute to both. These factors all contribute to changes in the sorption properties of archaeological woods. All decay fungi are capable of causing drastic changes to physical, chemical and strength properties of wood.

White-rots, brown-rots, and soft-rots are the three major categories in use, but they are not true taxonomic divisions and thus not very precise, so there is some overlap (Blanchette *et al.* 1990). Brown-rots are produced by a group of fungi that attack primarily the carbohydrates in the cell wall. White-rots are produced by a group of fungi that attack both carbohydrates and lignin in the cell wall. Species of the *Basidiomycotina* are responsible for both these types of rot, and tend to be primarily active on wooden artefacts before they are buried. Since soft rots are significant to post-depositional decay of waterlogged wood their discussion is reserved to section 2.4.1.

Both white-rots and brown-rots consist chemically of 80-90% polysaccharides, the remainder composed of proteins and lipids. Chitin is an especially characteristic constituent and can be used as an identifier where grosser morphological evidence is absent (Swift 1973).

Both of these types will tolerate a wide range of environmental conditions, but four requirements are critical: free water, non-extreme temperatures, molecular oxygen, and favourable pH. Water acts as the diffusion medium for enzymes, oxygen (a reactant in hydrolysis), and solubilised degradation products, as well as the capillary swelling agent aiding in penetration. Minimum moisture requirements are levels above fibre saturation point (40% EMC), and maximum are levels under saturation (80% EMC), because of the need for oxygen for respiration. This is the main reason why fungal activity is restricted in waterlogged wood, where water has gradually replaced air in the cell lumena. Since void volume varies inversely with specific gravity, high-density woods such as oak are likely to show significantly limited fungal activity even in drier conditions. Temperature optima are 15-45°C. Temperature controls the rate of reactions and, at higher levels, disrupts the stability of enzyme structures (Zabel and Morrell 1992). Atmospheric oxygen is needed at relatively low levels for most fungi. Free oxygen is the ultimate electron and hydrogen acceptor in the fungi's energy-yielding aerobic oxidation-reduction reactions. The higher tolerance of soft-rot fungi to low oxygen concentrations (compared to that of white- and brown-rot fungi), may explain their prevalence as decay agents in water-saturated woods (Duncan 1961). Carbon dioxide is toxic to fungi at higher concentrations, thus wood degrading in tightly enclosed spaces (e.g., archaeological wood packaged in sealed polythene) may stop deteriorating after a while because of the build-up of carbon dioxide levels by respiring fungi. In submerged conditions the diffusion rate of oxygen is very small, partly because of low solubility in water and diffusion through wood. Hydrogen ion concentration defines the optimal level for many enzyme reactions and protein stability. The optimal pH range for decay fungi is pH 3 to 6. Other important factors are growth nutrients such as nitrogen and iron, and also low levels of visible light.

The progression of attack on wood cell-wall components can be generalised for all decay fungi:

1. hyphal penetration
2. use of moisture to diffuse enzymes into the cell wall
3. breakdown of shielding by chemical bonds of lignin (or those between lignin and hemicellulose) by enzymes, thus facilitating enzyme access to carbohydrates
4. attack of hemicelluloses in the amorphous zones of the microfibrils occurs first, with removal of substituent groups and polymer debranching, either before, during or after depolymerisation of the polymer backbone
5. breakdown of cellulose and lignin in a series of step reactions
6. absorption of simple sugars and hydrocarbon fragments (byproducts of the decay process) by the hyphae.

(from Zabel and Morrell 1992)

Certain basic differences however exist between the decay actions of white rot fungi and brown rots:

White-rot *Basidiomycotina* degrade all the major components of wood, though certain species preferentially destroy lignin leaving behind a wood residue rich in chemically-altered polysaccharides (cellulose and hemicellulose) and of the white colour that has given this decay type its name. White-rots have been identified in fossil and waterlogged archaeological wood samples (Blanchette 1984), thus underlining the significance of preburial decay. They will tolerate very low oxygen concentrations, but will not grow under truly anaerobic conditions: for this reason, waterlogged artefacts may contain non-active white-rot that can reactivate after excavation. The actions of white-rot fungi leave skeleton cells without middle lamella, which gives a fibrous texture to the wood. Cell walls become highly perforated by hyphae, and permeability is increased.

All white-rot fungi degrade lignin, and Blanchette *et al.* (1990) have established that the removal of lignin takes place before the removal of carbohydrates, indeed is necessary to give access to fungal enzymes. The only regions to resist attack are the cell corners, that are less accessible to fungal enzymes in terms of spatial arrangements. Syringyl lignins are preferentially degraded over guaiacyl lignins explaining the attack of fibre cells before vessels. The lignin-degrading enzymes of white-rots are oxidative, and create a variety of chemical changes that Hedges (1990) has determined to include decreases in methoxyl, phenolic and hydroxyl contents. They also cause benzene ring cleavage and side-chain oxidation. The residual, oxidised lignin is characterised by elevated oxygen content, greater concentration of carboxyl groups, and elevated yields of acidic chemical degradation products. This altered material does not tend to accumulate in the wood tissues but is remineralised by the fungi (Zabel and Morrell 1992).

Brown-rot *Basidiomycotina* preferentially degrade wood polysaccharides, leaving behind an altered (demethoxylated) lignin-rich brown residue, from which this decay type gets its name. All that remains

of polysaccharides is a highly soluble residue. The most distinctive identifiable manifestation of brown-rot decay is the cuboidal cracking of the wood surface. Rapid and severe losses to wood strength taking place early in the decay process produce extreme embrittlement of cell walls, giving a powdery texture to the wood. When advanced, brown-rot may lend a rather swollen and porous look to wood cells, not dissimilar to the characteristics of waterlogged cells (Blanchette *et al.* 1990). In general, there is much less variation to the sequence of attack on cell-wall constituents than exists with white-rot decay.
S2 layers of cell walls are attacked preferentially, but eventually degradation leads to merging of cell walls, and their development of a porous appearance. At extreme stages of decay, the residual lignin middle lamella skeleton is loose and the cells are no longer able to hold to a rigid structure.

Degradation of polysaccharides in the cell wall is effected through oxidative depolymerization. Losses to crystallinity in cellulose thus occur early on. In contrast to white-rot decay mechanisms, the oxidation of cellulose occurs faster than it can be remineralised by the brown-rot fungi; thus there is an accumulation in wood cells of high concentrations of hygroscopic, altered low-molecular-weight intermediates, that may dissolve out of wood in conditions of higher pH (Hedges 1990). At high levels of decay, even lignins do not escape chemical alteration. Chemical analyses of residual lignin from brown-rotted wood indicate that demethylation of aromatic methoxyl groups and limited cleavage and hydroxylation of the benzene ring have taken place, with substantial increases in solubility (Christman and Oglesby 1971). Other principal chemical changes include oxidation of some alcohol and aldehyde groups to carboxyls, and the introduction of some phenolic hydroxyls. No significant separation of the guaiacyl and syringyl units has been reported to have taken place (Zabel and Morrell 1992).

In general, brown-rot fungi are more restrictive in their environmental requirements than white-rot (Blanchette *et al.* 1990). This may provide a partial explanation for the lack of evidence of brown-rots in archaeological waterlogged woods.

Figure 2.1 below shows the typical macroscopic appearance of white- and brown-rot decay-affected wood. Surfaces of archaeological wood post-treatment often have a similar appearance, which should perhaps be attributed to pre-depositional fungal degradation rather than to failure of treatment.

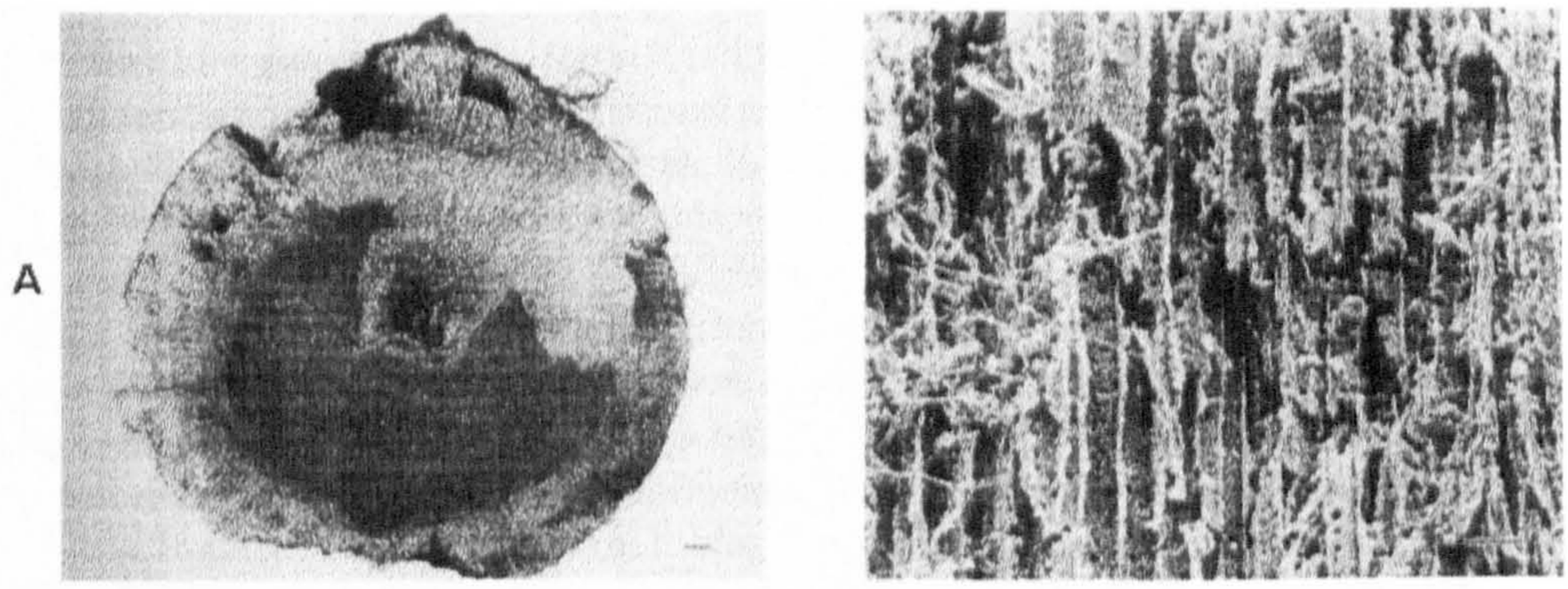


Figure 2.1 Macro- and microscopic appearance of white-rot (A) and brown-rot (B) decay in archaeological wood (Blanchette *et al.* 1990)

2.4 Post-Depositional Biological Degradation

Two types of microorganisms are active in post-depositional degradation of archaeological waterlogged woods, soft-rots and bacteria.

2.4.1 Soft-Rot Decay

Soft-rots are caused by microfungi (*Ascomycotina* and *Fungi Imperfecti*) that selectively attack the S2 portion of the cell wall under conditions of high moisture content and exposure to soil. Soft-rot fungi are variable in the materials and pattern of their attack. They perform both cavity formation and cell-wall erosion. Their erosion actions are very similar to those of white-rot fungi, resulting in thinning of cell walls. High lignin content discourages soft rot activity thus they largely restrict their activity to S2 layers in fibre and ray cells. Extended decay will lead to total destruction of the S2 layer, leaving an amorphous lignin structure and limited amounts of dark residues. The result of soft-rot erosion on the macro level is to make the wood very soft when moist or wet, and it is from this symptom that it receives its name. Upon drying of affected wood, a characteristic cuboidal checking of surface layers and darkening of surface occurs, though these surface layers may be abraded away in wood from wet or sandy environments (Figure 2.2). Nevertheless, despite appearances, soft-rot action is not simply a surface phenomenon.

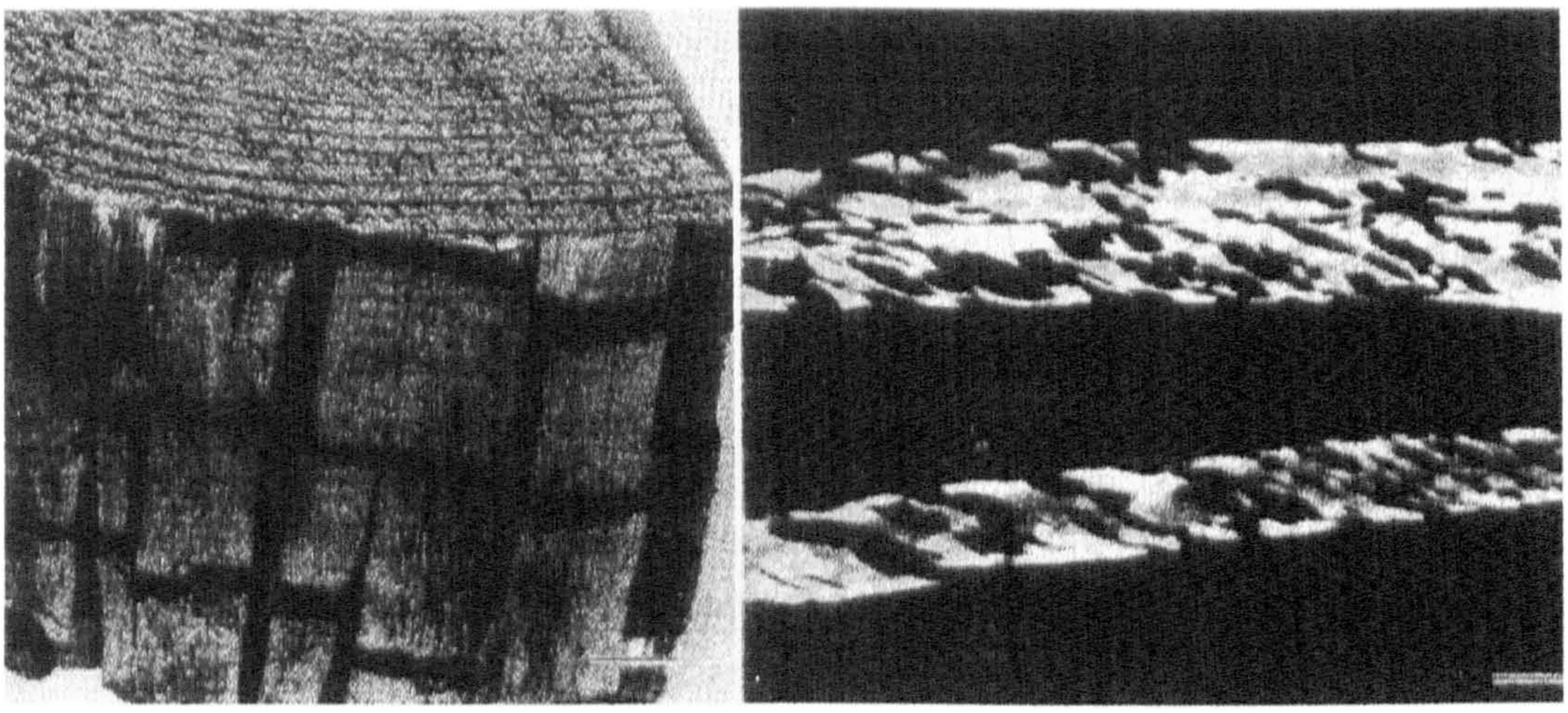


Figure 2.2 **Macro- and microscopic appearance of soft-rot decay (Blanchette *et al.*, 1990)**

Though soft-rots are active in above-ground environments, their liking for nitrogen and tolerance of high moisture levels mean that they will be more active in soil and aquatic environments. They are capable of being active at quite deep depths of burial. Soft-rots have been identified in archaeological woods (Nelson *et al.* 1995). Mouzouras (1986) claims that soft rots are the most common source of degradation of wood in aerobic waterlogged environments. This is partly because soft-rots can attack wood in a broader range of diverse environmental conditions than can the *Basidiomycotina*. Studies on waterlogged wood suggest that these fungi are able to attack at oxygen levels too low for basidiomycetes fungi, though they are not as tolerant as bacteria species (Blanchette 1991). Attack of wood in a waterlogged state, however, rarely extends further than the surface (Singh and Butcher 1990). Optimum pH levels vary from 6-8, and they are definitely more tolerant to extremes than basidiomycetes. This is also the case for moisture levels, where they function from very dry to waterlogged conditions. Despite this greater general tolerance, soft-rots are much slower to work than basidiomycetes and tend to be suppressed when in competition with them.

The chemical changes brought about by soft-rot fungi have been less studied than other wood-decaying microorganisms. They appear to be variable in their effects on components, sharing the features of both brown and white-rots. Soft-rots seem to be able to degrade lignins as well as polysaccharides, though under most circumstances (certainly with hardwoods) they prefer carbohydrates (Zabel and Morrell 1992). Indeed, soft-rot fungi have been reported to cause more lignin degradation than brown-rots, with losses as high as 40% (Nilsson *et al.* 1989). They do not achieve such pervasive depolymerisation, however, only minor demethoxylation, and wood decayed by soft-rot fungi does not contain high concentrations of alterations products of either lignins or polysaccharides (Hedges 1990; Zabel and Morrell 1992). Preferential attack of syringyl units has been observed (Nelson *et al.* 1995). Soft-rots remove glucans at a faster rate than hemicelluloses. During cavitation they may even attack crystalline cellulose, though rapid depolymerisation of cellulose is not as common as it is in brown-rot (Blanchette *et al.* 1990). Degradation products are used at the same rate as released. Relatively low lignin content is the explanation of soft-rot's predilection for hardwoods. Type of lignin is also significant as low

syringyl-guaiacyl ratios (as in oak) are less susceptible than higher to this form of decay (Galletti *et al.* 1995). Wood loses considerable strength even in the early stages of soft-rot attack, despite limited mass losses. Brash fracture is typical of soft-rot decayed wood.

2.4.2 Bacterial Decay

Bacteria are very small, unicellular organisms some of which (*Actinomycetes*) exist in filamentous form. Though found colonising wood, they do not appear to be able to degrade it on their own and thus are thought to work in tandem with wood-degrading fungi (Safo-Sampah and Wilcox 1988). Sulphur-reducing bacteria (*Clostridium)* are an exception to this. Like soft-rots, bacteria are primarily active in below-soil conditions, and are considered to be the major cause of deterioration in wood after burial (Kim 1990). They are very resistant to environmental extremes and can work either aerobically or anaerobically. They initially grow on wood surfaces, but are then carried into wood by microfauna, fungi and water menisci during wetting and drying cycles. They cause localised wall etchings and tunnels or cavities in cell walls, and in waterlogged wood are known to destroy parenchyma cells and pit membranes, causing significant increases to wood permeability (Zabel and Morrell 1992).

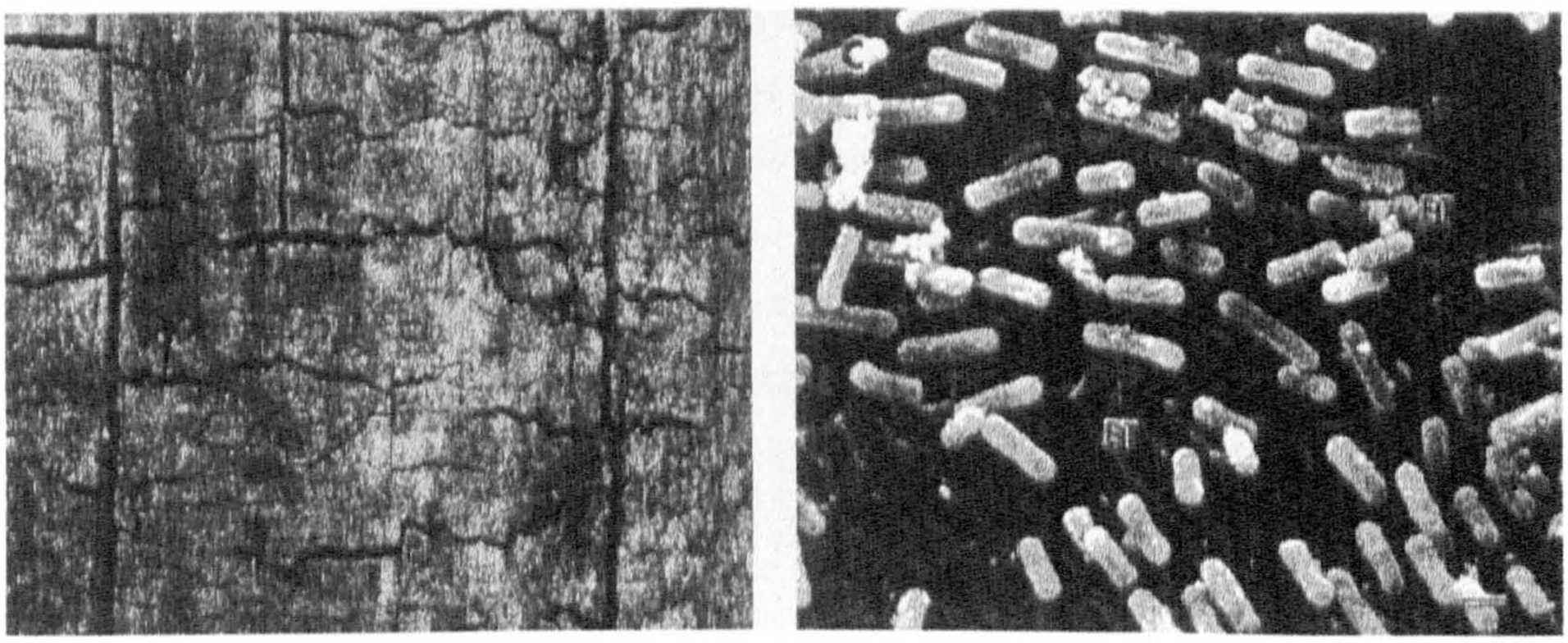


Figure 2.3 **Macro- and microscopic appearance of bacterial decay (Blanchette *et al.*, 1990)**

Under aerobic conditions, their effects on cell-wall components including lignin can be severe, though they work much more slowly than decay fungi (Christman and Oglesby 1971). As a result, current studies indicate that bacteria play only minor roles in decay in non-archaeological wood (Hedges 1990). In archaeological waterlogged wood, however, their influence is major. Recent studies of such material have shown evidence of bacterial decay prominent over any of the other types of decay (Mouzouras 1986), most probably because of their ability to take advantage of the inhospitable conditions of burial and waterlogging. Under anaerobic conditions, they are able to use compounds other than oxygen as electron acceptors for decay reactions. Sulphate-reducing bacteria reduce soil sulphates to hydrogen sulphide (Caple 1994). While bacteria certainly function in conditions of very low oxygen, Blanchette *et al.* (1990) has pointed out that degradation by bacteria under completely anaerobic conditions has not been demonstrated unequivocally.

High levels of lignification discourage bacteria, so sapwood will tend to be more effected than heartwood, and hardwoods degraded more quickly than softwoods. It explains why bacterial attack is often so closely associated with soft-rot decay, the latter achieving the initial delignification (Singh and Butcher 1990).

Perhaps the commonest manifestation of bacterial attack in wood is a pronounced increase in permeability brought on by the degradation of pit membranes, cell-wall erosion, tunnelling, and cavitation. Cell-wall degradation tends to be much less common, so much so that only recent investigations have provided evidence for this type of attack to the lignocellulose matrix (Daniel *et al.* 1987). They tend to affect all three layers of cell walls equally. In macromorphological terms, bacteria tend to leave wood with darkened, eroded surfaces and, once the wood is dry, with cross-grain checking similar in appearance to desert craquelure (Figure 2.3).

Little is known about specific chemical changes associated with wood-degrading bacteria, suggesting it might be a significant direction for future research into waterlogged archaeological wood. In general, bacteria concentrate their effect on the carbohydrates in wood, leading to an accumulation of lignin. Anaerobic bacteria are known to decompose crystalline cellulose as well as pectins and hemicelluloses, though the degree of polymerisation of cellulose has been reported as only slightly reduced (Passialis 1997). Normally, undegraded lignin will tend to act as a physical barrier to wood bacterial enzymes (Hedges 1990). As well as carbohydrates, however, bacteria are able to utilise many of the low-molecular-weight lignin degradation products left by already partially-decayed lignin. Crawford (1981) reports the ability of some bacteria to degrade lignin in a manner similar to that of white-rot fungi, in a process involving substituent oxidations and cleavage of both 2-carbon fragments from propyl side chains and aryl ether linkages.

2.5 Waterlogging

As has been pointed out in the introduction to this chapter, the term *waterlogging* is usually used to refer to the complete filling with water of all pore spaces in wood, both the capillaries and the microcapillaries (Grattan 1987). Waterlogging comes about through diffusion processes acting on the cell wall. Wood in an undegraded condition, and in particular oak wood, will tend to resist complete saturation by water, as conservation scientists have discovered when attempting to artificially waterlog wood samples for study (Andersen 1991). However, any degradative factor tending to lead to increases in wood porosity or permeability will allow waterlogging in wood located in sufficiently moist conditions. Such factors include bacterial and fungal attack on pit membranes and cell walls, delignification, solubilisation of heartwood extractives, and depolymerisation of cell-wall constituents, especially cellulose. Destruction of pits and hyphal perforation physically increases porosity. Solubilisation of extractives and delignification both involve mass losses that leave physical space for more moisture to penetrate, besides enhancing the accessibility of the cell-wall carbohydrates for

depolymerisation (Hoffmann and Jones 1990). Chemical deterioration of cell-wall carbohydrates is, however, probably the greatest single contributor to increases to wood moisture contents (Figure 2.4).

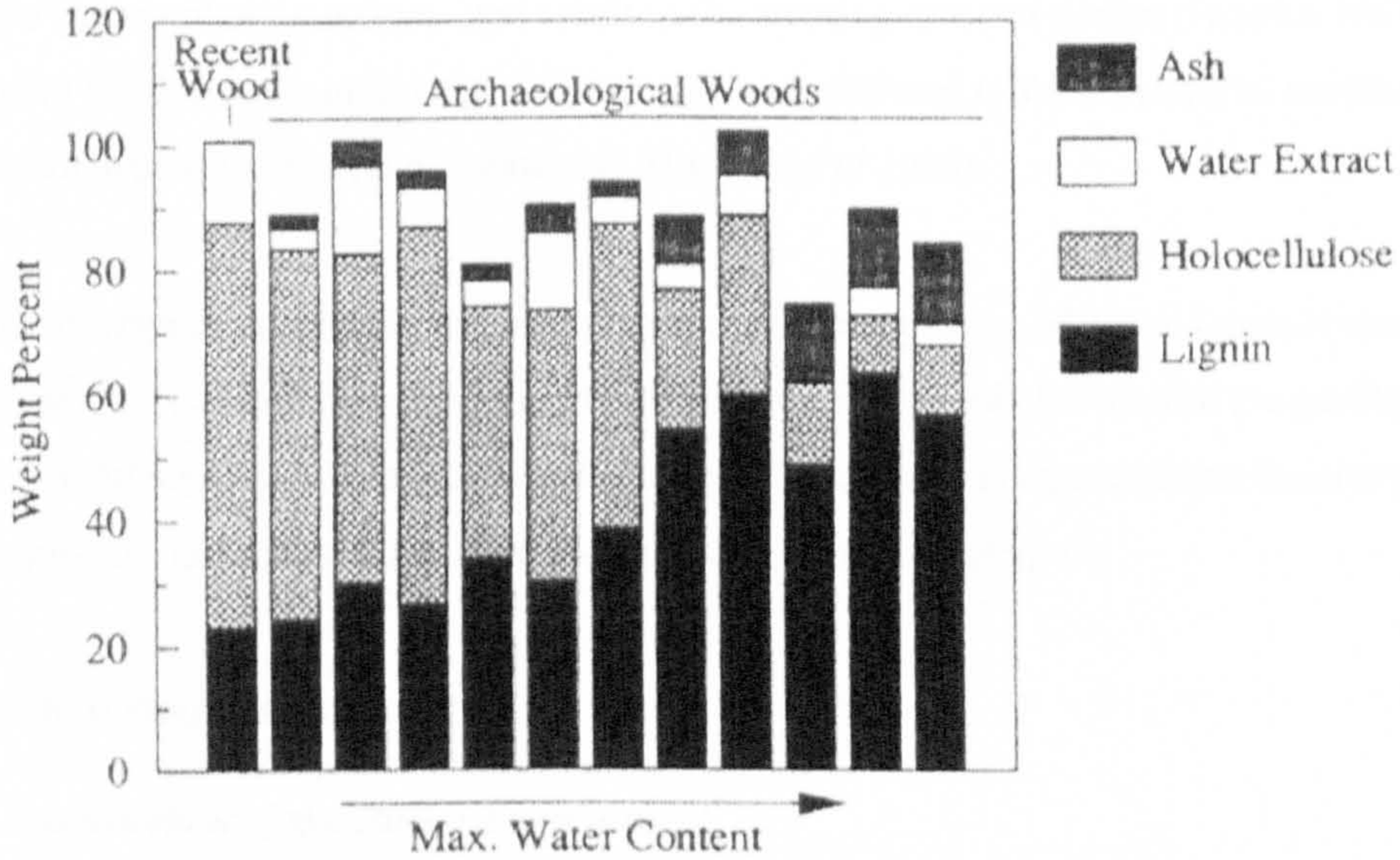


Figure 2.4 **Graph of change in constituent proportions with rise in water content** **(Hedges,1990)**

Most significant changes in waterlogging are centred around changes to the proportion of amorphous to crystalline phases within the reinforced cellulose fibre matrix. Amorphous zones are, of course, affected before crystalline zones because of the contribution to hydrolysis of structural water acting as molecular bridges between the micro-fibrils in these areas. Amorphous zones also contain more open bonding sites available for reaction. Diffusion of water from a wet burial environment through the amorphous zones in the cell-wall fibre matrix produces waterlogging by bonding readily with exposed polar sites on polysaccharide molecules and then filling microcapillaries situated between the fibrils, causing them to expand to maximum diameter and volume. This swelling process will, under extreme conditions (and aided by extremes in pH) eventually lead to the breakdown of crystalline areas through hydrolysis and oxidation. The greater the density of a particular species of wood, the greater the swelling that can take place in its tissues and, under waterlogged conditions, species such as oak can have an equilibrium water content of anywhere between 100% and over 900%, and experience increases in volume of up to 10.6% (Grattan 1987).

The degradation to cell-wall constituents undergone in association with waterlogging leads eventually to the dissolution of these materials and considerable mass losses to the wood. This factor alone, as well as the decrease in order within the reinforced fibre matrix, are responsible for the extreme reductions in strength experienced by waterlogged wooden artefacts. As in green wood, water acts to support wood cells and to plasticise fibrils so that it can better accommodate mechanical strain. In deteriorated waterlogged wood, water will support the wood tissues by bulking the frail remains of middle lamellae and any of the fragile, sheet-like cellulose that still remains. So waterlogged artefacts maintain their original structure and shape but, as mentioned earlier in this chapter, the excess water may hide the true

condition of the wood, causing it to appear much more strong and cohesive than it in fact is. Swelling also tends to hide use-life damage by closing up cracks. Waterlogging tends to produce darkened wood with a soft, cheesy texture. Some of this darkening is from byproducts of bacterial/fungal attack, which tend to increase chromophore reactions and result in the staining of wood tissues (Grattan 1987). Some has been found to result from complexing of iron compounds diffused in from the burial environment and humic (lignin byproducts) or tannic materials (Iiyama *et al* 1988).

The main factor of importance during waterlogging is the inhomogeneity of water's distribution throughout the wood. The differing areas of permeability are responsible for most of the problems faced by conservators in attempting to bring the wood into equilibrium with normal ambient humidity levels, without differential drying stresses that material this weak cannot stand up to.

2.6 Chemical Degradation

2.6.1 The Contribution of the Burial Environment

The burial environment is unquestionably the single most important factor determining the level and type of purely chemically-induced deterioration that will take place in any single piece of archaeological wood. The ideal conditions for preservation are rapid burial at a depth in a wet, immobilising sediment that eliminates light, oxygen, and anaerobic bacteria. Such conditions do exist in wet clay soils, in river sediments, in peat bogs and under the sea. There has been substantial research into determining which of the factors prevailing in peat bogs are responsible for good preservation (Painter 1995; Waksman 1952; Christman and Oglesby 1971), and some of the results are equally applicable to other burial conditions in which archaeological wet wood is likely to be found.

Low oxygen levels are considered to be the most significant of preservation factors in the waterlogged environment. But while there is, indeed, no molecular oxygen below the top 30-50 cm of a water-saturated soil, this does not mean that there is no decay. Waksman (1952) identified both aerobic and anaerobic decay in considerable concentrations throughout the layers of a peat bog. It must be accepted that anaerobic bacteria are potentially just as effective as aerobic ones in breaking down polysaccharides in wood, since these are hydrolytic reactions that require only the presence of water and not molecular oxygen. In contradiction to Zeikus' (1980) conclusions, even oxidative reactions can be carried out by anaerobic bacteria, though only by reducing other substances such as carbon dioxide to methane, sulphate to sulphur or hydrogen sulphide, or nitrate to nitrogen or ammonia. Oxidation will cease if these compounds are no longer available, and incompletely-oxidised substances build up as end-products, e.g., (in the case of cellulose) lactic acid, succinic acid, ethyl alcohol, and short-chain fatty acids, many of which have been identified in Py-GC/MS studies (Diaz-Vaz *et al.* 1991; Saiz-Jimincz *et al.* 1987; Wilson *et al.* 1993). That anaerobic bacteria find lignin particularly difficult to break down is thought to be because its breakdown entails oxidative steps right from the beginning (Colberg 1988).

pH conditions are also considered paramount in determining preservation under waterlogged conditions. But Painter (1995) considers this to be much exaggerated. In terms of direct chemical degradation caused by extremes of pH, it has been determined that acids will primarily degrade wood carbohydrates, while alkalis restrict their attack primarily to lignin and, to a lesser extent, to hemicellulose. Alkalis thus may be responsible for exposing cellulose to chemical degradation by attacking the integrity of the lignin/hemicellulose matrix and forming soluble lignin-alkali complexes (Zabel and Morrell 1992). Wood so affected becomes fibrous and bleached in appearance, swells, and experiences steep reductions in strength, effects easily confused with those of white-rot decay. Acid causes hydrolysis of the α 1-4 glycosidic linkages in cellulose and hemicelluloses, resulting in drastic reductions in tensile strength. This depolymerisation makes wood brown and brittle, results easily confused with the effects of brown-rot decay. However, most wetlands have pH conditions of only pH 5.5-6.5. Since they are flushed continuously by water, they tend to be buffered by dissolved calcium bicarbonate and are thus only slightly acidic—optimal for bacteria and decay fungi. Sea water is more extreme, at a pH range of 7.5-8.4 (Florian 1987), and precipitation-watered bogs can be very acidic (pH 3.2-4.5) as a result of cation exchange reactions by the holocellulose fractions present sequestering calcium and other multivalent metal cations. Even in these conditions, however, anaerobic and aerobic bacteria have been found (Painter 1995).

The cationic exchange mechanisms mentioned above are highly significant for the preservation of wood. Pectic acids are particularly involved, and they become released from the holocellulose fraction in wood during the early stages of its breakdown. Humic acid has been found to be produced from the conversion of pectic acid keto-uronic acids (5KMA's) under mildly acidic conditions, and it is this that sequesters multivalent cations, iron in particular (Painter 1995). As long as humic acids are able to keep up with available metal cation concentrations in the soil, they may act to inhibit bacterial growth by depriving them of the nutrients they need, but where high concentrations are available (such as where there is an association of wooden artefacts with metal ones), then bacterial activity will be actively encouraged. In peat bogs, the amino-nitrogens that bacteria need are in sequestered form, inaccessible to bacteria. Wetland sites, polluted now from groundwater runoff from agricultural soils, are a new danger for still-buried artefacts (Painter 1995). Hedges *et al.* (1985) have determined, using elemental analysis (CHN), that nitrogen fractions (some of which come from the very small protein content of wood), tend to increase with the degradation level in wood.

Sulphur is another of the soil nutrients that affect the chemical stability of wood constituents. It is used by anaerobic sulphate-reducing bacteria to produce the oxygen necessary for oxidative metabolism of cell-wall polymers. This is a two stage process: first hydrogen sulphide oxidation, then sulphate reduction. It is generally accepted that the first reaction is catalysed by the presence of ferric ions, while the second reaction requires an organic acid such as the lactic acid produced as a by-product of bacterial

fermentation processes in the soil. These reactions tend to be self-feeding, with oxidation of ionised hydrogen sulphide back to sulphate, thereby continuing the cycle (Cork and Cusanovich 1979).

1. Hydrogen Sulphide Oxidisation

$$HS^- + 2O_2 \longrightarrow SO_4^{2-} + H^+$$

2. Sulphate Reduction

$$2CH_3CHOHCOO^- + SO_4^{2-} \longrightarrow 2CH_3COO^- + 2HCO_3^- + H_2S$$

Equation 2.1 Sulphate reduction in the burial environment (after Cork and Cusanovich 1979)

The presence of polyvalent salts in burial soils can have a serious influence on the rate of decay of the wood buried there. Though some acid salts such as copper oxides have been found actually to increase strength in some woods (Baker 1974), others have a very severe effect on its preservation. Iron is the major polyvalent ion to affect the chemical integrity of wood. Its role in encouraging microbial action has previously been mentioned. Prolonged contact of wood with iron (III) causes localised embrittlement and loss in tensile strength (Baker 1974). Iron salts are inherently acidic, as a consequence of the hydrolysis of the ferric ion. As iron oxidises to form ferric hydroxide, it catalyses the oxidation and depolymerisation of cellulose into oxycellulose. Iron present in, or in association with, wooden artefacts will tend to affect the moisture retention characteristics of the material, since iron actively corrodes at relative humidities above 20% (MacLeod *et al.* 1994; Emery and Schroeder 1974). Continued conversion of iron to hydrated iron salts within wood may thus cause severe mechanical damage to even treated artefacts as a result of the extreme volume changes associated with this conversion (Jesperson 1989).

Peaty waterlogged soils contain phenolic compounds, not unlike the tannins common to oak heartwood. If exposed to oxygen, they tend to oxidise and may then form the iron tannate complexes often presumed to cause the darkening of waterlogged wood. We have seen, however, that there are many other possible contributors to the darkening (largely a surface phenomenon) of waterlogged wood. Painter (1995) suggests that it might be produced by a Maillard or melanoidin reaction, a complex chemical transformation that occurs whenever reducing carbohydrates (also perhaps aldehyde and ketone breakdown products of lignin) react with proteins or amines under mildly acidic conditions (Ellis 1959). The result is dark brown, nitrogen-containing polymers, found in degraded wood because they are more or less resistant to microbial attack. These will only break down slowly in wet conditions by aerobic bacteria, if nutrients and molecular oxygen available. (Painter 1995). A more serious effect of tannins is the hydrophilic characteristics they tend to give polymers they are tied to.

Water itself in the wet burial environment appears to be responsible for reducing the chemical deterioration of wood constituents. Painter (1995) has drawn up a model from experimental results

which suggests that enzymes secreted by microorganisms into the water surrounding an artefact will have a tendency to become trapped and inactivated on the surface of buried woody substrates. These include cellulases, hemicellulases and pectinases. For this reason, in peat bogs the biodegradation of any polymeric substance too large to be ingested whole by bacterial cells will be suppressed.

In this section we have discussed reasons for the high variability of wood preservation in different wet environments. In the following sections we will see how these elements, if not excluded from the burial environment, cause the deterioration of the chemical constituents of wood.

2.6.2 Trends in Degradation of Waterlogged Archaeological Woods

2.6.2.1 Zonal degradation

Only in a few species and at the end of the deterioration process is degradation in waterlogged artefacts evenly distributed. Oak wood is particularly noted for its uneven or zonal degradation and it is this that makes it so difficult for the conservator to treat. (Figure 2.5)

Hoffmann and Jones (1990) recognised a distinct progression to decay in waterlogged oak wood. Degradation begins first in latewood vessels and parenchyma cells, progresses to fibre cells, and finally to the larger earlywood vessels which are highly resistant (for reasons of proportion of constituents discussed previously). It progresses along a distinct front (sharp in hardwood species such as oak, and more diffuse in other species) parallel to the wood surface and not influenced by anatomical planes in the wood. It moves from cell layer to cell layer in the cells at the several-millimetre-thick front, leaving only cell corners and middle lamella, before moving on to a new zone.

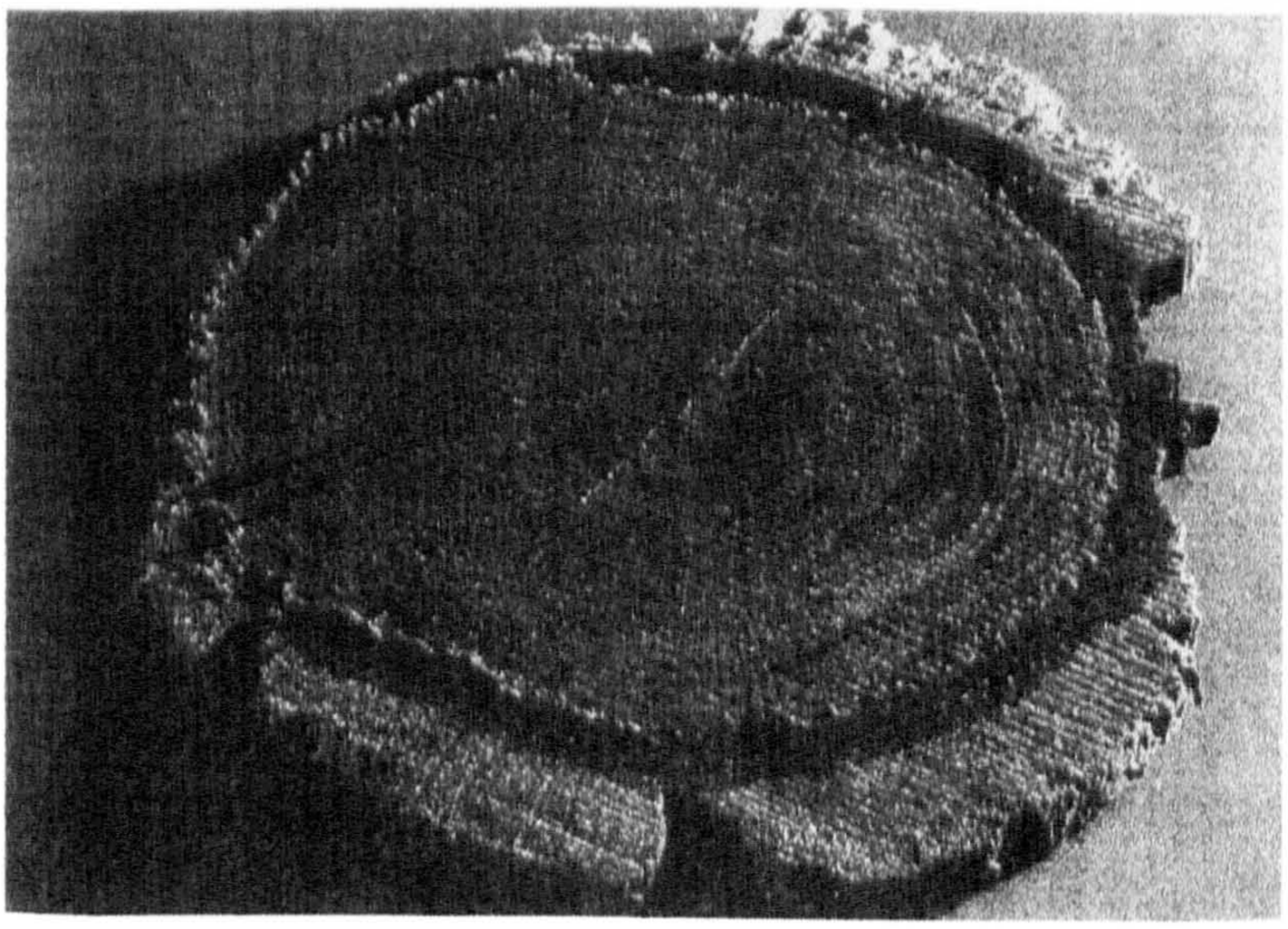


Figure 2.5 **Zonal degradation in waterlogged oak** **(Hoffmann and Jones,1990)**

2.6.2.2 Order of degradation of cell walls

Hoffmann and Jones (1990) are also responsible for plotting the progression of dissolution particular to waterlogged wood from observations made at zonal boundaries by microscopy backed up with chemical analysis. The process is, briefly, as follows:

1. Swelling of S2 and S3 causes loosening of lignocellulose complex.
2. Hydrolysis of hemicellulose begins in secondary cell walls and spreads rapidly.
3. Cellulose begins to break down from lumen inwards, losing crystallinity.
4. Cellulose degradation continues to total dissolution leaving middle lamella lignin honeycomb. (Barbour and Leney (1986) have determined that this middle lamella skeleton contains some cellulose in crystalline form, that has been protected by the relatively higher amount of extractives encrusting the area).
5. Lignin breakdown begins when 6/7 original cell wall substance gone.
6. Amorphous remains of middle lamella begin to lose cohesion (by 0.1g/cm^3 specific gravity) and wood is left with consistency of fudge.

Figure 2.6 (below) shows the micromorphological changes to archaeological wood at approximately stage 5 above.

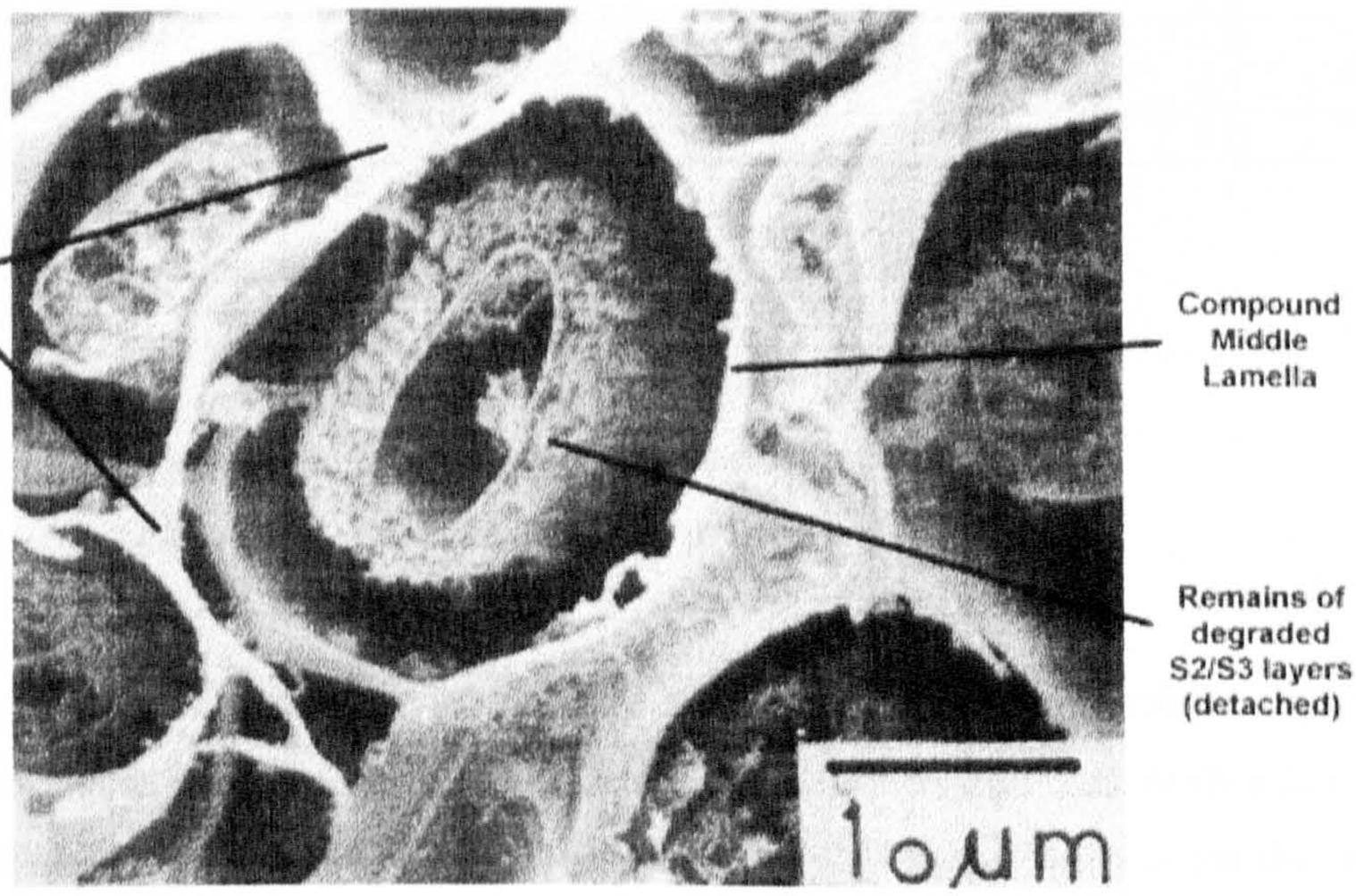


Figure 2.6 **Degradation of cell walls in heavily degraded oak (Hoffmann and Jones,1990)**

Nothing is known about what governs the rate of degradation in wood. Hoffmann and Jones (1990) believe it to be dependent on burial conditions, on the chemistry of the ground water, on inherent permeability and, to a lesser extent, on chemical constituent differences such as lignification and extractives. Hatcher *et al.* (1981) and Wilson *et al.* (1993) have established that the age of the specimen is not a significant factor.

2.6.2.3 Mass loss

Chemical degradation of polymeric substances involves such diverse processes as crosslinking and chain scission. These do not necessarily presume net mass loss, especially since the opening up of new bonding sites resulting from such degradation allows for new chemicals in the environment (e.g., humic acids and minerals) to bond into the material. In archaeological wet wood, however, there appears to be ample evidence of deterioration of constituents to soluble complexes
(Passialis 1997; Wilson *et al.* 1993). The wet burial context guarantees their dispersal. Table 2.1 below gives constituent values for a number of degraded archaeological oak samples in contrast to undegraded oak.

Constituent Ratios (weight percentages based on oven dry wood)							
Total Holocellulose	Cellulose	Hemicellulose	Lignin	Other Polysaccharides	Organic Extractives	Ash	Source
73.2	41.1	23.3	29.6	12.2	0.4	0.3	[1]
62.9	/	/	22.6	9.1	/	2.6	[2]inn
19.5	/	/	53.6	10.9	/	10.6	[2]out
52.8	/	/	30.2	14.0	/	4.0	[3]inn
12.9	/	/	49.0	0.4	/	12.4	[3]out
48.7	/	/	38.8	4.3	/	2.6	[3]inn_b
28.6	/	/	60.3	6.5	/	7.0	[3]out_b
77.9	38.3		24.7	/	3.4	0.3	[4]
61.1	37.8		25.8	7.7	0.78	7.6	[5a]
54.2	35.7		30.9	9.9	2.86	5.5	[5b]
55.4	25.5		20.6	15.3	0.67	4.0	[5c]

Sources:
[1] Fresh Oak (*Quercus robur*) Fengel & Wegener, 1984
[2]Arch. Oak (*Quercus robur*) Hoffmann & Jones, 1990
[3]Arch Oak (*Quercus robur*) Hoffmann, 1982
[4]Fresh Oak (*Quercus alba*) Fengel & Wegener, 1984
[5]Arch Oak (*Quercus alba*) Grattan & Mathias, 1986

Note: Percentages not mass normalised, i.e. constituents artificially concentrated by mass loss.

Table 2.1 Constituent ratios characteristic of degraded *Quercus spp.* wood

This mass loss is reflected in changes to density measurements, though increased mineral content may interfere with the directness of this relationship (Zabel and Morrell 1992). Hoffmann (1982) has determined that lignin is absolutely as well as relatively preserved, so the implication is that the loss must be ascribed to the holocellulose (total carbohydrates) fraction alone. However, this would seem unlikely, taking into account the work of microorganisms responsible for much of wood degradation. Even if we accept that archaeological waterlogged wood is primarily degraded by bacteria and soft-rot fungi, both of these agents do depolymerise lignin, even if to reduced extents. The question would thus seem to be whether these depolymerised fragments are left unmetabolised by the microorganism and thus identifiable by chemical gravimetric analysis. We are told that soft-rots and bacteria do not appear to leave lignin alteration products (Blanchette *et al.* 1990), but rather are reported able to utilise the low-molecular-weight fractions (Hedges 1990; Zabel and Morrell 1992). White-rots also metabolise all breakdown products (Zabel and Morrell 1992). It seems necessary to conclude, then, contrary to Hoffmann, that losses to lignins are a significant proportion of the total. It is important to establish this

point, because conservation treatment programs are often chosen on assessments of wood-deterioration level based only upon density measurements. Chapters 7 and 9 investigate this.

2.6.2.4 Order of degradation of constituents

Waterlogged wood is subject to spontaneous reactions with ambient chemical agents. The chemical changes in wood polymers, such as alteration of chemical characteristics, loss of crystallinity, changes in solubility, oxidation, and hydrolysis, will tend to be expressed in the wooden artefact as loss of strength, permeability, hygroscopicity, and other physical changes. Coniferous woods are generally more resistant to corrosive chemical attack than are most hardwoods, since chemically-resistant woods are generally those species high in α-cellulose and lignin and low in xylans. However, oak, with its relatively high lignin fraction, displays relatively high resistance.

Analyses have shown that the order of chemical stability in the polymers present in wood cells is, from most stable to least stable: β-Hydroxyl and vanillyl lignin structural units are the most resistant, followed by syringyl lignin units, followed by pectin, then α-cellulose, and finally hemicelluloses (Hedges *et al.* 1985). Van Krevelen plots of results from CHN analyses of archaeological wood samples (Hedges 1990), and work by Spiker and Hatcher (1987) comparing $^{13}C/^{12}C$, O/C, and H/C ratios in stable carbon isotope analysis confirmed with CP-MAS ^{13}C NMR, unambiguously show this preferential preservation of lignins over polysaccharides. Lignins are also the least hygroscopic of the major components, with cellulose occupying an intermediate position and hemicelluloses being the most hygroscopic. It is reasonable to assume, therefore, that the deterioration of these chemical constituents is highly correlated with increases in the hygroscopicity of wood (Schniewind 1990a).

2.6.3 Degradation of Hemicellulose

Hemicelluloses are vulnerable to dissolution in alkaline conditions and, because of their highly amorphous nature, some portion of them may also dissolve spontaneously under very wet conditions. Hemicelluloses also undergo breakdown by acid hydrolysis and through the enzymatic actions of fungi and bacteria, with consequent effect on the wood's elasticity. (Figure 2.7)

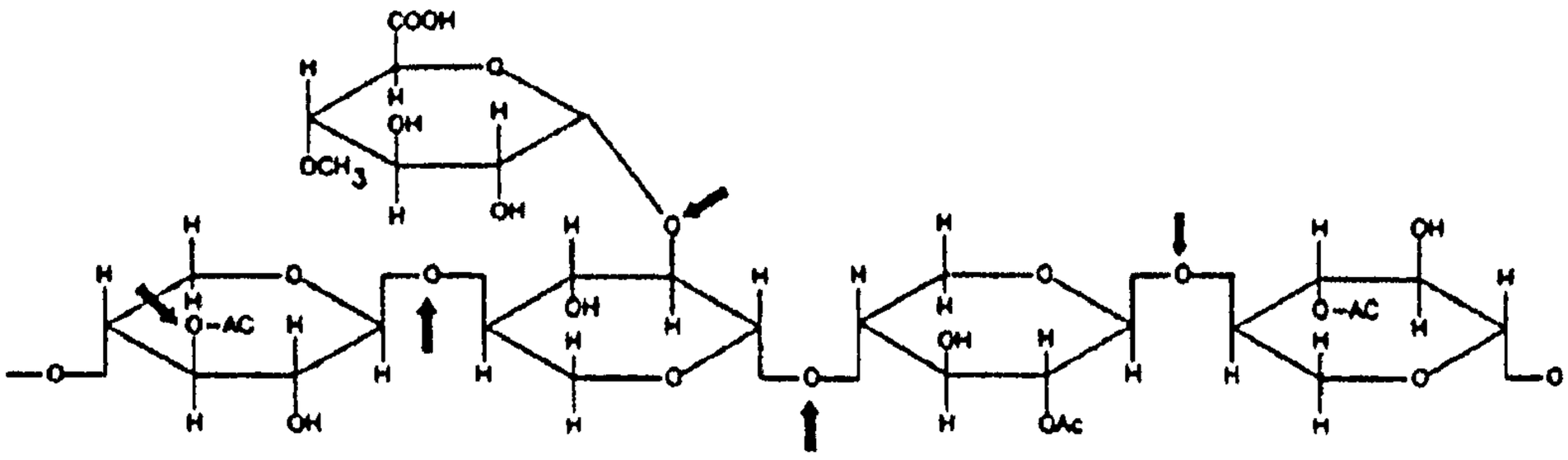


Figure 2.7 Sites for hydrolytic cleavage in hemicellulose (Zabel & Morrell,1992)

Bacteria and fungi will also metabolise hemicellulose, leaving no byproducts. Hemicelluloses are usually the first to be degraded, probably owing to their shorter chain lengths, inherent solubility and exposed locations around the cellulose microfibril. The processes of hemicellulose degradation are only now beginning to be elucidated, because of the complexity inherent in the variety of side branches, substituent groups and variations in sugars involved. It is known that the initial tendency is the stripping off of side groups from the polymer backbone and the separation of the polymer into xylose, mannose and galactose, and oligomers, as well as acetyl side chains. The end result of hemicellulose dissolution can be the production of proteins (Zabel and Morrell 1992).

2.6.4 Degradation of Cellulose

2.6.4.1 General

Breakdown of the cellulose polymer chain, occurring under waterlogging conditions, often follows from the access of water to the cellulose molecule via exposed polar sites in its amorphous regions, but is carried out by the chemical deterioration processes of photo-oxidation and acid hydrolysis. Since, under usual circumstances, both of these processes require acidic, aerated environments, open to high temperature and ultraviolet light—hydrogen and oxygen atoms contributed to the reaction process by the first two conditions and activation energy by the last two—it appears likely that purely chemically-initiated processes occur before the artefact has become fully waterlogged, and that afterwards primarily enzymatic processes prevail (Sjöström 1981).

2.6.4.2 Enzymatic hydrolysis

Enzymatically-induced dissolution of the cellulose polymer occurs in the presence of bacterial and fungal microorganisms. White-rots utilise a series of exo- and endo-β1,4 glucanases that achieve depolymerization of cellulose by a series of hydrolytic and oxidative reactions, details of which are given in the following sections. The initial pathway for enzymatic cleavage of cellulose is hydrolytic and involves the site of the glycosidic bond. (Figure 2.8)

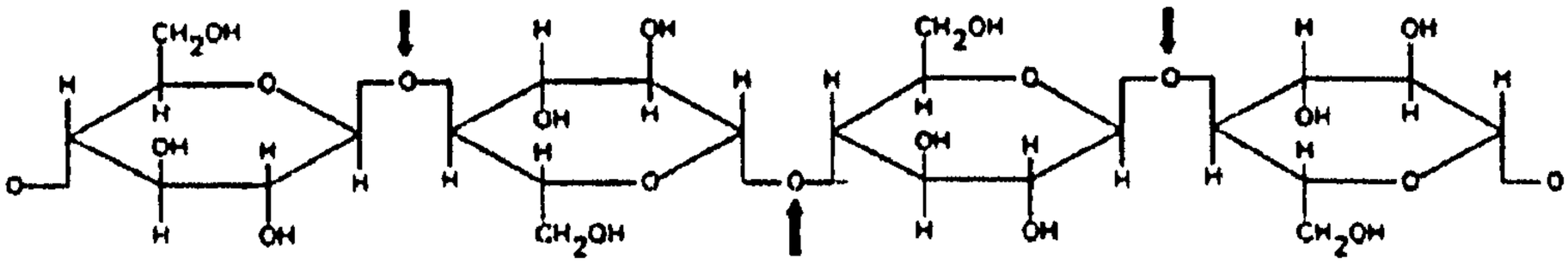


Figure 2.8 Sites for hydrolytic cleavage in cellulose (Zabel & Morrell, 1992)

The end products are oligosaccharides, cellobiose (2 glucose units) and glucose. Secondary decomposition pathways are both hydrolytic and oxidative, and involve the break-down of cellobiose to glucose, most of which is absorbed by the fungus (Zabel and Morrell 1992). Brown-rot fungi degrade cellulose in a manner that differs from that of white-rot. Though the decay mechanisms are less well

understood, a nonenzymatic oxidative depolymerizing agent has been proposed, perhaps aided by the H_2O_2 /Fe^{2+} system (Koenigs 1974). This step achieves separation of the cellulose chains in the crystalline zones, and is followed by cleavage of the cellulose polymer in a fashion similar to that of white-rots. This degradation occurs very early in the decay process. Soft-rots usually limit their activities to the amorphous zones of cellulose, though otherwise use much the same decay mechanisms as brown- and white-rots (Zabel and Morrell 1992). The visual results of enzymatic hydrolysis are generally localised crumbling and darkening of wood tissues, accompanied by drastic strength losses.

2.6.4.3 Oxidation

Chemically-initiated oxidation of cellulose always begins at the amorphous areas along the molecular chain, though it also may take place on the surface of the crystalline areas at the H^+ sites (Fengel and Wegener 1984). It requires the presence of heat or light for activation energy. Oxidation causes changes in the functional groups on the ring compounds that form the cellulose chain, the most obvious visible result being the production of chromophore groups that cause yellowing or browning of cellulosic materials. These changes eventually lead to breaks in the chain, weakening the molecule and opening it up to further chemical attack, especially by means of acid hydrolysis. Another result of photo-oxidation is the formation of free radicals; these will be responsible for the continuation of oxidative and hydrolytic degradation of cellulose, even in the absence of light (Hon 1979). Visible changes resulting from oxidative deterioration are a fuzzy appearance to the wood and, in extreme cases, the crumbling of tissues. The presence of iron oxides in the burial environment of the wood may contribute to auto-oxidation of cellulose through electrolytic actions (Florian 1987).

2.6.4.4 Acid hydrolysis

Chemically-induced hydrolysis of cellulose begins at the glycosidic bond or at the sites of carboxyl groups produced during oxidative degradation of the cellulose polymer. Activated by the presence of acids and water, oxygen links between glucose units on the chain are broken, thus reducing overall chain size and rendering more surface area open for attack or solubilization (Passialis 1997). End-products of acid hydrolysis are glucose and small amounts of disaccharides. (Figure 2.9) The most obvious visible result of hydrolytic reactions is brittleness of the cellulosic material and, in extreme cases, dissolution of cellulose.

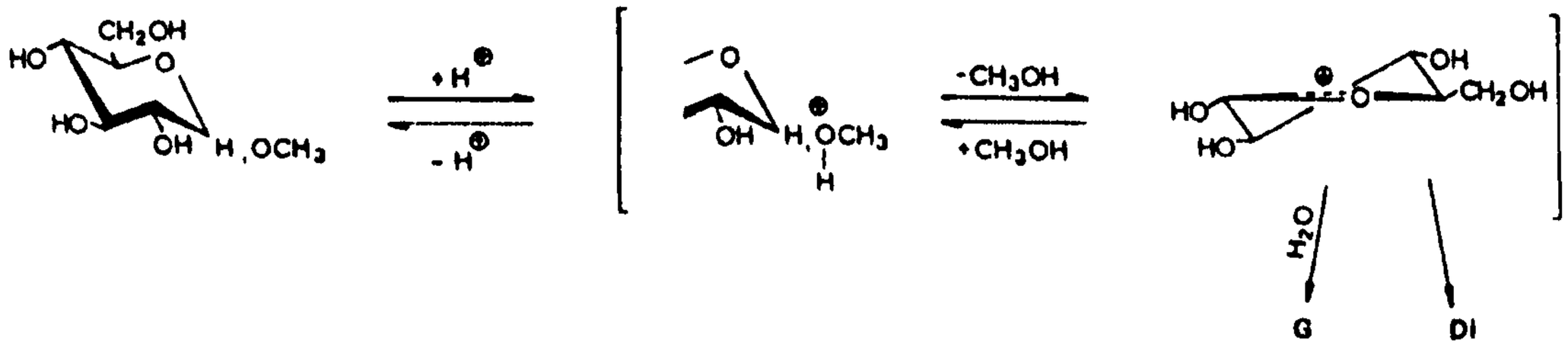


Figure 2.9 **Acid-catalyzed hydrolysis of cellulose** **(Sjöström,1981)**

2.6.5 Elevated Lignin Concentration

Elevated lignin concentration (proportional to holocellulose) is the most commonly-reported chemical property of ancient wood, and is consistent with woods from diverse environments (wet, dry, geological deposits, saltwater). As with wood carbohydrates, this trend does not appear to increase with the age of the sample in any regular fashion, which Hedges (1990) points out indicates that spontaneous abiotic chemical reactions are probably not the primary degradation mechanism. Increase in proportional lignin and decrease in polysaccharide are, however, related in a regular fashion to increases in water content, and also to losses in density (Figure 2.4).

Reservations about Hoffmann's (1982) claim that lignin fractions are absolutely as well as relatively preserved against diagenetic removal have already been expressed in an earlier section. Zabel and Morrell (1992) recommend caution about reliance on lignin determinations made by gravimetric solubility determinations. While there is also no evidence to show that polysaccharide degradation products are blocking the solubility of lignin for measurement (Hedges 1990), remnants of polysaccharide have been shown to continue in intimate association with cell-wall lignins, resisting removal by the concentrated acids used in these analyses, and thus remaining to contribute spuriously to measured residual lignin (Zabel and Morrell 1992).

2.6.6 Degradation of Lignins

As the primary role of lignin in the wood cell wall is to protect the structural carbohydrates from chemical and microbial attack, we can expect it to be inherently resistant to degradation. But because of its complex chemical structure, its mechanisms of degradation have only recently begun to be understood. It is known, however, that lignins are depolymerised primarily by oxidative enzymes that separate carbon-to-carbon bonds or ether linkages, and also separate various functional groups, side chains and aromatic rings randomly from the huge, amorphous lignin macromolecule (Figure 2.10). Unlike the carbohydrates, these cleavages are not uniform hydrolytic cleavages (Zabel and Morrell 1992).

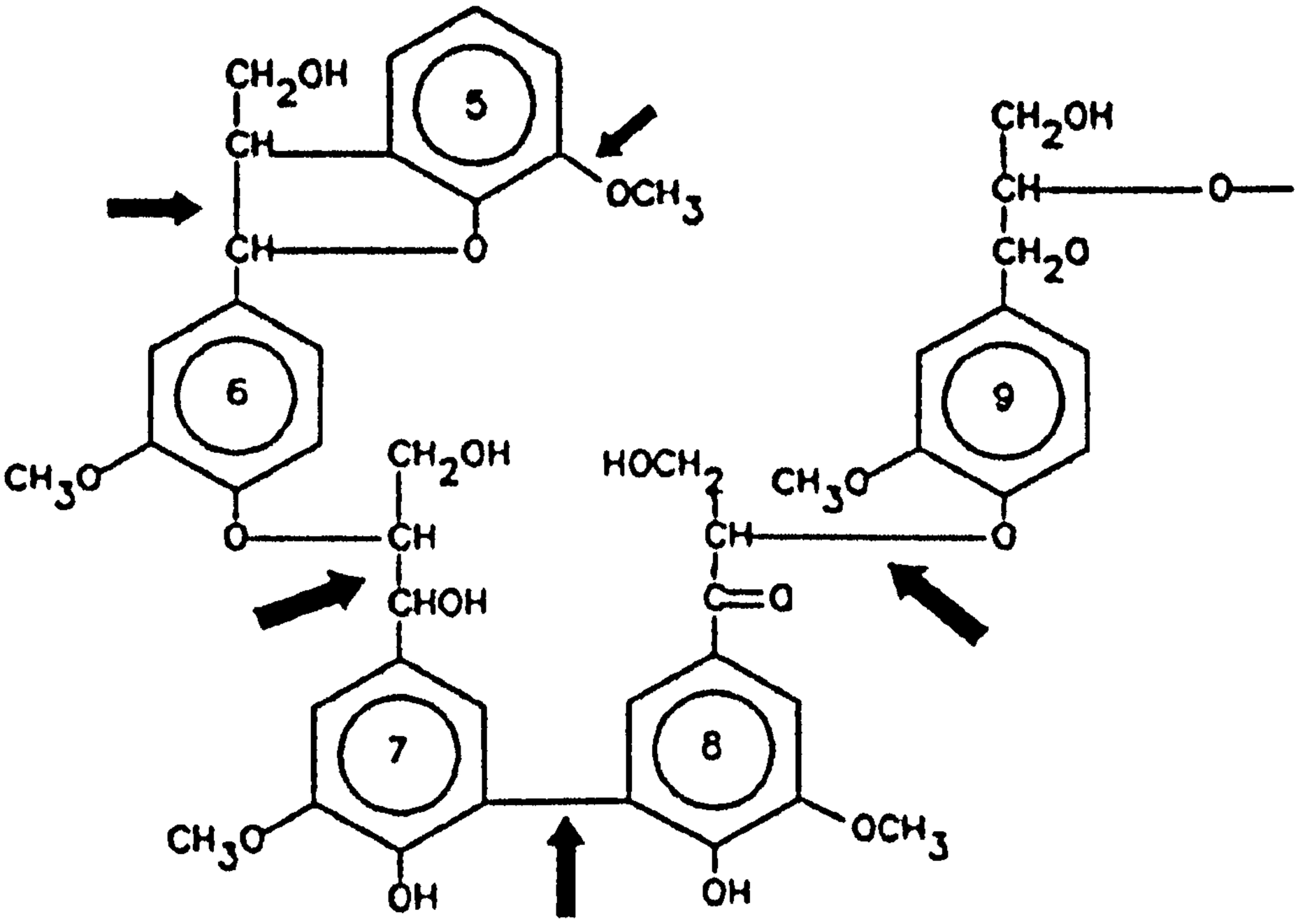
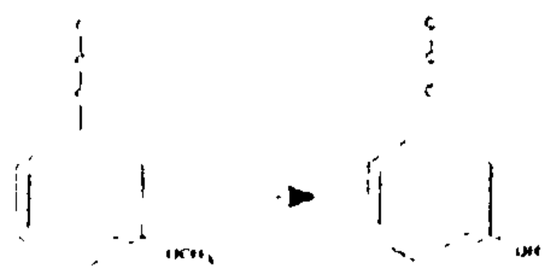


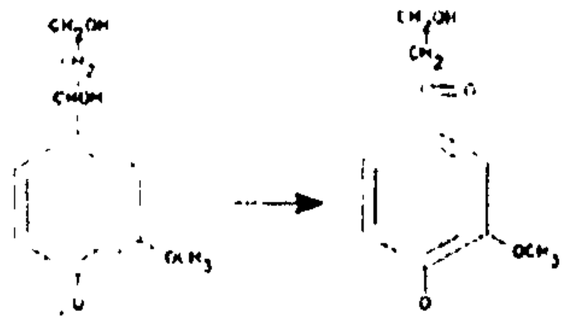
Figure 2.10 **Sites for oxidative enzymatic cleavage of lignin** **(Zabel & Morrell, 1992)**

White-rots, soft-rots and bacteria all employ the same mechanisms in decaying lignin. This process of decay is characterised by substituent oxidations, cleavage of 2-carbon fragments from propyl side chains and aryl ether linkages, a steady loss of methoxyl groups and an increase in oxygen and hydroxyl contents. Major structural changes caused to lignin include include:

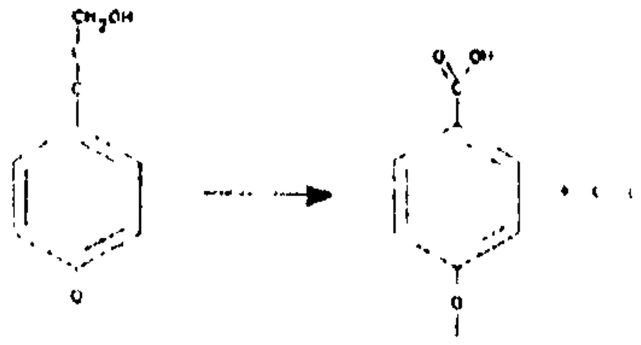
1. Demethylation



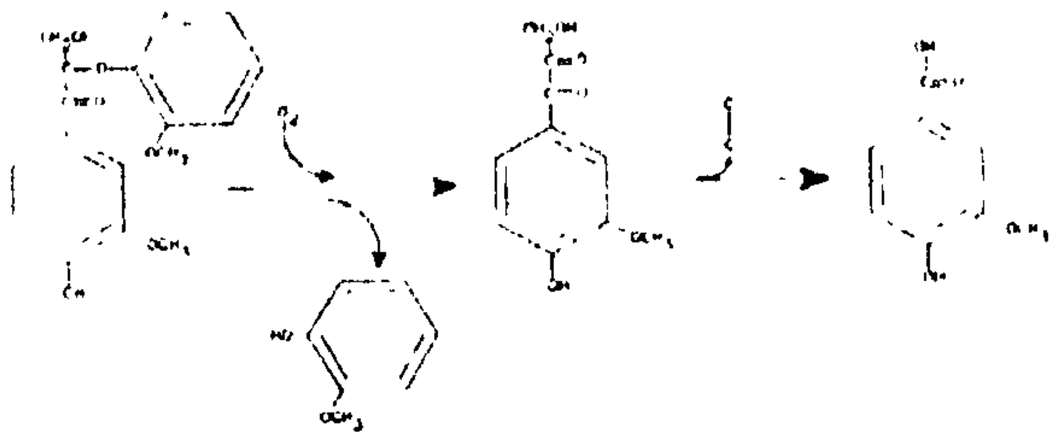
2. Oxidation of α-carbon atoms



3. Cleavage of the side chains between the α and β carbons of the phenyl propane units



4. Direct cleavage of an arylglycerol-β-aryl ether linkage



5. Hydroxylation and dioxygenase cleavage of aromatic rings

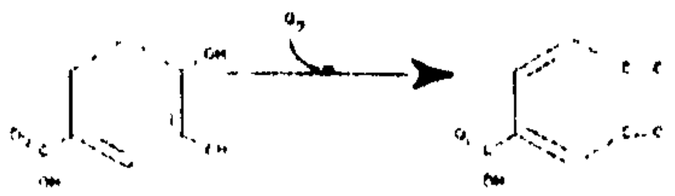


Figure 2.11 **Chemical modifications in decayed lignin** **(Zabel & Morrell, 1992)**

Wood degraded by white-rot fungi shows characteristically elevated yields of vanillic acid versus vanillin (Hedges *et al.* 1988). Soft-rot fungi appear to preferentially attack syringyl units (Nelson *et al.* 1995). There is, in fact, evidence that brown-rot fungi engage in lignin degradation (Kirk 1975).

Chemical analyses of residual lignin from brown-rotted wood seem to indicate substantial increases in solubility. The principal changes observed include decreased methoxyl content, oxidation of some alcohol and aldehyde groups to carboxyls, and the introduction of some phenolic hydroxyls. No significant separation of the guaiacyl and syringyl units appears to have taken place.

Typical low-molecular-weight products resulting from lignin degradation include vanillin, syringaldehyde, coniferyl aldehyde, vanillic acid, syringic acid, and a wide range of aliphatic or aromatic acids and phenols (Figure 2.12).

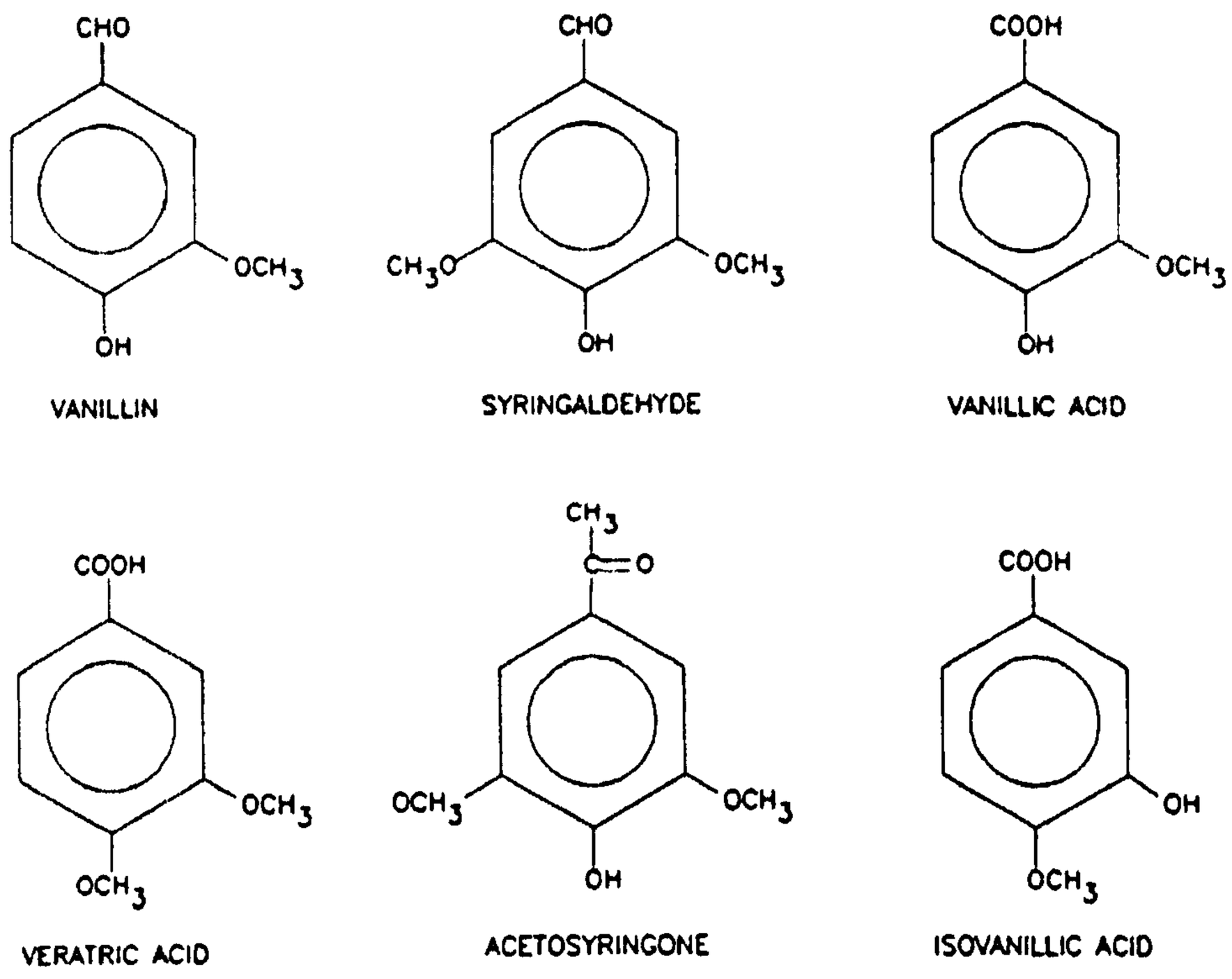


Figure 2.12 Low molecular weight degradation products of decayed lignin (Zabel & Morrell,1992)

Lignin is particularly sensitive to photo-oxidative deterioration. It is also affected by alkaline conditions, that cause increases in its overall crystallinity. There is a generalised increase of brittleness and friability of tissues (Florian 1987). Colour changes are produced by phenol-oxidizing enzymes.

2.6.7 Elevated Ash Content

Ash content has been observed to increase directly with degradation of cell-wall polymers and elevation of maximum moisture content. Levels have been measured as high as 20% in severely-degraded oak wood, an immense increase on the average 0.2% of fresh wood. Some of this increase may result from metabolic actions of fungi on the wood tissues, but much is attributed to the reduction of iron salts present in the burial environment by the action of sulphate-reducing bacteria (Hedges 1990). The deteriorative effect of these iron sulphides (FeS_2 pyrites) on wood polysaccharides has been discussed in a previous section. Prolonged contact of wood with iron minerals causes localised embrittlement and

losses in tensile strength (Baker 1974; Kim 1990). Schniewind (1990a) points out the contribution of elevated ash contents to increases in density, and cautions against judgements based solely on such data.

2.7 Changes to Physical and Mechanical Properties

2.7.1 General

Many changes occur during deterioration, ranging from drastic effects on wood strength to subtle modifications in properties such as density, hygroscopicity, and dimensions. The changes in one property are invariable associated with changes in other properties (e.g., changes in physical properties are a reflection of anatomical and chemical changes in the wood, brought on by degradation).

2.7.2 Bulk Losses and Reduction in Density

Losses to mass resulting from degradation of waterlogged wood have been discussed already in previous sections. The breakdown and removal of cell-wall components leads to reduction in overall mass. While degradation is only advanced as far as the relatively accessible components, relatively minor weight losses of 1-3% and minimal loss of strength is incurred. However, once the more chemically complex components such as lignins begin to be broken down and metabolised, weight losses of as much as 97% in some cases are incurred (Zabel and Morrell 1992). While mass loss can be a useful comparative measure of deterioration, it does not accurately measure the magnitude of decay effects on other properties of the wood, such as strength.

Density makes a better measure of wood deterioration for this purpose, and the degree to which density deviates from values for recent wood is commonly used as a measure of the extent of deterioration (Figure 2.13). Reduction in cell-wall density is thought to be the result of degradative losses of carbohydrates from the cell-wall lignocarbohydrate complex (Schniewind 1990a). Changes in density have generally been closely correlated with changes in certain strength properties, in particular with bending strength (Zabel and Morrell 1992). But it is not unusual to find that archaeological wood has suffered significant decreases in strength properties without any associated reduction in density (Schniewind 1990a). This could be to do with elevated ash contents.

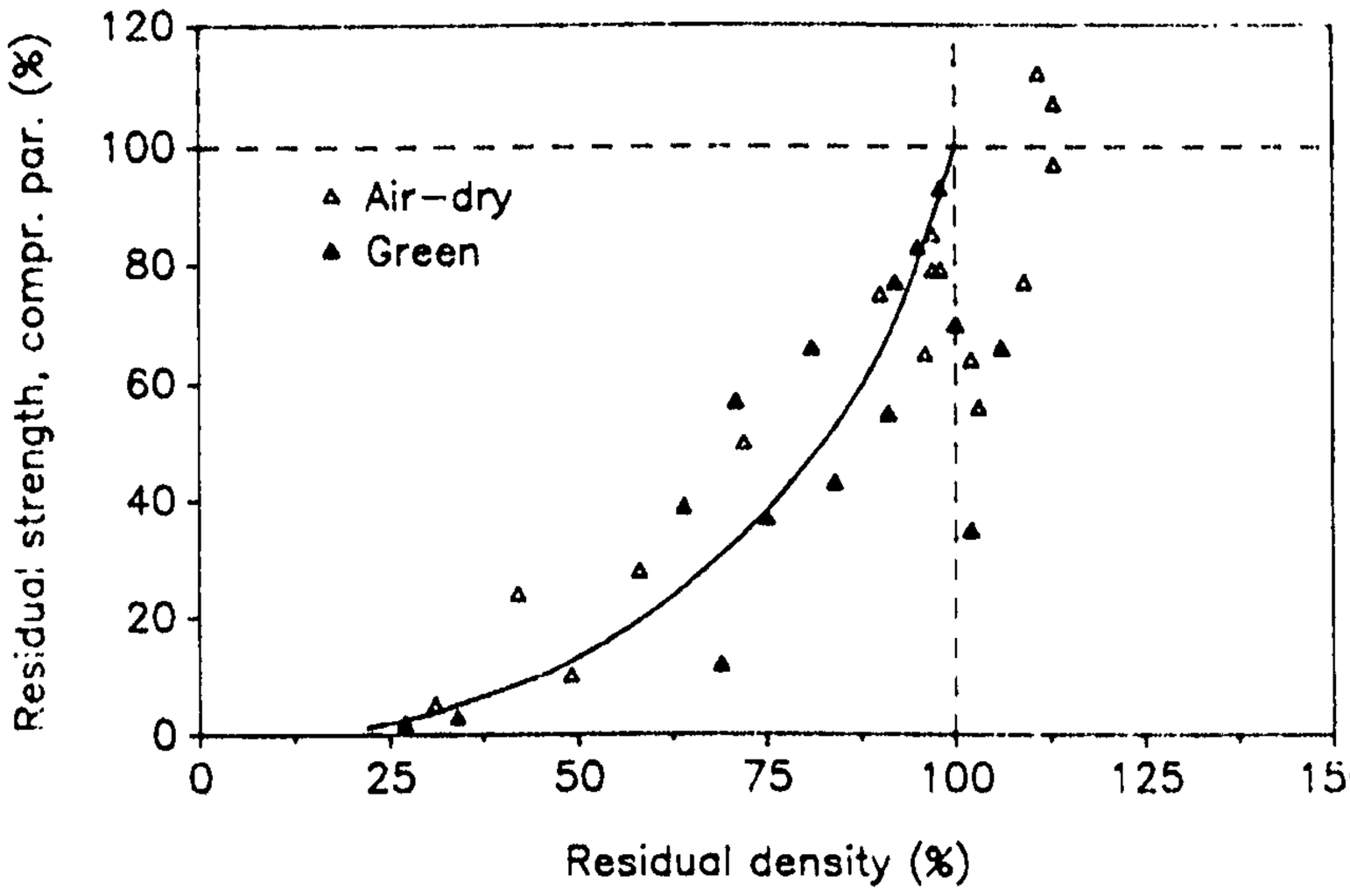


Figure 2.13 **Residual compression strength as a function of residual bulk density for a range of archaeological woods (Schniewind, 1990a)**

Reservations about the exclusive use of density as a gauge for deterioration have already been stated. Further reservations lie in the difficulty of making accurate measurements (especially of wood volume) since, as an organic colloid, it is affected enormously by changes to moisture content. Furthermore, while some fungi (white-rots) cause substantial weight loss without much change in wood volume, others (brown-rot fungi) cause substantial volume reduction as well (Zabel and Morrell 1992). Density reductions in wood decayed by these means would thus not be comparable.

A distinction must also be made between bulk density measurements and cell-wall density measurements. Most claim there to be no change to the latter even with large changes to the former. Measurements of bulk density of waterlogged wood are made using the maximum moisture content method, which is based on the assumption that the density of the cell-wall substance itself has remained unchanged. Certain conservation assessments (e.g. PEGCON, see Chapter 4) are based on this assumption, too. In addition, since the density of cell-wall substance is generally assumed to be constant, the density of a piece of wood obtained by measuring its overall weight and volume becomes a measure of wood porosity—and of many other properties. It is difficult to accept that there will have been no change to the density of the cell wall with selective dissolution of its components. Taniguchi *et al.* (1986) found some evidence of losses to the cell wall density of degraded waterlogged wood, but claim them to be small enough (1.38 g/cm^3, down from the accepted value constant for all species of 1.5 g/cm^3) not to affect basic density calculations. Reductions in cell-wall density have been shown to accompany increased accessibility (see Figure 2.14 below; also Figure 2.16).

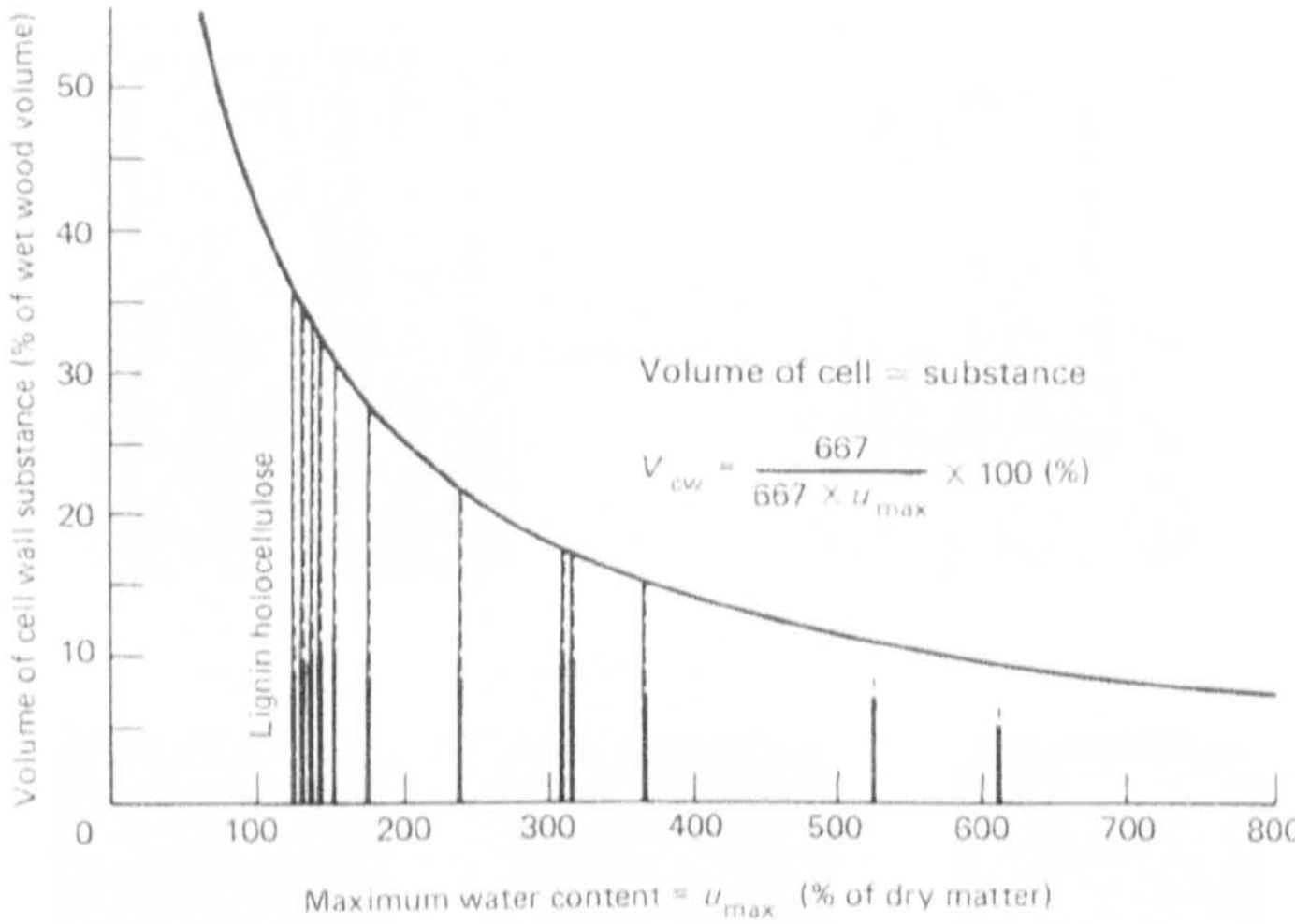


Figure 2.14 Graph of relation of water content to volume of cell-wall substances (Grattan,1987)

Changes in the bulk density of oak, usually expressed as *residual density*, can range from 20-140%. This increased density can be ascribed to natural variation within wood species, as density figures are compared to the mean values of recent wood that may have developed under very different growing conditions. This is another reason for caution about density figures.

2.7.3 Hygroscopicity

There are two ways of considering the effects of increased moisture content in waterlogged wood—hygroscopicity and permeability. Hygroscopicity is the tendency of a material to absorb moisture. As degradation of the ligno-carbohydrate matrix proceeds, it initiates changes to the moisture-holding capacity of the wood cell wall. These changes in turn alter equilibrium moisture contents (EMC), or the amount of water the wood is able to hold at any one level of ambient humidity.

Hemicellulose is the most hygroscopic of the principal components of wood, cellulose is intermediate, and lignin is the least hygroscopic. It is no coincidence that this, too, is the order of deterioration of the cell-wall components of wood. Moisture content has been used as the basis of a classification scheme for the degradation level of waterlogged archaeological wood meant to aid conservation treatment decisions (Christensen 1970; de Jong 1977). It groups wood according to the percentage of sound wood versus degraded wood (Figure 2.15).

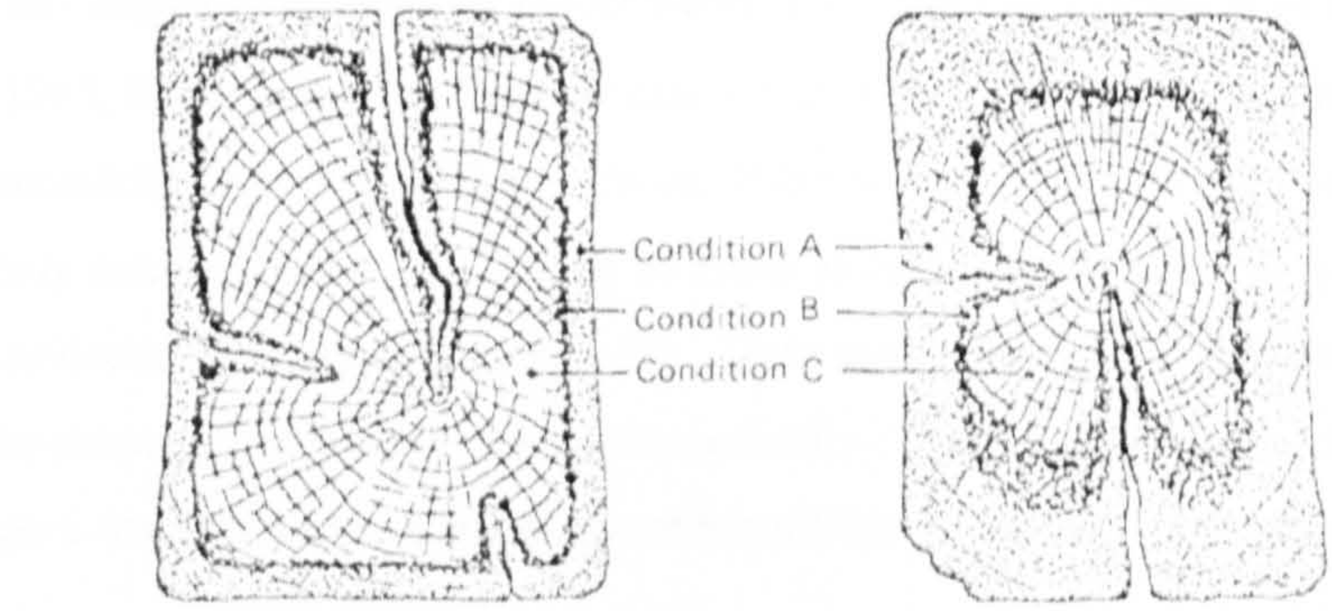


Figure 2.15 **The three classes of wood deterioration** **(Grattan 1987; after Christensen 1970)**

This system fails to be reliable where the artefact has undergone crushing or collapse or is not fully waterlogged. If lignin is the component of highest preservation in deteriorated wood, more severely deteriorated wood might be expected to be less hygroscopic than sound wood. Data available not only do not support this, but show the opposite to be true (Noack 1965; Hoffmann 1985). An explanation for this must be the increase of accessibility produced by the break-up of cellulose, more particularly its crystalline structure.

Generally, the EMC of brown-rotted wood is lower than that of sound wood, while that of white-rotted wood is higher, especially after weight losses of 60% have been incurred. Increase in EMC begins at 40% weight loss in white-rot, while in brown-rot there are sharp drops in EMC in the early stages of decay. These brown-rot results probably reflect preferential attack on the amorphous cellulose, which is usually responsible for retaining higher levels of adsorbed water than the crystalline cellulose; its removal in the early stages of decay decreases the overall moisture-holding capacity of wood. The absence of changes in EMC in early stages of white-rot decay probably reflect the uniform removal of all wood components, and the increases in EMC during the later stages of decay by these fungi may reflect selective attack on crystalline cellulose (Zabel and Morrell 1992).

Although comparatively little data on sorption characteristics of archaeological wood have yet been amassed, in such work as has been done EMC values for deteriorated archaeological wood are

consistently higher than those for recent wood, and appear so regardless of species (Noack 1965; Hoffmann 1985; Barbour and Leney 1982). This difference is much more noticeable at higher humidity levels, e.g. 80% and above. Fibre saturation point (FSP) values (see Chapter 3) are thus particularly increased, in some cases by as much as twice the usual levels, as shown in Schniewind's (1990a) collected data below (Figure 2.16). Fibre saturation point is important since it is the EMC where the properties of a wood change dramatically. This explains the tendency of archaeological waterlogged wood to undergo shrinkage at humidities just below 100% (Noack 1969; Barkmann 1975).

Sorption Characteristics of Buried Wood

		Density		*EMC at 98–100% RH[c] (FSP)*		
Species	*Age, years*	*Residual,[a] %*	*Basis[b]*	*Old Wood, %*	*New Wood, %*	*Ref.*
Abies alba	900	98	2	26.8	23.2	23
Quercus spp.	570	94	3	52.0	32.0	17, 43
Quercus spp.	700	88	2	34.3	30.8	22
Quercus spp.	800	104	2	36.0	30.8	25
Quercus spp.	800	106	2	36.7	30.8	22
Quercus spp.	800	109	2	34.5	30.8	22
Quercus spp.	900	111	2	29.5	23.0	38
Quercus spp.	1000	75	2	36.4	30.8	22
Quercus spp.	1100	102	2	36.3	30.8	22
Quercus spp.	1100	140	2	38.7	30.8	22
Quercus spp.	1600	96	2	33.3	30.8	22
Quercus spp.	4700	103	2	32.0	30.8	24
Alnus rubra	2500	42	3	60.0	30.0	21, 55

[a]Density of old wood relative to that of recent wood.
[b]1, OD weight and volume; 2, weight and volume at 12% MC; 3, conventional density (OD weight and green volume).
[c]RH is relative humidity.

Figure 2.16 **FSP values for archaeological waterlogged wood from various studies (Schniewind,1990a)**

Where FSP values do not show significant increases from sound wood values, it can be assumed that the wood is in good condition. Grattan (1987) points out, however, that once the cell wall becomes severely eaten away , the internal volume will begin to decrease again and the fibre saturation point will fall correspondingly. (Chapter 3)

2.7.4 Permeability and Porosity

Permeability is the facility with which a material permits the passage of a gas or liquid. Changes to accessibility or porosity in degraded woods produce associated changes in EMCs. Any change to porosity also changes the ability of the wood to accept treatment chemicals, and changes the stability of these treatments once in place. Increased porosity is also associated with increased chemical and biological attack.

Permeability is regulated by the control of liquid flow through wood, which is carried out by the pits, with the pit membranes acting as plugs. Pit integrity represents the major limiting factor in fluid flow through wood cells. The majority of decay fungi penetrate wood through pits, though some few do penetrate the wood cell wall directly. Bacteria can completely destroy the pit margo, leaving the torus non-functional. Damage or removal of the pit membrane makes wood markedly more receptive to movement of water, increasing the adsorption and desorption of water in comparison to that of sound wood (Flournoy *et al.* 1993). The process of pit damage or removal by bacterial action in waterlogged or saturated wood is relatively slow, though over several years this can show up in a substantial loss in volume.

The formation of tyloses in oak heartwood can render it almost completely impermeable. The internal deposition of iron tannates, iron salts or calcium salts, common in marine waterlogged wood, will yield equivalent results. In very degraded wood, pits have sometimes become fully aspirated for one reason or another, thereby leaving the cells impermeable. Wood permeability is thus not so easily related to wood degradation level, and this factor may have an affect on sorption data for the wood.

2.7.5 Dimensional Change

In green wood, water acts to support the wood cells and to plasticise the fibres of the wood so that it can better accommodate mechanical strain. In deteriorated waterlogged wood, water serves the same purpose though what it has to support is so much more depleted. Uncontrolled loss of water from archaeological waterlogged wood may result in collapse, shrinkage, distortion, splitting, embrittling, checking, delamination, and even complete disintegration. It may also result in wood that is relatively unaltered. This high unpredictability of results is one of the greatest concerns for the conservator of archaeological wood. The effects are much more severe on waterlogged wood than the drying stresses brought to bear on green (fresh cut) wood during seasoning (Figure 2.17). Because green wood contains considerable amounts of air, the movement of free water is more restricted and surface tension effects are thereby lessened in contrast to fully water-saturated waterlogged wood (Grattan 1987).

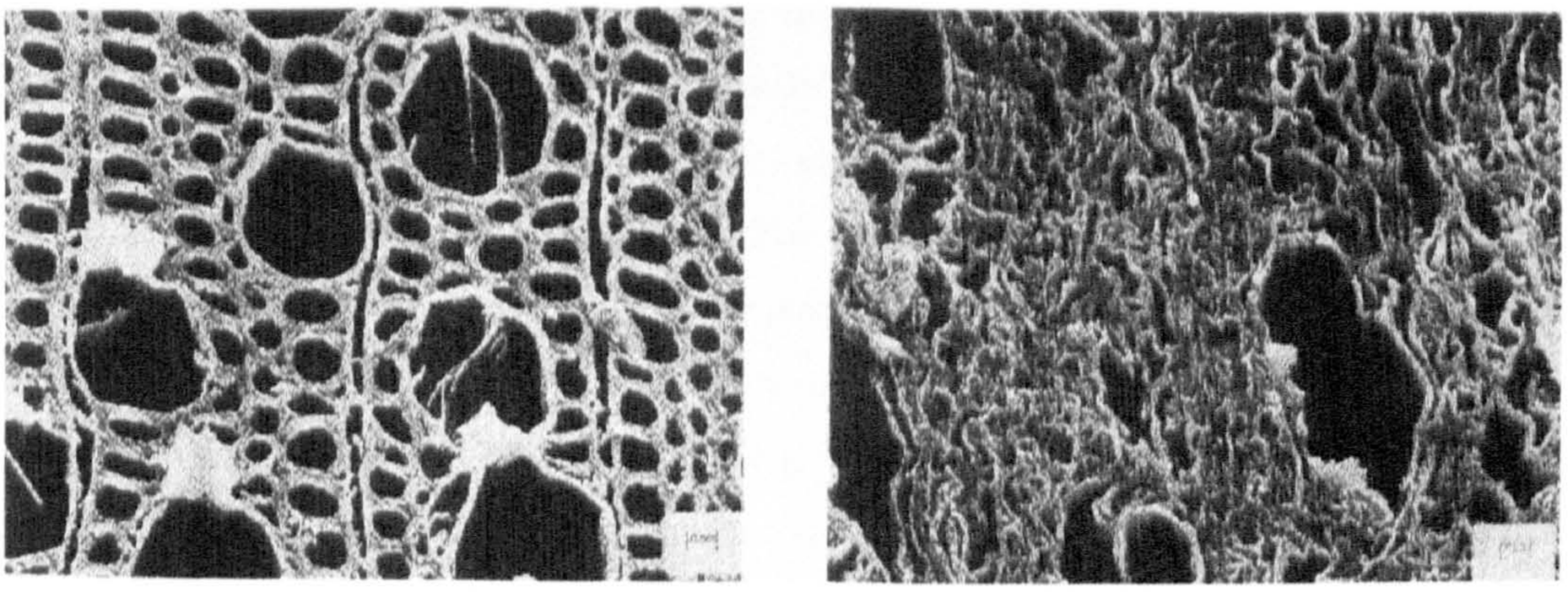


Figure 2.17 **Drying effects in fresh vs. waterlogged archaeological wood** **(Florian, 1990)**

Conditions produced by degradation that affect permeability of the wood are likely to be key factors in deciding whether deteriorated waterlogged wood will undergo extreme dimensional change on drying. Dimensional change is affected differentially in the different planes of wood. More important is the different moisture content at which significant changes in drying characteristics take place. Wood tissues under restraint—either within its internal system, or because of the construction of the artefact (e.g., at the joints of a box)—will be affected much more severely by dimensional changes, as they will tend to resolve themselves through the opening up of cracks or checks in the wood. All of these water-governed processes are discussed in greater detail in the next chapter.

2.7.6 Changes to Strength Properties

The effects of decay on the wood strength of recent timbers have been intensively studied (Zabel and Morrell 1992). Much less research has been carried out on the strength of archaeological wood.

Any alterations to chemical structure (especially to the carbohydrates of wood) that lead to decreases in mass will cause alteration to the mechanical properties of wood, for the most part sharp reductions. Most changes are readily measurable before the wood has exceeded a 5% weight loss (Zabel and Morrell 1992).

Of the many strength properties, work to maximal load, toughness, and impact bending are reported to be the most sensitive in detecting the early stages of degradation (Wilcox 1978). Most studies of the effects of degradation on modern timbers have used bending strength as a measure, testing large pieces of wood. From this data, modulus of elasticity, modulus of rupture and work to maximal load are calculated from stress-strain relationships. Uneven decay, however, is known to make such tests less meaningful (Zabel and Morrell 1992). Pockets of degradation produce failure zones that can magnify strength losses in small areas of the cell wall or wood tissues. For this reason, the strength testing of archaeological wood is very difficult. When smaller specimens are used, accuracy has been found to be variable. Measures of toughness are an exception to this. Reductions in toughness are a very good gauge of the early stages of degradation. Good results have also been achieved from longitudinal (bending) and radial compression, which are especially sensitive to the early stages of polysaccharide degradation (Wilcox 1978). The strength property most sensitive to slight amounts of decay, is the toughness or resistance to impact loading test, followed closely by static bending properties. Results from these measurements have shown that decay mechanisms that produce greater strength losses at lower weight losses (e.g., brown-rot, soft-rot) early in the process produce wood that is more damaged than that caused by other mechanisms of decay (e.g., white-rot) (Zabel and Morrell 1992). In later stages of degradation, little difference can be observed in the degree of strength loss resulting from different mechanisms of polysaccharide degradation.

Methods of measurement that have proved useful on archaeological samples include ultrasonic pulse tests (sensitive to losses in degree of crystalline structure) (Miura 1976), and various hardness-testing methods such as the Pilodyn needle impact hardness tester (Jones *et al.* 1986) and the Sibert resistance drill (Panter and Spriggs 1997). Most published results on this matter come from the work of the latter authors. These methods have proved relatively reliable in showing a linear relationship between hardness and maximum moisture content (Figure 2.18), and a semilogarithmic relationship between hardness and compression strength of a wide range of waterlogged samples in different states of degradation.

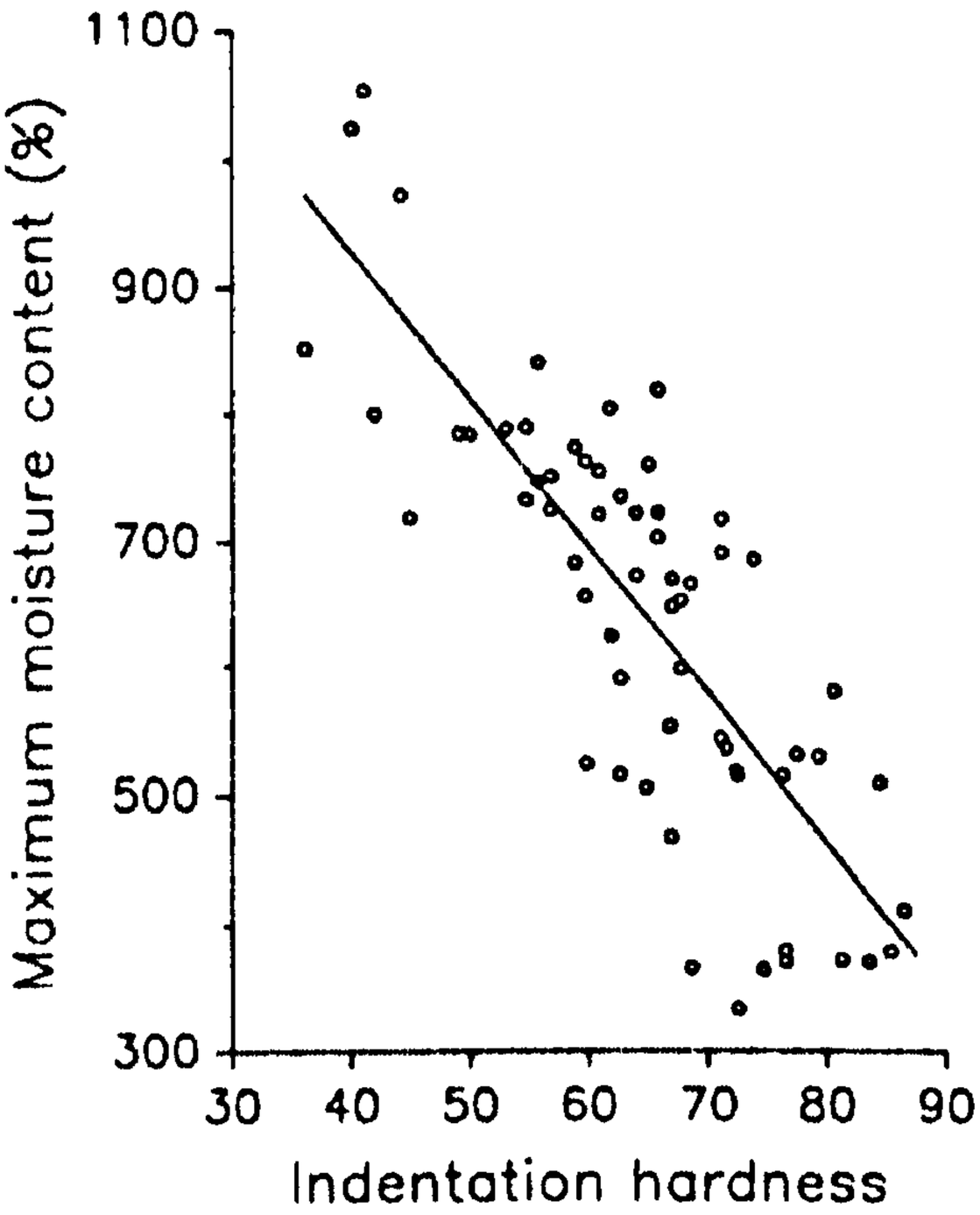


Figure 2.18 **Relation between max moisture content and hardness** **(Schniewind, 1990a)**

The usefulness of this resistance measurements as a diagnostic techique for degradation of archaeological timbers is investigated in Chapter 6.

Shock resistance, or impact bending strength data are generally most sensitive to the early stages of decay. Schniewind (1990a) reports values that show a great deal of variability. High values have been attributed by Hoffmann *et al.* (1986) to increases in plasticity, and to low stiffness values. Average residual impact bending strength is in the region of 68% and matches closely the residual bending strength values for the same samples. This failure to match the tendencies of modern wood undergoing above-ground decay processes appears to indicate that the mechanisms governing the deterioration of waterlogged wood are somewhat different.

Schniewind (1990a) provides a table of values for a number of strength tests carried out on buried waterlogged archaeological wood. In all cases, and in contrast to dry archaeological wood, strength

values are lower than for sound wood of the same species. He also plots residual strength values as a function of residual density (Figure 2.13), based on values from the above table, and shows clearly that loss in strength in this wood is proportionally greater than the mass loss, with moisture content controlled for. This suggests that strength losses in archaeological waterlogged woods are not directly proportional to, or due to, mass losses. He suggests that this may be because degradation in the integrity of the remaining substance (lignin for the most part) has also taken place. Chapter 8 investigates this. In the case of dry archaeological wood, it is thought that initial increases to cellulose crystallinity are responsible for maintenance of strength properties, though deterioration of cell-wall chemicals has also inevitably taken place.

Schniewind (1990a) makes the interesting observation that figures for tensile and bending strength are similar to those for compression strength, and modulus of elasticity and rupture are also reduced to about the same extent (51-53% on average). With early deterioration to cell-wall carbohydrates taking place, it would be unusual for these strength values to have decreased to the same extent. The relationship between density and compression strength is, however, displayed in oakwood in good condition. More highly deteriorated oakwood does not display such a high correlation between density and residual strength values.

2.8 Summary

We now have a clear picture of the effects waterlogging and burial have on archaeological wood.

Preburial degradation, including the effects of chemical weathering and decay fungi, appears to play a significant role in the degradation of the wood, though visual evidence of its influence may have become covered up by post-depositional degradation. We need to bring elements of this discussion into our own models for the degradation particular to waterlogged wood.

Factors affecting preservation include inherent properties such as growth characteristics, tissue variation (sapwood/heartwood), permeability, lignification, and heartwood extractives, as well as burial conditions, and chemistry of the ground water. The age of the specimen is not significant.

Post-depositional degradation appears to be weighted heavily towards soft-rot and bacterial degradation, with spontaneous abiotic chemical reactions unlikely as primary degradation mechanisms. The process of waterlogging itself is a contributor to degradation in wood because it decreases crystallinity and opens up the fibre structure to decay mechanisms. This process does not, however, initiate spontaneously in the presence of excesses of water, but is rather brought on by biodegradation, solubilisation and chemical deterioration, all of which cause net increases to wood porosity and permeability. Denser woods such as oak are more extremely affected by waterlogging than other woods.

It has been demonstrated that there is an order (distinctive to waterlogged archaeological wood) in the progression of dissolution of wood tissues, and within cell-wall constituents. Other distinctive trends in this material include mass losses, zonal degradation, iron and sulphur catalysed deterioration, and increased ash content. This latter is one of the main reasons for caution in making judgements based on wood density measurements of this material. We have been shown a direct relationship between increases in maximum moisture contents and degradation of constituents. A surprising fact has emerged through comparisons of inherent hygroscopicity of major wood constituents and increases to hygroscopicity brought on by degradation. Lignin is least hygroscopic, yet proportional increases in lignin content with increased degradation are not accompanied by decreases in hygroscopicity. Increases in accessibility, resulting from loss of crystallinity and depolymerisation of cellulose, appear to be the stronger factors here. Data in Chapter 5 will be seen to back this up. The matter of whether lignin is absolutely as well as proportionally preserved in degraded waterlogged wood requires further investigation, and Chapter 7 does just this.

The fibre saturation point of waterlogged archaeological wood is consistently and proportionally increased with degradation level, which explains the conservator's concerns in treating and storing this material. Severely degraded wood, however, may fail to show proportionately increased values because internal volumes have been severely reduced. Dimensional changes accompanying drying from such elevated FSPs are highly unpredictable because of the effects on diffusion of irregularity of decay and anisotropy of tissues. Further investigation of some of this variability would prove useful. .

Change to strength varies indirectly with degradation level and appears relatively linear with such measurements as maximum moisture content and density. They do not appear to be directly proportional to mass losses, however. The fact that they do not mirror the tendencies of above-ground decayed wood suggests that the degradation mechanisms that operate after burial are different and carry stronger weight in the final mechanical condition of waterlogged wood.

The factors summarised in this chapter will illuminate the content of the following chapters, where their direct relationship to conservators' concerns will become apparent, and the focus of analysis addresses some of the questions raised here. The comparative success of certain methods of analysis over others in obtaining the information the conservator needs will be assessed as part of the main aims of this research.

3 Water Relations in Wood

3.1 Introduction

Hoffmann (1982) remarked that it is with the capillary system of the cell wall that the conservator must work if he wants to stabilise his waterlogged wooden object. In discussing what materials and methods could most appropriately or successfully be used, it would be helpful to know the dimensions and characteristics of this complex capillary system. Since the atmospheric humidity determines the moisture content of wood, and this in turn determines the dimensions of the capillary system in wood, the interrelationship between humidity, water bonding, and the void system of wood can be expected to be of vital concern.

This interrelationship controls wood movement, strength, and permeability, and is itself a reflection of the deterioration level of the wood and the likelihood of future stability. Until now, wood-water relations have largely been the province of the wood scientists, who have published a large body of research. However, very little work has yet been carried out on the subject as it applies to waterlogged archaeological wood (Christensen 1970; Noack 1969; Barbour and Leney 1982; Hoffmann 1990; Schniewind 1990a). The concerns of wood scientists very closely echo those of conservators on this subject. Not only are they both dealing with wood, they share the same aims—to dry saturated (i.e. fresh) wood as fast and economically as possible to a stable equilibrium with the ambient environment, while producing minimal physical stress and damage to the material. But conservation has to treat with caution the conclusions drawn by wood science about wood behaviour when applying those conclusions to ancient wood. The last two chapters have established that ancient wood can be radically different to modern timber, both in inherent nature (age of tree, species) and in deterioration level and form. Thus we must expect water relations in archaeological wood also to be different.

In addition, most studies by wood scientists modelling water relations in wood look at moisture movements below the fibre saturation point (FSP), the problems of modelling being less complicated here than studies above FSP because of the presence of free water (Fakhouri *et al.* 1993). Moisture movement modelling below FSP is of limited use to those trying to predict the behaviour of drying wood, since this wood is *above* FSP because of having been in direct contact with liquid water rather than moisture. The movement of free liquid water in the wood system is considered to be highly complicated Comstock 1963; El Kouali and Vergnaud 1991).

3.2 Properties of Water

3.2.1 Chemical Characteristics of Water

The term *water* applies to water in all of its phases: liquid, gas, and solid (Cotterill 1985). The single water molecule is composed of two hydrogen atoms and an oxygen atom, configured in such a way as to form a slightly distorted tetrahedral configuration where the oxygen atom lies at the apex between the positively charged hydrogen atoms, and its own pair of negatively charged lone-pair electrons. It is this arrangement that confers upon water its characteristic and highly significant polarity, and its excellent ability to form hydrogen bonds.

The bonding of one water molecule to another is achieved largely through this hydrogen bonding. The three-dimensional arrangement of adjacent water molecules is controlled by their polarity: two molecules bonded via hydrogen bonds from their hydrogen atoms to a central oxygen atom, and two bonded covalently from their hydrogen atoms to the central oxygen's free radical end This structure is non- rigid and allows rotation of the water molecules on their axes (Laidler, 1978).

Earlier studies of water saw the liquid state as composed of a mixture of small aggregates of water molecules. This, however, did not take into account the fact that water molecules do not stay bonded to each other for more than a small fraction of a second. More recent models of water's liquid state take into account the observed regular arrangement of water molecules while in the liquid state. The hydrogen bonding between water molecules imposes certain restrictions on the possible spatial arrangement of the molecules, readily seen in water's solid phase, ice. At the higher temperature conditions of the liquid phase, there is distortion of these hydrogen bonds, but they remain intact, producing an irregular but still four-coordinated arrangement of the molecules. This is similar to the glassy state. Both have been given the term 'random network' for their instantaneous structure (Cotterill, 1985). Despite the basic stability of this network structure, individual water molecules within it oscillate within one area of the structural lattice for a short while and then jump into an adjacent section. At the same time, water molecules spontaneously undergo dissociation.

Water chemists are attempting to refine this molecular picture of liquid water (Finney 1981; Franks 1989, 1990). Their work stresses that while the older instantaneous, random-network models of water's liquid structure are sufficient on many levels, they are inadequate to aid understanding of the more subtle solvent-related effects observed in biological processes, or in explaining the strength of water-biopolymer interactions. These, they feel, lie in a much more detailed and exact understanding of the water-water hydrogen bond. The water-water hydrogen bond, however, is itself under reappraisal. It appears that in the liquid state the tetrahedral of the water-water interaction is considerably less than used to be believed. Such effects as cooperativity, molecular mobility, and perturbations close to

biomolecular surfaces change the magnitude and type of attraction between one water and the next and especially between water and biopolymer surfaces—in other words, for adsorption of water onto these polymers (Finney, 1981).

Water can exist in three general states or phases—solid (ice), liquid, or vapour—depending upon the temperature and pressure to which it is exposed (Figure 3.1).

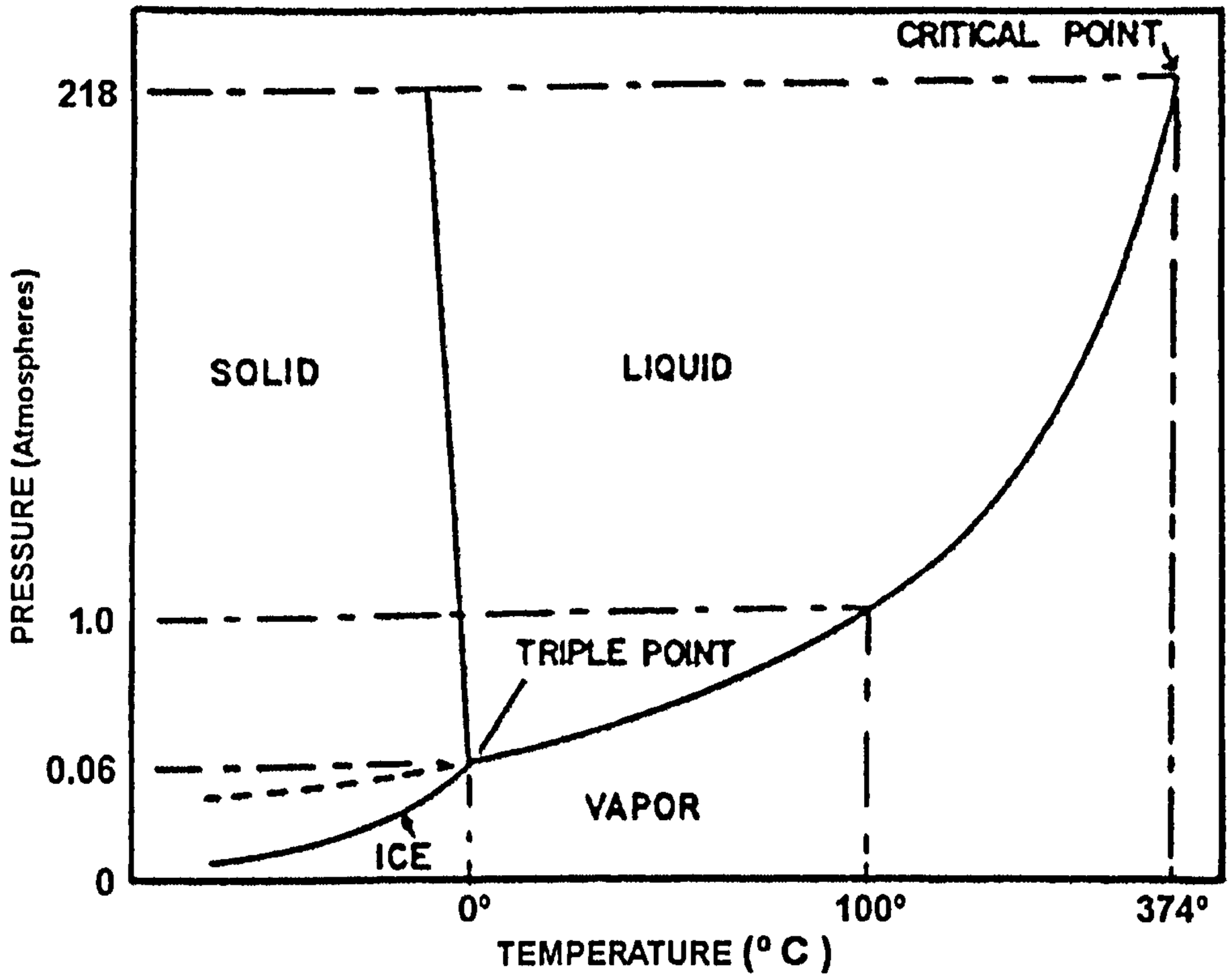


Figure 3.1 **Phase diagram for water (not to scale).** **(after Skaar, 1988)**

The kinetics of all three phases are significant to the conservation of wood: the liquid phase for deterioration and impregnation and for the initial phases of drying; vapour for drying and use-life; and ice for treatments such as freeze-drying. However, its vapour form is what most concerns us because it is the principal actor throughout all of these processes.

Certain of the new models appear in the discussion of sorption model thermodynamics in later sections, and in the discussion of the results from sorption analyses in Chapter 5.

3.2.2 Physical Properties of Water

3.2.2.1 Saturation vapour pressure

With sufficient vibrational energy to overcome the attractive forces of the liquid, water may escape and become a vapour molecule. Because of their high kinetic energy, these vapour molecules exert a pressure against an enclosure called the *vapour pressure* of the water. The higher the temperature of the liquid water, the greater the number of water vapour molecules and the higher the vapour pressure (since more can escape) and the higher the kinetic energy of the vapour molecules.

On this is based the temperature dependence of the vapour pressure of water:

$$\ln p_0 = 51.29 - 6651/T - 4.531[\ln(T)]$$

where: p_0 is saturation vapour pressure and T is temperature.

Equation 3.1 Temperature dependence of the vapour pressure of water (Skaar 1988)

Saturation vapour pressure (p_0) is the partial vapour pressure existing where the rate of evaporation is in steady state equilibrium with the rate of condensation in an enclosed space, and where the air can hold no more water at the specified temperature.

3.2.2.2 Relative humidity and water activity

The atmosphere is normally not saturated, the existing vapour pressure p generally being lower than the saturated vapour pressure p_0 (or p_s). The ratio p/p_0 is defined as the relative vapour pressure (h). Relative humidity (H) is defined as the ratio of the partial vapour pressure in the air to the saturated vapour pressure, expressed as a percent.

$$H = p / p_0 \times 100\%$$

where: H is relative humidity, p is vapour pressure, and p_0 is saturation vapour pressure.

Equation 3.2 Relative humidity (Skaar 1988)

Relative humidity is thus equal to the ratio of the absolute humidity of the air to the absolute humidity at saturation at the same temperature, expressed as a percent, and may be termed the *activity* of the water when in the context of the wood-water system.

In a closed system, humidity or activity mostly undergoes changes in response to changes in temperature (since this determines p_0) and is dependent also on vapour pressure p. Within enclosed spaces it is

temperature differentials that lead to variations in relative humidity, despite the fact that vapour pressure is generally constant. Usually activity is less than unity, i.e., vapour pressure p is less than p_0. But if the temperature is lowered within the space, or a substance's temperature is lowered, p_0 is lowered, and a condition known as *dew point temperature* may be reached. This is the temperature (T_d) at which moisture begins to condense from the atmosphere onto a cold object. This is an important consideration within the smaller enclosed capillary spaces of wood.

3.2.3 Water Interactions within the Wood Matrix

3.2.3.1 The internal surface

There needs to be a clear picture of where water is held in wood. Barkas (1949) describes wood as a sort of colloidal substance and as a gel, and summarises the characteristics of gels that are significant for wood. Wood fibres make up a swelling substance that, with the addition of adsorbed water, readily forms a solid solution—water-fibre polymer-water. These fibres are penetrable to different extents by water because of their hemicelluloses and lignin coating. There are two types of internal surface in wood to which water may bond: the permanent capillary system and the internal contact area of the cell wall fibre system. The cell system, as well as external interfibre surfaces, makes up the permanent capillary system of wood. These comprise a series of graduated capillaries (lumena), interlinked by pit openings. The intrafibrillary surfaces and internal voids between fibres make up the contact surface of the cell wall, also termed *second order space* (Skaar 1988) or *transient capillary zone* (Zabel and Morrell 1992), the non-pre-existing surfaces produced when water or other swelling agents are taken up by the cell wall, producing a solid solution (Stamm 1964). The proportions of these two types of internal surface determine the type and level of water interactions that occur within wood, and the physical condition of these two systems of capillaries determines the extent of water-wood relations.

The capillary system is extensive, its total area dependent on species, and capable when completely saturated of carrying up to 150% of the dry weight of sound wood in water (Grattan,1987). It has a surface of 100–200 m^2 for each cubic centimetre (Hoffmann 1982). The contact area of the cell wall fibre system, however, is a great deal more extensive (perhaps as much as 1000 times the capillary surface area) and though it carries only 20–30% of the dry weight of water in seasoned timber, after the swelling effects of waterlogging it is responsible for water contents of as much as 400% or more.

Stamm (1964) provides methods for estimating the extent of both types of surface area present in a piece of wood.

$$V_s = 1 - g\left[\left(1/g_w\right) + \left(m_s + m/\rho\right)\right]$$

where: V_s is the solid volume, g is the specific gravity of the wood, and g_w is the cell wall density, m_s is the saturation moisture content, m is the moisture content, and ρ is the density of water.

Equation 3.3 **Calculation of the void volume in wood** **(Stamm, 1964)**

Estimations of the volume of second order space in wood are not without problems, and therefore have undergone continued examination with a variety of approaches. Polymer exclusion methods have had some success (Stone and Scallan 1968a). Solution calorimetry has been used to measure heats of wetting for wood, and from them to calculate total heat of wetting, this being an indication of the total number of sorption sites within the cell wall accessible to water. Hatzikiriakos and Avramidis (1994) used the method of fractal dimension to characterise the internal surface of wood both in descriptive terms and in terms of area estimation. They found that methods of estimating the surface area of wood by determining the number of molecules of water corresponding to monolayer formation is not accurate. The fractal region calculated established that the internal surface is indeed much closer to being a three-dimensional one, and surface irregularities of the internal surface are extensive.

It is the change in this internal surface area resulting from deterioration that we are trying to measure indirectly by plotting the sorption isotherms of archaeological wood.

3.2.3.2 Bonding of water to internal surfaces

In the permanent capillary system, water will replace air as equilibrium vapour pressure rises. In the fibre system of the cell walls, water acts to increase the total surface area, and water then adds to water until the chemistry and thermodynamics of the system can admit no more (Berendsen 1975). Water is able to enter freely the amorphous regions of cellulose, where it is adsorbed onto the available hydroxyl groups. It is adsorbed only on the surface of the crystalline regions because of the unavailability of internal bonding sites already tied up by linkage with other cellulose molecules (Hedges 1990). The amount of water admissible to the fibre system of the cell wall, and consequently the amount of swelling that may take place at any one equilibrium vapour pressure, is dependent on the number of bonding sites made free on the fibre polymers (partially dependent on deterioration level), as well as the chemistry (iron content, alkalinity) of the water itself (Stamm 1964).

The thermodynamic constraints deciding whether, where, and how much water will bond to the internal surface is the subject of a great deal of discussion (section 3.6). Binding of water is not as simple as one molecule per binding (-OH) site. As Berendsen (1975) points out, it is probable that there need to be two free -OH bonds available to attract a water molecule to the surface of a biopolymer since, in the

liquid state, two bonding sites per molecule exist between water molecules. There is thus quite a considerable thermodynamic potential that must be created for one molecule to break away from its neighbours and bind with a fibre surface. The binding of further layers of water to the fibre could be expected to be less strong or permanent in nature (probably Van der Waal's forces rather than -OH bonds). Thus an increase or decrease in the number of bonding sites available along wood fibres will not have a direct relationship to the amount of water capable of being adsorbed, but instead an exponential relationship at certain points along the sorption curve. There is widespread confusion about the distinction between water bonded to wood and the hydration of wood. Binding to specific sites on the biomolecule is termed *specific hydration* and involves a higher binding energy, less motional freedom, and an extended lifetime at the binding site. It is distinct from *general hydration*, which is the sum of all water interactions in wood capillary systems (Berendsen 1975). Both general and specific hydration must be taken into account when attempting to get the fullest interpretation from sorption data (Laidler 1978). This is particularly illustrated in sorption hysteresis (section 3.3.2.3) and also determines the type of water within wood.

3.2.3.3 Types of water: levels of attraction

As well as solid, liquid, and vapour, a fourth, pseudo-phase for water is often mentioned in conjunction with wood-water interactions (Skaar 1988)—*hygroscopic water*, found only in the wood cell wall. Wood moisture may appear in three general forms, capillary water in the cell cavities and possibly in the cell wall, water vapour in the cell cavities, and hygroscopically bound water in the cell walls (Figure 3.2). Stamm (1964) outlines very clearly the distinctions between ways in which water is held in wood. They are summarised below.

Water of constitution is integral to the cellulose molecules and other carbohydrate-based constituents of wood. Though provisionally a permanent part of the polymer, this water can in fact be removed if sufficiently high degradation processes have occurred in the wood polymers to initiate their breakdown, as may be the case with waterlogged archaeological material. *Hygroscopically bound water* is generally accepted to be the monomolecularly adsorbed water which is believed to be held by hydrogen bonds to available sites, usually free hydroxyl groups, on internal wood surfaces. It is governed by theories of monomolecular adsorption.

Bulk water is the water adsorbed beyond the monomolecularly held water—i.e., water held in layers two to eight or nine molecules thick. It is a type of water largely unacknowledged by wood scientists, who tend to lump it in with the hygroscopic adsorbed proportion of water. Bulk water does not include capillary condensed water, or only the small fraction (<2% of cell wall volume) held in pre-existing capillaries or voids in the cell wall. It is held in solid solution in the cell walls, where it holds the fibres apart. This water is governed by thin film theories (Clifford 1975).

Capillary condensed or *free water* are terms that apply only to the take-up of water by *ab*sorption into capillary structures, such that a solid-air interface is replaced by a solid-liquid interface. (Stamm 1964). The capillaries involved may be so small as to approach molecular dimensions, and it will also occur to a limited degree within the discontinuous void volume of the cell walls (2% of cell wall volume in fresh wood, but very likely more in waterlogged wood), though only after all true capillary spaces are practically saturated. This water is governed by capillary theory.

Equations can be applied to calculate the average number of molecular layers of water adsorbed up to the point where capillary interactions start to take precedence (Stamm 1964). This can be very useful for predicting the behaviour of water in the cell walls. That this is an average, however, reflects the complex nature of the progression from one type of interaction to the next in the sequence of increasing or decreasing the water in the system. What this specifically expresses is the fact that, at any one relative vapour pressure some of the fibres will have adsorbed the maximum number of layers, whereas some fibres will have adsorbed less—the result, presumably, of different sorption sites exerting differing levels of attracting forces for the water.

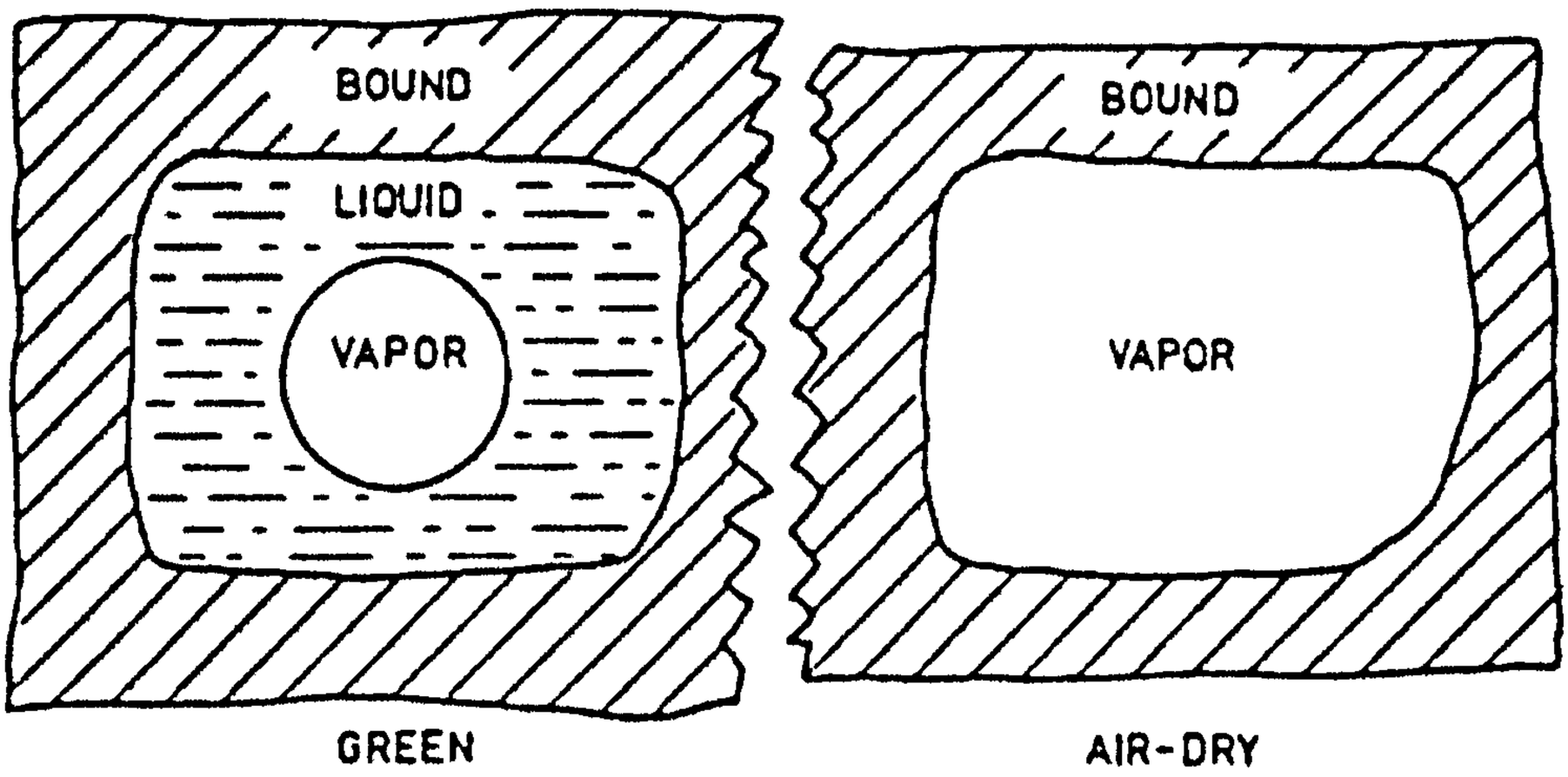


Figure 3.2 Schematic diagram of three kinds of moisture in green and dry wood (Skaar, 1988)

Adsorption that occurs on pre-existing surfaces is small compared to the take-up of liquid within the solid substance. For the most part, just two of the above categories are distinguished for attention in wood-water studies, the capillary or free water, and the hygroscopic or bound water. To be able to fully describe the sorption isotherm for wood, detailed information of how water interacts with wood at a molecular level has to be obtained.

3.2.3.4 Recent research

Research during the last decade has brought new insights into the structure and behaviour of water that sorption theories previously did not consider. Nuclear magnetic resonance (NMR) analysis has played an important role in these matters, because of its ability to provide insight into structure and dynamics at a molecular level,and it has been used extensively to investigate the wood-water system. Early studies recognised two states of water (Childs 1972; Froix Nelson 1975), free and bound. Later, *layering theories* were most well accepted (Caulfield 1978), arguing for decreasing energies of interaction between water and biopolymer with each layer of water molecules laid down. More recent NMR studies (Peemoeller and Sharp 1985) defined as many as three different phases in adsorbed water alone, depending on the strength of influence of the biopolymer on the water. IR work (Luck 1976) appeared to establish that at low moisture contents the bond energy between a binding site and the monolayer decreases as adsorption increases. When this was not clearly upheld by more recent NMR work, researchers such as Hartley *et al.* (1992) introduced *cluster theory*, where water molecules at hydration sites are thought to interact with each other to form clusters (Figure 3.3) with varying size and influence on the biopolymer. Clustering is thought to be what influences water-wood interactions below FSP.

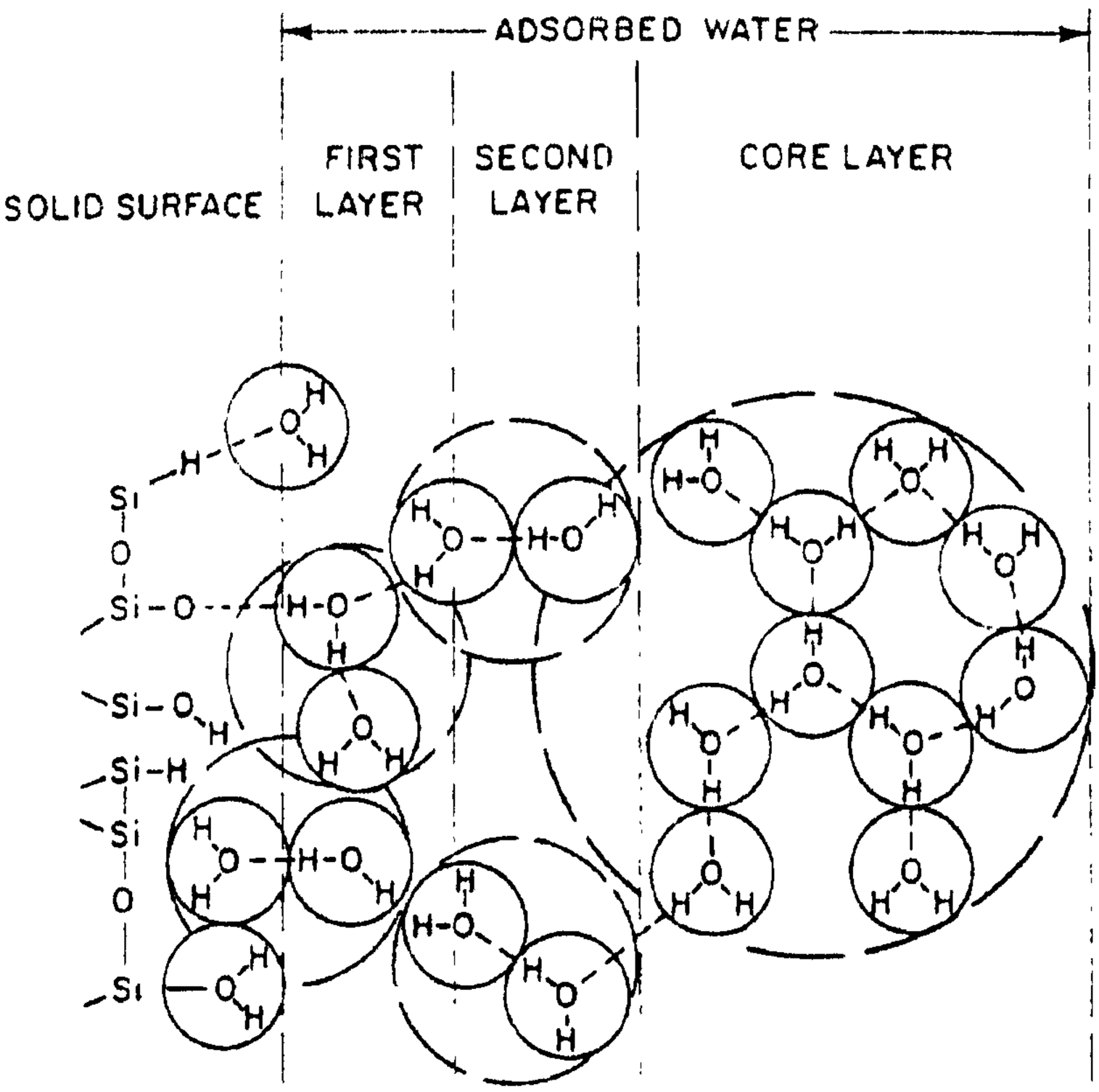


Figure 3.3 Cluster formation at a hydration site (model tested using glass) (Hartley et al., 1992)

Hartley and Avramidis (1993) further pursued this matter, to determine at which moisture contents clustering of water molecules occurs, both for adsorption and for desorption. Among others, Pizzi *et al.* (1987a & b) made the important point that the adsorption of water into wood must take into consideration water's heterogeneous nature. It is accepted that water attaches to available hydroxyl sites

upon adsorption into wood. But wood is not homogeneous in terms of morphology or site energies. Thus not all sorption sites (e.g., crystalline sites and amorphous sites) have the same ability to adsorb molecules, for example because of the strong influence of neighbouring hydroxyl groups. Their work indicates that it is possible for a water molecule to adsorb onto a site that already has a water molecule, rather than attach to an empty site. It can be seen from these conflicting views of water interactions that the equilibrium conditions and movements of water within the wood system and thus wood sorption isotherms are not open to simple interpretation and understanding.

3.2.3.5 Moisture content

The total moisture content is commonly used to summarise the total level of water-wood interaction taking place at a particular time. The moisture content of wood is usually expressed as a fraction of its dry weight (m), or as a percentage (M):

$$M = 100.\frac{w_m - w_o}{w_0}$$

where: M is % moisture content, w_m is moist weight of the wood, and w_o is the dry weight of the wood.

Equation 3.4 Moisture content (Skaar, 1988)

Moisture content is not easy to measure with any accuracy. A large number of different methods have been developed: gravimetry, distillation, nuclear magnetic resonance, Karl Fisher titration, electrical moisture meters (resistance and dielectric), and gamma radiation. Skaar (1988) reviews earlier critical discussion of these methods and others. He also comments on the significance of previous adsorption history to the moisture content of small wood samples. This is one of the most ubiquitous measures of wood science on which much other analysis depends, for example, constituent analysis, adsorption, density, porosity, etc. The problems with its quantification remain to be resolved.

3.2.3.6 Equilibrium moisture content

Since the balance between the different kinds of moisture in wood is regulated by ambient moisture conditions, when wood is exposed to atmospheric conditions it will tend to adjust its moisture content by evaporation or by adsorption until at balance with the surrounding atmospheric relative humidity. This moisture content is designated as the equilibrium moisture content (EMC) and is always approximately proportional to ambient relative humidity. Species or tissue type, temperature, mechanical stress and chemical deterioration can all be seen reflected in EMC values.

The effect of previous sorption history on EMC values is the subject of much recent work in sorption theory and modelling, and of particular relevance to the study of water interactions of waterlogged wood.

3.2.3.7 Fibre saturation point

The term *fibre saturation point* was created to mark the most significant EMC for wood—the point at which a changeover occurs between the two major types of water in wood. Traditionally, this point has been defined as the moisture content at which wood cell cavities contain no liquid water though the cell walls are still fully saturated with moisture (Tiemann 1906) (Figure 3.4).

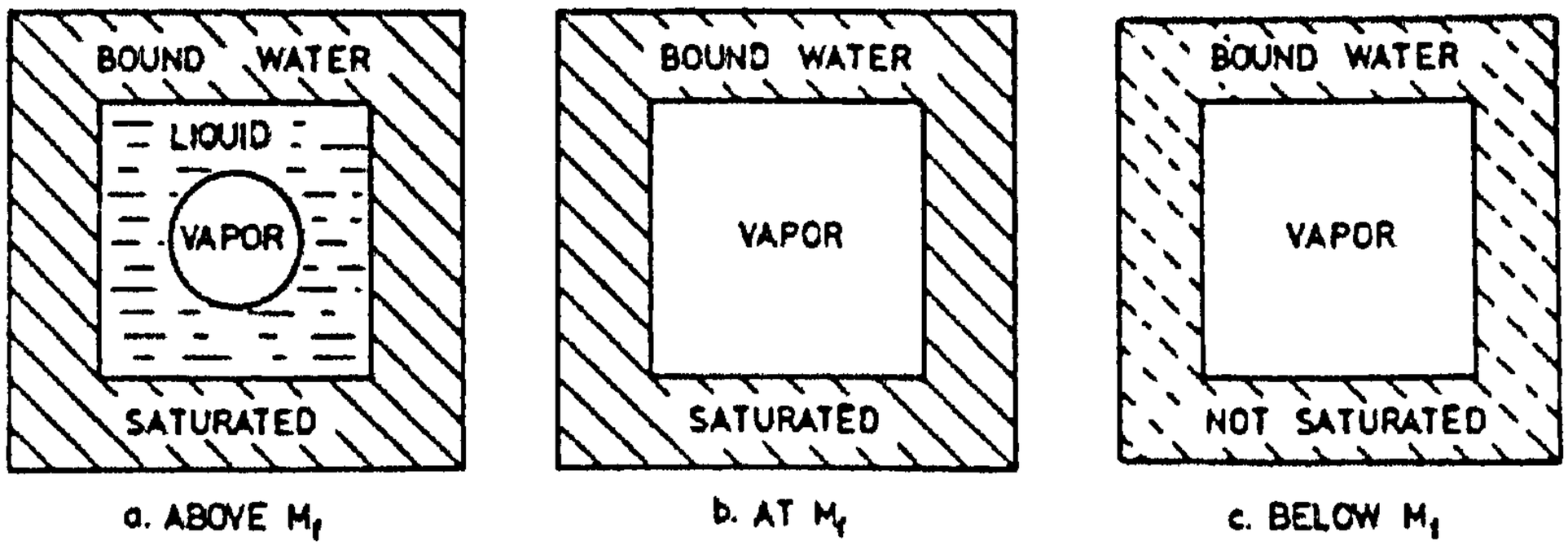


Figure 3.4 Schematic representation of FSP moisture distribution (Skaar, 1988)

Barkas (1949) and Siau (1984) pointed out the problems with Tiemann's definition of FSP. In light of the discussion of water potential (section 3.6.6), there appears to be no firm line of division between bound and free water. This increases the uncertainty in defining FSP. It is now known that loss of both free and bound water may, to a certain extent, take place simultaneously, a factor that further complicates calculation and understanding of this important point.

Later it was noticed that the mechanical properties of wood increase gradually and continuously up to this point, after which they act independently of moisture content. FSP is now, thus, usually defined as the moisture content corresponding to abrupt changes in physical properties in a piece of wood (Siau,1984). The point of interchange between where free water and where bound or bulk water holds sway is thus the point at which water interactions determine the physical properties of wood. Because free water cannot cause normal swelling or shrinkagein wood, since the cell wall is already saturated by the much more tightly bound hygroscopic water, it does not determine the physical properties of wood.

As with other equilibrium moisture contents, FSP is temperature-dependent and decreases about 1% for each 10°C increase in temperature (Stamm, 1971a). Values for FSP will also vary with species of wood. Stone and Scallan (1967) and Stamm (1971a) used polymer exclusion to measure values for hardwoods ranging from 12% to 33%. Resistance measurements of northern hemisphere hardwoods gave values in the more restricted range of 28% to 32%. FSP values will also vary with density and extractive content. It is worth remark that principal constituent (cellulose-lignin) ratios have not been found to influence FSP. This, however, is likely to be because measurement were made largely of sound wood samples where differences would not be so marked as in deteriorated wood.

For the conservator, FSP is most significant for heralding the point at which capillary collapse changes over to shrinkage as major contributor to dimensional change during the drying of waterlogged wood (section 3.4.2.1). The presence of free water in wood drastically increases its decay susceptibility as well as the possibility of fungal attack.

3.2.3.8 Problems in determining FSP: recent work

FSP is very difficult to measure experimentally, partly because of variation throughout wood tissues, and partly because it occurs at somewhere close to 0.9998 vapour pressure, a point very difficult to measure accurately with current technology (Stamm 1971a). Hawley (1931) reviewed many of the methods for estimating FSP. Stamm (1971a) critically appraised nine methods. More detailed comparison of these methods occurs in Chapter 5. Often FSP is measured indirectly through such physical properties of wood as electrical (Myer and Rees 1926), which allows FSP estimation from measurements of the heat of wetting of wood samples.

Since cells empty one by one along a sorption front, FSP is also difficult to generalise for the whole of a larger piece of wood. The small diameter of a significant proportion of wood capillaries (microscopically visible) means that water vapour will undergo condensation at relative vapour pressures of less than unity. The presence of water-soluble salts and sugars will further encourage this (Hart 1984). For this reason, the sorption-isotherm extrapolation method may prove subject to error. The porous pressure plate method was developed to overcome these problems (Stone and Scallan 1967), and produces significantly higher values for FSP than the standard isotherm extrapolation technique. Feist and Tarkow's work (1967), using the polymer exclusion principle, avoided the problems associated with use of a swelling medium such as water or those of capillary condensation, as the whole is carried out in the liquid state. This is assumed to be the most accurate method for estimating FSP. The same work also established the fact that density was of significance to FSP, in that low-density woods exhibit higher FSP than high-density woods, assumed to be because of thin walls providing less swelling resistance than thick walls or the high extractive contents often characteristic of such woods.

3.3 Characterising Moisture Movements in Wood

3.3.1 General

Wood structure and chemistry is such that it is continually in a process of change in its relations with the water mixed in with it. It changes moisture content and distribution during drying processes, during treatment with impregnants, and during use after stabilisation. Changes in wood moisture content that depend on ambient conditions of atmospheric humidity and temperature will be sporadic or cyclic or both. For this reason, moisture and related gradients are usually present in wood whatever its condition or status of use.

Discussion of the transport of water or any fluid through wood must make the distinction between two main governing processes: *bulk flow* and *diffusion*. Bulk flow involves the movement of fluids through the interconnected voids of wood structure under the influence of a static or capillary pressure gradient. This is the process that governs the impregnation of wood with bulking chemicals. Above fibre saturation, capillary forces and related thermodynamic diffusion potential gradients operate to cause liquid flow. The flow rate is determined by the combination of these forces and wood permeability, particularly that between cells. Diffusion includes both the transfer of water vapour through the air in the lumens of the cells and bound water diffusion, which takes place within the cell walls of wood. This process controls drying treatments, moisture migrations of *in situ* timbers, and dimensional changes in objects in response to changes in environmental temperature and humidity. Though both bulk flow of free water and diffusion of bound or water vapour contribute to the shape of the sorption isotherm, water vapour diffusion is considered the governing process of the two. Diffusion models dealing with the hygroscopic (below FSP) range are most controversial and occupy the bulk of discourse in wood science, and thus in this chapter. Bulk flow will, however, be discussed in detail at the end of this chapter.

3.3.1.1 Diffusion

Diffusion is a very general phenomenon involving the spontaneous movement of one material in another from a zone of higher concentration to a zone of lower concentration, in an effort to equalise the concentration and thus increase the entropy of the system (Stamm 1964). In the case of porous, swelling solids such as wood, diffusion may involve the movement of a gas or a vapour through or into the void structure, the movement of a bound liquid through or into the gel substance, or the movement of a solute (e.g., PEG) through or into the solvent-saturated solid. This last should not be confused with the movement of a liquid into the coarse capillary structure, which is due to capillarity rather than the tendency to equalise the concentration. Fick's first Law of diffusion is the simplest expression that governs diffusion, and is the starting point for sorption modelling in wood.

The diffusion coefficient is the proportionality constant in this expression. In wood, which is affected most by swelling vapours and solvents, the diffusion coefficient is dependent on the concentration. In the case of the passage of moisture through wood under a relative vapour pressure gradient, swelling from diffusion exists layer to layer, each to a different degree. This causes a moisture concentration gradient to be set up. However, the nature of the penetrating liquid is all-important, since the penetration of the cell wall void system will increase with an increase in the swelling power of the liquid (e.g., salt water). The nature of the wood itself is important, as woods of high permeability (such as highly-degraded waterlogged wood) experience enhanced vapour diffusion.

Fakhouri *et al.* (1993) point out that since wood is an anisotropic medium, there are three principal axes of diffusion with three principal diffusivities within this material. Below FSP, these principal diffusivities are thought to depend on moisture content (Siau 1984; Droin-Josserand et al. 1989). Above

FSP the principal diffusivities can be considered as constant (Mounji *et al.*, 1991b). Thus the stage of absorption (or desorption, as in drying) of moisture beyond FSP, which is of principal significance to the conservator of waterlogged wood, will be most accurately described by a few parameters—the principal diffusivities, the moisture content at equilibrium, and the rate of evaporation from the surface expressed in terms of the RH of the surrounding atmosphere. Fakhouri *et al.* (1993) claim that with these parameters, the kinetics of the absorption-desorption history can be determined, as well as the concentration distribution through certain planes of the wood, regardless of shape. These are the basis of the various mathematical models created to describe the wood sorption isotherm.

3.3.1.2 Capillary absorption/condensation

Capillary condensation is the process governing the movement of water through the permanent capillary structure of the wood. Bulk flow results from normal surface tension forces and involves the replacement of a solid air or solid vacuum interface with a solid-liquid interface. But *capisorption* or diffusive vapour condensation will take place only in the grosser pore structure of the wood and after levels of 0.9 relative vapour pressure have been reached (Stamm 1964). Where the capillaries involved are so small as to approach molecular dimensions, considerable vapour pressures may be present. Stamm (1964) provides a table of the capillary sizes that will fill with water in the vapour phase when in equilibrium with various relative vapour pressures.

Size of Capillaries That Will Fill with Water Under Different Relative Vapor Pressures

Calculated from the Kelvin Equation

Relative Vapor Pressure	Capillary Radius (microns)
0.90	0.010
0.95	0.020
0.97	0.035
0.98	0.053
0.99	0.106
0.995	0.210
0.999	1.060
0.9999	10.60

Table 3.1 **Capillary size and relative vapour pressure** **(Stamm, 1964)**

Hunter (1991) studied capisorption and developed energy relationships that show how the surface geometry is related to the isotherm, thereby modelling liquid surface profiles. They found that increases in temperature cause increases in capillary radius even when moisture content is constant. This clearly indicates that as the temperature is increased at a constant total moisture content, water comes out of the chemical structure and resides in the surface layer, which itself becomes thicker.

3.3.1.3 Complications in explaining water movements in wood

The behaviour of water, its properties and movements, is clearly very different depending on whether it is bound water, bulk water in a thin film, or capillary condensed free water. Each of these may require a different model of explanation. Impurities in the water, particularly surface active impurities, produce anomalous effects. The magnitude, range and permanence of these effects on the properties of water are still much debated. The highly disordered porous and diffuse interfaces such as exist within wood are a further complication, because nothing happens continuously over such surfaces: different effects are almost certainly taking place simultaneously along the length of the delineating interfaces (Clifford 1975). Delineating where a surface begins and ends when dealing with biological substances (which are often in a state of constant interchange) is also complex (Ninham 1982). Moreover, with larger pieces of wood, what occurs on the surface and what is occurring on the inner layers of wood differs because of the lag while diffusion catches up. The same applies to differing layers in wood, more especially in highly zonated woods such as oak. These are just a few of the problems in producing models from sorption data to explain the behaviour of water in wood.

3.3.2 Quantifying Moisture Movement

3.3.2.1 Sorption defined

Definitions of sorption which follow current IUPAC regulations (Jakubke and Jeschkeit 1993) describe sorption as the uptake of a substance by a sorbant material, resulting in a distribution of the sorbed substance (*adsorpt*) between different phases without any accompanying thermal phase change, such as evaporation, condensation, or crystallisation. Where the sorbed substance is taken up onto the surface, the term *adsorption* is used, and where it is taken up into the interior, the term *absorption* is used.

Depending on the magnitude of the heat released by either of these processes (under constant pressure), a distinction is made between *physisorption* and *chemisorption*. Physisorption is due mainly to van der Waals forces between the adsorpt and the sorbant material, while chemisorption is due to chemical bonds between the two. Consequently, physisorption is reversible without any chemical change effected on either adsorpt or sorbant substrate, while chemisorption is not. The reversing of sorption is termed *desorption*. Both physisorption and chemisorption hold a place in wood-water relations.

Adsorption of water into wood has been measured by resistance, dielectric measurements, NMR, FTIR, DSC, mercury porosimetry, membrane diffusion, and water vapour adsorption gravimetry: all of these are compared critically in Chapter 5.

3.3.2.2 The sorption isotherm

The sorption isotherm is a graphical plot of the relationship of equilibrium moisture content and ambient relative humidity. Because of the effect of temperature on the thermal energy of water molecules, the sorption isotherm is always plotted from data taken at a constant temperature. The sorption isotherm is used to express the equilibria established at surfaces, and graphically relates the amount of water intimately attached to the surface of wood macromolecules to the concentration of the water present. Depending on the availability of bonding sites on the macromolecule, and on the properties of the water, wood surfaces may become completely covered by a unimolecular layer of the substance or it may cover the surface at intermittent sites only (Laidler 1978). Under certain conditions this take-up is only one molecule thick; when polymolecular it rarely exceeds an average of 10 molecules thick. Considerable adsorption will occur at low vapour pressures, which is a reflection of the greater attractive force of the adsorbent for the adsorbate rather than the attractive force of the adsorbate for itself.

Water sorption isotherms, and in particular their components at low relative humidities (the monomolecular level of the sorption process), have been used in the past to calculate the internal surface area and porosity of various wood species (Stamm 1964). Both characteristics are useful tools in the evaluation of heat and mass transfer phenomena in wood, such as in drying and in gas or liquid impregnation. Furthermore, in processes like chemisorption and physisorption of water vapour by wood, the entire sorption isotherm (monomolecular and polymolecular component) has been used to evaluate energy liberation, sorbed water molecular distributions and degrees of freedom, fraction of wood surface covered by molecules, and possible alterations to the surface structure during the sorption process (Stamm 1964; Skaar 1988; Adamson 1990). Labusa (1984) gives a bibliography as well as a discussion of the measurement and use of moisture sorption isotherms, including their application in evaluating the moisture condition of fibre-based products.

Five different types of adsorption isotherm have been recognised, though only three are directly applicable to the wood-water system (Urquhart 1960). (Figure 3.5)

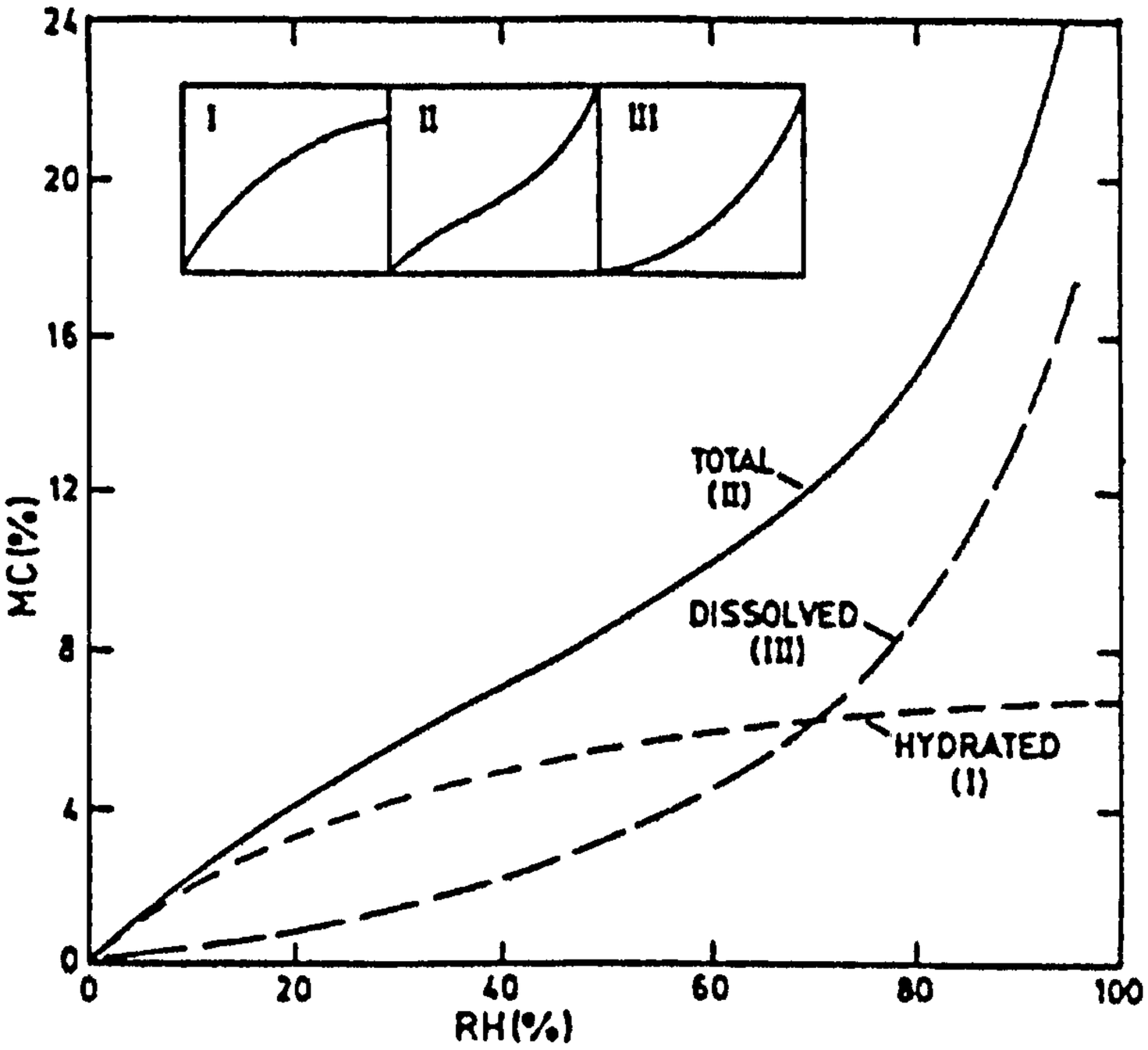


Figure 3.5 **Three main types of isotherm** **(Skaar 1988)**

The Type 2 sorption isotherm, also referred to as *sigmoid*, is typical of the plotted sorption values of wood and other hygroscopic polymers. It plots the behaviour typical of the formation of a solid solution within a swelling solid. It appears to be a composite of Types 1 and 3 sorption isotherms, representing in its lower section, hydrated water (Type 1) and in its upper section, dissolved water (Type 3). Thus, assuming Hailwood-Horrobin theory (section 3.6.2), and accepting the layer theory of adsorption, the Type 2 isotherm represents both monolayer and polymolecular adsorption. It involves the evolution of significant heat of adsorption. Type 1 adsorption is also referred to as *Langmuir adsorption*, and represents only monomolecular adsorption. In this type of sorption, vapour is also assumed to form a hydrate with the substrate and the attraction between the sorbent and sorbate is much greater than that between the sorbent molecules themselves in the liquid state. Type 3 sorption is a version of Type 2 adsorption, differing in that it occurs with negligible heat of adsorption, because the attractive force of the adsorbent for the adsorbates is almost the same as the attraction of the adsorbate for itself. This begins to be the case in wood above FSP, once a sufficient bulk of water has built up (e.g., multilayered sorption or clustering).

3.3.2.3 Deconstruction of the sorption isotherm

Though sorption, strictly speaking, only deals with the surfaces and void system of the cell walls, and does not involve capillary movements, the complete sorption isotherm, when plotted from a relative vapour pressure of 1.0 down to 0.0, plots the interchange of the three types of water in relation with wood. According to Hartley *et al.* (1992), each curve can thus be divided into three relative humidity regions. Region I is the monomolecular bound water and covers the range from 0.15-0.3 relative vapour

pressure. Region II is the polymolecular bound water (or thin layer) and covers the range from 0.2-0.9 relative vapour pressure. Region III is the capillary bound free water and covers the range above 0.9 relative vapour pressure. The points of interchange for all three of these are always closely related to the physical and chemical condition of the woody material and the behaviour of water in wood during sorption. We would expect these ranges of these regions to be somewhat altered in waterlogged archaeological wood.

According to Hartley *et al.* (1992), proponents of cluster theory define these three regions in a descriptive, slightly different way. In region I (0.0-0.3 relative vapour pressure) there may be a decrease of slope in moisture content change from the initial value. Chemical attraction between available sorption sites and water molecules is the dominant mechanism for sorption in this region and water is attracted to sorption sites at random, which explains the high attraction between the two (Hartley and Avramidis 1993). In region II (0.3-0.55 relative vapour pressure) there is no noticeable change in slope. This region might be considered an organisational region. Here the attractiveness of the sites becomes the same and the molecules reorganise to have all sites with the same energy. During this phase, too, more vapour molecules are being adsorbed and will increase the moisture content slightly. In region III (0.55-1. Relative vapour pressure) physisorption is the dominant mechanism. Molecules may be attracted to different sites, making water clusters there larger. However, at a particular point the hydrogen bond between the first molecule and the hydroxyl site will become weakened because of the presence of the cluster (Caulfield 1978), thus causing the cluster to move as a unit from site to site.

As wood adsorbs water its cellulose-cellulose bonds will separate, resulting in more mobile molecular chains. This swelling produces more free volume available for water molecules to adsorb, either on existing sites or on newly accessible sites (Froix and Nelson 1975). The adsorption of water will initially occur on sites that are weakly bonded to the neighbouring cellulose chains or on sites that are free. Additional moisture will penetrate fibre bundles and internal surface hydroxyl groups, swelling the cellulose and creating void spaces or free volume. The large rate increase in region III can be attributed to more such free volume caused by swelling of the polymer matrix, allowing more water cluster formation. Theincrease in region III may also be caused by condensation of water in the larger volumes in the wood, e.g., microvoids. For those wood scientists who accept cluster theory, this means that wood has two critical points: the FSP, representing completion of unimolecular adsorption, at which organisation of site energies begins (approximately 30% EMC in sound wood); and the critical RH (approximately 55% EMC in sound wood), the point where cluster formation begins.

Both cluster and multilayer theorists describe the process of adsorption as follows. As water first adsorbs to the wood, hydration sites are occupied by single water molecules. With more water added to the wood, the unimolecular hydration continues, but some of the water molecules will be attracted to sites already occupied, forming water dimers and perhaps trimers (cluster theory), or layers (multilayer

theory). At this level the bond to the cellulose substrate is generally expected to be weakened, with water layers or clusters experiencing increased mobility. In general summary, molecules are adsorbed randomly onto available sorption site, form bridges and small clusters that increase in size, becoming large near FSP. There is a tendency to cluster at lower moisture contents with increasing temperature (Hartley and Avramidis 1993).

During desorption, free water is considered to behave much like bulk water. The average size of the clusters or polymolecular layers are much argued over and difficult to analyse. A maximum of 10 is usually agreed on (Siau 1992). There is some evidence that, during desorption, the size of these clusters or layers initially decreases rapidly, desorbing randomly without interaction with other water molecules.

The main distinction between multilayer and cluster theory of water sorption in wood is that two critical points are identified with cluster theory during adsorption, though only one during desorption, as in multilayer theories of sorption.

3.3.2.4 Sorption hysteresis

The amount of water held by wood is not only dependent upon equilibrium relative vapour pressure, but also upon the direction from which equilibrium is approached. In all cellulosic materials, it appears that the amount of water adsorbed from the dry condition is always less than the amount retained on desorption at any fixed relative vapour pressure. Thus initial desorption shows higher EMCs than subsequent resorptions and desorptions. (Figure 3.6) All conservators of waterlogged material deal with this fact daily, and experimental data for both sound and waterlogged wood bears it out (Skaar 1988; Stamm 1964). Called *sorption hysteresis*, this important characteristic of wood represents irreversible changes in the water binding capabilities within wood ultrastructure produced through drying history, and has great significance for permanent change to wood properties.

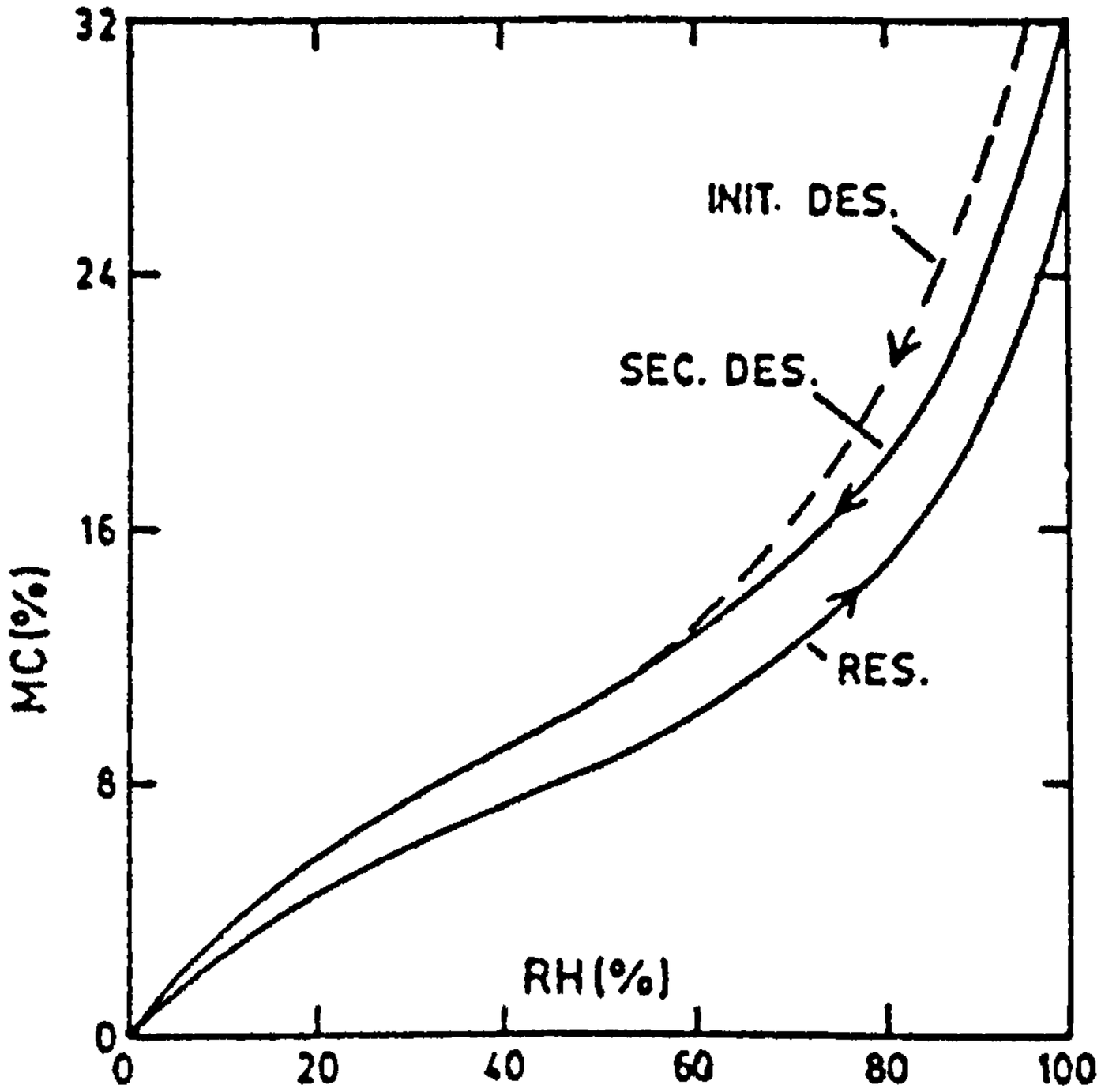


Figure 3.6 **Sorption hysteresis curves** **(Skaar, 1988)**

It is of significance that the lag in EMC occurs only down to about 50% RH, after which values reflect the original desorption values, indicating that the major irreversible change is to the amount of free or bulk water that can be adsorbed to the wood. This phenomenon is termed *cyclic* or *reversible hysteresis*. *Closed* or *irreversible hysteresis* occurs with successive cycles of desorption and resorption.

Hysteresis has been under discussion for a long time. Earlier theories explained it in terms of bad experimental method or the presence of trapped air (Stamm, 1964). Fortin (1979) established mathematically the "ink bottle" effect (which explains some of the hysteretic effect), as attributable to the fact that wood cavities are connected by narrow channels. At the present time, hysteresis is thought to be caused by reductions in the availability of bonding sites caused by shrinkage phenomena (permanent rebonding of adjacent cellulose molecules). Why this re-bonding should be permanent may be explained by the fact that gels are not perfectly elastic and thus the wood gel may undergo permanent deformation under swelling or shrinking (section 3.4.4). In addition, externally imposed stresses may reduce the hygroscopicity of cellulose as a result of increasing its crystallinity.

In fact, the complete cycle hysteresis loop of cellulose represents the boundary of an equilibrium area, any point within which may represent the moisture sorption by the cellulosic material under suitable relative vapour pressure. Size of wood can affect hysteresis; the hysteresis curve of larger pieces of wood appears to give an intermediate curve falling within the hysteresis loop obtained from sorption measurements made on small specimens. This is due, apparently, to the simultaneous occurrence of both desorption (from the core) and adsorption (from the surface) in a large specimen (Stamm 1964).

This partial or *incomplete desorption* followed by subsequent adsorption tends to produce narrower hysteresis loops, as do oscillating cycles of desorption/adsorption and temperature (Figure 3.8). This is due to bonding sites being progressively lost through drying effects. The magnitude of hysteresis increases with the degree of desiccation

The presence of extractives effects hysteresis. The bulking effect inhibits aggregation and reduces void volume: consequently the glucose anhydrides within the cell walls of wood will be more accessible than those in relatively extractive-free wood. The persistence of hysteresis in bulked wood is thought to be due to the freeing of formerly stable hydroxyl bonds as a result of the greater swelling. These liberated hydroxyls become active in sorption then, but the magnitude of hysteresis in this treated wood is due to a reduction in number of accessible hydroxyls and the bulking action of the treatment chemical.

When the wood-water system is being considered, the sigmoid shape of the wood sorption isotherm, always exhibiting irreversible hysteresis, indicates the polymolecular nature of sorption and the large forces of attraction between wood and water molecules (Stamm 1964; Avramidis 1989, 1992; Adamson 1990).

3.3.2.5 R/D ratios

The ratio of area under the adsorption isotherm to that under the desorption isotherm in the regions of surface-bound, capillary-condensed, and total water sorbed has been shown to yield meaningful and repeatable results on differences in wood characteristics (Spalt 1958). The magnitude of hysteresis effects may be expressed as the ratio of resorption to desorption EMCs at a given relative humidity (because hysteresis severity will vary with RH). Stamm (1964) and Skaar (1988) have provided us with interesting data on the variation of hysteresis ratios between wood constituents and between different tissue zones within wood.

Variations in R/D ratios between species and tissue types are thought to reflect variations in constituents, most significantly extractives. Thus, deteriorated waterlogged wood could be expected to show higher R/D ratios than sound wood as a result of loss of extractives, but lower values as a result of loss to holocellulose proportion. The latter would appear likely to be the controlling factor in this case. Okoh (1976) and Spalt (1958) calculated mean R/D ratios that show comparative differences in hysteresis effect between softwoods and hardwoods. In general hardwoods show higher R/D ratios than softwoods. Many other comparative surveys of wood hysteresis ratios have been reported (Skaar 1988).

Past history of the wood affects hysteresis. It has been noted by comparing the results from single-step resorption (where the sample is oven-dried between each equilibrium step) to multi-step resorption (where the sample is exposed to increasing or decreasing steps in humidity after each equilibrium step)

(Prichanandra 1966). Results tend to give higher R/D ratios for one-step resorption than for multi-step resorption. The real-life experiences of wooden artefacts must fall somewhere in between these two types of resorption, but thought should be given to which is likely to be the contributing factor under a given circumstance. Urquhart (1960) has shown that the completeness of the isotherm measurements, whether the full range or only a mid-range of humidity equilibria was measured, is significant to the level of R/D ratio produced. More complete ones give more informative ratios, while cyclic isotherms carried out over smaller humidity ranges tend to produce equilibrium areas rather than precise loci.

Skaar (1988) points out that the R/D ratio should be treated with a certain amount of caution because of the difficulties lying behind the making of EMC measurements, the past history of wood specimens, and variations in sampled tissues. The commonest failing in R/D data results from incomplete attainment of equilibrium, common to sorption experiments because of the extreme amount of time required for steps where the molecular rearrangements occurring are slow as the structure accommodates itself to swelling forces (Skaar *et al.* 1970). In general, the effect of this is to increase R/D ratios, thus underestimating the effect of cycling humidities on permanent change to wood hygroscopicity.

3.3.2.6 Degraded wood and sorption characteristics

Few studies of the sorption characteristics of archaeological waterlogged wood have been carried out (Noack 1965; Rosenqvist 1975; Barbour and Lency 1982; Barbour 1983; Kommert 1986; Schniewind 1990a). The most comprehensive of these are the studies carried out by Barbour (1983) and Barbour and Lency (1982), though they are mainly pilot studies, with some interesting observations and indications for future research directions.

Very early in studies of waterlogged wood it was realised that both sorption curve and FSP of archaeological wood differ noticeably from those of sound wood (Rosenqvist 1975). Stone and Scallan (1968b) point out that the cell wall of wood is a gel composed of carbohydrate and lignin macromolecules. Any process that brings the wood gel into contact with an excess of water involves a constant modification of the ligno-cellulose gel as chemical and mechanical treatments remove material from within it or rupture bonds that hold the matrix together. The structure of this gel is clearly an important factor in determining its reactions to changes in available moisture.

Hedges (1990) has laid out a scale of increasing levels of reactivity to deteriorative processes of the cell wall components, with hemicelluloses as most vulnerable and lignin least vulnerable. Hoffmann (1982) provides data for the changes to wood sorption EMCs as chemical constituent ratios change. What effect the loss of each one of these constituents has individually is more difficult to determine.

It is generally accepted that, of the principal components of wood, hemicellulose is the most hygroscopic, cellulose intermediate, and lignin the least hygroscopic. It is no coincidence that this too is the order of deterioration of wood cell wall components. However, limited data are in fact available for the adsorption values of isolated wood components. In certain hardwoods the holocellulose has been found to have considerably higher sorption values than the wood itself. Lignins from hardwoods, however, may have only slightly lower sorption values than the original wood (Stamm,1964). The combined sorption values for the holocellulose and the lignin are often significantly higher than those of the wood itself because of problems in experimentation. Yet if lignin is the constituent in highest proportion in deteriorated wood, it might be expected that more severely deteriorated wood was less hygroscopic than sound wood. Available data not only do not support this, but show the opposite to be true (Noack 1965; Hoffmann 1982). An explanation for this must be the increased accessibility produced by the break-up of cellulose, more particularly its crystalline structure. Sorption data for individual constituents, therefore, does not tell us all it might. The extractive techniques used to separate wood fractions usually cause changes to their chemistry and thus to their sorption values. Moreover, the constituents do not exist in isolation in wood, thus even after deterioration we are still dealing with a complex macromolecular mixture.

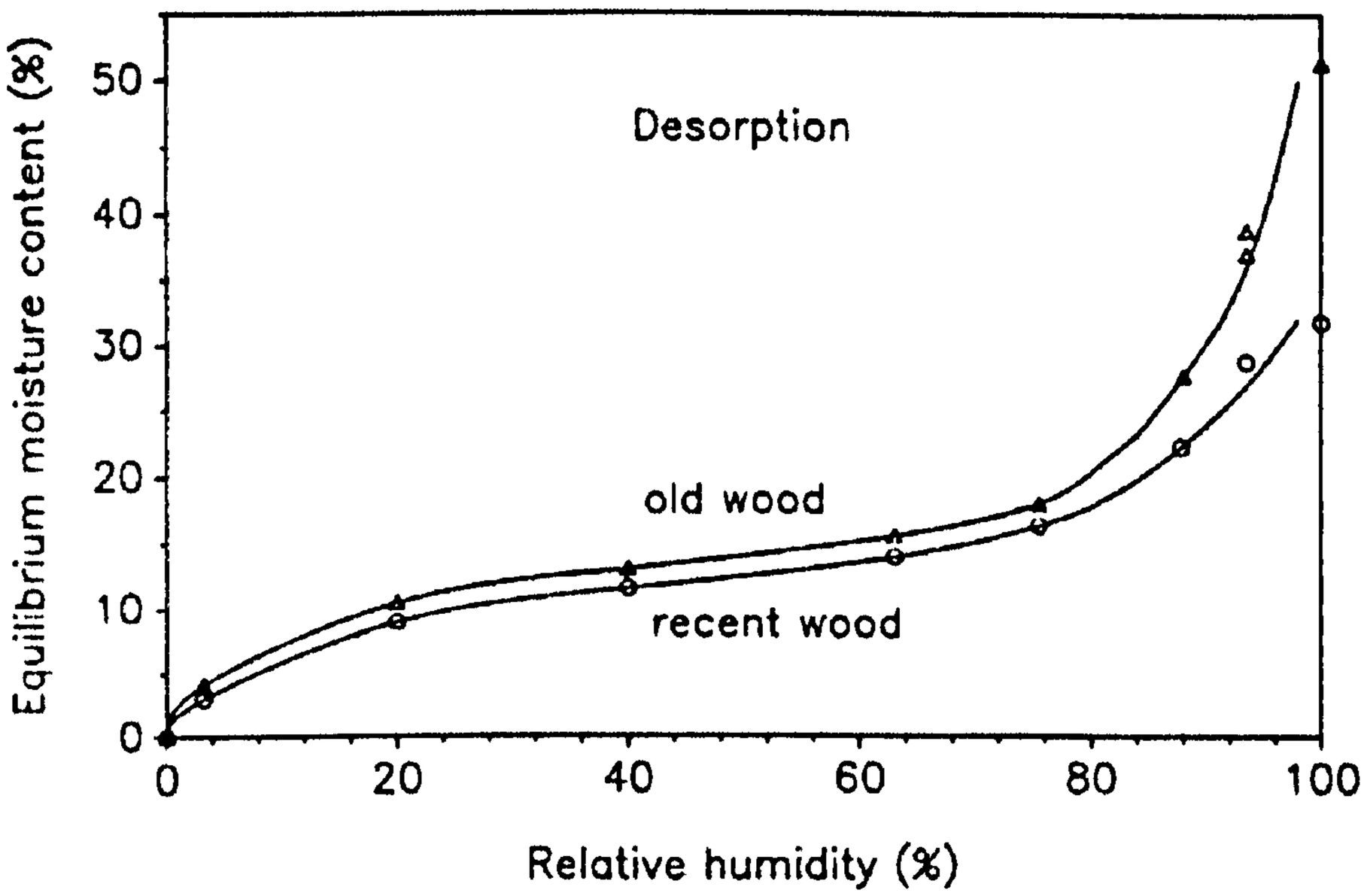


Figure 3.7 **Sorption isotherms for archaeological vs recent wood** **(Schniewind, 1990)**

EMC values for deteriorated archaeological wood are consistently higher than those for recent wood (Figure 3.7), and this appears to be the case regardless of species (Noack 1965; Hoffmann 1982; Barbour 1983), though comparatively little data on sorption characteristics of archaeological wood has yet been collected. This difference has shown to be much more stressed at the higher humidity levels (>80%RH). This explains the tendency of archaeological waterlogged wood to undergo shrinkage at RHs just below 100% (Noack 1965; Barkmann 1975). FSP values are thus particularly affected: Barbour (1982) reports as much as twice the levels in his archaeological alder over the entire range. Despite the physical effects

of waterlogging, in a proportion of these cases FSP values reported are not much higher than those for sound wood. This may suggest that the material from these sites was in good chemical preservation.

The study of brown- and white-rot deterioration of wood can shed light on some of the anomalies surrounding constituent loss and change to sorption characteristics. Wood that has brown-rot (loss of holocellulose) measures lower EMCs than sound wood, while wood with white-rot (loss of both holocellulose and lignin) measures higher EMCs (Zabel and Morrell 1992). This anomaly is thought likely to arise from preferential attack on the amorphous cellulose, which is usually responsible for retaining higher levels of adsorbed water than the crystalline cellulose. Its removal in the early stages of decay decreases the overall moisture-holding capacity of wood. The absence of changes in EMC in early stages of white-rot decay probably reflects the uniform removal of all wood components, and the increases to EMC during the later stages of decay by these fungi may reflect selective attack on crystalline cellulose.

Exposure to alkaline conditions and certain salts can affect the water-carrying capacity of wood, by swelling fibres and increasing median pore size and total pore volumes (Rowland *et al.* 1984; Stone and Scallan 1963). These conditions also cause component removal. Insoluble salts will have a reverse effect (Grethlein 1985).

Loss of extractives from the wood appears to increase adsorption values, since these open up for water adsorption areas previously blocked in the cell walls (Stamm 1964). The blockage of cell wall fibre cavities and lumen with deterioration products, however, appears to contribute to the raising of EMC figures for the wood because of the augmented hygroscopicity of these carbohydrate fractions (Hoffmann and Jones 1990). The effect of bulking treatments aimed at blocking or deactivating surface layer hydroxyls in order to stabilise or waterproof wood appears to achieve overall reduction of sorption and alteration of the nature and magnitude of hysteresis (Spalt 1958). But this is not thought to be due to loss of active surface hydroxyls, rather to the bulking effect on capillaries.

The effects of extractives, ash and differential chemical deterioration on EMC values indicate why density/specific gravity is not a good indicator, either of the water binding characteristics of wood or of its permeability. Nevertheless, most conservation treatments are based on this assessment (Grattan 1982b). It is apparent that it is not only the changes to constituent ratios but the physical loss of matter and the plastic deformation produced by excessive swelling that affect the sorption characteristics of deteriorated wood. Reductions in cell wall density have been shown to accompany increased accessibility. Though Buck (1978), in his study of old panel paintings, concludes from sorption trials that ancient dry wood that has not undergone abnormal chemical change still possesses its characteristic response to moisture, ancient wet wood in good chemical preservation can not be presumed to be unchanged, because of the added effect of the physical actions of waterlogging.

A complicating factor in extrapolating the effects of deterioration to the sorption characteristics of wood is the unevenness of the deterioration of a piece of wood. Hoffmann and Jones (1990) showed the variation caused to chemical constituents as a deterioration front moves through a piece of wood. Increased general porosity and changes to pore volume ratios caused by constituent loss has been found to increase EMC values, partly through creation of new sites, and partly through swelling effects. Thus it is probably for physical reasons that loss of lignin also has been observed to lead to increases in sorption EMC and FSP (Flournoy *et al.* 1991).

Physical changes from waterlogging, such as breakdown of the cell structure, discontinuous surfaces produced with cell wall lamination, swelling into the lumena, and filling of lumena and void spaces with breakdown products will all affect sorption values. Berendsen (1975) commented that discontinuous surfaces produce significantly different shapes of sorption curve than the ideal. As collapse and shrinkage take place, stresses are generated within the wood. These stresses must either be tolerated or dissipated through a realignment of the wood structure. How this happens depends on the characteristics of individual cells and on the general wood structure. Barbour and Leney (1982) delineate two forms of drying stresses, intracellular stress and intercellular, that result in more- or-less permanent changes to the ability of the wood to take up water upon subsequent hydrations.

Changing temperature affects the sorption isotherm in two ways. The reversible effect is to change the EMC at a given RH as a result of changes to the activity of the sorbed water in the conditioned wood. The irreversible effect is to cause permanent change to the hygroscopicity of the wood. This latter depends on the temperature change and duration of exposure, as the effects are equivalent to a hysteresis effect precipitated by changes in relative humidity. A decrease of 1% in FSP has been measured with increase of temperature of 10° C. This holds significance for treated archaeological wood in storage or on display. The decrease of EMCs noted in temperatures below freezing is in opposition to the above trend, reflecting the more rapid decrease in vapour pressure of ice with decreasing temperature than that of sorbed water. This phenomenon is responsible for "coldness shrinkage" and is of considerable significance to the conservator because of storage of waterlogged finds in outside ponds and in freezers prior to treatment.

Wood-deteriorating microorganisms work in both chemical and physical manners to affect the sorption characteristics of wood. The supply of free water on surfaces of cell lumena is used by fungi in the hydrolysis of carbohydrates. Hydrolysis of cellulose has been found to cause a general increase in bonding sites (Grethlein 1985). In addition, many fungi release metabolic water during the decay process (Zabel and Morrell 1992).

Among other treatments, gamma radiation is known to effect the sorption characteristics of wood (Skaar 1988). It lowers the EMC over the entire sorption range, though the effect is reduced with smaller

dosages. This phenomenon may be of significance to conservation, where the use of gamma radiation in the treatment of waterlogged wood against microorganisms has been proposed (Jones 1990). It is not clear whether this effect is permanent or reversible.

Barbour and Leney (1982) found that the shapes of the adsorption and desorption curves for waterlogged wood are quite similar in shape to those for sound wood—i.e., they are sigmoidal Type 2 in form. As well as raised EMCs and FSP, variation in the shape of the curves for waterlogged archaeological wood also shows up. Sorption curves for sound wood show an abrupt increase at a relative vapour pressure of about 0.9, attributable to capillary condensation in fine permanent capillaries. Barbour found that deteriorated waterlogged wood showed its rapid upturn at 0.8 rather than 0.9. This would seem to suggest an increase in the number of these fine capillaries. Pore volume studies examining the effect of constituent losses appear to show similar results (Stone and Scallan 1963; 1967; 1968b).

Other studies are in general agreement with these results (Schniewind 1990), producing the generalisation that the amount of increase in sorptive ability of archaeological waterlogged wood is dependent on the extent and the mechanism of deterioration, rather than on length of time buried.

3.4 The Effects of Moisture Movement in Wood

3.4.1 Volumetric Hygroexpansion

One of the main concerns of water relations in wood is the effect moisture change has on dimensional change. Moisture movement in wood is defined as the change in EMC in response to change in environmental conditions. Since these environmental conditions are rarely constant, it is rare that wood's moisture content is equal to its EMC. What is most significant to the conservator is that dimensional change accompanies these fluctuations in moisture movement. This is what is termed *movement* in wood. *Volumetric hygroexpansion* is the term given to all dimensional change caused by movement. It covers both *initial shrinkage* and subsequent movement, in other words, dimensional change during use. The type of shrinkage undergone by waterlogged wood when dried to ambient conditions falls under the term *initial shrinkage*, just as does the initial shrinkage associated with the seasoning of green wood (Stevens 1963).

Both the inherent characteristics of the wood and its level of deterioration will effect the severity and permanent consequences of hygroexpansion. Skaar (1988) and Panshin and deZeeuw (1980) have provided most of the detailed discussion of density, specific gravity and density index as they relate specifically to wood hygroexpansion. Stamm (1964), Skaar (1972), and Siau (1984) have discussed the factors that affect cell-wall density, but for simplicity in hygroexpansion calculations, an approximate or average value of 1.5 g/cc is conventionally used.

Hygroexpansion in wood is traditionally given in terms of percent shrinkage (s) or percent swelling (S), and these two differ in terms of the reference starting point used, e.g., shrinkage from wet dimensions and swelling from oven-dry dimensions. *Percent dimensional change* is a commonly-used term for studies of treatments of waterlogged wood, and when compared to success of a treatment in preventing dimensional change it is often expressed as *anti-shrink efficiency* (ASE). A further useful index of hygroexpansion is the ratio of the relative dimensional change to the moisture change that has occurred. Swelling gradient, defined by Kollmann and Coté (1968), differential swelling (Keylwerth 1962), hygroexpansion coefficient (Skaar 1972), and various other similar indexes have been defined.

For wooden artefacts after treatment and drying to ambient conditions, it is often important to know the hygroexpansion properties of the wood with respect to humidity changes such as those to which the wood is exposed in storage or on display. This information can be obtained from the sorption isotherm using the following equation.

$$Y_v = \left(\frac{1}{v}\right)\left(\frac{dv}{dh}\right) = ZX_v$$

Where: $Z = \left(\frac{dM}{dH}\right) = \left(\frac{dm}{dh}\right)$

where: Y_v is the volumetric humidity expansion coefficient, v is the volume measured at moisture content m, d_v and d_h are the differential indices of volumetric hygroexpansion, Z is the slope of the sorption isotherm, X_v is the volumetric moisture expansion coefficient. M (m) is equilibrium moisture content, and H (h) is relative humidity or vapour pressure.

Equation 3.5 Humidity expansion coefficient (Skaar,1988)

The standard case for wooden objects, however, is one of oscillating sorption, and in this case hysteresis also reduces the effective slope, as illustrated below in Figure 3.8. M_d refers to moisture contents during desorption, while M_r refers to those measured during resorption.

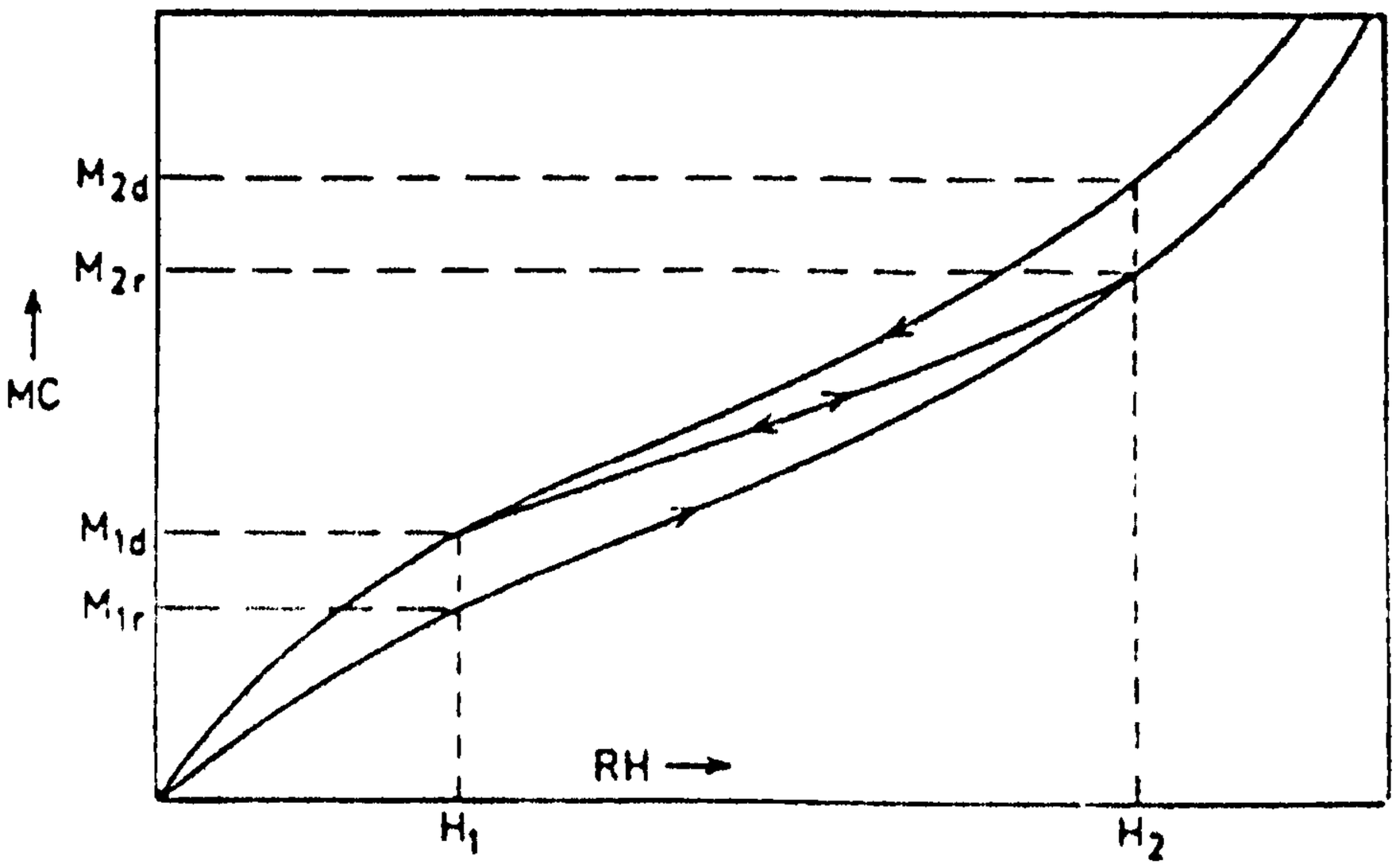


Figure 3.8 **Oscillating sorption and the humidity expansion coefficient.** **(Skaar, 1988)**

The humidity expansion coefficient (Y)can thus be seen as a more important wood property than the moisture expansion coefficient (X). Unfortunately, the former is more difficult to measure, and more data exists for the constants used in the equation for the latter. The slope of the sorption isotherm relates X and Y and it is obvious that any number of variables in wood properties will affect this, more particularly in relation to sorption hysteresis.

Directional hygroexpansion is examined where shrinkage or swelling along one of the principal structural planes of wood is of interest. This tends to become of particular significance because of the anisotropic nature of wood. Most equations for wood, however, deal with changes in hygroexpansion within the cell wall of wood rather than the bulk mass, and thus anisotropy is neglected.

Sorption models use numerical solutions of the wood diffusion equation to predict the general moisture response characteristics of wood samples subjected to sinusoidally varying humidity (i.e., unsteady-state conditions), but employ analytical solutions for the steady-state case (i.e., when the response is repetitive in succeeding cycles).

3.4.2 Deteriorative Movement due to Hygroexpansion

3.4.2.1 General description

Shrinkage phenomena are the main source of concern for conservators of waterlogged archaeological wood, and what all of their treatments are aimed to counteract.

In green wood, water acts to support the wood cell and to plasticise its fibres so that it can better accommodate mechanical strain. In deteriorated waterlogged wood it serves to support by bulking the frail remains of middle lamella and any of the fragile, sheet like cellulose that still remains, allowing it to maintain the original structure and shape of the wood (Hoffmann and Jones 1990).

The uncontrolled loss of water from wood whose water content is above the fibre saturation point (i.e., both green wood and waterlogged wood) may result in wood that is relatively unaltered or may result in collapse and shrinkage. These are two distinct processes, influenced by capillary tension and drying stresses. The consequences of these are distortion, splitting, embrittling, checking, delamination, and even complete disintegration of the wood tissues. It is the high unpredictability of results that is one of the greatest concerns for the conservator of this material.

Sound wood in the green state contains air in practically all its cell cavities (Grattan 1987). This leads to behaviour on drying that is different from that of waterlogged wood, since the movement of free water in green wood will not engender the massive capillary forces that occur in waterlogged wood.

Hygroexpansion affects larger timbers in a more complicated fashion. Grattan (1987) describes the drying behaviour of larger pieces of waterlogged wood as a type of hydraulic system, where the core can be regarded as a single hydraulic unit. In it, drying proceeds by diffusion until the capillary tension forces created by the largest pores to the saturated core equals the pressure created in the system by loss of water. The core will undergo elastic deformation and the meniscus in the largest exposed capillary then moves until it reaches the wider interior of the opening, at which point the forces of capillary tension decrease dramatically, relieving the pressure on the core and producing a rapid sucking effect on the contents of the emptying cell as the deformed capillary springs back.

In a general fashion, then, the process of uncontrolled drying of wood above FSP has two phases: *collapse*, which takes place largely above the fibre saturation point of the wood, and *shrinkage*, which takes place below the fibre saturation point. Capillary tension effects control the first of these processes, and arise as a pressure differential develops when the free water evaporates from the capillaries that form the permanent void structure of the wood. Desorptive diffusion controls the second of the processes, and involves the removal of bound water from intermolecular association with the cell wall

substance. In the two phases of this process, the larger capillaries will tend to empty first and one at a time, and the smaller ones remain full because of the greater surface tension coupled with the reduced saturation vapour pressure of water present in them. Wood science tends to use the term *collapse* to describe both phenomena (Skaar 1988).

3.4.2.2 Collapse

Collapse produces gross distortion of the cell, during which capillary forces from the retreating water may reduce the lumen volume to zero. In green wood this phenomenon is usually confined to the heartwood, whereas in archaeological and waterlogged wood it is often the sapwood that is affected most (Grattan 1987). This type of hygroexpansion is in fact controlled both by diffusion (producing drying stresses) and flow phenomena (producing capillary tension effects). Capillary tension is, however, thought to be the principal factor.

Pressure inside the cell will be governed by the radius of the largest capillary connecting it to free air space. Where a small capillary leads to a cell full of water, it will induce a substantial compressive force on the cell wall (Figure 3.9). Where wood is most highly degraded (e.g., in the sapwood regions of waterlogged wood), the system of microcapillaries has been severely disrupted through the destruction of pit membranes. The maximum capillary tension force likely to be developed would thus be derived from the whole pit diameter. Whether or how much collapse occurs will depend on the elastic limit of the wood's strength compared to the capillary forces brought to bear upon it.

The elastic limits of degraded waterlogged wood can be assumed to be rather low because of material losses to the load-bearing secondary cell wall and increased plasticisation from the ingress of water into the cell wall. Thus, despite the relatively larger capillary diameters present in degraded wood, these forces will be able to have a substantial effect on the cell wall with uncontrolled drying (Grattan 1987). The condition of the cell wall and its pits is thus likely to be a key factor in deciding whether deteriorated waterlogged wood will collapse on drying.

The other cause of collapse, *drying stress*, arises from the fact that the water saturation of tissues at the core of the piece of waterlogged wood differ to that at its surface—during drying the outer surface has almost no moisture content, while the interior is fully saturated. Shrinkage thus occurs first in the outer layers, initiating internal stresses. These large compressive forces being brought to bear on the wood in the core then lead to its collapse. In this case the drying stresses outlet themselves on the outer zone of wood, producing surface cracks and checks.

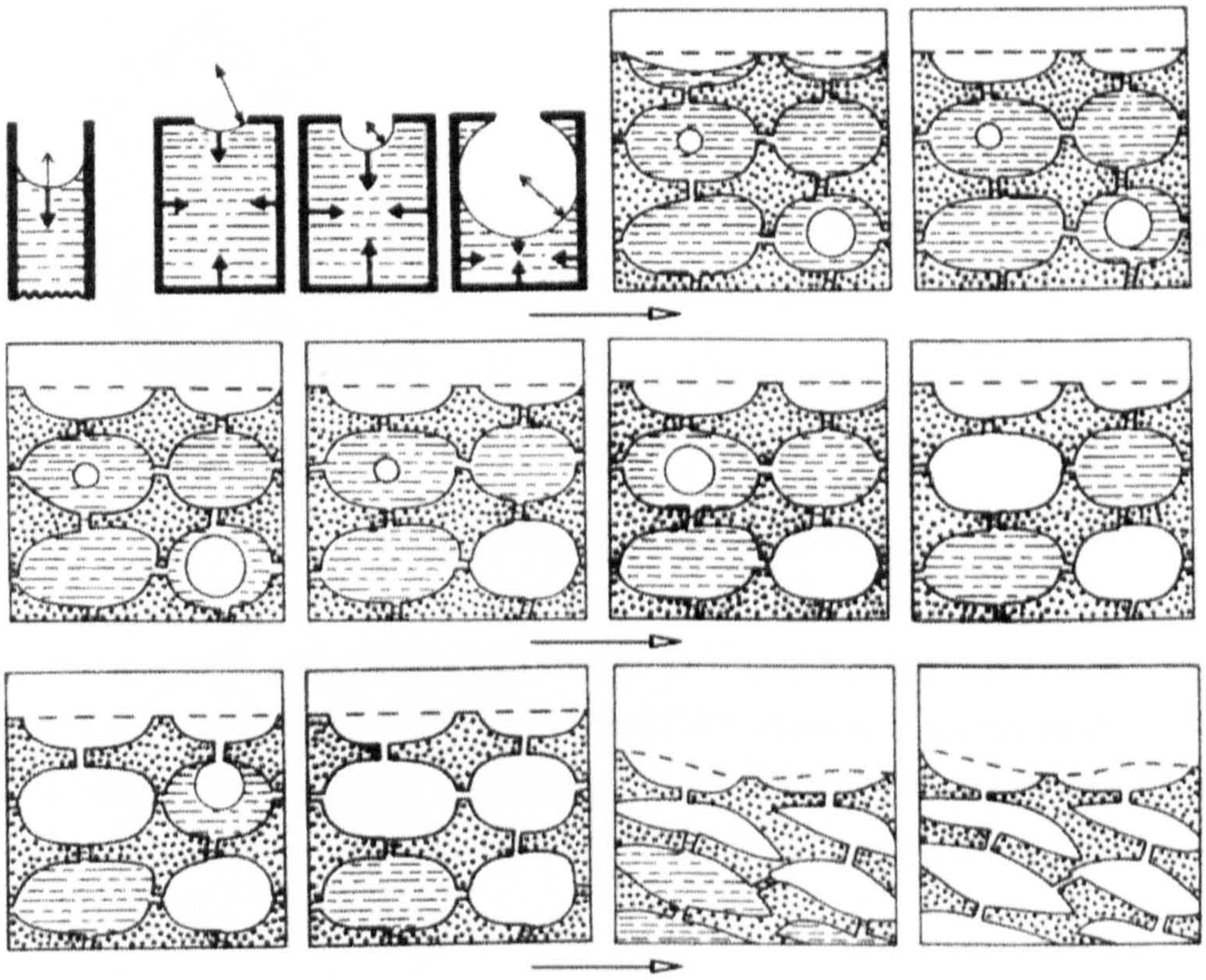


Figure 3.9 **Evaporation of free water from wood** **(after Siau,1984)**

Collapse shrinkage may also occur. Drying causes tension in the water within the fibre lumens (Kauman 1964). A physical flattening of fibres induced by this internal tension causes collapse shrinkage (Figure 3.9). A problem in the study of collapse has been the lack of information in the literature as to the conditions that accompany the onset of collapse. Innes (1995) has developed a model to analyse the stress and strain in the walls of hardwood fibre cells in order to predict the onset of collapse. This model demonstrates that the stresses and strains in the fibre cell wall are sensitive to changes in temperature of the order of 5° C. This has serious implications for waterlogged wood on display after treatment, or while waiting for treatment during storage.

3.4.2.3 Shrinkage

Shrinkage refers specifically to the shrinkage of the microcapillaries and second order space in the cell walls in wood. Loss of the bound water that lies as lubricator between cellulose fibres and within cell voids results in the pulling together of the fibres and the loss of much of the flexible strength lent to them by the plasticising effect of the water. It is to a certain extent reversible (i.e., it will fluctuate) with moisture absorption and desorption, at least in unaltered sound wood. Permanent shrinkage can occur in the highly disordered chemistry of deteriorated wood. This results in an enormous increase in the total crystallinity of the fibres and a corresponding increase in their brittleness, even to the point of fracture (Figure 3.10).

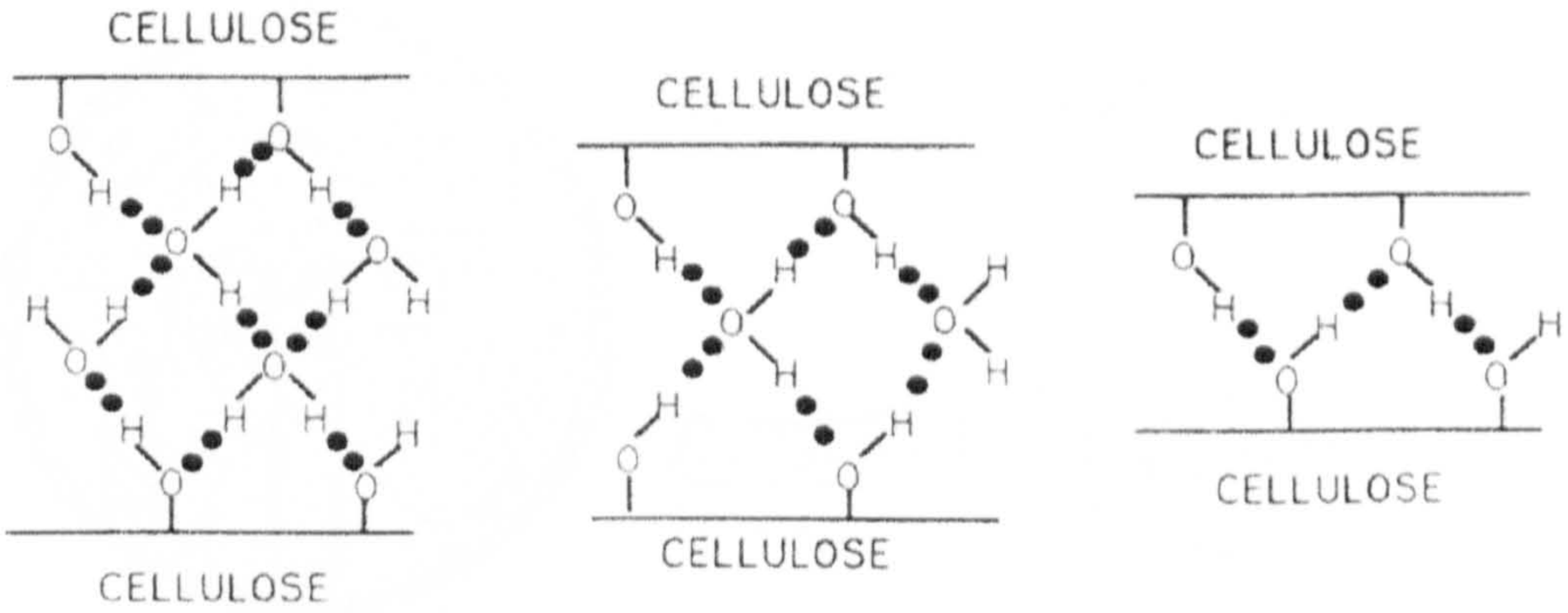


Figure 3.10 **The effects of water loss on orientation of cell wall polymers** **(Zabel & Morrell, 1992)**

While collapse causes general reduction in dimensions, shrinkage causes distortion in wood. This is a result of wood anisotropism, which means that the fibres will tend to undergo much greater shrinkage laterally than along their length (Figures 3.11 and 3.12). The presence of amorphous and crystalline zones along the cellulose molecule will mean that these zones react to differing extents when drying or swelling takes place in wood tissues.

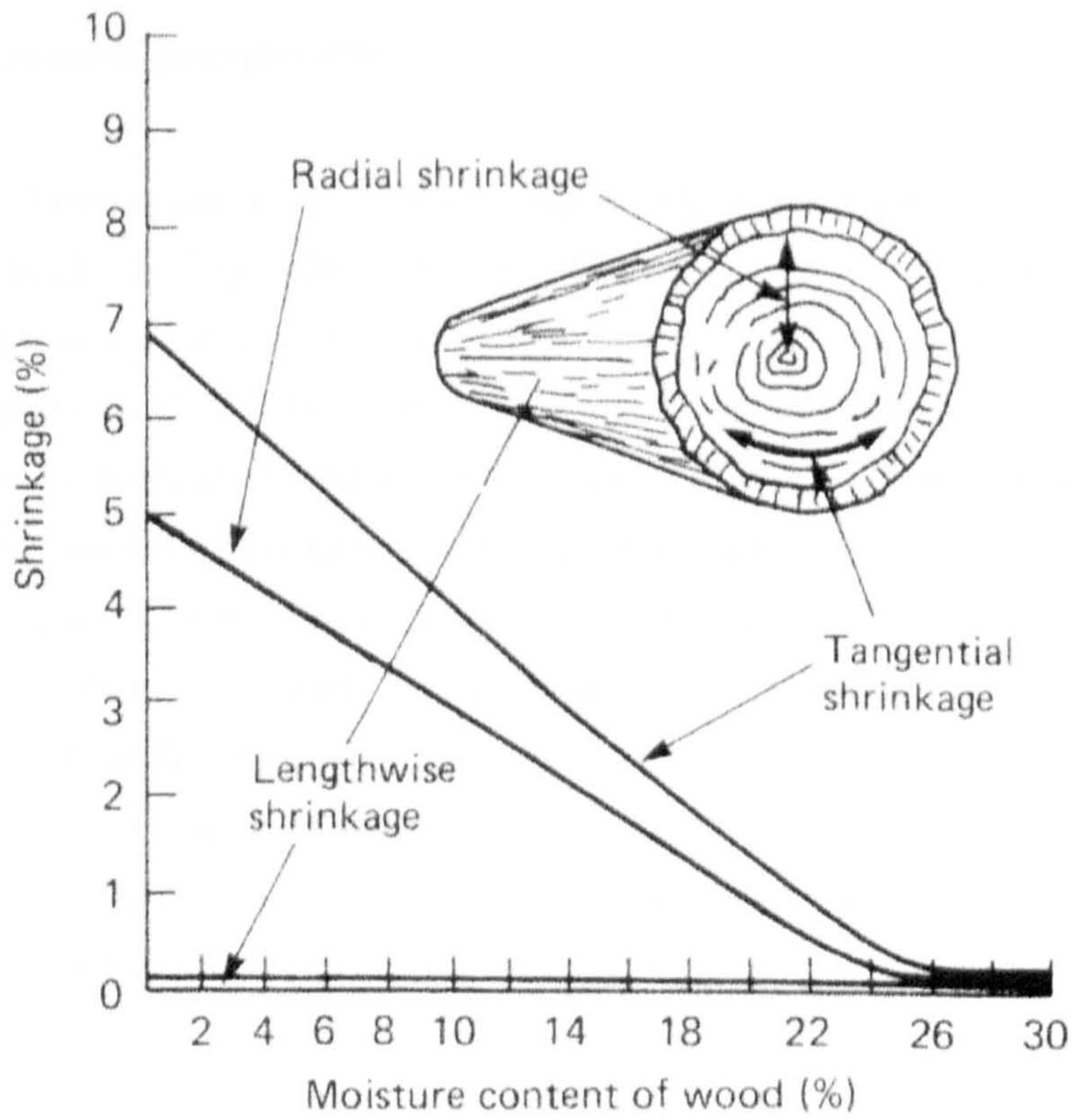


Figure 3.11 **Anisotropic shrinkage** **(Grattan,1987)**

Because shrinkage effects are related to the fibre structure of wood, the greater the density of wood the greater the shrinkage. However, the great distortions that cells undergo during collapse and before shrinkage effects begin, greatly complicate the dimensional changes occurring to the wood, making them hard to predict with any preciseness or reliability.

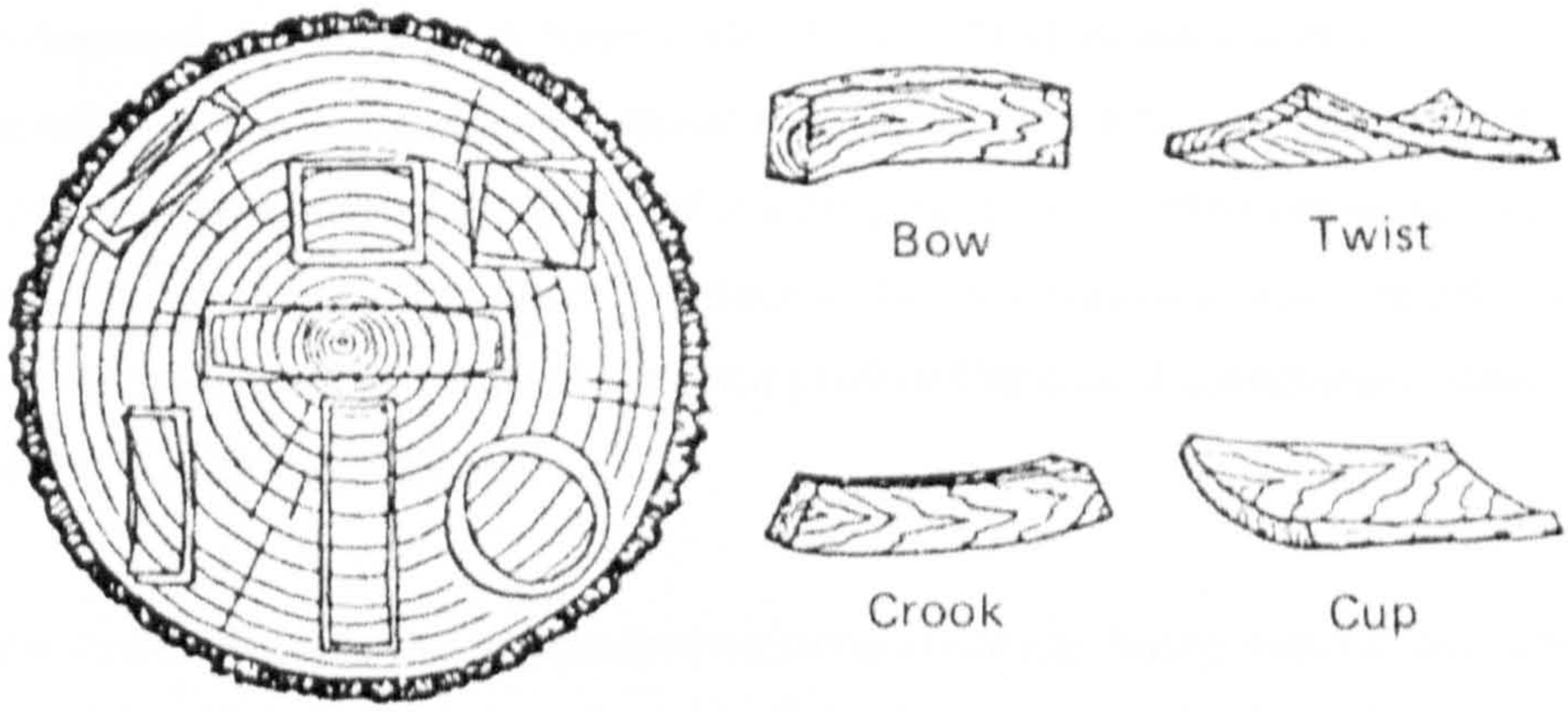


Figure 3.12 Dimensional behaviour of different cuts of wood (Grattan,1987)

In places where the wood tissues are under restraint—either within its internal system, or because of the construction of the artefact (e.g., at the joints of a box)—considerable stresses that may arise from such dimensional changes will tend to resolve themselves through the opening up of cracks or checks in the wood, usually either following the line of ray cells or running through the larger voids produced by the open ends of vessels.

3.4.3 Directional Hygroexpansion

Under normal circumstances, the greatest shrinkage is tangential, followed by radial, and then longitudinal (which is too negligible to be taken into account except in very deteriorated wood, where only the primary wall is left with its perpendicular orientation of fibrils (Grattan,1987)). Barber's generally-adopted view (1968) that the ligno-cellulose matrix construction works to restrain hygroexpansion in the direction parallel to fibril axes would tend to suggest that waterlogged wood might experience significant longitudinal shrinkage as a result of the deterioration of the cementation between adjacent walls. Hoffmann and Jones (1990) observed the decrease in length of microfibril resulting from increase in fibril angle caused by swelling in waterlogged oak wood. Volumetric shrinkage is usually slightly less than the total of the three separate directional shrinkages. Skaar has provided an equation for calculating accurately the value of total shrinkage (Skaar 1988), though the T/R ratio (tangential/radial shrinkage), is most commonly used to describe the dimensional movement characteristics of wood.

The coefficient of volumetric moisture expansion describes dimensional change associated with moisture change after initial drying, and can be calculated for directional hygroexpansion as well as volumetric hygroexpansion, although Meylan (1972) reported that longitudinal shrinkage in sound wood decreases with increasing moisture content. There is evidence that the T/R shrinkage ratio is not constant over the entire hygroscopic moisture range, differing depending on the direction involved. Shrinkage intersection point is roughly equal to the FSP (the estimated value of moisture content below which shrinkage begins). It is consistently higher for tangential than for radial hygroexpansion.

Such a degree of anisotropism in dimensional change sets up extreme stresses within the wood. Mathematical analyses of shrinkage behaviour of timber during drying, such as those carried out by Imata (1975), who applied the concepts of mapping theory to calculate the magnitudes and distributions of stresses during drying, have direct relevance to the conservation of waterlogged archaeological timbers where the weakened state of the wood produced by loss of constituents makes it particularly vulnerable, even to small stresses.

The area measured under the curves showing stress occurring during sorption and sorption hysteresis is proportional to the mean difference between resorption and desorption isotherms and thus equal to the R/D ratios measured for the given sample of wood (Skaar 1988; Barkas 1949).

The hygroexpansion of wood subject to cyclic humidity changes has been termed *movement* (Stevens 1963). Movement is considerable smaller for a given range of humidity change than is shrinkage during the initial drying of green wood.

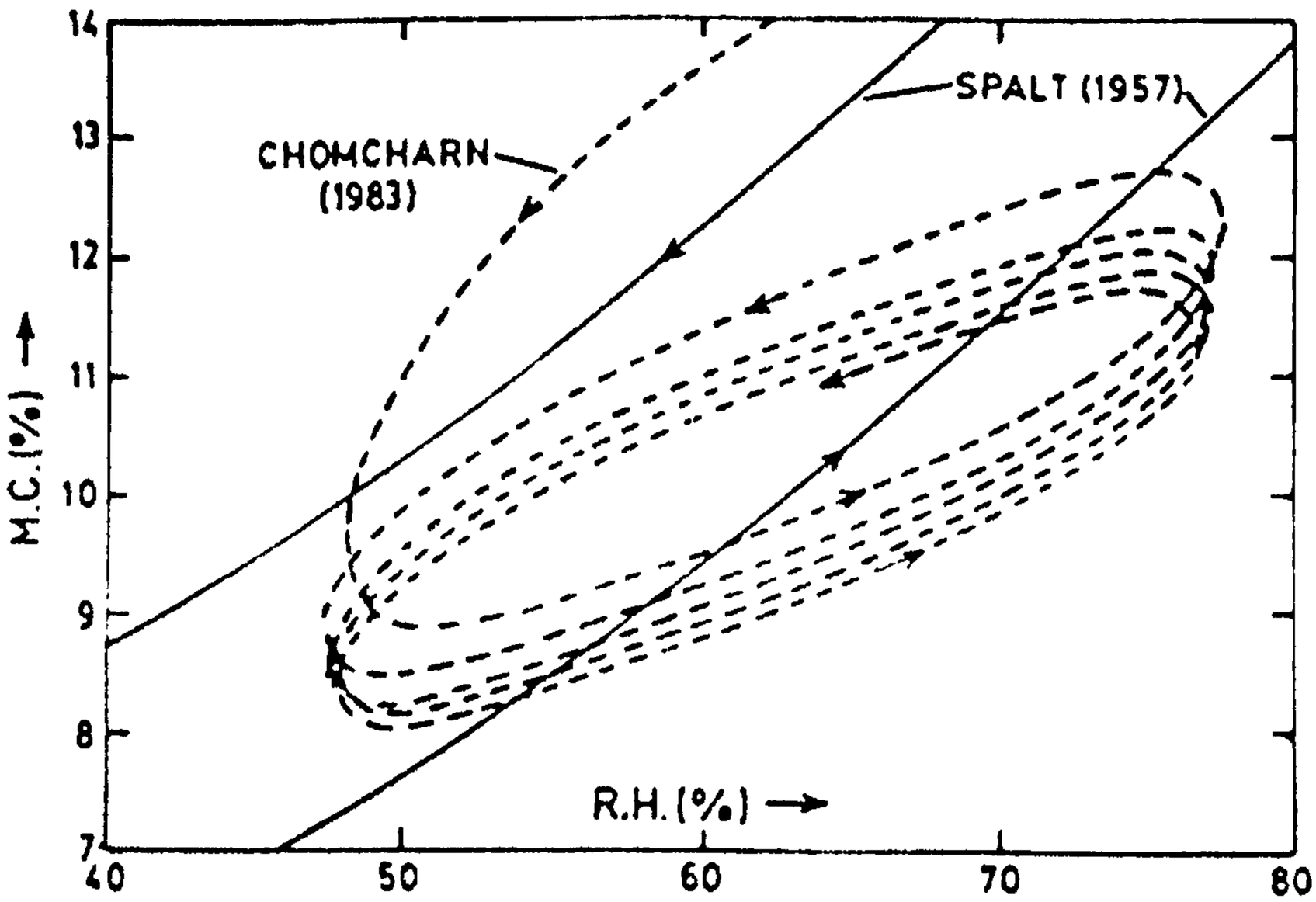


Figure 3.13 **Cycling humidity change effect on the sorption isotherm** **(Skaar,1988)**

Chomcharn and Skaar (1983) studied sinusoidally varying humidity cycles and monitored changes in moisture content and in radial and tangential dimensional change. They found a lag between the dimension change and the change in RH, though both were sinusoidal. The phase lag decreased and the amplitude increased with increased cycling period (Figure 3.13). Here lies the danger for archaeological wood on display. Moisture diffusion coefficients appeared to decrease with increasing cycling period and increase with decreasing wood specific gravity. The dynamic moisture expansion coefficient was found to be relatively constant during cycles. The dynamic moisture sorption coefficient decreased with each cycle and with decreasing cycling period, and was heavily affected by hysteresis.

3.4.4 Hygroexpansion and Stress

3.4.4.1 Mechanical stress

Mechanical stresses arise from a number of causes, such as moisture gradients, mechanical restraints, macroscopic tissue swelling anisotropy, and microscopic and submicroscopic anisotropy within the cell wall. Stresses such as restraint may in themselves reduce EMC values (Barkas, 1949), or their effect on dimensional change may be direct mechanical deformation of the elastic or inelastic forms. Moisture gradients are of particular concern to wood scientists and conservators because their effect is largest and common. It is impossible in practice to eliminate stresses completely during moisture changes in wood (Skaar 1988).

Skaar (1988) describes how larger pieces of sound timber go through a number of cycles or stages of differential stress during the drying process. Inner wood and outer wood often set up opposing stresses that result in surface checks (creep/tension), core collapse (compression), and case-hardening (compression set). Case-hardening can be removed if the wood is subjected to a high humidity and temperature for a short time just before finishing drying. In general though, inner layers will always undergo more shrinkage than outer layers.

Stresses are also set up during impregnation treatments as a result of the restraint imposed upon swelling by the stronger dry core and the weaker wet surface. Anisotropic effects are of particular significance.

The effect of mechanical restraints on hygroscopic dimensional change is very marked in wood because of the large component of rheological or inelastic deformation associated with mechanical stress in this material. These effects occur also in the micro, involving fibril interactions and submicroscopic anisotropy.

3.4.4.2 Swelling pressure

Gels such as wood adsorb less at a given EMC when under restraint. Within the cell wall of wood the restraint to swelling is inherent in the intertwining and crosslinking of the long cellulosic molecules, as well as in the layered structure of the microfibrils. Wood swelling under restraint will exert considerable and increasing swelling pressures with time. The maximum pressure that will develop will be limited by the compressive strength of the wood. Eventually, however, there is a decrease in this pressure caused by a large rheological flow component in the wood (Skaar 1988). It is this time factor that regulates whether a wooden object will crack or check under swelling conditions or whether it may accommodate them. Dense woods such as oak are likelier to suffer more from sudden changes to moisture content, since there is less cell cavity space to accommodate the swelling (Skaar 1988).

Since portions of wood under restraint will tend to absorb less moisture than unrestrained wood, artefacts containing wood of varied conditions may have radically differing EMC at a given RH condition, further complicating the artefact's adjustment to changes in ambient humidity. It is possible to see here a potential explanation for sorption hysteresis, since severe losses of bound water that occur below FSP will tend to lead to an increase in the level of interfibrillar bonding, involving bonding forces that will be very difficult to reverse or overcome. For an anisotropic gel such as wood, there are shear strains involved even when it is subjected to hydrostatic pressures that are uniform on all surfaces (Barkas 1949). While the totality of stress brought to bear on wood during sorption can be calculated from thermodynamic equations (osmotic pressure equation), experimentally measured values are always lower (Simpson 1971), though the variation pattern with wood moisture content is the same.

Molinski *et al.* (1991) stress the usefulness of acoustic emission studies to explain the mechanism of desorption-caused cracking of wood occurring in consequence of moisture-induced stress during its drying. Useful studies have also been published that apply this technique to explain the mechanism of cracking produced from stresses set up during soaking or immersion pre-treatments of wood with polar or swelling media, e.g., PEGs (Polisko *et al.* 1989). This data may explain the dangers and difficulties of re-treatments of waterlogged artefacts, or the reversing of conservation treatments, or the effects of osmotic collapse during normal treatment of waterlogged wood from the wet state. Most of the damage has been found to be along the radial planes of the wood, though some occurs along the border of growth rings, due to shearing between these layers of differential density, (especially in oak). This is due to the formation of greater tensile stresses in the tangential direction. In general, swelling stresses (hygroexpansion coefficients) increase with increasing moisture content.

3.4.4.3 Hygroexpansion and strength properties

Despite the stresses mentioned above, it is generally recognised that the strength or mechanical properties of wood generally increase with decreasing moisture content below fibre saturation point and do not change in any noticeable way above this point with changes in moisture content. Loss of moisture from the cell wall results in an change in mechanical properties, while loss of capillary or free water from cell cavities has no effect at all on these properties. Empirical observations have established that this relationship is guided by the following exponential equation taken from Skaar (1988):

$$S_m = S_{12}(1+B)^{(12-M)}$$

where: S_{12} and S_m are the strength properties at moisture content m and 12% respectively, and B is a coefficient representing the fractional increase in the particular strength property per percent decrease in wood moisture content.

Equation 3.6 Moisture content related to strength (Skaar,1988)

3.4.5 Reducing Hygroexpansion in Wood: Bulking Treatments

Considerable research has been carried out, both by wood scientists and conservators, into practical and economical methods of reducing the natural tendency of wood to shrink and swell with changes in ambient humidity (Chapter 4). Some of the elementary principles that lie behind such treatments can be discussed here.

Of the five different ways proposed by Kollmann *et al.* (1975) to reduce hygroexpansion in wood, only chemical treatment with bulking agents to reduce shrinkage is in common use by conservators of waterlogged wood —largely for practical reasons dictated by the condition of the material but also because of conservation ethics. Chemical treatment to induce crosslinking of wood constituents has appeared with certain of the *in situ* polymerisation treatments, e.g., formaldehyde-based (Grattan 1982), but is not in common use. It is interesting to note that any increase in crosslinking will cause a decrease in toughness, in abrasion resistance and resilience and in other mechanical properties that are related to its hygroscopicity (Skaar, 1988). The parameters used to evaluate the effectiveness of treatments include anti-shrink efficiency (ASE), or percentage reduction in shrinkage, defined as:

$$ASE(\%) = 100.\frac{S - S_x}{S}$$

where: S and S_x are the shrinkages before and after treatment.

Equation 3.7 Anti-shrink Efficiency (ASE) (Skaar, 1988)

ASE can also be defined in terms of the reduction in hygroscopicity between any two limits of humidity, useful for wood in use or after treatment. Shrinkages are usually measured in the maximum dimension only, tangential.

Most treatments used on waterlogged wood are water-soluble bulking chemicals, non-water-soluble ones being introduced only after an initial low surface tension drying with an organic solvent, and often polymerised *in situ* by heat or radiation. Several water-soluble chemicals have been used, including salts (alum treatment), sugars (sucrose treatment), and polyethylene glycol. Immersion in such chemicals causes displacement of some of the water present. Because of the reduction in activity of the remaining water and the bulking effect of the chemicals themselves, the wood remains almost fully swollen at relatively low ambient humidities. Problems with salt treatments are that the wood surface remains damp at ambient humidities higher than those at which shrinkage begins in each case, and the salts are corrosive in combination with this moisture. Sugar solutions are noncorrosive in their actions on the surface but are attractive to biological organisms unless dried without mould-activated depolymerisation.

If this occurs they will tend to be hygroscopic as well, thus biocides are often added. Polyethylene glycols are the most universally successful bulking agents for wood.

Bulking treatments are only effective in reducing hygroexpansion if they can work evenly throughout the thickness of the wood. Getting these chemicals evenly dispersed throughout the wood tissues is a difficult if not impossible task, largely because of physical barriers such as high localised vapour pressures within microcapillaries and extractives present in the wood. The mechanisms of diffusion and permeability are largely responsible for the success or failure of bulking treatments and are discussed briefly in following sections.

3.5 Sorption Thermodynamics

Thermodynamics of the wood-water system are useful to consider in calculating the approximate magnitude of certain observed properties of the system. Avramidis (1992) points out the increasing significance of thermodynamics of sorption in modelling processes such as drying in wood. More precise determination of thermodynamic parameters provides better insight into the sorption mechanism, allows for fuller interpretation of sorption isotherms, and allows further refining of sorption models. Thermodynamics in the wood-water system is, however, complicated by the fact that, as a result of sorption hysteresis, it is not truly reversible.

Sorbed water has a lower vapour pressure than ordinary liquid water. Its activity is therefore less than unity, and its enthalpy, entropy and molar free energy or chemical potential are all lower or more negative than those of liquid water at the same temperature.

Certain thermodynamic properties of water that are particularly affected by its interaction with wood are of particular interest. Changes in enthalpy (dH) appear likely to provide a measure of the energy changes occurring upon the mixing of water molecules with wood during sorption, and give an indication of the binding forces likely involved. Changes in free energy (dG) have the potential to indicate the sorbent's affinity for water. Changes in entropy (dS), which occur during sorption, may help define the spatial arrangements occurring within the water-wood interface in certain states. Measurements of changes to free energy and entropy during moisture sorption have given us models for the level of order, and the layering and bonding and organisations of the various types of moisture within wood (Skaar 1988). Enthalpy-entropy compensation exists in wood, as was established by Avramidis (1992).

Avramidis determined that enthalpy and entropy changes in the water-wood interface at different stages of water sorption are independent of temperature, that the forces of attraction of water molecules by sorption sites decrease as moisture content increases, and that the entropy decrease during adsorption

can be attributed to an increase in order in the sorbed water molecules. Thermodynamically, the fourth pseudo-phase of water, the *hygroscopic water* (mentioned previously), is analogous to the frozen or solid state of ordinary water until FSP, when liquid properties take over. Hunter (1995) challenges the assumption made without exception in sorption theory that the enthalpy of sorbed water is constant throughout. Where water is sorbed on wood this assumption does not seem to apply, either from a physical point of view or from published results. Hunter argues that the specific enthalpy of water sorbed on wood is by no means uniform throughout the sorbed water, and that as more water is adsorbed, the enthalpy of any of the water previously adsorbed will usually change and probably decrease in magnitude.

Enthalpy equations can also be used to calculate the observed lower vapour pressures of capillary water compared to that of ordinary water, explaining the observation that capillary condensation may occur as low as relative vapour pressures of 0.9. Skaar (1988) discusses other equations that support observed data about wood-water relations.

Differential heats of sorption for wood can be calculated from the Clausius-Clapeyron equation and may be used to check thermogravimetric measurements of moisture sorption in wood. Problems arise with this equation because it assumes reversibility in the sorption isotherm which, as a result of sorption hysteresis, is not the case. Nevertheless, the trends it shows are accurate.

Differential heat of sorption $(Q_s)_0$ is a measure of the excess binding energy of the water molecules to the wood substrate over that between water molecules in the liquid state. Total heat of wetting is interpreted to be proportional to the total number of sorption sites in the wood available for sorption of water. Measurements of total heat of wetting are made directly by calorimetric measurement and thus avoid the problems associated with the indirectly calculated differential heats of sorption (Skaar 1988). Values measured for $(Q_s)_0$ for cellulosic materials tend to be within the same range, and Stamm (1964) points out that this is also in the range of those for hydrogen bonding. Thus more hygroscopic woods, including waterlogged woods, are characterised by a higher total heat of wetting as a result of their larger numbers of sorption sites per unit of dry mass. This further means that total heat of wetting is related linearly to FSP. Kajita (1977) established the contribution of each of the chemical components of wood to the total heat of wetting of wood, and thus to its hygroscopicity and FSP. Loss of extractives was found to increase heats of wetting (hygroscopicity) and loss of hemicelluloses was noted to decrease heats of wetting (hygroscopicity). Waterlogged wood would seem to be an exception to this case, until the increased heat associated with the opening up of the cell-wall structure by sorbed water is taken into account.

3.6 Sorption Models

3.6.1 Basic Background

Because of the difficulty in producing error-free sorption data from experiment, many attempts have been made to express the sorption process mathematically (Spalt 1958). Most of them make certain assumptions about the system and incorporate certain generalisations in order to simplify the sorption equation. Current efforts are mainly directed towards making sorption models more generally applicable (i.e., able to explain all observed characteristics of wood)—adsorption/desorption hysteresis, temperature effects on adsorption, and the adsorption/desorption ratio. Most models are designed to fit test data, and strive to be consistent with them. But though they often achieve this, they do not always provide thermodynamic constants of the expected magnitude. New work on sorption models is mainly aimed at resolving these inconsistencies.

Some of the many equations that have been proposed and tested for describing the moisture sorption isotherms of wood are purely empirical, some are semi-empirical, and others are based on theoretical considerations (Skaar 1988). Some have been derived from classical thermodynamic considerations, others from statistical considerations, and still others from combinations of these or other treatments. There are two general approaches: sorption considered as a surface phenomenon and sorption as a solution phenomenon. In both cases, strong sorption sites are assumed for bound water, but in the first approach these sites are the primary surface layer, and in the second these sites are distributed throughout the volume of the sorbate but equally accessible to water (Skaar 1988). In both cases equations take the same form, and both assume two components to bound water, one strongly and the other weakly bonded. It must be stressed that these assumptions and described mechanisms are of necessity idealistic, mainly because of the complexity of the polymer structure of wood (Hartley *et al.* 1992).

Sorption equations have tended to be grouped into four categories, based on the physical models assumed in their derivations. The categories are: localised monolayer sorption models; multilayer sorption models (homogeneous sorption, polarised sorption layers, liquid film, capillary condensation, etc.); sorption models used in polymer science (solution models, localised sorption and solution, etc.); and empirical models (partially theoretical, fully empirical). Simpson (1973, 1979) discussed the principal models applicable to wood.

Because of the differences in complexity involved in modelling the movements of the three different types of water in wood, sorption models tend to be grouped around which part of the isotherm they are attempting to model, either that above the FSP or that below. The latter is considered to be less complicated to model than the former (Comstock 1963; El Kouali and Vergnaud 1991), because it has

only bound water transport to deal with; as a result, it has attracted most sorption studies. Stamm (1964) and Siau (1984) discuss in detail the mechanisms of bulk water transport above FSP. Moisture transport above FSP is of significance for its potential to describe both the drying of waterlogged wood and its subsequent reactions to local environment, especially surface phenomena such as temperature-induced condensation. It is also of significance to retreatment of artefacts, perhaps to remove a failed treatment (e.g., alum) or to prepare it for analysis (^{14}C dating).

Bound water transport in wood, (i.e., below FSP) attracts two main schools of thought. One, representing the majority of wood scientists, believes that this transport is described by Fickian diffusion, with moisture content concentration gradients the driving force. Many attempts have been made to measure the diffusivity either of the bound water diffusion or of the combined bound water and water vapour diffusion (Stamm 1960; Skaar 1958; Choong 1965; Comstock 1963). The other school believes that bound water diffusion takes place in response to a vapour pressure gradient rather than to a moisture content gradient. The technique of determination of diffusivity tends to have a large effect on the actual values recorded for a wood (Comstock 1963).

Direction of diffusivity also interests wood scientists. It has been found, in general, that transverse diffusivity increases with increasing moisture content, while longitudinal diffusivity decreases with increasing moisture content (Choong 1965; Siau 1971; Avramidis and Siau 1987). During absorption, diffusivity has been found to depend on an exponential relationship with moisture content (Rosen, 1976; Skaar, 1958; Avramidis and Siau, 1987).

Most wood sorption models lay claim to describing one or more of the following diffusions: isothermal, nonisothermal, steady-state, or nonsteady-state.

Earlier equations for the wood-water system (e.g., those of Langmuir, Freundlich) restricted themselves to *isothermal moisture diffusion*, which refers to analyses of moisture movement in wood that have been carried out under constant temperature conditions. Though there is, of course, always some transfer of heat during moisture movement, due to the transport of energy with the water molecules (and this may result in slight temperature differences and thermo-effects), these tended to be neglected in the earlier models as they were felt to be too small to be measured conveniently (Skaar 1988).

Nonisothermal moisture diffusion or *irreversible thermodynamics* applies where there is some coupling of heat and moisture transport (thermal diffusion or *Soret effect*), as under conditions where moisture diffuses through wood under the influence of a temperature gradient. Most drying processes occur under these conditions, since a thermal gradient is required in the process. In addition, the response of wood to varying environmental conditions, such as caused by temperature gradients in exhibition galleries on site, applies here. Choong (1963), Siau and Babiak (1983), and Siau *et al.* (1986) have all demonstrated

that when wood is subjected to a temperature gradient it will not remain at uniform moisture content, but will achieve nonuniform moisture distribution.

The most commonly used approach to adequately describe these conditions is that of irreversible thermodynamics, which can occur under *steady-state* or *nonsteady-state* conditions. The transports of heat and moisture are not reversible because true thermodynamic equilibrium does not exist. Equations describing this coupling of heat and moisture or mass transport bring together Fourier's Law of heat conduction and Fick's Law of mass flow. Equations relating these two processes and factoring in the Soret coefficient (to take account of the coupling of heat and moisture transfer) are provided by Siau (1984) and Skaar (1988). These equations are used to determine the effect of temperature change on EMC readings for the sorption isotherm (Stamm 1964).

Insights into the importance of steady state, non-isothermal diffusion in wood were provided largely by Babbitt (1940) and Choong (1963), and recently reappraised by Siau (1980). Nonisothermal moisture movement can be analysed as due to one of the following: a gradient of activated moisture molecules (Siau and Babiak 1983; Keene 1992), a gradient of chemical potential (Siau 1983a, 1984; Keene, 1992), or to water potential. More recently, Siau (1992) has pointed out the problems with the first two of these. Equations for the gradient of activated moisture molecules do not account for the effect of the sorption isotherm on nonisothermal diffusion. That for the gradient of chemical potential was marred by one of its values, and thus did not fit experimental data. Siau re-examined these models in terms of thermal diffusion; the modified equations yielded a model that improved the agreement between experiment and theory for available sorption data, particularly at higher relative humidities.

Steady-state diffusion may occur under either isothermal or non-isothermal conditions, but always where flux and gradient are non-variable in both space and time. This type of flow is not, in fact, relevant for most processes in wood treatment (e.g., impregnation, heating, and drying) where there is no net change in the conditions inside the wood over a period of time. Steady state diffusion coefficient determinations (towards which most of this type of modelling is directed) are largely based directly on Fick's law, in which a moisture-content or partial pressure gradient may be used with equivalent results, provided conditions are isothermal. Though this is the case with thin barriers, it is not the case with thick barriers such as cell walls. Here *activated diffusion* is now considered to be taking place (section 3.6.3), where the diffusion coefficient increases rapidly with temperature in accordance with the Arrhenius equation. Surface losses will also tend to make steady state equations irrelevant, since surface resistance may influence adsorption results to a significant degree (Siau 1984). Variations in air velocity also change adsorption results significantly enough to affect the validity of steady state equations. These factors are more adequately taken into account with non-steady state diffusion models. Since, however, unsteady-state equations are derived from steady-state relationships, a great deal of attention in wood science/physics has focused on refining of steady state expressions.

Nonsteady-state diffusion occurs when flux and gradient are variable in both space and time. This type of flow has relevance for most processes in wood treatment because there is a net change in the conditions inside the wood over a period of time. Nonsteady-state equations are usually derived from steady-state relationships, with the adjustment for heat flow using Fourier's law. The thermal diffusion coefficient is then numerically equal to the rate of temperature change, depending on the gradient change. The factors influencing thermal diffusivity (and thus the time taken to dry) are thermal conductivity, specific gravity, and moisture content. Nonisothermal, nonsteady-state moisture movement requires the emendation of the standard nonsteady state and nonisothermal equations in order to take into account the effects of temperature and moisture content upon the diffusion coefficient. Hailwood-Horrobin theory (section 3.6.2.3) was the first attempt at doing this.

The most important practical application of nonisothermal nonsteady state moisture movement is in the drying of wood. Where comparison of moisture content profiles with temperature show lowest values of moisture content on the surface and highest in the core of a piece of wood, and temperature profiles the reverse, it can be seen how the thermal gradient partially counteracts the effect of moisture content gradient during the drying process.

When attempting to determine the value of *diffusivity*, wood scientists adopt models of either steady or unsteady state flow. Most commonly, unsteady state flow is the method chosen. In this method the flux and gradient are variable in both space and time, conditions that are more important in common wood treatments than steady state flow, since the former is present whenever the wood is impregnated with liquid or undergoing drying (Droin-Josserand *et al.* 1988, 1989). During absorption, in the contact with liquid water, there is not considered to be any external resistance to moisture flow. But for desorption of moisture, the process is assumed to be controlled by diffusion within the wood and evaporation on the surface, with the rate of evaporation being proportional to the difference between the moisture concentration on the surface and at equilibrium (Droin-Josserand *et al.* 1988). El Kouali *et al.* (1991) believes that absorption can be described by diffusional processes, and that desorption can be described by evaporation and diffusion. He feels he has determined that a constant diffusivity is observed at all stages of evaporation and desorption, and is the same value in the two cases. Others do not subscribe to this concept. (Avramidis 1992; Hunter 1995)

Some of these others aim at defining theoretically exact values of the sorption energies of single molecules of water on all available sites of both crystalline and amorphous cellulose, hoping to aid better modelling of the complexities of wood. The affinity of a water molecule for a given chemical site should allow construction of a theoretical sorption isotherm at least at the water monolayer level for each successive molecule adsorbed or desorbed. (Pizzi *et al.*, 1987 a & b)

3.6.2 Ground Models for Sorption in Wood

Detailed reviews of the development of sorption models and current theory have been published. (Skaar 1954; Spalt 1958; Stamm 1964; Siau 1984; Skaar 1988; Cloutier and Fortin 1991). As has been mentioned before, two primary concepts govern these theories: one a multi-molecular layer concept and the other a polymer-solution concept. Most models still incorporate a proportion of Langmuir's equation, since the initial part of the isotherm fits it quite well. It acknowledges the dynamic nature of the process, but fails to recognise the non-ideal adsorption that takes place where surfaces are not uniform, or where there are interactions between adsorbed molecules (known as *cooperativity*), e.g., Zone II on the isotherm. Freundlich made some headway in defining these non-ideal systems. His model acknowledges the observed dependence of amount absorbed to concentration of sites filled.

Brunauer, Emmett, and Teller (1938) have made modifications to the Langmuir equation to allow for polymolecular adsorption (the B.E.T. equation). However, they made the same assumption that Langmuir did, and also assumed that the heat of adsorption is confined to the formation of the first monomolecular layer, which is not true. It is quite useful, however, for calculating the amount of adsorbate required to form a monomolecular layer (Zone I). The B.E.T. equation, however, remains the best-known equation for water adsorption by wood, despite these wrong assumptions.

These earlier theories are based on the layering concept (Figure 3.14).

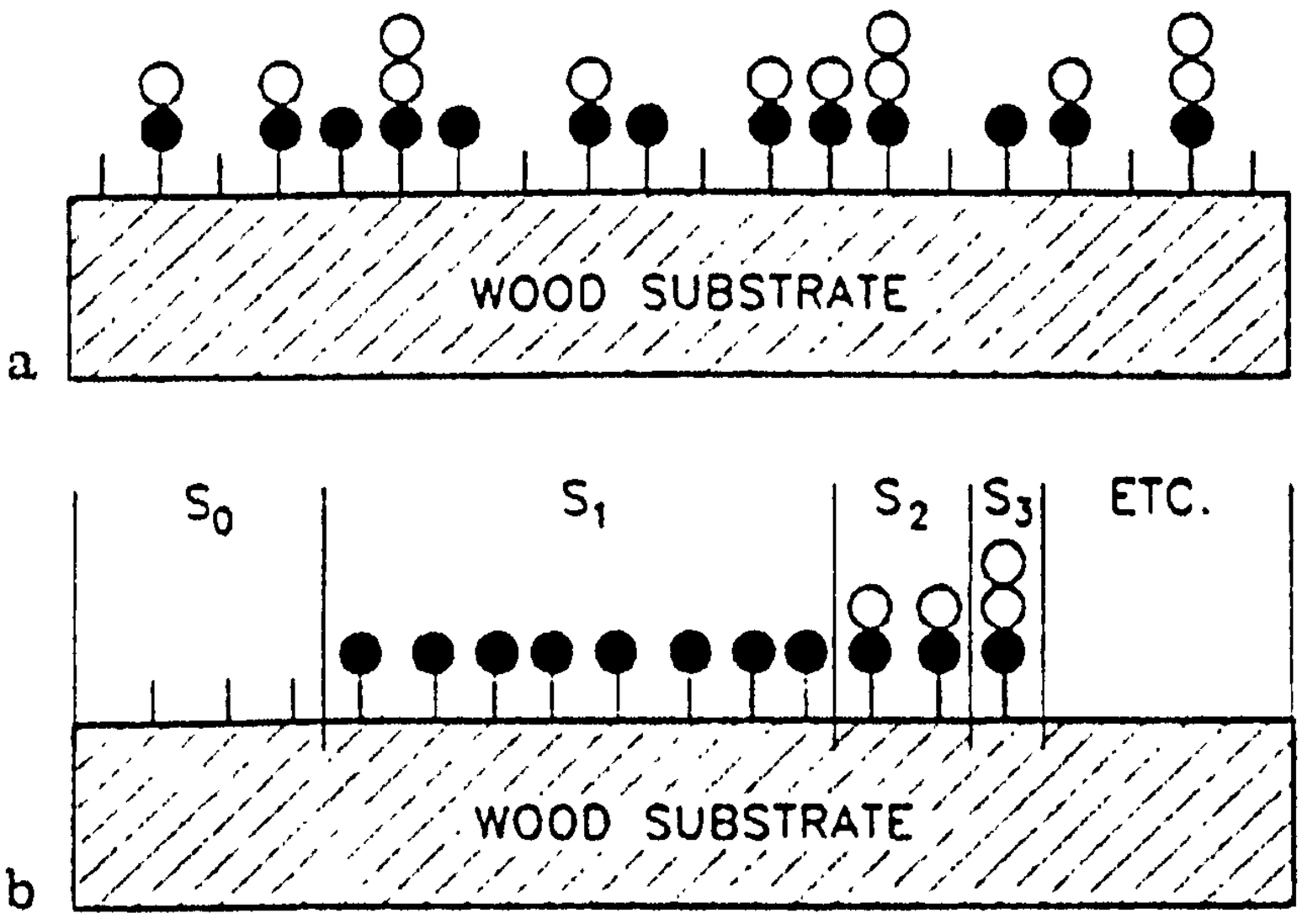


Figure 3.14 Schematic view of formation of layers in multi-molecular layering (Hartley *et al.*,1992)

3.6.2.1 Brunauer-Emmett-Teller (B.E.T) theory

B.E.T theory forms the basis upon which many other wood sorption theories have developed. As an extension or emendation of the Langmuir theory, it assumes polymolecular multilayered sorption. It is particularly useful in calculating surface areas and energies of sorption. Though the theory works well with experimental data at water vapour activities below 0.4, it is not accurate any higher. This is partly because B.E.T. theory assumes that the thermodynamic properties of the secondary water are identical with those of ordinary liquid water.

$$\frac{h}{M(1-h)} = \frac{1}{M_m C} + \frac{(C-1)h}{M_m C}$$

where: M is the percent moisture content , h is the relative vapour pressure ,M_m is the fractional moisture content , and C is the BET constant.

Equation 3.8 Standard form of the B.E.T. equation (Skaar, 1988)

The B.E.T. equation was eventually modified by Brunauer *et al.* (1938) to improve the fit of experimental data from the higher relative vapour pressures. This was done by restricting the maximum number of layers permissible on any one sorption site.

$$\frac{h}{M(1-h)} = \frac{1-h+Ch(1-h^n)}{M_m C[1-(n+1-nh)h^n]}$$

where: M is the percent moisture content , h is the relative vapour pressure, M_m is the fractional moisture content , n is the number of layers of water, and C is the BET constant.

Equation 3.9 Brunauer's modification of the B.E.T. equation (Skaar,1988)

The average number of layers at any relative vapour pressure could be estimated from the ratio of the total moisture content to the moisture content of the monolayer. All versions based on the B.E.T. model consider a multilayer adsorption, assuming a monolayer tightly bonded to the wood substrate and secondary and higher layers having similar characteristics to liquid water.

3.6.2.2 The Dent theory

Dent's more recent modification of B.E.T. theory (1977), closely matches the observed isotherms because it advances B.E.T. theory to include the realisation that the water in secondary layers is not the same as liquid water. The theory assumes that the properties of water in the secondary layer is the same for all subsequent layers of water. The Dent model established the important fact that some sorption sites remain vacant even at saturation humidity. At equilibrium, evaporation from one area of sorption

sites will be condensing on another area, and the rates of these two processes will be equal, and proportional to the vapour activity at constant temperature, i.e., equilibrium RH.

Data plotted from this model reveals that the curve for primary water is typical of the type 1 isotherm (i.e., monolayer sorption) and the secondary water isotherm is typical of the type 3 isotherm (i.e., multilayered sorption). The two added together form the typical type 2 isotherm.

One of the significant drawbacks to the B.E.T. and Dent sorption models is that neither can quantify sufficiently the energy changes behind restrained sorption. Within the cell wall of wood, the restraint to swelling is inherent in the intertwining and cross-linking of the long cellulosic molecules, as well as in the layered structure of the microfibrils. In his work with textiles, King (1960) modified the B.E.T. equation to incorporate these factors, and established that swelling at low moisture contents does not involve significant swelling stress, as apparently the take-up of primary water is not accompanied by sufficient bond deformation in the fibre structure to resist the swelling, and the cell wall structure is sufficiently porous and flexible to absorb this without stress. It seems likely that the same would hold true for waterlogged wood during use.

3.6.2.3 The Hailwood-Horrobin theory

Hailwood and Horrobin (1946) provided the next significant move in sorption theory, though they moved away from the multilayer concept to do so. They developed a model for sorption that assumed that the process leads to part of the sorbed water forming a hydrate with the wood polymers, and the balance forming a solid solution in the cell wall. Two distinct kinds of hydrate have been incorporated into their model. The cell wall is presumed to consist of three chemical species: dry wood, hydrated wood, and dissolved water acting as an ideal solid solution. The mixture of polymer, polymer hydrates and dissolved water forms the single solid phase—wood. The two-component system, water and polymer, exists in two phases, and the dissolved water molecules in the solid phase are assumed to be mobile (Hartley *et al.* 1992). The Hailwood-Horrobin model is now used more extensively than models based on multilayering theory.

This model satisfactorily produces the sigmoid Type 2 isotherm normally found for wood. It has been criticised for some of the assumptions used in its derivation, but it does provide a satisfactory estimate of certain fundamental sorption parameters, and is similar in this to the Dent model.

$$\frac{h}{m} = A + Bh - Ch^2$$

where: $A = \frac{1}{m_0 K_d (K_h + 1)}$: $B = \frac{K_h - 1}{m_0 (K_h + 1)}$: $C = \frac{K_h K_d}{m_0 (K_h + 1)}$

where: *A*, *B*, and *C* are three empirical constants that vary depending on the physical model assumed, *h* is the relative vapour pressure, *m* is the moisture content, m_o is the moisture content at total monolayer hydration, and K_h and K_d are equilibrium constants.

Equation 3.10 Hailwood-Horrobin sorption model (Skaar, 1988)

Thus the Hailwood-Horrobin and Dent sorption theories predict the same empirical parameters and three fundamental equilibrium constants, one for each hydrate, as well as m_0. The magnitude of certain of their constants are, however, slightly different.

Not only does this theory provide a measure of the water bound directly to the polymer and that condensed in the void volume of the polymer, it also provides a measure of the degree of orientation within the polymer structure. One limitation of the Hailwood-Horrobin theory that cannot be overlooked is its failure to account explicitly for hysteresis in sorption (Spalt, 1958). The success of this theory is based on the constants derived by Simpson (1973). Hartley *et al.* (1992) suggest that a combination of the Dent multilayered concept and the Hailwood-Horrobin solution-based concept would more adequately explain the behaviour of water in wood.

Most other isotherm equations available have proved to be able to be rearranged into the above form, though the value of their constants may be slightly different. The Hailwood-Horrobin model has been criticised by Simpson (1979) for not predicting satisfactory values of change in Hh and Hd. This has come about because of the simplifying assumptions that creep into most sorption theories and preclude accurate predictions of the heats of sorption. More recent models are all attempts to produce more satisfactory values. Using a non-linear regression technique, Simpson (1973, 1979) applied Hailwood-Horrobin equations to USDA Wood Handbook data in order to determine the values of constants contained within the equations. The resulting regression equations have found wide use in more recent attempts at wood sorption models.

Peirce's contribution (1929) was to produce an equation that has been used to relate moisture content exponentially with several of the mechanical properties of wood at or below FSP. The relationship of mechanical strength to primary water, according to the Peirce model, is based on the assumption that these strength properties are determined by the number of hydrogen bonds crosslinking cellulose and other constituents in the non-crystalline regions of the cell wall. Sorption of primary water presumably

involves rupturing these hydrogen bonds in proportion to the amount of water. Peirce's model also accurately predicts the reduction of the mechanical properties of wood with increasing temperature.

Enderby (1955) and King (1960) used statistical thermodynamics to derive equations identical with those of Hailwood-Horrobin equations. The model attempted to quantify the different types of sorption sites. Bradley (1936) incorporated the concept of dipole attractions to define loss of bonding energy between successive layers of sorbed water molecules.

3.6.2.4 Simpson's modifications and capillary condensation

Most sorption models tend to underestimate the actual sorption values obtained at high humidities. It is thought that this may be due to capillary condensation at these high humidities. This has been shown to exist in the smaller capillaries of wood even when the ambient atmosphere is not fully saturated, established by the Kelvin equation:

$$r = \frac{2V_w S}{RT \ln(1/h)}$$

where: r is the capillary radius, R is the gas constant, V_w is the molar volume, S is the surface tension, T is the absolute temperature, and h is the equilibrium relative vapour pressure.

Equation 3.11 The Kelvin equation (Skaar, 1988)

This only works to values for h=0.8 since the calculated radii are getting close to the size of the water molecule itself (30 times), and surface tension operates under the assumption that large numbers of molecules are present. The assumption that pre-existing capillaries in the cell wall enlarge as moisture content increases (thus increasing their capillary radii and corresponding equilibrium humidities) also only operates with higher humidities.

Sorption hysteresis has also been attributed at least in part to capillary condensation, since the contact angle of the receding meniscus in a capillary during desorption is smaller than when it is advancing during resorption, thus causing more sorbed water to be present during desorption in a given meniscus radius and ambient humidity, than during resorption (Figure 3.15).

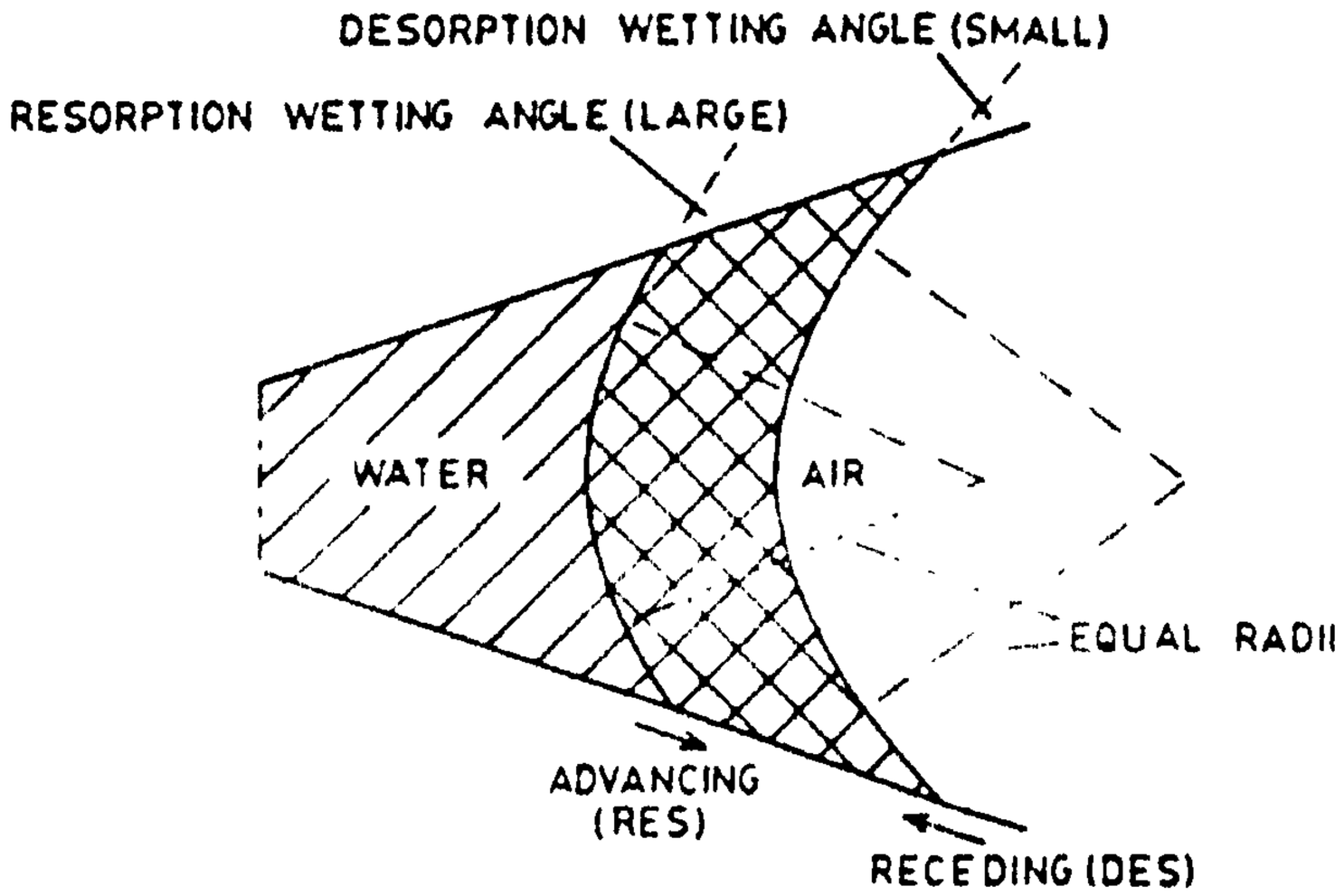


Figure 3.15 **Meniscus during desorption/resorption** **(Skaar, 1988)**

Simpson's (1973) modifications of the B.E.T. model, using the Kelvin equation, attempted to predict this hysteresis effect and produced the following sorption curves (Figure 3.16):

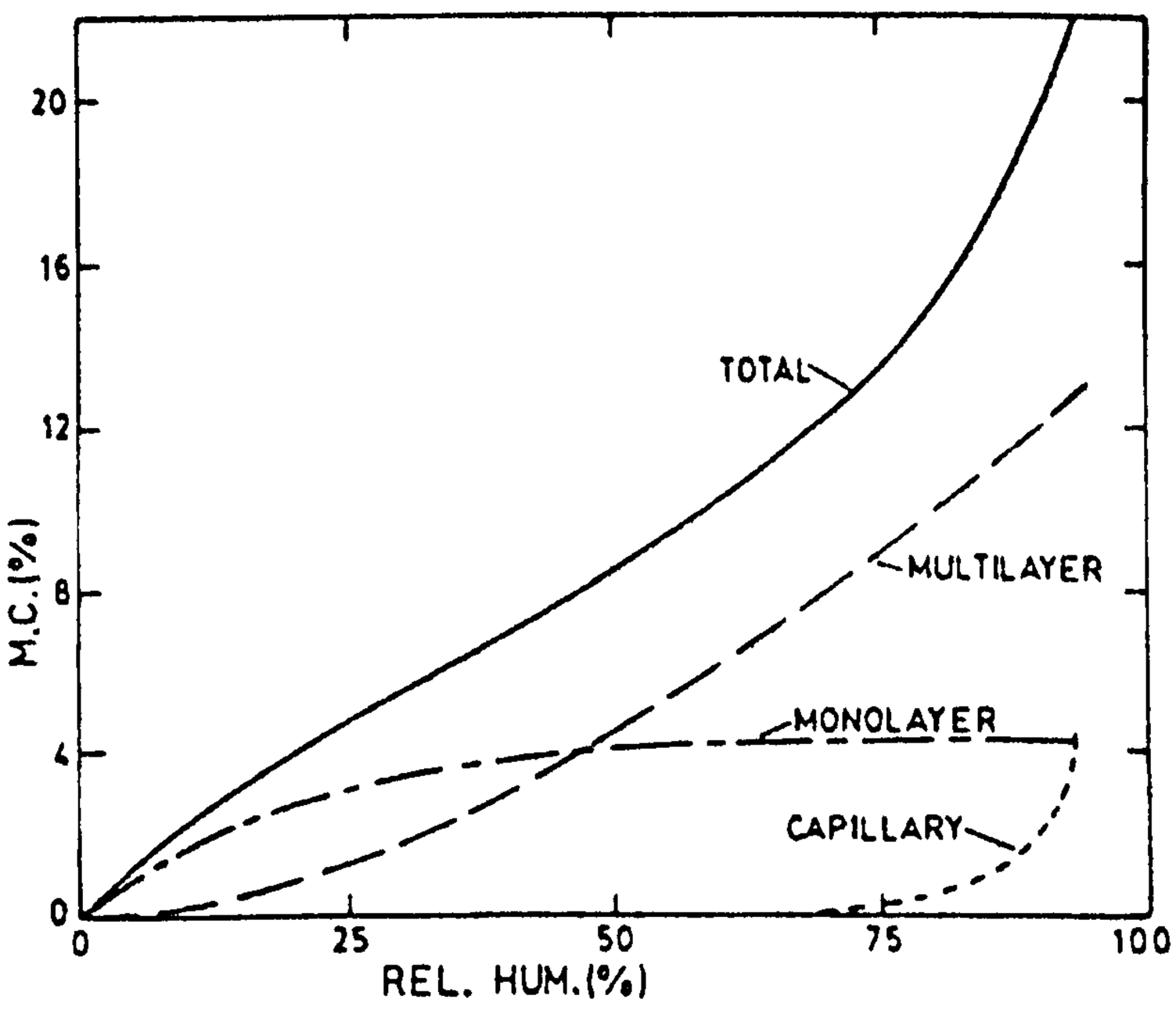


Figure 3.16 **Modifications to B.E.T. to incorporate capillary condensation** **(Skaar,1988)**

3.6.2.5 Malmquist's sorption model

Malmquist's sorption model (1958, 1959, 1967 in Siau 1984) treats the sorption of water by wood in terms of the space-dimensional factor within the cell wall. It also considers the cohesive properties of the cell wall that might limit the swelling associated with water sorption and therefore the extent of water sorption by the wood. This model brings up for the first time the concept of sorption occurring within two-dimensional surfaces or three-dimensional volumes. Malmquist's theory considers that there

is a sorption space within the cell wall that sorbed water molecules can occupy, and also defined the surrounding vapour space as the space that the water-vapour molecules occupy.

He brings in the cohesion factor to account for the limits to sorption imposed by the resistance of wood to swelling. He attributes sorption hysteresis to two factors: an increase in saturation pressure during resorption compared with desorption, and the matter of soft or linear sorption, defined elsewhere.

3.6.3 Recent Discussion

3.6.3.1 General

Bramhall (1995) outlines the current agreed understanding of water diffusion, and its connection and significance to the drying of wood. The generally accepted view is that once drying is under way, the wood surface assumes the EMC corresponding to the temperature and RH of the surrounding air and, driven by the difference in moisture content between the interior and the surface, diffusion takes place. This diffusion requires the conduction of heat to the interior and the activation of water molecules. The molecules progress by a series of *random jumps* from one hygroscopic site to the next until they reach the surface. At any hygroscopic site a molecule may be *captured*, but when it is captured it must give up its heat of activation to a neighbouring molecule that then continues the journey. This process is called *activated diffusion*, and is adequately described by Fick's equation or minor adaptations of it (Skaar 1988). Fick's law represents the relationship between the flux and the concentration gradient under steady-state conditions, and in its unmodified form is considered to apply only to the bound-water proportion in wood.

Wood scientists are now concerned with the problem of how to measure the concentration gradient. Often this can be achieved by the measuring of moisture content profiles. When testing sorption equations, however, wood scientists usually concentrate on the bound-water fraction because of the complication of modifying these equations to factor in the mixture of capillary bulk movement and diffusion that characterise free-water movement. Various workers are also experimenting to find values for the diffusion coefficient and to see how it varies with temperature. They have usually proceeded by measuring drying rates at various temperatures under essentially isothermal conditions. Invariably the relationship is found to be:

$$D_T = ke^{-E/RT}$$

where: D_T is a proportionality constant dependent on temperature, k is the Boltzmann constant, E is the activation energy, R is the appropriate gas constant, and T is the absolute temperature.

Equation 3.12 Diffusion coefficient varies with temperature (Bramhall, 1995)

Bramhall points out the similarity of this equation to the equation defining the vapour pressure of water, causing some to assume that the diffusion coefficient is proportional to the vapour pressure (section 3.6.3.9).

3.6.3.2 Driving forces

Most of the attention paid to moisture migration has been focused on the movement of bound water through wood (Stanish 1986). Until very recently this process has been generally accepted to be diffusive in nature (Bramhall, 1995). In keeping with Fick's laws of diffusion, it is natural to express the rate of bound water diffusion as the product of a diffusion coefficient (or *diffusivity* or *conductance*) and a driving force (or *gradient*). The identification of the proper driving force has, however, been a source of controversy for many years. Most of the recent discussion surrounding sorption models for wood continues to centre around differences in stress on one or other of the possible driving forces for diffusion.

The focus of much current discussion is just how far Fick's law can be taken in the context of wood-water relations. Fick's experiments were necessarily isothermal, to counteract convection currents. He conducted his experiments at several temperatures and concluded that the rate of diffusion was proportional to the concentration gradient and that the diffusion coefficient was proportional to the absolute temperature. The controversy around the application of Fick's law to wood moisture movement lies with its assumption that moisture concentration is the potential or driving force for this process and that a single diffusion coefficient controls it. Babbitt (1950) stated that if Fick's law is to be more generalisable it must take on the assumption that the diffusion coefficient is not a constant but is dependent on the concentration.

There are a number of alternative ways of expressing the potential that drives moisture through wood. There is moisture content, partial water vapour pressure in equilibrium with the wood, relative humidity in equilibrium with the wood, chemical or water potential, and spreading pressure. Skaar (1954) showed that calculations of isothermal moisture transport made with concentration, moisture-content, or partial-vapour pressure gradients produce identical results. Early investigators (Skaar 1954; Stamm 1959, 1960; Comstock 1963; and many others), chose to use the gradient of the concentration of bound water (moisture content) as the driving force, which they did with considerable success. Unfortunately, the diffusion coefficients they derived remained strongly dependent on moisture content, temperature, and wood properties.

Other driving forces have been suggested, and their discussion follows. Each of them is associated with a particular transport coefficient K, which is the only point on which these other theoretical models differ significantly from Fick's law. Skaar (1988) gives a useful summary of these potentials and their relationship to Fick's law.

Until this decade, *moisture content gradient* was the most generally accepted approach used to model both bound water and free water in wood (Moschler and Martin 1968; Nadler *et al.* 1985; Cunningham *et al.* 1989). As far back as 1950, however, Babbitt pointed out that where there is an interaction between the diffusing gas and the solid, this approach is not valid; instead, a potential function should be used, since its space derivative gives a true force for driving the diffusion.

Bramhall (1976) recognised the same flaw, and proposed the *vapour pressure gradient* as a better choice of driving force for bound water diffusion. This precipitated a lively exchange of discussion (Rosen 1976; Babbitt 1977a; Bramhall 1977; Wengert 1977; Babbitt, 1977b; Bramhall 1979) and a general reconsideration of sorption models. During this time *chemical potential gradient* as driving force was introduced (Kawai *et al.* 1978). Kawai and co-workers applied this to an nonsteady-state diffusion equation to model isothermal drying rate experiments. The derived diffusion coefficients were related exponentially to moisture content, but with a lot of scatter that the authors attributed to heterogeneity, drying stresses and temperature gradients. Stanish (1986) believed the scatter to have been due to failing to incorporate water vapour diffusion to the overall drying rate.

The *water potential-moisture content relationship* is an approach that has been adopted in the last two decades to bring together elements of both moisture content gradient-led and chemical potential-led theories (Cloutier *et al.* 1991). The water potential concept can explain both the actions of bound water and free water, and thus can be used to describe wood behaviour both above and below FSP (Fortin 1979; Siau 1984, 1988). However, the moisture content-water potential relationship (M-ψ) must be known. Evaluation of this relationship has been carried out by only a few researchers (Griffin 1977; Fortin 1979; Choong and Tesoro 1989). Since water potential takes capillary forces into account (i.e., free-water movements), variations in the shape of the M-ψ relationship will occur both at high moisture content and between species that have anatomical differences. Temperature may also effect this relationship significantly, the water potential increasing with increase in temperature at any given moisture content. A directional dependency (*transient diffusion*; *three-dimensional diffusion*) may also exist within wood tissues/planes, and this is currently a matter for much discussion (El Kouali *et al.* 1991; Mounji and Bouzon 1992).

Siau (1980) looked at the contribution of thermal diffusion (also known as the *Soret effect*) to nonisothermal bound-water migration behaviour, and thereby added the *temperature gradient* to the chemical potential gradient to express a new driving force. While theoretical considerations showed that the thermal diffusion coefficient should be equivalent to the activation energy for water vapour diffusion, experimental nonisothermal drying data produced thermal diffusion coefficients that were inconsistent with the reported activation energy. Skaar and Siau (1981) then developed a theoretical expression for bound-water flux based on the assumption that bound-water diffusion is an activated process (*activated diffusion*), i.e., that bound water molecules must attain a certain minimum energy level in order to

migrate from sorption site to sorption site. Their expression included a thermal diffusion term to calculate the necessary activation energy. Siau (1983a) then took up the concept of the chemical potential again, attempting to adapt it to the nonisothermal case, defining bound-water flux in terms of a chemical potential gradient, which was expressed in terms of temperature and moisture content.

Nelson (1991) criticised the models of Siau (1980) and Skaar and Siau (1981) for finding that the molar heat of transfer and the molar activation energy were equivalent. His equations established that the heat of transfer for adsorbed water exceeds the activation energy for bound water diffusion. He proposed the explanation that diffusing molecules may carry energy in excess of the minimum required for participation in diffusion (i.e., activation). While his model only covers steady-state conditions, he believes that experimental data could expand this to nonisothermal conditions. He maintains that *nonequilibrium thermodynamics* can describe both isothermal and nonisothermal conditions in wood.

Work continues with an emphasis on moisture content-water potential forces. Recently Bramhall (1995) contributed an important paper re-establishing the relevance of the Fickian equation for the wood-water relation, and through his critical appraisal of years of misinterpretation of this law, argues convincingly for the transcendence of vapour pressure as a driving force.

3.7 Permeability and Pore Volumes

3.7.1 General

As stated previously, bulk flow is a significant mechanism in wood moisture transport, particularly as it applies to the transport of impregnation chemicals into wood structure. It is also significant to a small extent in moisture movements above FSP. The magnitude of bulk flow of a fluid through wood is determined by its permeability. It is important to make a distinction between porosity and permeability. *Porosity* is the volume fraction of void space in a solid. *Permeability* is a measure of the ease with which fluids are transported through a porous solid under the influence of a pressure gradient (Siau, 1988). While a solid must be porous to be permeable, not all porous solids are permeable. Wood will only be permeable where its void spaces are interconnected by openings. Where wood pits have become occluded (drying stress), or where they have become encrusted (e.g., by iron salts or calcium compounds), or if the pits are aspirated, the wood will assume a closed-cell structure and exhibit a permeability of close to zero. Movements through the cell wall bound-water, material (i.e., as sorbed or bound-water) are not included under this concept.

The three-dimensional network that is wood substance expands at saturation vapour pressure to a maximum, with complete dissolution prevented by crosslinks. This swollen network contains submicroscopic voids (second order space) in which water is condensed immediately. Some average or effective size of void will impose an upper limit to the size of molecule a water-borne or swelling solute

is capable of diffusing into or through the cell walls into these new spaces. The concept of pore volumes is significant to such processes as openness of wood to deteriorating chemicals and micro-organisms; the penetration of preservation and bulking chemicals; the bonding of adhesives; and the removal of chemical breakdown products (e.g., wood constituents), or salts (e.g., iron and lime) during treatment processes (Tarkow *et al.* 1966). Hoffmann (1982) relates wood capillary sizes with the size of some common treatment molecules used in the conservation of wood (Table 3.2 below).

Capillary system of cell wall	
Fissures within elementary fibrils	1nm
Capillaries between elementary fibrils	10nm
Capillaries between fibrils	up to 80nm
Pores in pit membranes	up to 150nm
Dimensions of some molecules	
Water	0.2nm
PEG 400 (length x width)	2 x 0.25nm
PEG 1000 (length x width)	4.5 x 0.35nm
PEG 4000 (length x width)	18 x 0.35nm

Table 3.2 Capillary sizes (Hoffmann, 1982)

3.7.2 Types of Flow

The steady-state flow of fluids through wood is governed, as in other porous solids, by Darcy's law.

$$K = \frac{Flux}{Gradient} = \frac{Q/A}{\Delta P/L} = \frac{QL}{A\Delta P'}$$

where: K is conductivity or permeability, Q is the volumetric flow rate, L is the length of the specimen in the flow direction, A is the cross-sectional are of specimen perpendicular to the flow direction, and ΔP is the pressure differential.

Equation 3.13 Darcy's Law for Liquids (Siau, 1984)

Conductivity is assumed to be constant in steady state flow conditions, and is equivalent to permeability.

Darcy's law runs into problems with the complexity of wood, and its assumptions and limitations are discussed by Siau (1984). From the following summary of its principal assumptions it is easy to see where some modification of Darcy's law is required when it is to be applied to wood permeability.

1. Flow is viscous and linear. (Siau and Petty (1979) have determined that nonlinear flow will occur where fluid is moving from a large to a small capillary.)

2. The fluid is homogeneous and incompressible. (Conservation treatment chemicals for wood such as PEGs are mixtures of various molecular weight fractions, even those designated with a single molecular weight, e.g., PEG 3000 (Skinner, 1994). While liquids are essentially incompressible, gases aren't. Vapour phase treatment, e.g., *in situ* monomer polymerisation treatments, would not fit this assumption.)

3. The porous medium is homogeneous. (Woods have an extremely complex and non-homogeneous structure, especially hardwoods such as oak.)

4. There is no interaction between fluid and substrate. (This is certainly not true of either water or water-based chemicals' interaction with wood, because of their interaction with hydroxyl sites on the cell-wall surface. It is this that explains why non-polar solvent-based treatments for wood are found to more thoroughly permeate the entirety of a wooden object.)

5. Permeability is independent of the length of the specimen in the flow direction. (Bramhall (1991) and Siau (1972) pointed out that while specimen length in woods of relatively high permeability is usually independent of permeability, permeability decreases with length in woods of low permeability, tending to become greater as permeability decreases.)

Despite these restrictions, Darcy's law remains the basis for models of bulk flow in wood.

Various kinds of flow occur within wood—viscous or laminar flow, turbulent flow, non-linear flow, and molecular slip flow or Knudsen diffusion. Siau (1984) reviews the participation of each of these in detail.

The extreme non-homogeneity of wood structure is one of the principal reasons why it is difficult to correlate the steady-state gas permeability of wood with its treatability with preservative liquids, since this involves unsteady state transport. The flow of a liquid into a porous body is governed by different principles than the diffusion of vapour within it, because the liquid enters as a front with liquid-gas interfaces in the capillaries. Nonhomogeneity of flow is conventionally factored into Darcy's equation to help cope with this.

3.7.3 Measurement of Pore Volumes

If the conservator could calculate the overall porosity of his wood and the relative proportions of pores of different sizes, he could make better choice of the type of bulking chemical to use in stabilising his wood. Microscopic procedures have been used to calculate void volumes, as well as moisture adsorption isotherms, X-ray scattering techniques, or polymer exclusion. The problem with the use of the sorption isotherm for this purpose is that, though in principle analysis of the isotherm will relate the relative vapour pressure at which a vapour condenses in an existing capillary to some characteristic size of the capillary, in practise it is not so applicable to wood whose gel contains only a very small content of truly pre-existing or permanent capillaries. Its voids are best considered as being created when the substance goes into partial solution. Even solvent replacement and nitrogen adsorption techniques that avoid the problems of swelling capillaries experience substantial shrinkage during the final replacement of the fluid by evaporation from swollen wood below the critical temperature for the fluid.

The use of bulking chemicals in the measurement of pore volumes (*solute exclusion*) can similarly experience problems, especially as many of these (e.g., PEGs) may in fact have a small swelling effect on the wood in themselves (Jensen, 1997), since finding chemicals of very precise molecular weight and spherical section is difficult, and since the high concentrations necessary may impose osmotic collapse upon inner wood (Skinner, 1994). This technique is also, of necessity, temperature-dependent. What also has to be taken into account is the increased surface interaction capacity, the reactivity of the swollen wood substance. Wood may often also contain barriers to the diffusion of polymers into its voids (e.g., tyloses in oak; iron or calcium carbonate salts; cell layer composition). Nevertheless, this technique is considered the most accurate and least error-prone for determining void volumes in wood (Siau, 1984). Lin *et al.* (1987) used solute exclusion (both PEGs and sugars) monitored by a differential refractometer to determine pore size distribution and micropore size in wet cellulose. They found the need for replicate samples and a statistical approach to data analysis because of sample-to-sample variability. The method proved useful for wet, hydrophilic polymers. Since the ratio of concentration for penetrating molecules inside the pore to that of the bulk phase is termed the *penetration coefficient* and is a function of both the shape and radius of the pores, the apparent pore-size distribution from this method thus reflects the shape as well as size of the pores of wet wood. A simple slit model was been indicated for wood cellulose. The differential refractometer made easier precise determination of small changes in polymer concentration.

The situation for waterlogged wood is slightly different. Tarkow *et al.* (1966) discovered the limiting size for the penetration of a water soluble material into green wood substance to be the PEG 3000 molecule. As a result, this size has been adopted as maximum for treatments of waterlogged wood, although loss of constituents and excess swelling may have produced voids larger in size. Griffin (1977) defined FSP as the condition when all voids of a radius greater than 1.5μ are devoid of free water. But

the raised FSPs measured for waterlogged wood would seem to suggest a larger void size. There is, however, a great deal of discussion as to whether waterlogged wood is indeed swollen beyond its original dimensions (Grattan, 1987). At temperatures significantly above room temperature, e.g., the 60°C at which certain treatments are carried out, Goring, (1963) discovered softening of lignin and hemicellulose to occur. This may explain a portion of the increased permeation by PEGs achieved at this temperature. All of these factors suggest that the use of polymer exclusion to measure pore volumes might be problematic in waterlogged wood specimens, as indeed Skinner (1994) discovered.

3.7.4 Pore Volume Ratios and Permeability Models

The simplest model of permeability applicable to wood is the uniform parallel circular capillary model, upon which the Poiseuille equation is based.

$$Q = \frac{N\pi r^4 \Delta P}{8\eta L}$$

where: Q is the volumetric flow rate, L is the length of the specimen in the flow direction, N is the number of layers, and ΔP is the pressure differential.

Equation 3.14 Poiseuille Law for Liquids **(Siau, 1984)**

In the main, this model is applicable to the open vessels of diffuse porous hardwoods in the longitudinal fibre direction. In more heterogeneous woods such as oak, where areas of high conductance (vessels) abut on areas of low conductance (inter-vessel pits), Petty's model for conductance in series has been found to be more relevant (Siau *et al.*, 1981), and is generally extended to apply to three-series components, and can be corrected to take into account short capillaries.

3.7.5 The Characterisation of Wood Structure from Permeability Measurements

Where there is a need to establish how open to impregnation by a particular liquid a wooden object is, an accurate mathematical picture of its pore volume ratios must be obtained, as well as an indication of the interconnectivity of those pores. Equations to calculate radii for each type of wood pore, numbers of pores present, and radius and number of pit openings (significant because of their deterioration in waterlogged wood) are readily available (Siau, 1984). Other aspects of the use of permeability and capillary phenomena to characterise wood structure are discussed in detail by Siau *et al.* (1981) and Jensen (1997).

Stone and Scallan (1968a) experimented with permeability measurements as a tool to describe wood structure. Using the polymer exclusion method, they were able to make accurate measurements of wood fibre saturation points, both for fresh and for deteriorated wood. They equated FSP with total pore

volume or total inaccessible water. By equating accessible water with inaccessible water subtracted from total water of swelling, they were able to predict the permeability of particular woods to treatment chemicals and to removal of chemicals (desalination; re-treatment) and breakdown products. In measuring the inaccessible water by using a series of penetrating molecules of increasing size, their method plots out the pore size distribution. Stone and Scallan (1968a) visualised pore size distribution curves as divided into two sections, the small pore region of the curve corresponding to micro-reticular or intra-lamellar pores (up to 25Å), and the large pore region corresponding to macro-reticular or inter-lamellar spaces. Since the curve is smooth, it suggests that there is considerable overlap in the distribution of the sizes of the two types of pores. They concluded that since pore sizes were narrowest towards the lumen, cellulose is more densely packed in this region. They also concluded that lignin, which has little ability to hold water, is most concentrated between one cell wall and the next. This matches up well with current knowledge. They also used this technique to predict the condition of the cell wall during deterioration. Cellulose losses would create larger porosity towards the lumen, reversing the trend of sound wood. And because of this, total hygroscopicity could be predicted to rise despite the loss of most of the water binding cellulose.

Cunningham (1992) studied effective penetration depth and effective resistance, using lumped modelling to simplify certain of the physical complexities of the wood system, in order to further elucidate moisture transfer in wooden structures. *Effective penetration* gives an indication of the depth that moisture penetrates into a material under transient and cyclic conditions, while *effective resistance* gives an idea as to the amount of moisture transfer resistance the mean moisture content of a material encounters in transferring into and out of that material. These quantities have been shown to be equivalent, though different aspects of the same thing. Significantly, however, the effective penetration depth was found not to be dependent upon the surface resistance of the boundary layer or surface. The diffusion equation for the amplitude and phase of the main moisture content for a periodic driving potential was used in defining these concepts.

3.7.6 Effect of Moisture Content and Drying on Permeability

The effect of drying of fresh wood results in high capillary forces at the surface of the free-water. These forces may cause aspiration in pits of softwoods where impermeable tori are present, but in hardwoods that do not have pit tori, the permeability is unaffected in this manner. Permeability in waterlogged woods is likely to be increased by the factor of generalised pit membrane dissolution by bacteria, but decreased with ash content. In oak wood it will also tend to be affected by zonation, being highest in highly permeable outer layers and lowest in the central less permeable layers, explaining the greater general success of conservation treatment of highly degraded wood over less degraded oak artefacts. Zonation in wood produces non-Darcian behaviour of fluids (Siau, 1984). Some of this effect is inherent to the species itself, where the zonation is parallel in nature. Certain conservation treatments (such as the acetone-rosin treatment) involve a step to increase permeability, e.g. pre-soaking in HCl or disodium

EDTA. Solvent exchange drying and freeze drying where surface tension forces are significantly reduced, reduce the lowering of permeability induced by drying effects.

Waterlogged wood's permeability can be reduced if only partially saturated, either because of incomplete waterlogging or through partial drying after excavation. This is because high capillary pressures must be overcome to force air bubbles through minute openings. Hardwoods generally exhibit increasing longitudinal permeability with increased moisture content, perhaps due to increase in the fractional volume of the vessels.

Variations in permeability due to object size exist under certain conditions. The effect appears to be greater in specimens of lower permeability (Bramhall, 1991). Bramhall explained this by a model in which there is an exponential decrease in the effective area for conduction with increasing length due to a progressive closing off of parallel flow paths within the wood, expressed mathematically as,

$$\text{Effective conductive area} = Ae^{-bL}$$

where: A is the cross-sectional area, L is the length, b is the positive exponential coefficient obtained from the slope.

Equation 3.15 Influence of specimen length on permeability (Siau, 1984)

In certain hardwoods, permeability appears to increase sharply with length up to a certain length and then to level off. Bramhall attributed this to non-linear flow due to kinetic-energy losses at the entrance of the vessels. This effect could be expected to increase as the length to diameter ratio of the vessels decreases. Condition of capillary end surfaces would also hold significance, with smoother surfaces resulting in increased permeability.

3.7.7 Changes in Pore Structure Caused by Degradation of Wood

Certain of the changes to pore volume ratios have been made apparent already in preceding sections. Grattan (1987) has discussed the relation of level of deterioration in wood to changes in its density and permeability. From work published by Hoffmann (1982;1985) and deJong (1979) he draws a connection between water content and volume of cell wall substances as affected by deterioration. (Figure 2.14)

Wood with lower levels of remaining cellulose exhibits higher water content, explainable by the fact that as materials are removed (either chemically or by bio-organisms), there is a general increase in the internal volume of the cell wall and therefore a corresponding increase in the FSP of the wood. Grattan (1987) points out, however, that once the cell wall becomes severely eaten away, internal volumes may begin to decrease again, with a corresponding fall in FSP.

One of the classification schemes created to aid the treatment of waterlogged wood by impregnants makes use of permeability. It groups wood according to the percentage of sound wood versus degraded wood (Christensen 1970; Jagels 1982)

The condition of cell wall pits is a controlling factor in wood permeability, since they are responsible for control of liquid flow. Pits represent the major limiting factor in fluid flow through wood cells. The majority of decay fungi penetrate wood through perforation of its pits, though some few do directly penetrate the wood cell wall. Damage or removal of the pit membrane makes wood markedly more receptive to movement of water. This will increase its adsorption and desorption of water in comparison to sound wood (Zabel and Morrell, 1992). The process of pit damage or removal by bacterial chemical action in waterlogged or saturated wood is relatively slow, though eventually it amounts to a substantial loss in volume. The effect of pit damage on permeability in wood is responsible for severe drying stresses, increased hygroscopicity, increased effectiveness of bulking treatments and preservatives, and decreased effectiveness of adhesives. Increased permeability also leads to increased chemical and biological attack. Wood permeability is not always so easily related to wood degradation level, since sometimes in very degraded wood the pits have been fully aspirated for one reason or another, thereby leaving the cells impermeable. Inherent or imposed physical aspects of a wood can also cause misleading trends. The formation of tyloses in oak heartwood can render it almost completely impermeable. The internal deposition of iron tannates, iron salts or calcium salts (especially common to marine waterlogged wood) can yield the same effect. Of course, the physical changes induced with hygroscopic swelling are responsible, in themselves, for a proportion of the increase to second order space or transient capillaries and thus to permeability.

Flournoy *et al.* (1991) used a refined version of the solute exclusion technique to measure the pore volume changes induced by wood decay from brown-rot fungi, which selectively depolymerise hemicellulose and cellulose, making this a close model for degraded waterlogged wood. They investigated the effect of holocellulose losses on maximum and median pore diameters, and the point at which the sudden increase in total cell wall volume and accessibility takes place. They found that at 35% weight loss, the cell wall volume had doubled, and that maximum pore size remained fairly constant throughout degradation while median pore diameter tended to increase. These changes were attributed to the creation of new openings in the cell wall and, to a lesser extent, to the erosion of pre-existing pores and to the swelling of the cell wall as a result of the fungal action. Blanchette *et al.* (1989) studied white rot wood for similar purposes. This rot decays both lignin and holocellulose selectively. Their results suggested, in contrast to Flournoy's, that lignin removal opens up the cell walls generally. Flournoy *et al.* 's work suggests that changes other than increases in accessible cell wall volume are responsible for brown rot degradation. Mechanical disruption must also be a significant factor.

Reverse gel filtration, a similar technique, was used by Rowland *et al.* (1984) to study cellulose treated by various chemicals to make it more accessible to dyes (NaOH and ammonia). The substantial swelling caused by the NaOH and ammonia increased its accessibility to water. Stone and Scallan (1963) used the nitrogen adsorption technique to study the effects of component removal on the porosity and pore size distribution of wood. Their work concentrated around sulphite and kraft pulping, used to remove lignin and hemicellulose from wood. Both processes were found to swell the fibres and increase the number of pores, with a median size in the 20-40Å range, leading to shrinkage on drying. Such pores produced by component dissolution make up the slit-like spaces between adjacent lamellae, normally 35Å in width, and can lead to the splitting of cell walls into layers. Increases in the number of lamellae produces an increase in the number of pores and a higher total pore volume. Stone and Scallan (1963) found that the removal of either lignin or carbohydrate from wood fibres leaves small pores in the swollen cell wall. They also observed that, as material is removed from the cell wall, the porosity increases gradually until the swollen cell wall contains slightly more void than solid volume. When the pore volume was compared to the volume of material removed, it was found that the porosity varies with level of dissolution of components. At low levels of removal, the pore volume is approximately equal to the volume of the material removed; at medium levels, it exceeds the volume of material removed, because swelling of the cell wall occurs; at highest levels, swelling was found to decrease and the pore volume indicated a net contraction of the cell wall. A later study by Stone and Scallan (1968) indicated that later levels of degradation produced steady swelling. They suggest that that this swelling causes such a disruption of the structure of the cell wall that the fibres are substantially weakened.

Grethlein (1985) pre-treated hardwoods by mild acid hydrolysis followed by enzymatic hydrolysis and determined their resulting pore size distribution. He concluded that, since cellulose is a heterogeneous porous substrate, its rate of hydrolysis is governed by the number of glucosidic bond sites that are accessible to the enzyme. Pre-treatments or chemical deterioration generally increase the number of these sites. Woods with higher non-carbohydrate content, e.g., those with high extractives and lignin or ash, would present a lower pore volume to degradation. He points out that in pore volume distributions the pore sizes are in fact only nominal values and may not be spherical. He also shows that it is possible to calculate internal surface area from the pore volume distribution curve.

3.7.8 Retention and Wood Impregnation Treatments

Retention is a measure of the concentration of preservative or other liquid in wood. It may also be expressed as the fraction of voids filled by liquid, which requires the volume of retained liquid to be divided by the void volume of the wood. During the conservation process, water-soluble impregnation agents are brought into the cell lumen and cell wall by diffusion from an outer surrounding solution. Since their purpose is both to replace a proportion of the water in the wood void spaces to reduce capillary action effects on drying and to lay down a layer of non-volatile bulking material on the surfaces of these spaces to support the weakened material, the level to which conservation treatment chemicals

can penetrate this system of permanent and transient capillary space and be retained there is vital to the success of the treatment. A discussion of all the models in current circulation to describe and predict this is beyond the scope of the present study. However, Jensen (1997) presents an exhaustive and enlightening discussion of the subject.

3.8 Summary

This chapter has attempted to summarise the main issues in the field of wood-water relations and apply them to the questions which are of paramount concern to conservators of waterlogged archaeological wood. It is clear that this field of research is complex and by-and-large still looking for answers for questions relating to sound wood material. They are dogged with problems caused by the fact that chemists studying the behaviour of water itself have not yet finalised their picture of the molecule, never mind its inter-relations with biomolecules such as wood. For the archaeological wood scientist the picture is still more complex since the material he is dealing with is changed in important ways from the original wood substance about which a body of research already exists. The field of research about archaeological wood however, is still in its infancy. Work especially remains to be done in the sub-specialism of diffusion models for waterlogged archaeological wood. Jensen's work (1996) has made a beginning, but his conclusions which apply to the field of conservation have yet to be put into use. The next chapter will clarify the importance wood-water relations holds for improving waterlogged wood conservation.

4 Issues and Approaches in the Conservation of Waterlogged Wood

4.1 Introduction

In the middle of this century, when the treatment of waterlogged wood first began to receive systematic study as a result of a great surge in wetland and underwater site excavation, understanding of the nature of the wood itself was restricted. Treatment approaches tended to reflect trends in wood technology timber treatments and older craftsman recipes. Larger structures, composite objects, and uncommon wood species proved unpredictable under treatment. Over the past 20 years, understanding of the influence of the types and severity of deterioration on the outcome of conservation treatments of wooden objects has greatly improved. Reasons for success and failure of treatments are much more clearly understood. Analysis of archaeological woods and treatment materials have made comparison of treatments more meaningful. Thus new treatments are devised from a stronger base than previously. As well, passive treatments have been developed and appraised with greater sophistication, so that the choice to delay immediate interventive conservation is no longer impractical.

Interventive treatment still, however, remains the focus of the conservation of waterlogged archaeological wooden artefacts. From previous chapters we know that the appearance of these artefacts can be highly deceptive, disguising the fact that all or part of the artefact may now be mainly a lignin matrix held up by water, organic debris and silt. Waterlogged wood is almost invariably extremely weakened and unable to hold its own weight, easily damaged and marked by handling, and impossible to dry out to ambient conditions without considerable and irreversible shrinkage and drying stresses in the form of cracking and warping.

This chapter concentrates on the issues behind the interventive treatments that have been and are currently used to treat waterlogged archaeological wood. A final section deals with current research into new approaches. Though somewhat neglected up to the present time, the contribution that studies of wood sorption properties can make to archaeological wood will be seen to be critical.

4.2 Problems in the Treatment of Waterlogged Wood

4.2.1 General

In the majority of cases, archaeological waterlogged wood demands active interventive treatment. In the wet, saturated state it is inaccessible for study and display and it is vulnerable to accelerated damage and degradation. Wet storage methods lead to further deterioration and monitoring of them is difficult. Frozen storage brings its own problems (section 4.3). Moreover, both options are expensive over the long term. Thus, at the present time, active stabilisation is the conservator's prime concern.

Many difficulties with the treatment of waterlogged archaeological wood lie in the nature of the material itself—size, variability, and barriers to diffusion. Age of the artefact does not affect the success of treatment, as used to be believed (Bräker and Bill, 1979). The other major difficulties are lack of

information on conservation materials, and cost. As more information is made available and techniques for retrieving the necessary information from the artefact are made more accessible to conservators, the problems encountered with its treatment will decrease.

4.2.2 Variability

When excavated, waterlogged wood is in a variety of conditions of preservation. This great variability depends on burial conditions, species and quality of the wood and, to a smaller extent, the duration of its burial in the wet medium (McCawley 1977). Heavily deteriorated wood is not more difficult to treat than less deteriorated; indeed, the increased porosity and equalisation of deterioration throughout (which occurs towards the end of the deterioration process) aids in the even diffusion of conservation chemicals into the artefact. The zonal nature of deterioration in much waterlogged wood (particularly oak) produces chemical and physical differences between layers in the artefact that may be extreme. (Chapter 2). The inherent chemical and physical nature of each species of wood will show through in the areas that have resisted decomposition (Chapter 1). In oak wood this may mean that the core wood continues to contain a high level of extractives, and that a proportion of its vessels are blocked by tyloses. Anisotropism and zonation are likely to ensure that the drying stresses on this material are unpredictable (deJong 1979). The consequence of such a high level of variation is that it is likely that a combination treatment rather than any one single treatment will be required for stabilisation of the object, and this has a serious impact on cost.

4.2.3 Size

The size of the artefact decides both the time required to treat it and the logistical problems entailed in doing so. Diffusion of treatment chemicals is heavily complicated by the thickness of timbers (Jensen 1966). Drying time and the effectiveness of the drying method are likewise affected (Ambrose 1990). Whole ships and large structures may impose restrictions on the type of treatment possible to undertake, as requirements for plant and conservation chemicals either must be scaled up to cope or compromises must be made (Hoffmann 1996; Håfors 1990). The larger the object, the greater overall variability will exist within it. This makes assessment of suitable treatment very difficult.

4.2.4 Information on Chemical and Physical Condition

One of the main problems in the treatment of waterlogged archaeological wood is the difficulty in obtaining sufficient meaningful information about the piece of wood under treatment. Suitably quick, reliable and accessible techniques for assessing this do not yet exist; as a result, conservators in general "eyeball" the assemblage of artefacts, making guesses at density from their experience of other wooden artefacts, and assessing zonal proportions and overall condition from subjective physical resistance tests such as Christensen's pin test (Hoffmann 1982; Clark and Squirrell 1985; Jagels 1982) Thus conservators are often aiming their treatments at wood constituents that are no longer present in significant proportion. Not being able to assess or map the areas of differential permeability in an

object, the individual conservator does not feel he has the information needed to make minor adjustments to the treatment process throughout its duration, as would happen in other fields of conservation. It also means that behaviour after treatment is difficult to predict, and the identification of particular objects in need of special care provisions is difficult as well. Moreover, the causes of later damage such as warping, bleeding of bulking agents, joint failures, and ageing effects are hard to assess. The relation between chemistry, permeability, sorption properties, and hygroscopicity are paramount here. Larger objects such as ships present logistical barriers to the precise assessment of chemical and physical condition of their constituent parts. DeJong (1979), responsible for systematising Christensen's three-grade system for waterlogged wood, recognised that the field lacks the body of materials research to generate the information necessary or the means suitable for predicting the individual artefact's response to treatment. The emphasis of earlier conservation research has always been towards the development of a single stabilising treatment that can cope with any variation in the material without specific information to advise it. In recent years, more sophisticated physical resistance monitoring techniques such as the Pilodyn (Mouzouras *et al.* 1990) and the Sibbert drill (Panter and Spriggs 1997); and improvements to electrical resistance monitoring (Crawshaw, 1994; MacLeod and Richards, 1994) are showing promising signs of providing the specific information the conservator needs to tailor treatment to artefact.

4.2.5 Information on Interaction of Chemicals with Wood

The conservator's other main problem lies in the scarcity of information about treatment chemicals and processes used with waterlogged wood. An accurate view of the diffusion of various conservation chemicals through the changed structure of archaeological wood is needed, as well as more accurate information on the pattern and processes by which water leaves this wood. Differences in species, size and direction of cut, different levels of degradation, the presence of iron or calcium salts and tyloses—all may affect diffusion and permeability in wood. The model that governs the PEGCON program (Cook and Grattan 1991) for determining correct concentrations and treatment times for conservation chemicals in specific wooden artefacts was a first move towards solving such problems, but its foundations are flawed (Skinner 1997). Work continues on establishing the exact interaction of conservation materials such as polyethylene glycol (PEG) and sucrose with the wood cell wall (Young and Sims 1989; Schmitt and Noldt 1994). However, at present the practical conservation of waterlogged wood continues to be heavily based on an inaccurate picture of the materials and processes involved. The shape of the PEG molecule may be the wrong shape to replace water next to the cellulose of the cell wall (Brownstein 1982), but we continue to view this as being the process taking place during bulking. Small sizes of PEG molecule and sucrose measure high hygroscopicities as materials alone, yet in conjunction with wood they lower its overall hygroscopicity. A high proportion of the void space in waterlogged wood is too restricted for freezing to take place, yet the freeze-drying process is rarely altered to take account of this fact. There is a great need for more over-reaching models of the behaviour of waterlogged wood and treatment chemicals and processes, particularly in a form that is accessible to the working conservator and to which the input of measured observations will produce a

selection of treatment options and adjustments. Recent work by Ambrose (1990), Jensen *et al.* (1994), and Jensen (1996) are directed to this end.

4.2.6 Expense

Increasingly, cost is the deciding factor in the choice of treatment for waterlogged finds. Budgets for excavations and museums are increasingly restricted. In addition, accountability to the public means that longer-term conservation projects must make some provision for public accessibility (Hunter and Nayling 1997). The consequence is to reduce the conservator's ability to carry out even the simplest of diagnostic tests to guide treatments and to press him in the direction of bulk treatment schemes using simplified processes and shorter overall treatment time. At the same time, the demand for guarantee of success and increased information about material increases. Health and safety regulations have introduced new restrictions. It is unlikely that conservation research can provide a single solution to all of these requirements. It is doubtful that it should attempt to do so (Clark and Squirrel 1982). It is more likely that improvements directed towards predictability of success in treatment will engender greater respect for these objects, so that time and cost will less often be the mediating factors in conservation treatment.

4.3 Aims and Approaches in the Treatment of Waterlogged Wood

4.3.1 General

The aim of all interventive treatments for waterlogged wood is the effective drying of the material, because through this it will achieve stabilisation. In waterlogged wood of any level of deterioration, it is the water that is now largely supporting the structure of the wood. Successful treatment of this wood must therefore achieve the removal of the water without collapse of the structure, dimensional change of any sort, or stress damage. It must furthermore retain in the wood its natural texture, colour and surface detail, while increasing its strength and stabilising the wood against further change over the long term. Peterson (1990) prioritises the attributes that guide the conservator's choice of treatment. He ranks form, dimensions, and surface detail highest, colour and texture in the middle, and composition and function lowest. The visual characteristics of treated waterlogged wood have tended to be subjective, and taste in these has changed over time. Level of dimensional change deemed acceptable, though more readily quantifiable (section 4.3.7), is also a matter for argument. Christensen (1970) claimed that a considerable amount of swelling (up to 15%) took place in wood while in the waterlogged burial environment. For this reason shrinkages up to this level were considered acceptable, if not actually desirable. Christensen's conclusions were based on laboratory saturation tests, rather than knowledge of soil chemistry-wood interactions which make the matter much less clear cut (Chapter 2). The current direction of thought is that the conservator should aim to produce artefacts with dimensions as close as possible to those of the original waterlogged dimensions (Spriggs 1987; Barbour and Lency 1981). Antishrink Efficiency (ASE) is now used to gauge the level of dimensional stabilisation achieved during a treatment. It is a more meaningful measure of this stabilisation than previous measures of shrinkage,

since it bases itself on comparison with the shrinkage of the particular wood if allowed to air-dry without treatment. It is only meaningful when the relative humidity at which it was measured is also stated. Ibbs (1990) makes valid criticisms of the level of error commonly introduced to such measurements. Treatments that achieve an ASE of 75% or higher are currently considered acceptable (Morgos and Setsuo 1994).

Some treatments achieve all the aims discussed above; many achieve only one or two. To select an appropriate treatment for any artefact, it is important to know which treatment will achieve which of the aims.

4.3.2 Control of Collapse

Since collapse comes about from the tension produced in cell walls when the free water in wood retreats with evaporation, the replacement of this water with an intermediate replacement liquid (a liquid of lower surface tension) will reduce this effect, as will the avoidance of the liquid state by sublimation of the water. Moreover, the addition of a water-soluble, non-polar bulking agent will also effect this reduction by removing water from its close association with the cell wall. Another approach is to prevent collapse by filling the void space with an impregnant that provides some structural support against the contractile stresses as it solidifies on drying. A further approach still is to induce crosslinking between cell wall constituents and another chemical, removing water from its close association with the cell wall and providing three-dimensional support within the capillaries.

4.3.3 Control of Shrinkage

The removal of bound water from association with the cell wall substance causes shrinkage, a process controlled by desorptive diffusion (Chapter 3). A proportion of shrinkage results from the reduction in void volume caused by collapse, and a larger proportion from the drawing-together of fibrils within the cell wall. The introduction of a bulking agent will provide a non-volatile substance to resist contraction of this second-order space when the water evaporates.

4.3.4 Control of Warping

Warping comes about as a result of the interaction of anisotropism in the wood and the stresses brought to the wood as a result of collapse and shrinkage. Archaeological waterlogged wood has lost the strength to resist stress. Conservation treatments that reduce collapse and shrinkage and that return to the wood a proportion of its original strength to resist will prevent warping.

4.3.5 Increase in Strength

The original relation between strength and weight in wood is upset by the degradation and loss of cell wall constituents. This means that waterlogged wood can usually no longer bear its own weight. It is also extremely brittle, particularly its surfaces. Only crosslinking or reacting treatments will effect a true chemical increase in the wood's strength. Use of higher molecular weight, non-reacting polymers may be able to achieve this physically.

4.3.6 Long-Term Stabilisation

Once wood is dried, it is left vulnerable to changes in atmospheric humidity. Archaeological wood has been measured to exhibit steeply increased hygroscopicity. Nishiura and Imazu (1990) discuss the dimensional change of waterlogged wood in ambient humidity after treatment. Certain treatments are able to reduce this change by blocking a proportion of the hydroxyl sites on the remaining cell wall chemicals. Coatings have not been found to block moisture movements in this wood (Grattan 1987). Lower molecular weight fractions of treatment chemicals have a tendency to migrate at high humidities. Moisture trapped in core wood as a result of incomplete conservation will move if the ambient humidity is too low. There will be a need for post-treatment environmental control if long-term success of treatment is to be achieved.

4.4 Early Approaches

4.4.1 General

Until the discovery and conservation of the *Wasa* in Sweden in the early 1970s, the preservation of large waterlogged timbers had been carried out either by air-drying, application of surface coatings, or by impregnation in hot solutions of salts or wax mixtures-- treatments adopted from those for dry wood. The lack of understanding of the nature and properties of degraded structural timbers led to the choice of often-inappropriate treatments, and the inhomogeneity of the wood was not generally recognised or systematised. Tests carried out on small fragments of archaeological objects were scaled up for larger objects. If test results were negative, the method was generally abandoned, whereas positive results led to its universal application (Christensen 1970). Christensen proposed a three-class system for waterlogged wood that made important changes to the way the conservator viewed the material and approached its treatment. Surface coatings were abandoned as impractical, and some conditions of treatment (such as the boiling of wood) were less extreme.

The first of a number of important cross-laboratory comparative treatment appraisals appeared in 1979 (Bräker and Bill 1979). That assessment acknowledged differences in wood species and cut, but chose the age of the artefact to summarise condition. It compared a number of resin-impregnation treatments, freeze-drying, polyethylene glycol impregnation and *in situ* polymerisation.

This study was followed by Clarke and Squirrel's assessment (1982). Their criteria were broader but their conclusions were drawn from theoretical considerations rather than empirical data. They compared the same treatments as the earlier study. After the conclusion of the First International Comparative Wood Treatment Study, started in 1983, Grattan (1987; 1989) carried out a more comprehensive review of all treatment approaches. His conclusions profited from the more recent understanding of the chemistry of waterlogged wood and its chemical and physical interactions with treatments. He clarified the distinction between the impregnation approach, in which the intention is to fill all internal cavities, and the bulking approach, in which only the cell wall is treated. Impregnation treatments included: total replacement with high molecular weight polyethylene glycols (PEGs); the acetone-rosin treatment; alum; TEOS (Tetraethyl orthosilicate); PEG/tertiary butanol; *in situ* addition polymerisation and condensation polymerisation of monomers. Bulking treatments included all those where low molecular weight and dilute solutions are used, such as PEG 400/freeze-drying, sucrose treatments, and some *in situ* polymerised vinyl monomer treatments. In 1990 there was a similar comparative treatment project, but specifically aimed at freeze-drying treatments (Hoffmann and Fortuin 1990), followed by one in 1993 on sucrose treatments (Hoffmann *et al.* 1994).

Barbour (1990) discussed three approaches to drying waterlogged archaeological wood without pre-treatment with chemicals—controlled air-drying, solvent drying, freeze-drying—and then outlined three other categories where pre-treatment chemicals are involved—coatings to block surfaces, bulking treatments to reduce cell wall shrinkage, and lumen filling treatments to prevent collapse and improve mechanical properties. He distinguished two further categories under bulking agents, *reactive* and *non-reactive* treatments. *Non-reactive treatments* are those in which chemicals enter the molecular structure of the cell walls, replacing water and holding the walls in their swollen or semi-swollen state. They are attracted to the cell walls by hydrogen bonding but do not form covalent bonds with the cell wall substance. PEG, sugars, and salt treatments are examples. In these, the attraction between the bulking agent and the wood substance is weak and, at least in theory, reversible. These treatments tend to reduce the stiffness of the cell walls. In *reactive treatments*, a chemical is covalently bonded to the cell wall. Crosslinking of the cell wall material may also occur. Such treatments sometimes swell the wood and sometimes cause it to shrink. Examples include alkylene oxides and thermosetting resins. These treatments are essentially non-reversible but they usually improve the mechanical properties of the wall. Because of the former, the conservation community is cautious about using them except where no other method would be effective.

The following discussion of methods is organised to roughly follow the development of treatments for waterlogged wood and the understanding that led to their development.

4.4.2 Air-Drying and Controlled Air-Drying

Akin to the seasoning of green timber, in this approach the wood is allowed to dry naturally. Drying stresses and damage can be controlled by limiting the development of moisture gradients within the wood. This is achieved by allowing the wood to come into equilibrium with progressively lower and lower atmospheric relative humidities. Objects may be wrapped in polythene, buried in wet sand or clay, or placed in controlled humidity enclosures to carry out this process (Barbour 1990).

The success of controlled air-drying is very much dependent on the state of degradation of the surviving wood and fastenings—a good state of preservation is required if the wood is to withstand the drying pressures satisfactorily (Barbour 1983). In fact, only collapse is minimised by this treatment, so it is common for change of shape to occur in wood treated in this fashion. Even wood in good condition will require treatment of its surface layer to prevent lamination (Rosenqvist 1959). When carried out sufficiently gradually, the procedure will require a long time to complete because of the vast quantities of water involved. During this period, it may be necessary to make use of biocides to control deterioration. Its advantages are that the wood is fully accessible throughout the treatment, and that it is inexpensive, with no need for specialist equipment.

In general, this technique is now only used for very large structures (such as ships) whose bulk cannot be accommodated by immersion treatments, and only in conjunction with a bulking pre-treatment.

4.4.3 Surface Treatments

Some of the first treatments of waterlogged wood were oils used in furniture restoration (beeswax, carnauba wax, linseed oil, tung oil and other drying oils) that were tried out as surface treatments (Barbour 1990). Though they achieved some filling of the lumens near the surface, their inability to diffuse fully throughout the wood void space meant that only stabilisation of the outermost layer of wood took place. They were also unsuccessful in blocking moisture movements in the wood, or at lending the wood increased strength. As a result, the use of these oils quickly lapsed in favour of other more effective treatment systems. Surface coatings following impregnation treatments, however, continued for some time, using high molecular weight PEGs or an epoxy resin after drying (Bräker and Bill 1979; Christensen 1970).

4.4.4 Silicate-Based Treatments

4.4.4.1 Alum

The earliest method to gain general usage as a treatment for waterlogged wood was the alum method, in which objects were placed in a hot saturated solution of potassium aluminium sulphate ($KAl(SO_4)$) aiming to replace the water in the pores with a mass that would congeal, preventing shrinkage on drying. After drying, a linseed oil treatment was applied to the surface, followed sometimes by shellac. This treatment achieved both successful bulking and surface tension reduction, but no increase in

strength. At times, problems with penetration led to interior collapse. Although used for many years, this method is no longer employed, because it does not prevent shrinkage entirely and produces a heavy, brittle end result. A variation on this treatment was the addition of glycerol to the alum, meant to solve the problem of excess brittleness. Unfortunately, objects treated with it were heavily darkened and extremely hygroscopic. As well, adsorption of water under humid conditions led to the alum gaining water of crystallisation, expanding as it did so, and leading to fragmentation of the wood.

4.4.4.2 The Thessaloniki process

Treatment with sodium silicate, more recently known as the *Thessaloniki process* (Borgin 1978), was used at the British Museum earlier this century (Scott 1923). In this process, after an initial phase of partial drying, silicates are precipitated in the wood in the form of barium silicate by immersion of the wood in concentrated barium hydroxide. High occurrence of collapse in wood undergoing this treatment has occurred as a result of the alkalinity of sodium silicate (Grattan and Clarke 1987).

4.4.5 Early Use of Polyethylene Glycols

4.4.5.1 Properties of polyethylene glycols

Because polyethylene glycols (hereafter PEGs) have the longest continuous history of use in the treatment of waterlogged wood, some discussion of their properties is called for.

PEGs are more accurately termed polyethylene oxides. Their correct chemical name is polyoxy 1-2 ethanediyl. These molecules possess two terminal hydroxyl groups and many oxygen atoms in the polymer chain available for hydrogen bonding. The success of PEGs lies in the fact that they are completely soluble in water in all proportions and thus have the ability to totally replace water in the cell wall of wood. A bulking agent with limited solubility is unable to do this, since precipitation within the cell wall prevents further diffusion of the agent (Grattan and Clarke 1987). Moreover, because they are non-reactive the effect is fully or close-to-fully reversible, even after ageing (Cooke *et al.* 1994).

PEG is available in a variety of grades which differ in molecular weight. In fact, these grades usually contain a mixture of sizes of molecule, with only the predominant size stated (Skinner 1993). The size of PEG molecules in aqueous solution is difficult to predict with certainty, since they are not rigid chain polymers, but on the contrary flexible polymers capable of random coiling, with numerous folds and twists throughout the chain (Brownstein 1982). This twisting increases with increasing molecular weight.

PEG is used both as a bulking treatment and as an impregnant, largely depending on the molecular weight and concentration used. A variety of different methods is used in its application depending on the requirements of the object (e.g., tanking, spraying, surface application). It is capable of achieving successful protection against collapse and shrinkage, and may also impart a degree of increased strength to the wood. This latter point is contested; while Jover (1994) attested to the success of high molecular

weight PEGs imparting strength to charred Palaeolithic wood, the tests of Caple and Murray (1994) contradicted his results.

The mechanism by which PEG stabilises the wood on a macro- and microscopic scale is complex and not fully known. Finney and Jones (1993) used laser microprobe mass spectrometry to probe the cell structure, and confirmed that PEG has penetrated the cell walls of conserved waterlogged wood. However, the interaction of PEG with individual cell wall components is much more difficult to establish.

PEG diffusion is relatively slow, so treatments of large objects take a long time to complete—15-20 years. Impregnation treatments also leave the wood heavy and dark. PEGs exhibit excellent stability at low pH but are susceptible to thermal degradation, which is augmented in extremes of pH (Bilz 1997). PEG solutions can sustain algae and bacterial colonies and thus may require the addition of biocides to control. PEG is incompatible with virtually all adhesive systems, leaving doweling as the only option where re-assembly is required.

4.4.5.2 Total impregnation

The earliest treatments using PEG involved placing the wood in a heated solution of PEG 2000 or 4000, the concentration of which was gradually increased to saturation levels (Christensen 1970). The remaining water was then allowed to evaporate, leaving wood cell cavities full of the wax-like, solid PEG, which had enabled it to resist collapse during drying. It was fairly inexpensive, easy to apply, and safe and stable over time, even in environments of high or fluctuating humidity (Jensen 1996). But its drawbacks were the dark, waxy finish produced, and the unnatural heaviness and obliteration of surface detail caused by the excess wax on the surface. Much work was required to remove this excess wax, a problem that remains with all air-dry PEG treatments to this day. Where more serious problems arose was with penetration, because of the large size of the PEG molecules used (see Table 3.2). This was particularly the case with larger timbers, and osmotic collapse was common in those of good condition with solid heartwood remaining. In theory, there should normally have been enough of the smaller PEG molecules within the PEG 4000 mixture to penetrate the more restrictive spaces in the cell wall (Jensen, 1996). The fact that this was not the case galvanised Christensen into studying the relationship between deterioration level, residual density, water content and permeability. The knowledge he acquired, applied to choice of treatment process, led to amendments of the PEG treatment to improve diffusion and to take care of the important problem of shrinkage (which total impregnation is not able to do to any significant extent). Two possible options existed for preventing shrinkage: use of a better diffusing medium (lower surface tension) or use of a smaller molecule. Christensen adopted the first initially in his PEG/tertiary-butanol treatment (section 4.5.5.4) and discarded the second because of concern over the hygroscopicity of smaller PEG molecules when measured in isolation (section 4.5.3.5).

4.4.5.3 Spray treatments for large structures

Because of the long periods required for the treatment of larger timbers (such as ships) by immersion, spraying provides a good option; it allows for public access and monitoring of the wood during the long treatment period. For this treatment to succeed, all surfaces must be kept continually wet with the solution to prevent air getting in and blocking diffusion, and to prevent capillary tension collapse initiated by the compression of the fully swollen inner core by a dry surface shell (Stamm 1959). Ambient relative humidity during air-drying should be close to saturation to reduce the steepness of the moisture gradient, and thus surface checking. This is not usually possible for practical reasons, as well as because of the associated health risks, and accounts for much of the failure experienced in using this method.

The technique continues to be used today for large structures such as the Mary Rose, and structures left *in situ* such as the platform timbers at Flag Fen. A mixture of molecular weight of PEG was recently used with success by spray technique to bulk some Neolithic bark bowls before freeze-drying (Ward *et al.* 1996).

4.4.5.4 The use of smaller molecular weight PEGs

Continuing work on the *Wasa* shipwreck saw the first experimentation with smaller molecular weight PEGs to cope with problems of collapse and surface checking (Håfors,1990). First PEG 1500 and then PEG 600 were tried. The success of these tests sparked a spate of experiments with different and smaller PEG molecules, to deal with the differing permeabilities of woods of different types and states of preservation.

This work established that hygroscopicity was in fact substantially reduced when these lower molecular weight PEGs were tied, however loosely, into the wood substrate. Their physical combination with higher molecular weight PEGs also appeared to be a factor. New treatments with mixtures of high and low molecular weight PEGs were adopted into general practise. The smaller molecule was meant to diffuse into the smaller capillaries and second order space, preventing shrinkage, and the larger PEG molecule was included to fill or coat the walls of the larger pores against collapse. Young and Wainwright (1982) confirmed PEG 400's ability to penetrate the smaller void spaces of the cell wall matrix, using microscopy with cobalt thiocyanate staining techniques. Just how much of each should be used and in what increments was matter for a great deal of discussion. Initially the emphasis remained on air-drying as the second step, but later on other drying methods were experimented with. A modification of this treatment is the most commonly used treatment for archaeological waterlogged wood today.

4.4.5.5 Heating of PEG solutions

Heating of PEG solutions is necessary to effect the initial melting of solid grades of PEG (1500 and above) and to allow them to remain in solution at any concentration. Heating was also thought to be vital for the improvement of penetration throughout larger timbers and for the shortening of treatment times. It was furthermore felt to be an advantage where reshaping of objects was called for (Christensen 1970; Jespersen 1979). Moreover, heating helps control micro-organism growth in treatment tanks (Zabel and Morrell, 1992).

Heating of PEG solutions, however, causes a number of problems. At temperatures significantly above room temperature, e.g., the 60°C at which impregnation is often carried out, Goring (1963) discovered that softening of lignin and hemicellulose occurs. Heat unfortunately also encourages osmotic collapse if correct steps are not taken. More recently, Bilz *et al.* (1994) pointed out the problem of thermally-induced oxidative breakdown of polyethylene glycol solutions with heating. They found that dilute PEG solutions are less stable than concentrated ones, that iron salts contribute to this depolymerisation, and that closed tank treatments help prevent it. The degradation of PEG was also reviewed by Glastrup (1997), who found that it produced noxious compounds such as formic acid and formaldehyde. The use of antioxidant BHA (butylated hydroxyanisole) was found successful at stabilising PEG against oxidation (Bilz and Grattan 1997). The use of oxygen scavengers after treatment storage has also been recommended by Bilz *et al.* 1994).

4.4.6 Freeze-Drying

4.4.6.1 General

The freeze-drying technique depends on the sublimation of ice within the wood such that the liquid phase and the drying stresses associated with its loss are avoided. A range of techniques fall under the term *freeze-drying* (also referred to as *sublimation drying* or *lyophilization).* All that is required is a frozen object, saturated with water or another solvent, and an environment that has a water vapour pressure less than that of the vapour pressure of the ice in the object. This may be achieved by the use of vacuum or desiccants or by air circulation, or a combination of all three. Depending on the condition of the timber, pre-treatment with a wax or similar bulking material may be required to minimise any shrinkage or distortion that may occur during the drying process, but total impregnation is redundant.

The use of these techniques to remove water from waterlogged wood remains ideal in theory; in practice, however, certain difficulties are encountered. These difficulties reside in the intrinsic complexity and variability of wood (Chapter 1), to which are added the complications of its degradation (Chapter 2) and in the complexity of removing bound water from frozen solutions in a diverse range of media, where there has been a general lack of experimental or empirical data (Ambrose 1990). The fields of cryotechnology in food science and biomedical industries have now provided some of this data, e.g., primary freezing damage, water vapour transfer efficiency, heat transfer efficiency, overall drying rates, cell distortion, chemical degradation, loss of physical qualities, and post-drying storage requirements.

But work is needed to apply this to waterlogged wood in a way of practical use to conservators. The application of freeze-drying to archaeological materials is dominated by efforts to deal with damage arising in treatment and to scale up the process to accommodate large structures while at the same time reducing costs.

4.4.6.2 Freeze-drying without pre-treatment

Experimentation with freeze-drying of archaeological wood began as early as the mid-1950s (Rosenqvist 1959). Initially, the technique was used in isolation, its advantage held to lie in its simplicity and non-interventionist approach to the material. But because of the damage that resulted, it did not become widely adopted until much later (Ambrose 1970). The initial freezing stage produced cracking and shattering of the wood; the vacuum drying stage produced shrinkage; and the final acclimatisation stage produced warping and delamination. Earlier trials followed up the treatment with wax or epoxy resin coatings to protect the surface and make it appear more like that of a historic wooden object.

The freeze-drying process can take from days to years to complete, the limiting factors being the size of the object and the quantity of water in need of removal. Vacuum freeze-drying is the fastest of the techniques but its plant is relatively expensive both to buy and to run, and monitoring of the condition of the wood throughout the process has to be carried out by remote means.

The decision as to when to stop the process has often been a matter for discussion, because both overdrying and incomplete drying can be a problem if the process is not monitored properly. The acceptable rate for re-adsorption of moisture on completion of the drying process has not received sufficient attention. Freezing-down temperature (-20°C) is based on the phase diagram for water, but fails to take into account the high vapour pressures existing in wood's smaller capillaries. Concern has been raised about the hygroscopic state the wood is left in if the bulking step is excluded. Ambrose (1990) discards this concern, pointing out that the decreased total cellulose-lignin ratio in degraded wood is reflected in its diminished swelling response and hygroscopicity once it has dried. The change reflects both the poorer affinity of lignin for water and the increased random hydroxyl bonding in degraded cellulose.

Nevertheless, freeze-drying treatments can never be totally successful on their own, as they cannot prevent the shrinkage caused by removal of bulking water. Franks (1981) summarised the damage caused by low temperature and freezing on organic systems. There is a need, then, for some added material to protect the cell walls against the expansion of water as it freezes, and something to provide strength and protection to more degraded layers. In a recent paper appraising freeze-drying techniques for archaeological wood, Ambrose (1990) ascribes this lack of success to the need for more precise information on its sorption properties.

Many of the problems with this treatment are due to the differing behaviour of adsorbed water and free water on freezing. Ambrose (1990) sketches out the changes these go through during each of the steps in the freeze-drying process. Water expands 13% on freezing, incremented with each further degree.

This expansion is further aggravated by meeting the increased viscosity, surface tension, and shrinkage of adsorbed water as the freezing front advances into the wood. The ultimate level of damage to the object will be determined by porosity, internal specific surface area, and the structural coherence of the wood. It is possible to see why data of the sorption characteristics of a piece of wood about to undergo treatment could, with the right modelling program, yield the information needed to tailor freeze-drying process parameters such as rate of freezing-down, maximum freezing temperature, rate of sublimation drying, relative humidity, and end point.

Ambrose's recent work provides the framework for new understanding and modification of the freeze-drying process. His underlining of the significance of temperature gradient in producing drying stresses has clarified the necessity of reducing the cooling rate drastically from the earlier "shock freezing" approach (Nielsen 1985; Bräker and Bill 1979).

The initial approach to lessening the extent of damage caused by freeze-drying was to introduce a pre-treatment step involving PEG.

4.4.7 Solvent Exchange Impregnation Treatments

4.4.7.1 The organic solvent-drying treatment

This method was developed with the same aims as the freeze-drying method. Here, the water in the wood is gradually replaced by solvent exchange with a liquid of lower surface tension and higher volatility than water. This is followed by controlled evaporation of the solvent from the wood, where contractile drying stresses on the wood are reduced through minimisation of surface tension. Though with fresh wood and archaeological wood in excellent condition this technique reduces both collapse and a proportion of shrinkage, in most archaeological wood solvent-drying often achieves neither because of the weakness of the remaining wood structure. In addition, solvents such as alcohols and acetone have been observed to cause a small amount of shrinkage (Stamm 1964), decrease in strength, and some reduction in bending resistance (Zabel and Morrell 1992). This may be responsible for some of the change in shape experienced by objects that have undergone solvent drying.

The method has had more success when used in conjunction with impregnants and bulking agents. Solvent exchange of water for a carrier solvent is followed by exchange of this solvent for an impregnation agent, often a non-polar resin such as rosin (colophony), dammar resin, beeswax, styrenes or methyl methacrylates. These latter belong to the category of *in situ* polymerisation treatments that use either heat/catalyst or gamma radiation to react monomers whose ability to permeate wood structure greatly exceeds that of larger molecules. Condensation polymerisation treatments include those such as the melamine-formaldehyde and epoxy-based treatments. Vinyl addition polymerisation treatments includes those such as methyl methacrylate (Munnikendam 1967) and styrene-polyester (Bräker and Bill 1979). These non-polar resins act only as impregnants; since they do not interact with cell wall constituents, they are not able to control cell wall shrinkage (Barbour 1990). Solvent exchange treatments that incorporate polar agents such as the tertiary-butanol/PEG and cellosolve-petroleum/PEG,

are able to control cell wall shrinkage as well. Variations of the *in situ* polymerisation process now being developed use water-soluble monomers that work as both bulking and impregnation agents (Barbour 1990).

In general, solvent exchange treatments have had limited acceptance because of the expense, the health and safety risks associated with the use of organic solvents on a large scale, and the specialist plant and personnel sometimes required to carry them out. Catalyst-based *in situ* treatments suffer from premature polymerisation, making adjustment of the process difficult and leading to surface deposition of the polymer (Grattan and Clarke 1987). All of these treatments tend to be irreversible. When used on individual or smaller objects, however, diffusion rate and efficiencies are greatly increased over other treatments.

4.4.7.2 The tertiary-butanol/PEG treatment

The tertiary-butanol PEG treatment has been perhaps the most successful of the solvent exchange treatments.

Once Christensen had defined the problems of zonality for the treatment of waterlogged wood, he developed this method of treatment to deal with the problematic Type III wood. The introduction of tertiary butanol (*t*-butyl alcohol) to the process improved the penetration of PEG 4000 by using a non-polar carrying agent during the impregnation stage, thereby reducing shrinkage protection. It also solved the problems of collapse associated with the drying stage, more by its exceptionally low surface tension than by sublimation of the alcohol (Jensen 1996).

This treatment is often included with vacuum freeze-drying methods because of its use of vacuum and the low freezing point of tertiary-butanol to evaporate off the solvent carrier. Strictly speaking, however, this is not a freeze-drying process, because the free water content has been removed long before the *t*-butyl alcohol is removed under vacuum (Jensen,1996). It involves solvent exchange as a first step followed by solvent carrier impregnation and then sublimation produced through the exceptionally low surface tension of tertiary-butanol, rather than through pressure *per se*. This final step is carried out slightly below 25°C, the freezing point of t-butanol, and will work at normal air pressure as well.

The PEG/*t*-butanol method is recognised to be somewhat complicated and hazardous, but until the advent of the PEG/freeze-dry treatment these concerns were felt to be outweighed by its excellent results—lightweight, natural-looking objects with high ASE, and increased strength. Post-treatment surface applications of PEG 4000 counteracted the occasional problem with cracked and fragile surfaces. This method continued to be used into the 80s in Denmark and Japan, but has more recently been dropped due to the expense of the tertiary butanol, and the health risks and danger of use of large quantities of the chemical under vacuum conditions.

4.4.7.3 The Lyofix DML method

The Lyofix DML method was developed in Switzerland by Haas (Bräker and Bill 1979) and has been demonstrated to be an extremely reliable method that gives excellent results.
Lyofix DML, the replacement product for the original Arigal C treatment, is a triazine resin (etherified melamine-formaldehyde precondensate).

Use was made of this water-miscible condensation resin in the conservation of wood from ancient lake settlements in Switzerland. Hardened by heating in association with a catalyst, its advantages included the strength it imparted to objects, the natural appearance of the treated wood, the simplicity of the procedure and the short treatment time. Its main disadvantage is its irreversibility, and the hazards of using formaldehyde. Moreover, it did not prove suitable for large objects, as the chemistry of the process allows only restricted impregnation time. The cost of chemicals also restricts its use to smaller objects. Though cracking and checking is very uncommon, interior cavities have been found to open up in the wood after a time as a result of the treatment's very shallow penetration of the wood. Because the treatment must take place under conditions of very high pH (pH 8 and above) to prevent the premature precipitation of melamine formaldehyde, there may be problems with composite objects—cracking and discoloration have been noted (Bräker and Bill 1979) Most commonly, the treatment is followed by a surface treatment of wax or varnish to protect fragile surfaces and improve aesthetic appearance according to the tastes prevalent at the time.

It is effective for all wood types, the only difference being the time needed for the impregnation step. Charred wood and bark were also successfully treated with this method. End results prove not hygroscopic and the presence of formalin discourages micro-organisms. Occasionally a slight (up to 5%) increase in volume was noted, probably the result of the swelling effect of high pH.

4.4.7.4 The alcohol/ether/rosin treatment

Adopted from work by Christensen in the 1950s, this method was used for small delicate objects such as the Vindolanda writing tablets, and was in use for some years (Bräker and Bill 1979). It had been chosen at the time as the method most likely not to obscure the writing surface of the tablets. The process involved dewatering the object first in ethyl alcohol, followed by an alcohol-ether exchange and then impregnation with rosin under vacuum, often in combination with various other natural resins and beeswax. Drying was also carried out under vacuum. The low flashpoint of the solvents, in particular ether, made this method very hazardous. Pre-treatment with ammonia and hydrogen peroxide probably improved both penetration and the appearance of the wood.

The process takes slightly longer than the Lyofix method for impregnation, and a similar time for controlled evaporation of the solvents. Occasionally, surfaces have needed cleaning with dichloromethane after treatment to remove excess resin.

The success of the process is heavily dependent on the condition of the wood, with moderately deteriorated wood responding better than undeteriorated. Dense and zonal woods such as oak and yew tended to end up with stress cracking, for which they are given an additional treatment with PEG 4000. Composite objects proved a problem because of anisotropic shrinkage. Objects treated with the alcohol/ether/rosin treatment are notorious for their fragility, though their colour, texture, and surface detail are very good. The process is restricted to small objects and is irreversible.

4.4.7.5 The acetone-rosin treatment

This is the only one of the solvent exchange treatments to have remained in use till the present. This is partly because of the good results it produces and partly because of its suitability as a treatment for wood-metal composites and as a field lab treatment.

The method was developed specifically to treat impenetrable oak and other dense woods. It uses a solvent of low surface tension in solvent exchange with the water in wood, and then as carrying agent for the impregnant, rosin. Much of its success has been attributed to the initial pre-treatment with acid, which removes material in the wood that would otherwise block penetration of the bulking agent (e.g., iron salts, tyloses in oak, soil residues and wood breakdown products). It results in a very even penetration by the resin, sound core wood as well as outer deteriorated wood. As a result, it provides protection for the wood against collapse and shrinkage during drying, though little or no increase in strength. The final product tends to be a light-coloured, medium-weight object retaining good surface detail. It is non-hygroscopic and allows gluing. Though object dimensions remain stable over time, despite earlier claims the treatment is not reversible (Fox 1989; Cooke *et al.* 1994).

The acetone-rosin method tends to be less successful on open-structured woods such as willow and poplar. There have been complaints that it produces an over-bleached look and brittleness (Cooke *et al.* 1994). The method is also not very safe, as it involves heating the acetone-rosin solution. Obvious advantages of this method are that, without its acid pre-treatment, it does not put metal-wood composites at risk, and that it requires no special circumstances for drying. This simplicity has made it ideal for use in field labs.

This process has been used to the present time for wood-metal composites and for smaller objects (Fox 1989). It has been adapted to fit current health and safety regulations, and the acid pre-treatment has been dropped without apparent effect on success (Grattan and Clarke 1987).

4.5 Current Treatment Methods

PEG treatments dominate the conservation of waterlogged archaeological wood today, although the emphasis of these treatments has changed. PEG impregnation treatments remain in use where size of object or other logistical considerations make it practical, but PEG bulking treatments now underlie most research programmes in the development of improved conservation techniques for waterlogged wood. While increase in knowledge about the nature of archaeological wood has been largely

responsible for this change, the treatment's record for general reliability, versatility (range of application techniques and MW of the polymer), low cost and easy application have also been factors. Its slow treatment time and the cost implication of this are now of concern.

Recent research centres on improvements to diffusion factors and drying efficiency. Because of the slow movement in this area over the last 20 years (Barbour 1990), treatment with sugars has received renewed attention and a great deal of interest and experimentation. Treatments involving resins play a lesser role than they used to, largely because of their irreversibility. Monomer radiation polymerisation treatments involving water-soluble impregnants are under development where facilities allow, and continue to have an advantage over PEG treatments where wood-metal composites are involved. The addition of corrosion inhibitors to PEG solutions has been introduced. Research into making passive treatments more viable is just beginning to yield results.

4.5.1 The PEG Two-Step Process

While it was recognised early on that differing grades of PEG could be useful in overcoming the problems of penetration in woods with two or more zones of differing deterioration, it was not until the current decade that Hoffmann (1990) produced his *PEG two-step process*. Previous treatments had already recognised the ability of high molecular weight PEGs to control collapse by providing support for the cell walls, and the ability of low molecular weight PEGs to diffuse far into the wood structure and prevent shrinkage by bulking out the second order space. But these treatments used the two grades together as a mixture. Hoffmann's two-step process showed a fuller understanding of the causes of osmotic collapse. The smaller molecule was introduced first at low concentration, and then in increasing concentrations, until sufficient moisture exchange from the central undeteriorated areas had taken place and sufficient PEG 400 had diffused throughout the void system to provide initial dimensional stabilisation against shrinkage. Only after this had been achieved was the larger molecule added to complete the bulking of the more deteriorated layers, achieving support of voids and lumens in a more mechanical fashion and thereby reducing collapse and imparting a degree of increased strength.

Because of its high level of success, this method has become the standard method for the treatment of waterlogged wood of all sizes and types. Only the mode of application (spray, immersion, surface application) and the drying method vary, depending on logistical considerations. However, the process is neither sufficiently infallible nor predictable in its results. A great deal of work has therefore gone into deciding just what levels of each grade of PEG are needed for an object. This has involved research into the chemical and physical nature of waterlogged wood and the interaction of the PEG molecule with it.

By now it is accepted that low molecular weight PEGs lower overall hygroscopicity in archaeological wood—both below that of untreated wood and below the PEG itself. The blame for dark, wet-looking PEG-treated objects must therefore be related accurately to flaws in the drying process. This was established first in experiments by Rosenqvist (1975), whose adsorption isotherms showed lower

moisture adsorption below 60% RH compared with untreated oak. XRD work by the same author seemed to suggest an increase in total crystallinity. More recent work by Grattan (1982) and by Cook and Grattan (1991) further supported the first of Rosenqvist's observations. These results argue for a degree of hydrogen bonding between PEG and wood constituents.

Incorrectly estimating the final concentration of low molecular weight PEG can potentially produce hygroscopic objects, just as overestimating high molecular weight PEG will cause a surface residue to be left, obscuring surface detail. This new understanding has resulted in abandonment of total impregnation treatments in favour of partial impregnation, where the wood is treated with only just enough PEG to satisfy the surface sorption requirements of the sample. Any excess will exhibit the same hygroscopicity as PEG on its own. Indeed in this excess state, low molecular weight PEGs will exert surface tension effects in the void space and capillary surfaces similar to that of water itself (Ambrose 1990). In air-drying treatments where their use is both as bulking agent and as surface tension reducers, low molecular weight PEGs may be used at concentrations well above the sorption capacity of the dried wood (Hoffmann 1985).

Understanding the optimum concentration of low-molecular weight that will just satisfy the sorption sites or specific surface in waterlogged wood is the subject of much of current research into PEG treatments. The measurement of specific surface in swollen degraded wood is problematic because of the variability in wooden artefacts. Increased knowledge of the sorption behaviour of archaeological wood could contribute greatly, but is rarely available. Grattan has provided a mathematical model (PEGCON) for estimating the optimum proportions, concentrations, and increments for these two chemicals in the two-step treatment (Watson 1982). It is calculated in balance with the relative loss of dry cell matter in the wood to be treated, compared with that of sound wood of the same species. This model and program has come in for some criticism of late (Skinner 1994) because of the necessity to incorporate a "fudge-factor" in order to make up for generalisations in the model that yield suggested concentrations of much too high a value. Hoffmann has adapted PEGCON calculations to take into account the FSPs of degraded woods (Hoffmann and Blanchette 1997). Ambrose (1990) suggests that the use of quantitative computer imaging systems in conjunction with stained microscope sections would allow a better assessment of relative ratios of cell surface area to volume in sound versus degraded wood. He believes that it would be much more accurate in what it tells us than the simple weight loss ratios used in PEGCON. Recently, Jensen (1996) has released a new computer program with a mathematical model called DIFCON that incorporates data for diffusion rates of PEG with sorption data for various wood species, and models for estimating accurate internal volumes. This program holds a great deal of promise but has been little tested as yet.

4.5.2 Freeze-Drying with PEG

The initial approach to lessening the extent of damage caused by freeze-drying was to introduce a pre-treatment step involving PEG. Ambrose (1990) explains the dangers to archaeological wood of freezing where the composition of the aqueous solution in the cells has changed through loss of constituents. Weak hydrogen bonding between water and other polar molecules in the wood is very sensitive to changes in temperature and does not change at the freezing point of water. The presence in cells of cryoprotectors, (simple carbohydrates, extractives, mineral salts, etc.) has long been recognised to lower the freezing point of aqueous solutions and protect against freezing damage (Franks 1981). Methods to alleviate freezing damage have been various. Christensen introduced the PEG/tertiary butanol treatment initially to cope with the ice expansion problem. The combination of a bulking agent with freeze-drying was discussed as early as 1960 (Ambrose 1970; Rosenqvist 1959; Organ 1959), but a lack of confidence in the method and in low molecular weight PEGs slowed its general acceptance.

Once these concerns had been allayed, PEG 400 was chosen for use with freeze-drying because of its good diffusion properties, its low volatility (meaning that it would not be removed with the water on sublimation), and for its ability to displace surface-bound water on the cell wall and the close proximity of its freezing range to that of water, both of which gave it the ability to lessen expansion damage during freezing. Whether PEG 400 indeed displaces water next to cellulose is brought into question by Brownstein (1982) (section 4.4.4.1). Its slightly biocidic properties gave it advantages over sugars. Moreover, less bulking agent was required and it had a quicker diffusion time than total impregnation treatments.

The use of PEG 400 in conjunction with freeze-drying continued until the need for a bulking chemical in addition to the surface tension reducing material was recognized. Freeze-drying from mixtures of PEGs became formalised on adoption of Hoffmann's two step process as the standard pre-treatment for freeze-drying. Indeed, for any artefact of a size to fit in the conventional freeze-dryer, this is now the standard treatment for almost all waterlogged archaeological wood.

Freeze-drying with PEGs yields excellent aesthetic results, much better than those from air-drying with PEGs. This is thought to be because freeze-drying prevents PEG being drawn to the wood surface (Grattan and Clarke 1987). A portion of the light colour of freeze-dried objects may be due to its lightening effects on humic acids reported by Omar *et al.* (Painter 1995). Painter claims this is a purely physical phenomenon, resulting from the special reflective properties of the surfaces created by freeze-drying.

Freeze-drying equipment tends to be expensive, both to purchase and to run. Few apparatuses are available with the internal capacity to treat very large timbers, never mind whole ships. This has tended to limit the use of this most successful of treatments to smaller artefacts and to conservation laboratories sufficiently well-funded to be able to afford the equipment. Freeze-dryers are getting larger; at the present time, they can be found up to 10 meters in length and 2 meters in width. This is greatly increasing the size of timbers and objects able to be treated in this fashion. These larger freeze dryers,

however, suffer from problems in achieving sufficiently high working vacuums and of removing the high water vapour yield of the objects (Ambrose 1990).

Hoffmann and Fortuin (1990) reported on an evaluation of a study on freeze-drying of waterlogged wood. Bernard-Maugiron *et al.* (1990) have recently commented on necessary adjustments to the PEG freeze-drying method for larger pieces of waterlogged wood.

4.5.3 Treatments with Sugars

4.5.3.1 Sucrose treatment

For a number of years now, studies have been undertaken to determine the effect of aqueous solutions of sucrose on reducing shrinkage in waterlogged wood during drying. Recently, Morgos (1994) published a comprehensive bibliography of this work. Parrent (1985) however, was the first to report favourably on its success with archaeological wood. Isolated studies since then have demonstrated its beneficial effects on wood stabilisation (Morgos, 1987;1994). In 1994, Hoffmann *et al.* brought together the results of a systematic study of the effect of sucrose at an optimum concentration on a wide variety of wood samples (Hoffmann *et al.* 1994).

The appeal of sucrose as a treatment is its low cost, non-toxicity, biodegradability, and ease of application (Hoffmann *et al.* 1994). These characteristics make it especially promising as a solution to the problem of conserving very large waterlogged objects. Its accessibility for use in countries whose conservation treatment resources are restricted is an added asset, since sucrose is a natural product, available throughout the world.

Sucrose's physicochemical properties seem particularly suited to the conservation of wet archaeological wood. Sucrose molecules are a similar size to those of PEG 200 and 400, but are more linear in structure and have a higher affinity to cellulose, thus an improved ability to diffuse throughout wood (Hoffmann *et al.* 1994). Because of its easy penetration, treatment times are much shorter than for PEGs, a few weeks to a month (Hoffmann *et al.* 1994). Microscopy of treated samples has shown its presence throughout the wood structure (Schmitt and Noldt 1994). At ambient temperatures, its limit of solubility in water reaches concentration of up to 70% g/g of sucrose in the solution, so that impregnation can be carried out without any heating being required (Hoffmann *et al.* 1994).

The stabilised wood is hard and brittle, and even very degraded woods can be handled reasonably safely. On solidifying, the sugar forms an amorphous glassy state over the cell walls (Schmitt and Noldt 1994). This confers strength to the cell walls and, in addition, has a considerable effect in negating the hygroscopicity otherwise expected with a sugar treatment (Parrent and Morgos 1994). Hygroscopicity at medium relative humidities is negligible, though problems have been reported at 75-80% (Hoffmann *et al.* 1994; Dean 1996). Between impregnation and drying, sucrose-treated wood can be bent and reshaped as much as the quality of the wood will permit (Hoffmann 1994).

Sucrose treatment produces objects that are quite natural in colour, feel and surface appearance. Surfaces only rarely require cleaning of excess impregnant. It has proved to be reversible and is safe for use with metal-wood composites.

As a follow-up of the ELN-study "Sucrose," Hoffmann (1994) carried out more stringent tests on this treatment, after which he was more cautious in his support of it. He found some of the same problems occurred with sucrose treatments as with PEG 3350 treatments on heavily zonated wood, suggesting that diffusion was not universally improved by this method. There was however, less difference between different types of wood, making some simplification if adapted for bulk treatment. Residual shrinkage could be high in some cases. Some of this shrinkage occurred during the impregnation period, suggesting that the impregnation was carried out too fast, with the initial sucrose concentration too high. Hoffmann called for more research into where the sugar gets deposited within the ultrastructure of the cell wall.

Because sucrose makes an ideal host for micro-organisms, a biocide must be used. Quite apart from the health risks and deterioration associated with intense mould growth, microbial actions on sucrose solutions cause depolymerisation of the sucrose into short chain sugars that fail to harden on evaporation and form a syrup that keeps the wood damp and sticky after drying (Hoffmann *et al* 1994). Micro-organism growth also blocks the diffusion of the sugar, through CO_2 production. Pre-treatment against biological agents involving Gamma radiation (Pointing et al. 1994) might possibly solve this most severe problem.

The implications of these recommendations lead to the conclusion that sucrose is not attractive as a replacement for PEGs in the treatment of waterlogged wood. It is hazardous and time-consuming. Achieving even distribution of the sucrose in the wood has been found to take as long as conventional two-step PEG treatments. Good results from the air-drying step can take as long as 15 weeks (Hoffmann 1994). The treatment tends, in fact, to be very expensive because of the high amount of sugar and biocide required. Hoffman observed a very characteristic 'washboarding', common regardless of degree of degradation, and believes it will be found to be related to uneven distribution of sucrose throughout the wood. This led Hoffmann (1996) to reverse his recommendation.

4.5.3.2 Mixed sugar treatments

For some time, mixtures of sugars have also been under investigation as wood treatments. A recent appraisal and comparison of sucrose, mannitol and a sucrose-mannitol mixture for a variety of hardwoods showed some promising results (Morgos and Setsuo 1994). Because mannitol has smaller molecules than sucrose, it can be expected to exhibit very good diffusion characteristics. However it has lower water solubility than sucrose, and crystallises sooner. This is thought to aid the treatment process in mixed-solution treatment because the mannitol will crystallise as the wood begins drying, acting as a protection against collapse, while sucrose, which has a higher molecular weight and forms large strong crystals, will bulk the void system. The combination seems a promising equivalent to the two-step

treatment of multi-quality timbers, but with the advantage of being able to be done in one step, saving time and money. End results appear to be stable over time.

Impregnation takes approximately one week for small items, carried out in increments at high temperature. End concentrations for sucrose are still required to be high for a good result. A biocide is necessary. Mannitol has a tendency to leave a white deposit on the treated wood surface, very difficult to remove. However, when used as a mixture with sucrose, this premature precipitation does not take place.

4.5.4 Treatments for Wood-Metal Composite Objects

If waterlogged wood-metal composite objects can not be taken apart for separate treatment, a problem arises with the standard aqueous PEG treatment given to these objects to stabilise the wood component. PEG solutions are mildly acidic in nature (pH 4.5-7). This has been given as a reason for adopting sucrose treatments for these objects.

Various studies have been undertaken to measure the corrosion rates of various metals in aqueous PEG solutions (Cook *et al.* 1985; Gilberg *et al.* 1989; Selwin *et al.* 1993). Cook *et al.* (1985) also tested a number of corrosion inhibitors for use in treatment solutions. They tested resins similar in structure to PEG which also contained corrosion-inhibiting functional groups (organic amines containing aliphatics, PEGs, and PPG). Selwin *et al.* (1993) also tested PEG solutions with a number of different corrosion inhibitors aimed at individual metals; they found reduced corrosion rates in solutions containing corrosion inhibitors. Most work of this sort has been carried out on clean metal surfaces, and the authors envisage different results from metals with thick corrosion crusts that may prevent the inhibitor from reaching the metal surface. The effect of the inhibitor on the efficacy of the PEG solution as bulking agent was not discussed. The added cost of these chemicals can be relatively high.

Argyropoulos *et al.* (1999) published results of tests for Hostacor (a trethanolamine (TEA) salt of acylamido carboxylic acid) as a corrosion inhibitor for iron composite objects undergoing PEG treatment. They measured the corrosion potential over time for the new, more biodegradable Hostacor IT on polished archaeological wrought iron without corrosion products. The results revealed that both types of Hostacor spontaneously passivated the iron, regardless of the concentration or grade of PEG used. A mechanism for this corrosion inhibition was proposed.

4.5.5 Radiation-Cured Resins

The use of radiation-curing resins continues to be to studied (Trân *et al.* 1990) at those facilities where the technology is available. Though they have been successful in adding strength and stability to waterlogged wood, they continue to be non-reversible, making their general adoption by the conservation community unlikely at the present time. Concern continues with the use of organic solvents in association with archaeological artefacts whose surface residues may be wanted for analysis.

4.5.6 TEOS

The use of oxysilanes to precipitate silicates within the remaining structure of degraded wood has been applied to modern wood. The treatment has had some success in providing dimensional stability (Irwin and Wessen 1976), but results have not in general proved consistent with archaeological wood (Jespersen 1982). For this reason the method is not in common use (Grattan 1987; Barbour 1990).

Tetraethylorthosilicate, however, has proved successful with smaller archaeological objects and with very dense woods such as yew (Jensen *et al.* 1997). It works by depositing silica in wood cell walls by a reaction with the water contained there. Ethanol vapour is a by-product. This method has not been suggested for use with heavy timbers and it is non-reversible.

4.6 Present Trends in Conservation Research

4.6.1 The Cellosolve/Petroleum Method

Detail of the cellosolve/petroleum method was published recently (Jensen *et al.* 1994). Dewatering of the object in cellosolve (1-ethoxy-2-propanol) is followed by solvent exchange of the cellosolve with petroleum. Both processes take place under controlled boiling either in vacuum or at normal atmospheric pressure. This is followed by a PEG/petroleum impregnation and a final vacuum drying. The process takes from 4 to 60 days. Though superficially similar to the earlier alcohol-ether treatment, this method is not as hazardous and involves less solvent, as well as achieving more thorough diffusion. Cellosolve is, however, toxic. Since it is used in this treatment only to aid the penetration of petroleum into the cell wall, it could be replaced by some other surface-active agent that would diminish the surface tension of the water (Jensen *et al.* 1994). One of the advantages of this method is that it is less expensive than freeze-drying methods (Jensen 1996).

Jensen *et al.* (1994) do not feel that the method is a replacement for more traditional conservation methods such as freeze-drying, but rather a supplementary treatment for small, delicate, and heavily-degraded objects, for metal-wood composites, for objects that need a very light and natural appearance or for objects that need quick treatment. Preliminary tests have been promising.

4.6.2 Chemical Modification of Cell Wall Polymers

4.6.2.1 Selection of treatment agent by its sorption properties

Jensen (1996) has remarked on the fact that the most commonly-used water-soluble impregnation agents have a very low affinity for the cell wall compared to that of water. This results in a high selective sorption of water and a low concentration of solute in the cell wall. A higher sorption of the water-soluble agent could be obtained by properly designed methods for dehydration in organic solvents, such as the cellosolve petroleum method discussed previously. But if water is still going to be the main solvent in conservation, other agents of higher affinity must be found. Investigations of synthesised

phenols, benzoic acids, and amines and amides have shown highly selective adsorption and the ability to swell modern woods beyond the water-swollen volume (Rowell 1984). Such agents have not been investigated yet in the context of archaeological wood.

Jensen proposes the use of a water-soluble agent along with a solvent exchange treatment. He has had success with PEGs and glycerol on smaller objects of heavily-degraded hardwood. Jensen hopes that, though it may not be possible to design impregnation agents with higher affinity than water to polar sorption areas on cellulose, it should be possible to design water-soluble agents with the ability to penetrate and swell the areas of residual lignin.

4.6.2.2 Treatment based on residual chemical components

Ambrose (1990) also suggests treating the chemical wood components themselves, rather than the physical wood mass. Basic differences in the degradative pathways of cellulose, lignin, and their end products greatly affect the response of saturated wood to drying. Conservators have not generally attempted to treat the major holocellulose and lignin components as separate problems, or to devise chemical treatments according to their relative proportion in degraded wood. This disregard of chemical differences has been possible because the standard treatment based around water replacement and bulking of the wood mass has by-and-large been a success. More recent work aimed at defining the chemical properties of water-degraded wood for conservation purposes has been used to predict diffusion behaviour rather than directed attention towards the need to work with the residual lignin as well as depleted cellulose (Cook and Grattan 1985; Hoffmann 1985; Young and Wainwright 1982).

Rowell (1990) suggests a number of treatments with the potential to chemically restore the cell wall-matrix and cell wall polymers to a condition simulating their original state. He believes conservators should pursue the course that was begun with some of the earlier treatments for waterlogged wood —reacting the remaining cell wall polymers using simple reactive chemicals, crosslinking agents, or polymerisable systems. In general, because of lack of polarity and large molecular size, these treatments did not achieve penetration of the cell wall. Their main functions were encapsulating the remaining wood structure, strengthening it, and reducing surface tension effects by use of solvent replacement systems. Newer theoretical approaches suggest using what is left of the cell wall polymers as part of the conservation system. Strength could be achieved by putting the remaining cellulose fractions back together through chemical reaction, either by crosslinking or bond-graft co-polymerisation. Difunctional epoxides and isocyanates have been used to crosslink hydroxyls on cellulose, hemicellulose, and lignin (Ellis and Rowell 1984). However, the results were non-reversible. Graft co-polymerisation of chemicals reacted with hydroxyl groups into network polymers has been tried with glycidyl methacrylate (Subramanian 1984; Meyer 1984). Another chemical system that has been investigated is the reaction of wood with maleic anhydride and allyl glycidyl ether (Matsuda *et al.* 1988), followed by copolymerisation with nitrile, acrylates, styrene or other vinyl monomers. Bioactive monomers such as Tri-*n*-butyltin methacrylate (Subramanian 1984) have been tested for incorporation into monomer blends before *in situ* polymerisation, and pentachloro- and pentabromophenyl acrylate

and methacrylate (Rowell 1990b) have been co-polymerised to achieve the same effect. Unfortunately, none of these studies included experiments with archaeological wood.

Narayanan *et al.* (1993) carried out one of the few trials using archaeological wood. They discussed the results of studies on tryhydroxyhexane, polyacrylic acid, pentaerythritol, polysodium-4-styrene sulphate, protein, caboxylated polybutadienes agar and gelatine gels. However, only one of them, polyPET, compared favourably with PEG. This product (probably pentaerythrityl sulphate) left a white haze on the surface of wood stored at medium humidities (58%), solvation and reprecipitation cycles. It requires heat and its long-term stability is questionable, making it unlikely to be adopted by conservators.

Zirconium compounds aimed at stabilising lignin residues have recently been tested by Sutcliffe and Wood (1997). Used as co-monomers with methyl methacrylates, zirconium has been shown to aid treatment of waterlogged wood after radiation polymerisation.

4.6.3 Other PEGs

Dean *et al.* (1994) investigated the potential of Breox 50w PAGs (polyalkylene glycols) as a replacement for lower molecular weight bulking agents to stabilise waterlogged wood. They felt that it showed good results as a single grade treatment for slightly degraded oak, as well as in combination with PEG 4000 in the two-step process for wood of mixed grades. This chemical has a lower hygroscopicity than the lower molecular weights of PEG, as well as low biodegradability and excellent ASEs. Diffusion rates are faster and the product is fully reversible.

4.6.4 Alternative Methods of Freeze-Drying

4.6.4.1 General

Freeze-drying is perhaps the most successful technique applied to the conservation of waterlogged wood. But it has always remained out of reach as a conservation treatment for large objects such as whole ships and other structures that can not be dismantled. The scale of operation in vacuum freeze-dryers is fine for objects up to a few kilos but rapidly becomes problematic as the mass of the object increases. This difficulty is a function of the need for much more energy and increased plant size to operate the larger chambers. More importantly, increasing chamber capacity cannot yield a commensurate gain in drying capacity for the larger timbers. Because of the diminishing yield of water vapour as wooden objects increase in thickness, the heat transfer to the ice surface necessary for sublimation has to be carried out through an ever-thickening dried layer. Manipulation of conditions in the chamber can help overcome this to a certain extent, but those techniques that use heat to increase thermal gradient cause extremely desiccating conditions at the outer surface and may, in addition, cause migration of PEG and swelling of wood components (Ambrose 1990; Watson 1987).

For these reasons, alternatives to vacuum freeze-drying have been sought for application to larger wooden objects.

4.6.4.2 Non-vacuum freeze-drying

Various approaches to non-vacuum freeze-drying have been experimented with, some based on exchanges of desiccants within a freezer facility (Diesen and Storch 1992), some relying on air exchanges effected by powerful fan systems (Ambrose 1975). Large composite artefacts have been successfully freeze-dried at normal air pressure in engineered environmental enclosures and similar techniques have been used successfully on entire ships (Drocourt and Morel-Deledalle, 1985; Amoignon and Larrat 1985).

Non-vacuum freeze-drying is normally carried out in freezing cabinets equipped with fans for air circulation over the object and an ice trap for drying the moisture laden air that is removed. The dried air will then undergo re-heating to approximately -5°C before being re-circulated over the wood in a continuous cycle. Provided the air vapour pressure remains less than the saturation or ice point vapour pressure of the ice surface at -5 °C, sublimation will continue successfully. The presence of light-weight fractions in PEG 400 aids in lowering the freezing range of the solution and contributes to a reduction in the potential evaporation, thus slowing the process (Ambrose 1990). The transport of water vapour through the dried surface during atmospheric pressure freeze-drying is up to eight times slower than with conventional vacuum freeze-drying, and the temperature gradient between ice surface and outer dried surface is also very small. As a result, non-vacuum freeze-drying has the advantage of avoiding the extreme desiccation of vacuum methods. Vapour transport rates, rather than heat transfer, determine the time taken to complete the process. This factor, however, may be thought to be of less importance than the reduction in plant and running costs effected. Experiments conducted at Canadian Conservation Institute, comparing the two systems in terms of total costs, concluded that non-vacuum freeze-drying cost 10% that of vacuum freeze-drying (McCawley *et al.* 1982).

Problems with this technique centre around incomplete and insufficient air circulation and flow rates, and leakage of moist air into the system.

4.6.4.3 Natural environment freeze-drying

The potential for natural freeze-drying in outdoor enclosures in cold climates has been recognised for some time (Grattan and McCawley 1978). Researchers at the Canadian Conservation Institute experimented with open-air freeze-drying of dugout canoes, using dry, cold winter conditions in Canada. Grattan *et al.* (1980) experimented in five locations across Canada and had considerable success with relatively non-degraded wood. The main limitation of natural climate freeze-drying is the length of the cold, dry season. Drying rates for this technique have been determined to be a function of the square root of object mass over time ($M^1/_2/t$) (Grattan *et al.* 1980). Weather patterns in the northern hemisphere were not able to provide sufficiently long a period to complete the drying of very large timbers. It was possible in this case, however, to remove the remaining water in controlled microclimate chambers indoors (Bergeron 1987).

Grattan and McCawley (1980) claimed the advantage of this technique over that of conventional total impregnation treatments to lie with reduced treatment time. Because this freeze-drying process requires only partial bulking of the wood before drying, the entire treatment took one third the time of the conventional treatment for such large structures. Ambrose (1990) has calculated the comparative vapour pressure deficits for non-vacuum freeze-drying, natural freeze-drying in Canada, and Antarctic freeze-drying. His data indicate the Antarctic to show most promise for this drying technique. Air flow and length of drying season in this area are also more suited to freeze-drying (Ambrose, 1994). The costs of transport to this region would still appear to limit its practical application.

Though little work appears to have been carried out since Grattan's initial experiments and treatments, Lan (1995) reported success in conservation of a heavily-degraded boat by natural climate freeze-drying. No pre-treatment with bulking agent was used. The lack of success in some timbers was attributed to the shortness of the freeze-drying period for the denser and larger wood.

The advantages of both these forms of atmospheric pressure freeze-drying over total impregnation for larger structures are the good surface aesthetics resulting, the lower drying stress experienced as a result of lower thermal gradients, and the savings in chemicals, energy, and capital costs. Because the process is relatively slow, it permits more careful monitoring and adjustment to suit the individual object. Its disadvantages lie in administrative and transport logistics, and provision of suitable housing against winds and rain.

4.6.4.4 Supercritical drying

A new variant of freeze-drying has been proposed by Kaye and Cole-Hamilton (1994) which, like freeze-drying, effects the negation of the liquid/gas interface, but does not require pre-treatment for success. This technique was considered safe for wood-metal composites, and was reported to leave wood with good storage and display characteristics. It is effected by a rapid process of solvent exchange with methanol, and then an exchange of the methanol for CO_2 by the addition of dry ice. This, then, is converted into a supercritical fluid by raising the temperature to 40°C and applying vacuum. The drying stage is completed overnight. Minimal shrinkages (6-10%) were noted on test samples. Its main disadvantages are the amount of methanol required and the necessity for vacuum plant. This equipment is, however, much less expensive than the cost of a conventional freeze-drier and it is cheaper and quicker to run. No bulking agents are required.

More recent experiments on larger archaeological samples resulted in spontaneous fragmentation (Panter *pers comm* 1996).

4.6.5 Extraction of Metal Salts

Graham *et al.* (1976) documented the problems encountered when damp or wet wood comes into direct contact with metal—where water-soluble wood extracts such as formic and acetic acids produce localised acidity next to the metal surface. The effects of corrosion products adjacent to wood, in particular iron, were seen to induce catalysation of hemicellulose decomposition (Marian and Wissing 1960). More recently, MacLeod *et al.* (1990) discussed the interactions of iron corrosion products with waterlogged wood. MacLeod and Kenna (1991) outlined the effects of corrosion on the mechanical strength and chemical stability of wood structure. A mechanism for cellulose degradation by metal catalysed hydrolytic auto-oxidation was given, and rates of it were measured. The problem of precipitated corrosion products replacing water in the swollen wood matrix was also discussed, as well as the consequences of pore blockages. Though mineral precipitation results in a certain amount of dimensional stabilisation by its bulking effect on wood, treatment is interfered with as a result of their unequal distribution. Post-treatment changes in corrosion salts also cause damage to wood structure. MacLeod and Kenna (1990) discussed the deterioration of archaeological wood by pyrites. The solubilisation of metal corrosion products can also be a problem during treatment, as they are able to depolymerise PEG. MacLeod and Richards (1997), using FTIR and NMR, report on the impact of metal corrosion products on the degradation of waterlogged wood from shipwreck sites.

Most conservators agree that there is a need for the removal of corrosion products and other salts from objects before treatment. However, methods cannot be developed to achieve this effectively until we better understand the mechanism of their formation.

Cole-Hamilton *et al.* (1995) evaluated the usefulness of nuclear magnetic resonance imaging to probe iron levels in wood under conservation. MacLeod *et al.* (1994) compared extraction chemicals for use during treatments involving metal-wood composite objects. They found 2% ammonium citrate solutions in association with 5% PEG 400 at neutral pH to be the most effective. Both substances were found to participate in its removal. This was an improvement on more traditional alkaline solutions that are less effective and have been found to cause dissolution of hemicelluloses (Marian and Wissing 1960). The treatment left no residues.

4.6.6 Biological Inhibitors

Fungi and bacteria have been found to degrade PEGs and impede their penetration into wood, in addition to releasing hydrogen sulphide and mycotoxins (Dean *et al.* 1990). Effective control methods must be sensitive to the quantity and type of micro-organism present, the physical and chemical properties of the object, and the storage environment or conservation process.

Physical controls such as brushing, lowered temperature, and special filter systems for the water in circulation were compared by Jones *et al.* (1986). These methods were found to inhibit micro-organism growth only. Chemical controls in the form of biocides were reviewed by Dawson (1982), and found in general to be unsatisfactory over the long term. Biocides can interfere with PEG solutions, and new

health and safety regulations reduce the choice for use. They are toxic and very expensive to dispose of. Few have been found to remain effective over time and they interfere with ^{14}C dating. Gould (1988) tested low oxygen atmospheres with some success. Dawson *et al.* (1982) experimented with the use of ultraviolet, but found it unsuccessful as a result of low penetrating power. Jespersen (1985) tested biological controls such as water snails and perch and found them to be successful.

Pointing *et al.* (1994) carried out preliminary experiments with thermal pasteurisation and ionising gamma irradiation. Their tests were limited to smaller timbers, however, and concerns have been expressed as to their effects on wood durability (Scheffer, 1963). Butterfield (1987) demonstrated that gamma radiation produces accelerated ageing of cellulosic materials. Pointing *et al.* (1994) recently carried out further investigations to assess the suitability of gamma irradiation for sterilising wrapped, waterlogged archaeological timbers destined for long-term storage. No detectable radiation-induced changes in moisture content, cellulose stability, or strength were observed except at doses far higher than those necessary to achieve complete sterilisation of the wood. Gamma irradiation does not result in any residual radioactivity in wood. Again, relatively small timbers were tested.

Physicochemical control methods, such as Spriggs' (1996) silver/copper sacrificial electrodes, have been shown to work effectively over time. They produce no interference with PEG, and are inexpensive to use. This method has been used with some success *in situ* at Flag Fen. Bacteria are known to immobilise copper, and may eventually pose a problem (Mouzouras *et al.* 1990).

4.6.7 Storage Systems and in situ *Reburial*

Reductions in funding leave large quantities of archaeological wood untreated for many years, which produces a need for successful long-term storage methods. Reburial and extended storage methods have been under discussion for a considerable time (Dawson *et al.* 1982). A comparative European project on storage methods was recently reviewed by Saetterhaug (1990).

Three approaches are conventionally used in the long-term storage of waterlogged wood—wrapping, tanking, and freezer storage. Recently, reburial has been given some attention. Problems with wrapping come about as a result of the permeability of the polythene by air (Lucas, 1982). Drying of timbers occurs when this method is used for long periods. Pitman *et al.* (1993) have reported the vulnerability of wrapped timbers to attack by the wharf-borer, a wood-boring insect capable of puncturing the polyethylene wrapping materials currently in use for waterlogged timber storage. Tanking, or the storage of timbers under water-saturated conditions (*ponding*), is not always satisfactory because continuing exposure to oxygen, changing water chemistry, problems with micro-organisms, and erosion cause continuing deterioration in the wood under store over time. Freezing suffers from the problems discussed in a previous section (section 4.4.5) and may be impractical for larger timbers. The problems with the development of a successful reburial environment lies with achieving truly anoxic conditions and a suitable burial chemistry in a relatively short period of time (Mouzouras 1994).

Mouzouras *et al.* (1990) compared the deterioration of timbers under wet storage by wrapping, ponding, and reburial on the sea bed. Using the Pilodyn resistance measurement instrument, they established that there was not much difference in condition between those wrapped in polythene and those ponded, and not very much decay had occurred to either in the ten years since excavation. They felt that the success of polyethylene wrappings lay with the depletion of oxygen within, the pH unsuitable for micro-organisms, and the little or no exchange of water causing build up of toxic metabolites. They did not comment on the possible effects of drying. Wood buried in the sea bed suffered greatly from erosion, and from fungal, bacterial, and borer damage.

DeJong (1981); Nelson (1982); Stevens (1982); Tuck (1982); Jespersen (1985); Jones and Rule (1990) have all experimented with reburial, mostly without success. Caple (1994) discussed the problems of modelling the nature of anoxic burial environment in order to either to preserve or create such environments for reburial purposes. Accurate determination of chemical parameters within soil deposits was found to be difficult without the disturbance of soil equilibria significant to the study. A later paper (Caple *et al.* 1997) establishes the correspondence of low Eh environments with good preservation conditions for organic materials.

Coles (1994) recognised the need for reburial studies to go hand in hand with wetland preservation carried out specifically to improve *in situ* preservation of archaeological material. He discusses a number of ongoing projects in Europe. Brunning (1997) reports on interim hydrological analyses of the Somerset Levels Trackway.

4.6.8 Treatments for Fossilised Wood

Work is being carried out to extend treatments for waterlogged archaeological wood to charred and fossil woods. PEG 300 with air-drying was successfully used to treat a fossilised Miocene tree trunk that was almost entirely lignified (Hoffmann and Blanchette 1997). This bulking agent was chosen for its ability to penetrate the compressed cellular structure and because it would not crystallise in the cell walls and risk destroying extraordinarily well-preserved ultrastructural information there. TEM established the full reversibility of this treatment, allowing later analysis.

4.7 Summary

"The major problem is not that we do not have adequate methods for the conservation of waterlogged wood, it is in recognising the limitation of these methods with respect to the size of object that can be treated within the restrictions of the amount of time, money and facilities available."
(Clark and Squirrel 1982).

This statement continues to summarise accurately the state of waterlogged wood conservation today. Clark and Squirrel recognised that conservators of archaeological wood continue to hope for a single "standard accepted treatment" that will fulfil all treatment criteria and that they can follow without the

need to individually assess each object, achieving success with all types and conditions of archaeological wood. This attitude is a natural response to increasingly tight conservation budgets.

If the conservator is to be able to get the information he needs in order to tailor his treatments individually to suit the object, he needs to be provided with more meaningful, more easily accessible, and less time-consuming techniques with which to assess the condition of waterlogged objects. Sorption studies are at the centre of most issues in waterlogged wood treatment. Permeability, diffusion rates, drying behaviour, and internal surface calculation all depend on the sorption characteristics of the wood. This study will attempt to correlate this information with some easily accessible techniques in condition assessment.

5 Sorption Analysis

5.1 Introduction

Water sorption is at the centre of our understanding of the behaviour of degraded wood under treatment. The conservator is concerned with three aspects of the water-relations of such material:

1. how to dry wood as rapidly as possible, and without physical damage, to a stable equilibrium with the ambient environment;

2. how to introduce chemicals into the wood in such a way that they are evenly and fully distributed throughout its fibre system;

3. how to predict the behaviour of a piece of wood after treatment, that is, in terms of its reactions to cyclic and sudden changes in environmental conditions.

Sorption analysis is the most systematic route by which to search for answers. But sorption tests are notoriously difficult to carry out without levels of error that make the results of any numerical form of analysis (e.g., pore volumes, R/D ratios, FSP) by-and-large meaningless (Skaar 1988; Wadsö 1994).

The initial brief of this research was to design a simple sorption apparatus, accessible (in terms of materials) to most conservators, and able to produce data of good quality, either for artefact appraisal or for conservation research. In order to test the performance of this apparatus, a systematic set of samples were sent through a series of cycled stepwise sorption trials and their characteristic sorption isotherms were measured. To obtain more information about the chemical and physical characteristics of the sample set tested, a number of other standard tests and analyses were applied (Chapters 6 to 8) and comparative degradation levels established. Once it became apparent just how impractical sorption analysis is for everyday assessment, these other analyses were focussed towards finding some other simpler diagnostic test that would correlate with sorption figures and form an indirect route to such determinations.

This chapter describes the sampling strategy and investigative approach of this thesis work. It continues with a description of the design of the sorption apparatus and an appraisal of the results obtained from it. The appraisal includes assessments of fibre saturation point, level of hysteresis, void volume calculations, and comparisons with trends shown in archaeological woods reported in the literature. The chapter concludes with an appraisal of the usefulness of sorption measurements to archaeological wood studies and conservation.

5.2 General Investigative Approach and Sampling Strategy

The aim in choosing a sampling strategy for this research was to investigate the ability of the tests carried out to reveal important differences between artefacts, and also to reveal the lesser variation that exists within the single artefact. The latter is not a matter of sheer intellectual curiosity, rather to test whether one small sample taken from a representative section of the artefact is able to yield information that can be applied meaningfully to the whole. The archaeological conservator is rarely in a position to take multiple samples from a single artefact. Except in dealing with large structural timbers, the taking of a sample wafer of a size to meet sorption analysis specifications (Section 5.5.3.1) may compromise the integrity of the artefact. Preference must always lie with techniques that require samples of only milligram proportions.

5.2.1 Sample Material

The first phase of investigation centred on samples taken from a single artefact—a plank 700mm x 162mm x 25mm taken from the oak lining of a well in the *vicus* of the Roman fort at Roecliffe (WD93; F73; Plank 3.2), dated to the 1st century AD. This artefact is radially split, with the remains of a thick layer of sapwood along its outer edge. Neither end is original, though losses are of old date and show the characteristic heavier degradation in comparison to wood from the plank's central region. Species identification determined it to be *Quercus robur*.

An initial set of samples was taken by sectioning this wooden plank through its length, in three dimensions. Figure 5.1 shows the sample cuts.

Series '*A*' samples contrast wood from the exposed ends of the plank with wood from the centre of the plank.

Series '*B*' samples consist of very intimately associated samples from the centre of the plank, allowing repeatability of results to be tested.

Series '*C*' samples were taken at even sampling distances along the length of the plank, to test variation throughout the object.

Series '*D*' samples consist of transverse slices through the thickness of the centre of the object, for comparison with one another.

Series '*E*' samples consist of fresh modern oak (E1) and seasoned historical (Durham Cathedral door, 16th C.) dry oak (E2), incorporated for comparison..

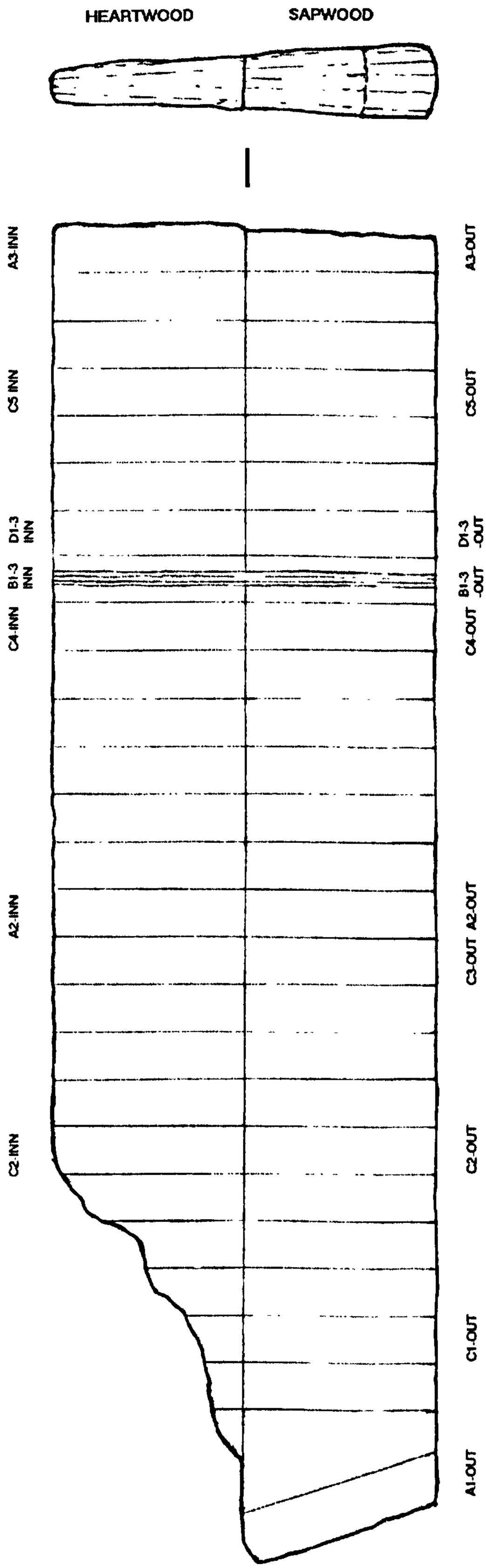


Figure 5.1 Schematic drawing of Roman plank showing sample cuts taken for various analyses.

The second phase of investigation centred around a group of seven oak artefacts from various sites in the U.K.—five rough-hewn roundwood stakes from Flag Fen (1000 BC); a portion of quarter-sawn structural timber from the drawbridge (Z-phase) at Wood Hall moated manor site (Mid-14th C.); and a roundwood stake upright from the Sweet Track (3800BC). These artefacts were chosen for their differing degrees of preservation, the Wood Hall wood at the top end and the Sweet Track wood at the lowest end. All came from freshwater environments, though of very contrasting soil chemistries (Caple *et al.* 1994). 'WH1' represents the Wood Hall timber; Series 'FF' represents the stakes from Flag Fen; and 'ST3' represents the stake from the Sweet Track. No sapwood was represented in this material, though outer layers were generally more degraded than the cores. Figure 5.2, below, provides diagrams of these artefacts in cross-section, with indications of the comparative level of degradation throughout the artefacts (Samples FF12, and FF9 have particularly hard inner cores, shown by boundary lines).

In samples taken for both phases, 'OUT' suffixes represent samples from the outer layers of the artefact, while 'INN' represents inner cuts. The material from these contrasting layers mirrors the problems met by the conservator in dealing with zonally-degraded oak.

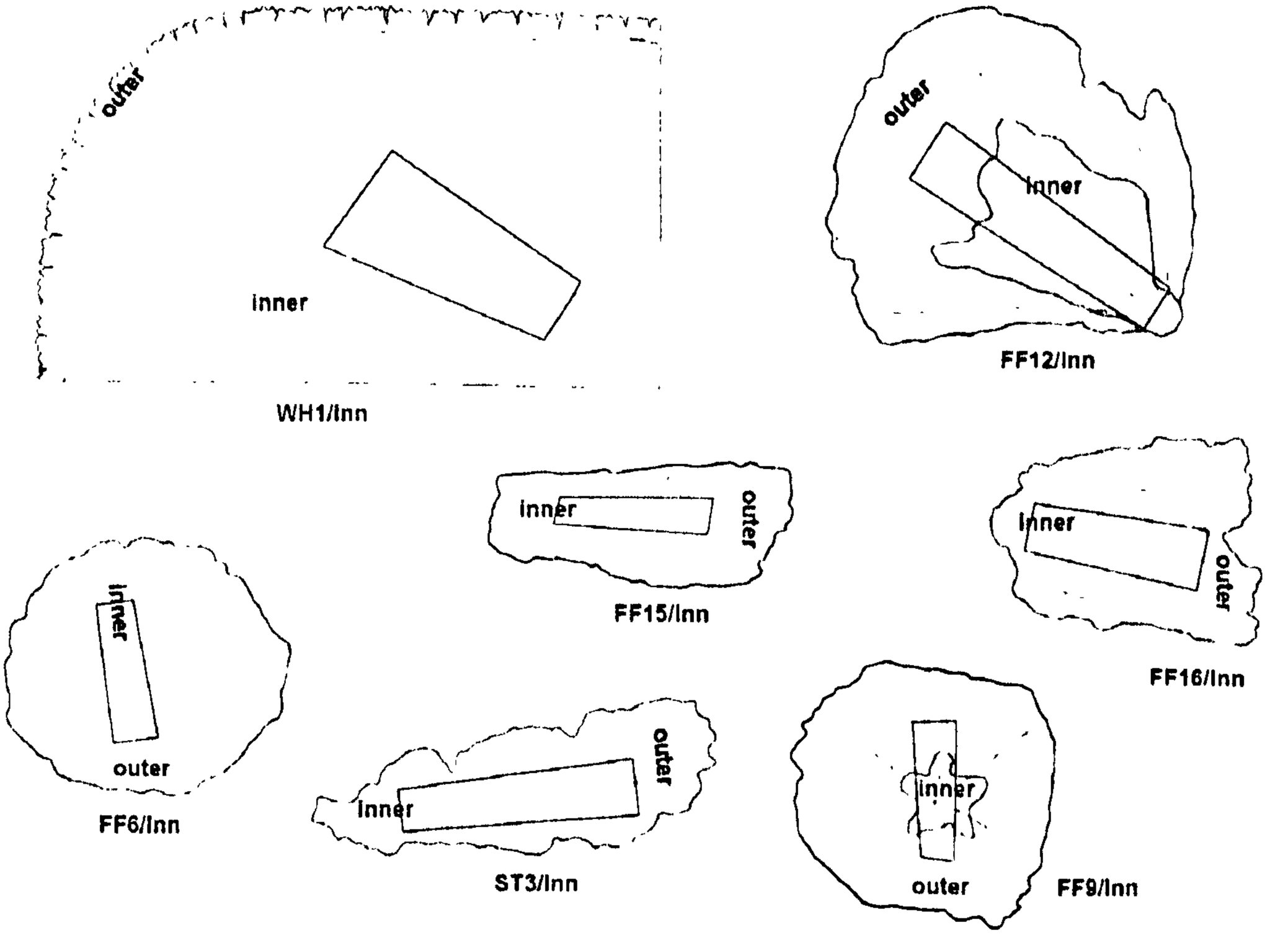


Figure 5.2 **Cross-sectional drawings of oak artefacts showing sampling and relative zonation. Relative sizes maintained**

5.2.2 Sub-sampling for Analysis

The sorption tests called for thin sample wafers of sufficient size (because of waterlogging) that their dry weights would still be accurately measurable using a three-decimal-place balance. The waterlogging factor decided the dimensions of all sub-samples taken for analysis. Figure 5.3 below is a schematic drawing of the method by which sub-samples were taken in order that relative homogeneity could be presumed for material set aside for the different analyses to be applied to each artefact.

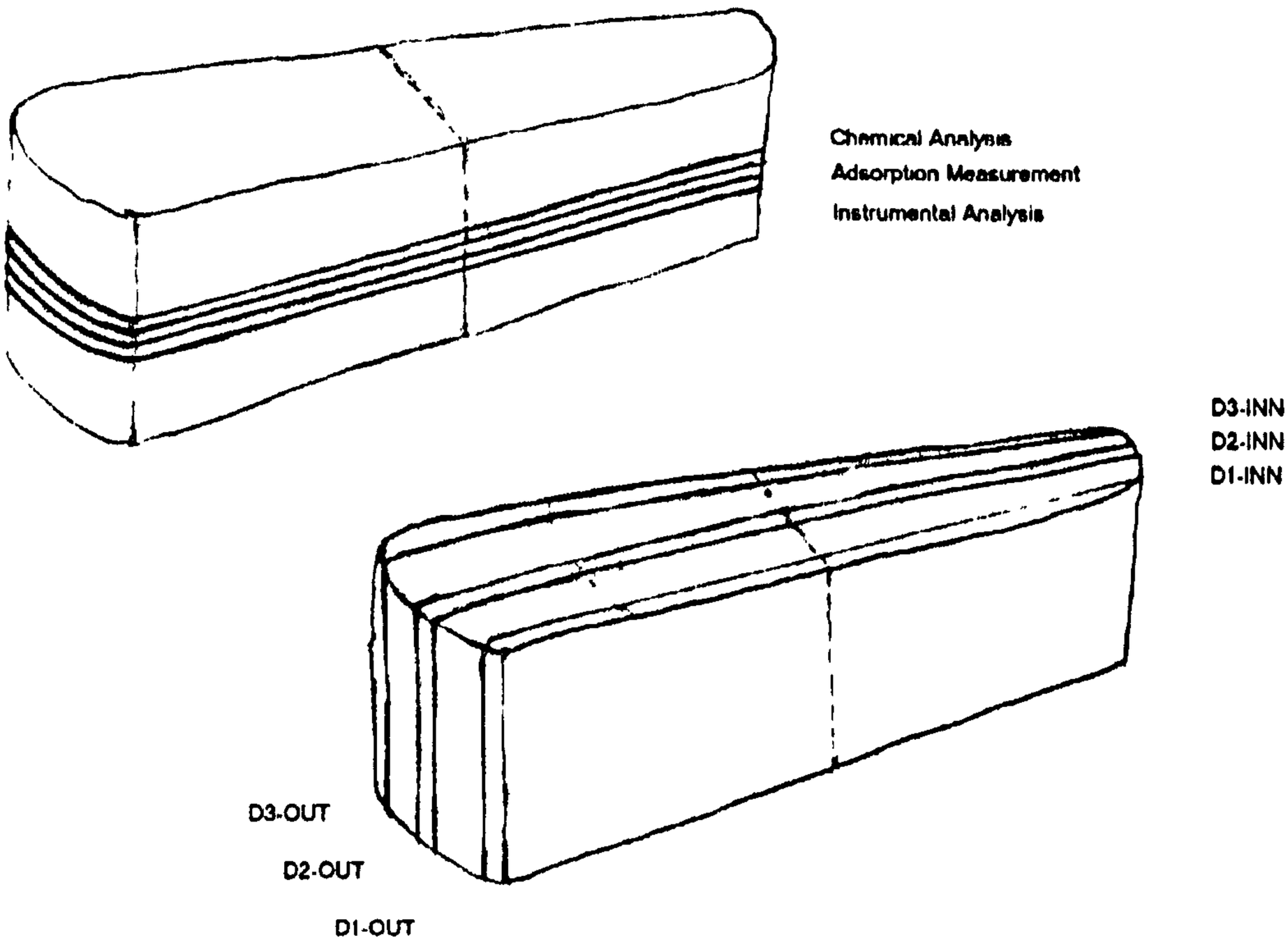


Figure 5.3 **Schematic drawing of sub-sampling of archaeological wood samples.**

5.2.3 Nature of Sample Material

The nature of degradation of archaeological waterlogged wood is very characteristic in some of its manifestations, discussed in detail in Chapter 2. In order to obtain a general visual picture of the conditions prevailing with the sample material under testing, scanning electron micrographs (SEM) were taken of one of the more degraded portions of the Roman plank (A3/Out).

The SEM photos shown on the following pages (Figure 5.4) illustrate features general to the conditions of degradation of most of the samples under study, if not of extent. Samples were prepared in the standard fashion, involving initial solvent dehydration and fixing in tetraethylorthosilicate (TEOS) (Dey *et al.* 1989); mounting in ABS solvent cement; and gold coating.

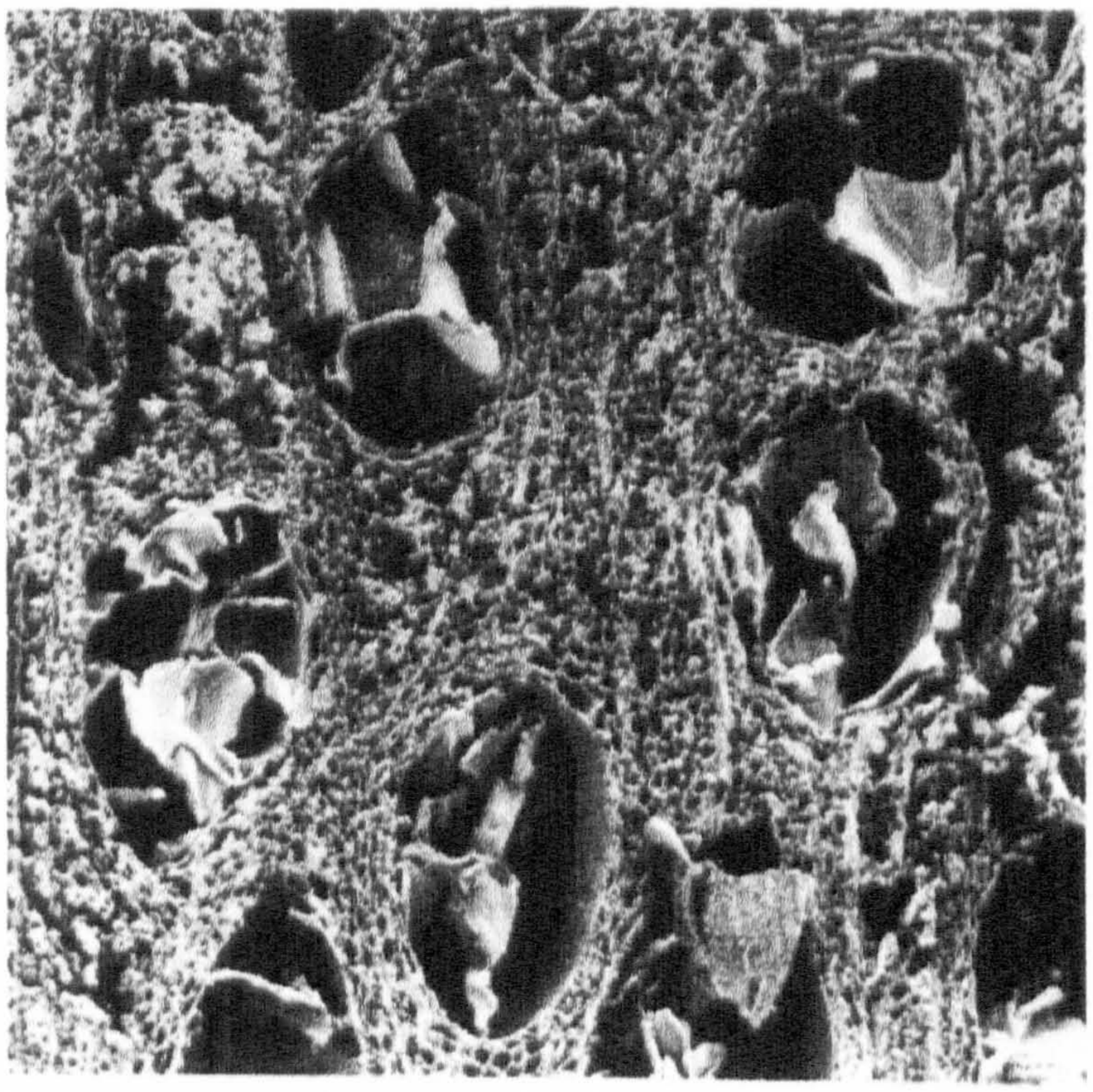


Figure 5.4a Typical appearance of degraded waterlogged oakwood (11% residual cellulose) in transverse section. Note tyloses. Slight collapse in vessel caused by sample preparation method. (X 120)

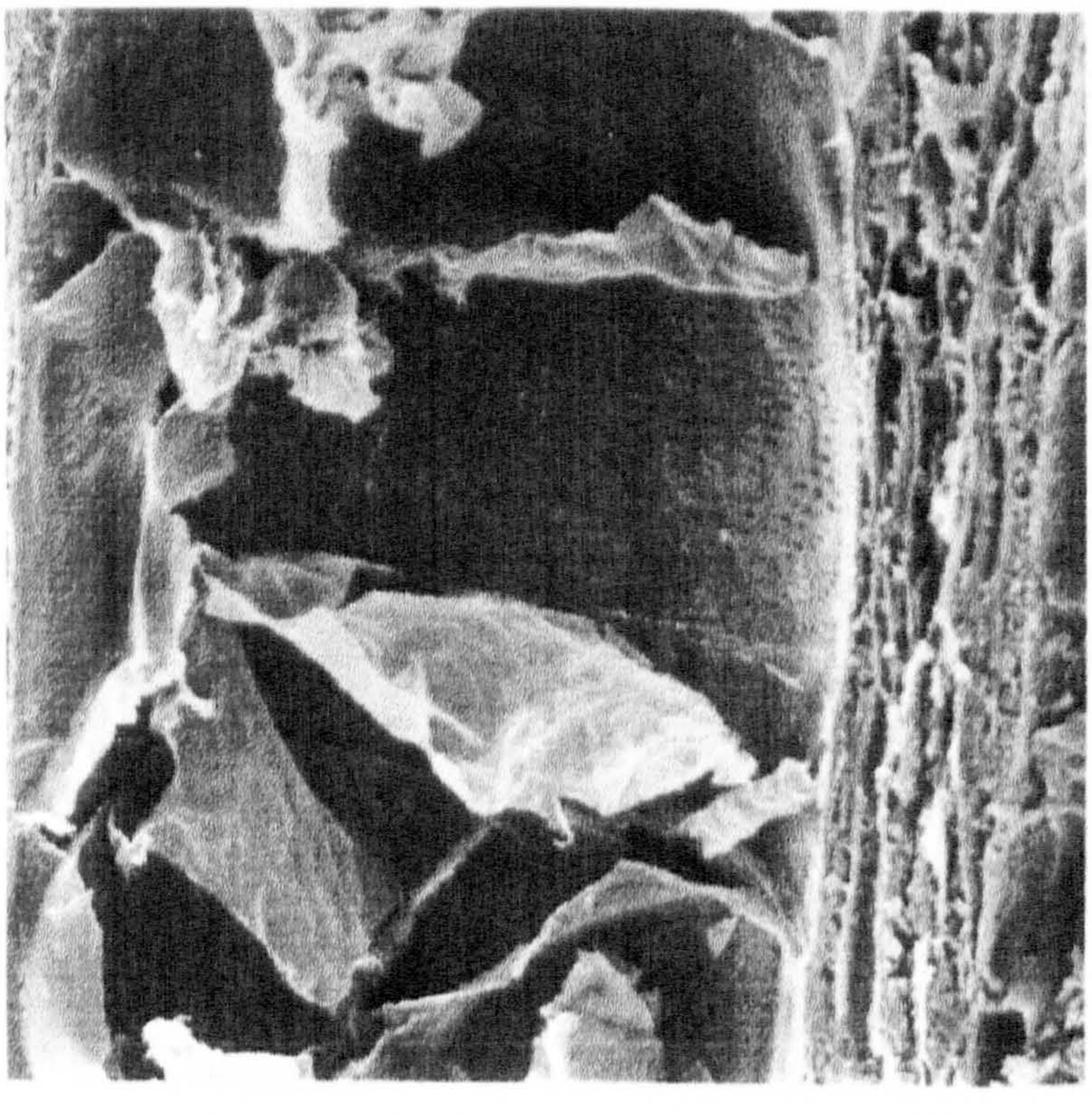


Figure 5.4b Close-up of tyloses in vessels. Signs of erosion of pit margins visible. (X 2500)

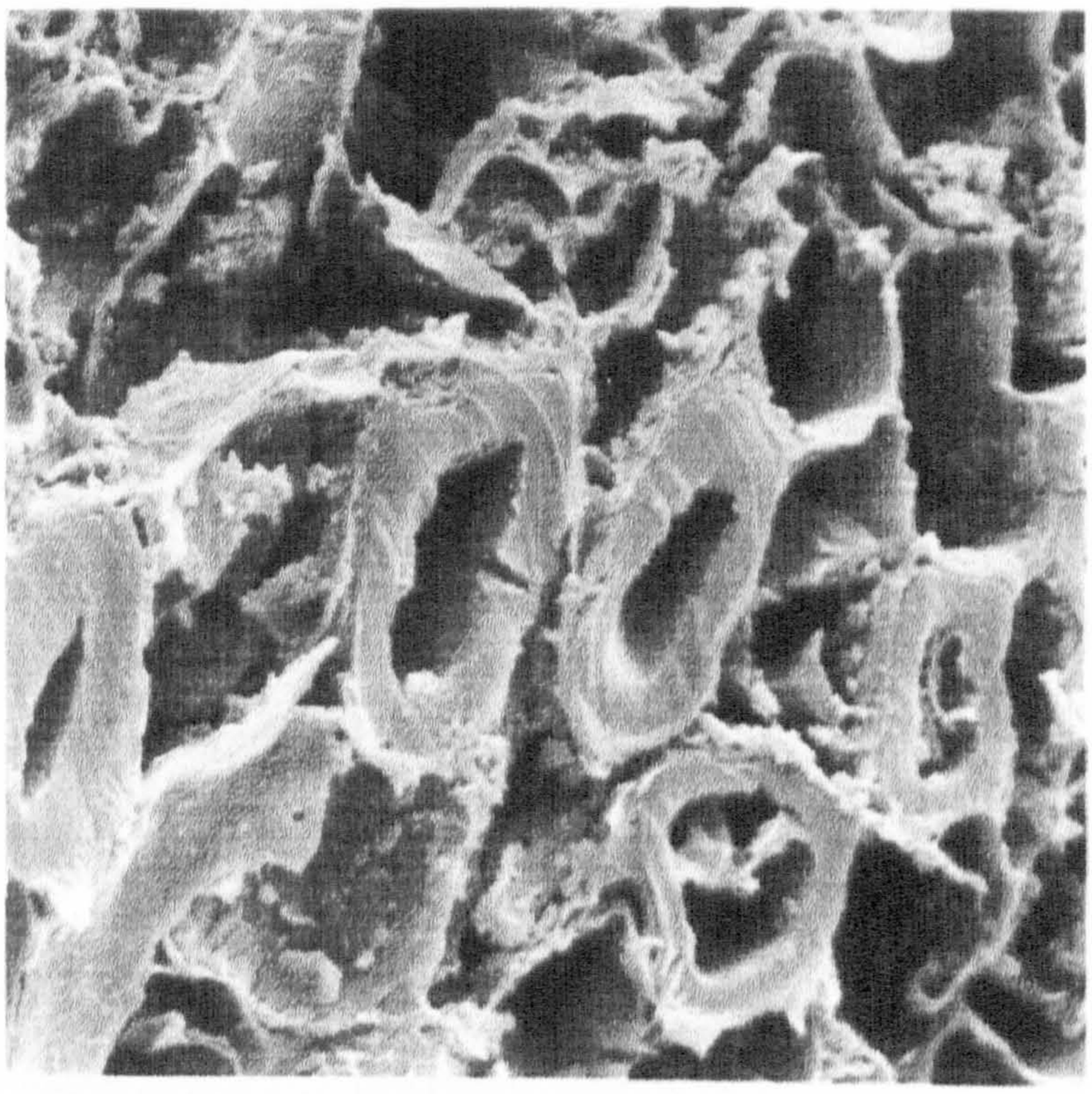


Figure 5.4c Combination of intact fibre cells and those with almost complete loss of secondary cell-wall layers. Detachment of S2 layer. (X 1500)

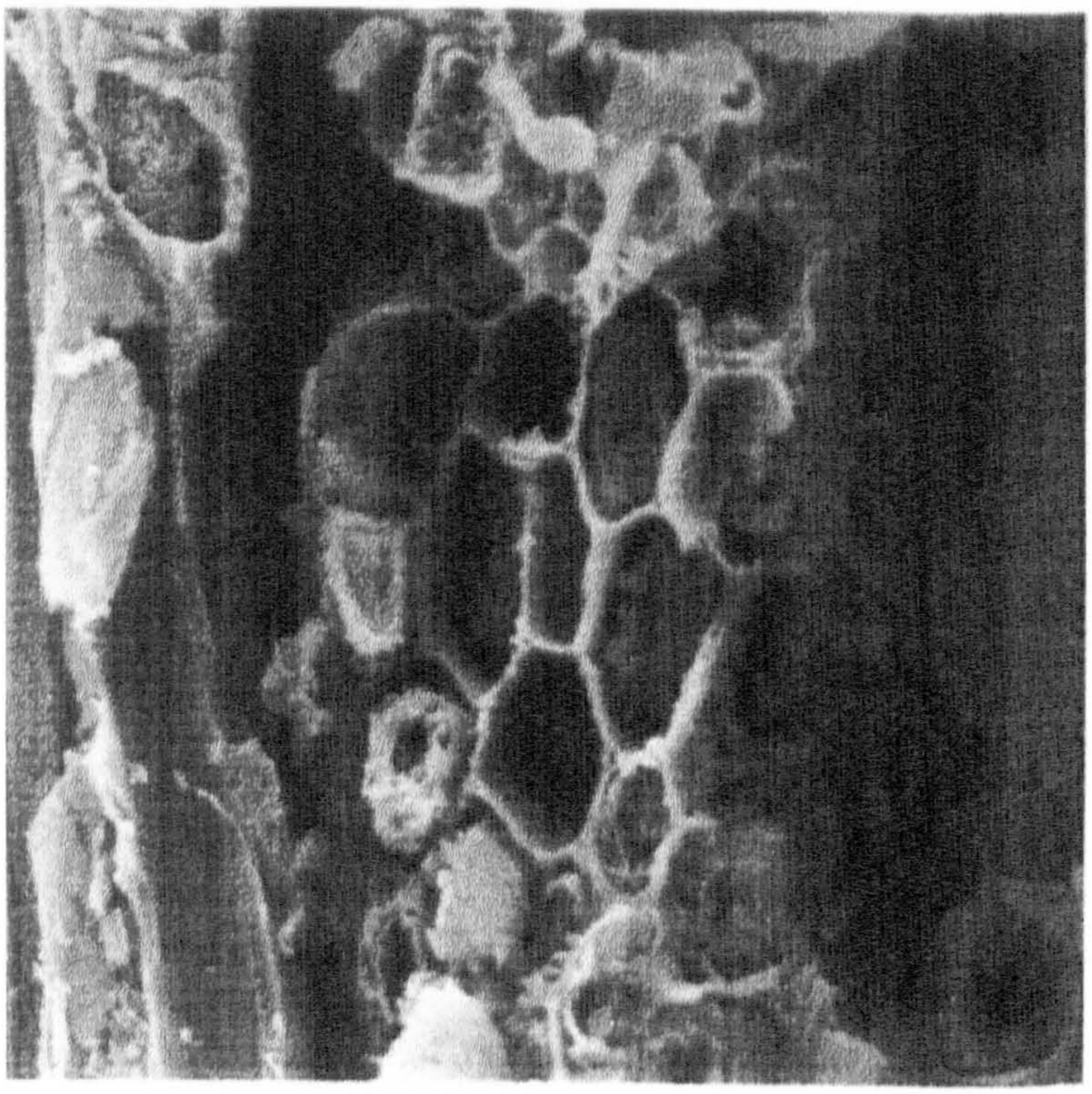


Figure 5.4d Thinning of ray cells visible in tangential section. (X 1300)

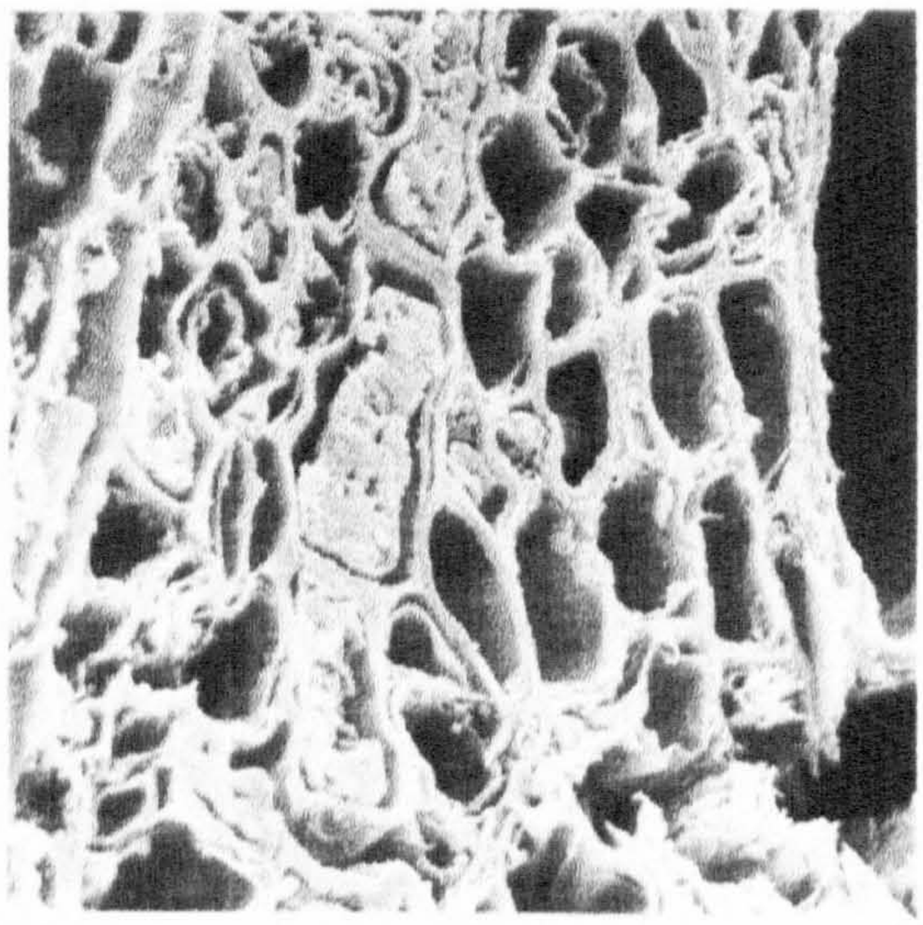


Figure 5.4e Parenchyma cells filled with amorphous mineral mass. Typical thinning to cells surrounding uniseriate rays. (X1000)

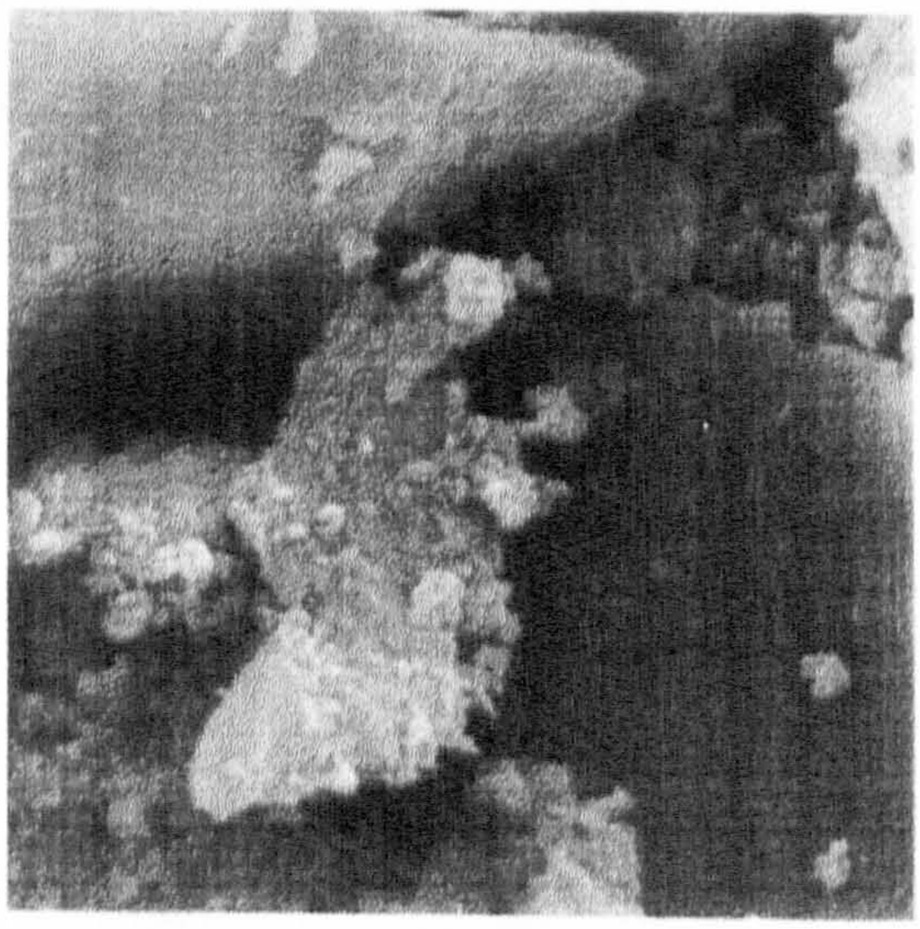


Figure 5.4f Close-up of contents of amorphous mineral mass filling parenchyma cells. (X 3000)

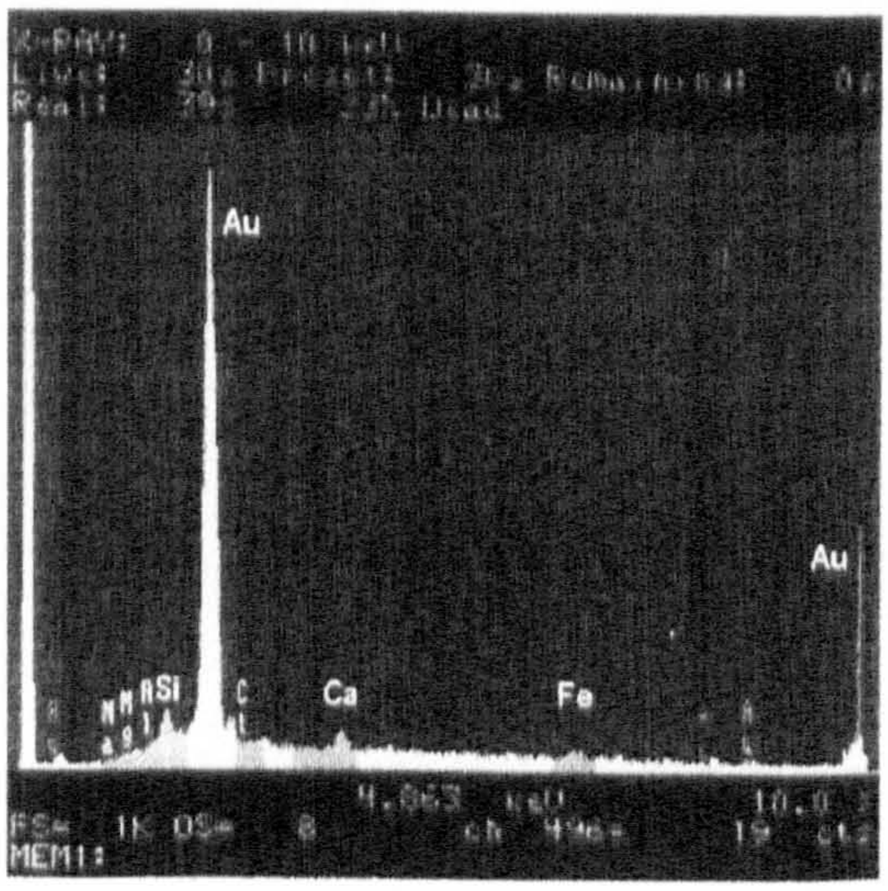


Figure 5.4g Results from EDXRF analysis of amorphous contents of parenchyma cells. Calcium/Iron organic complex.

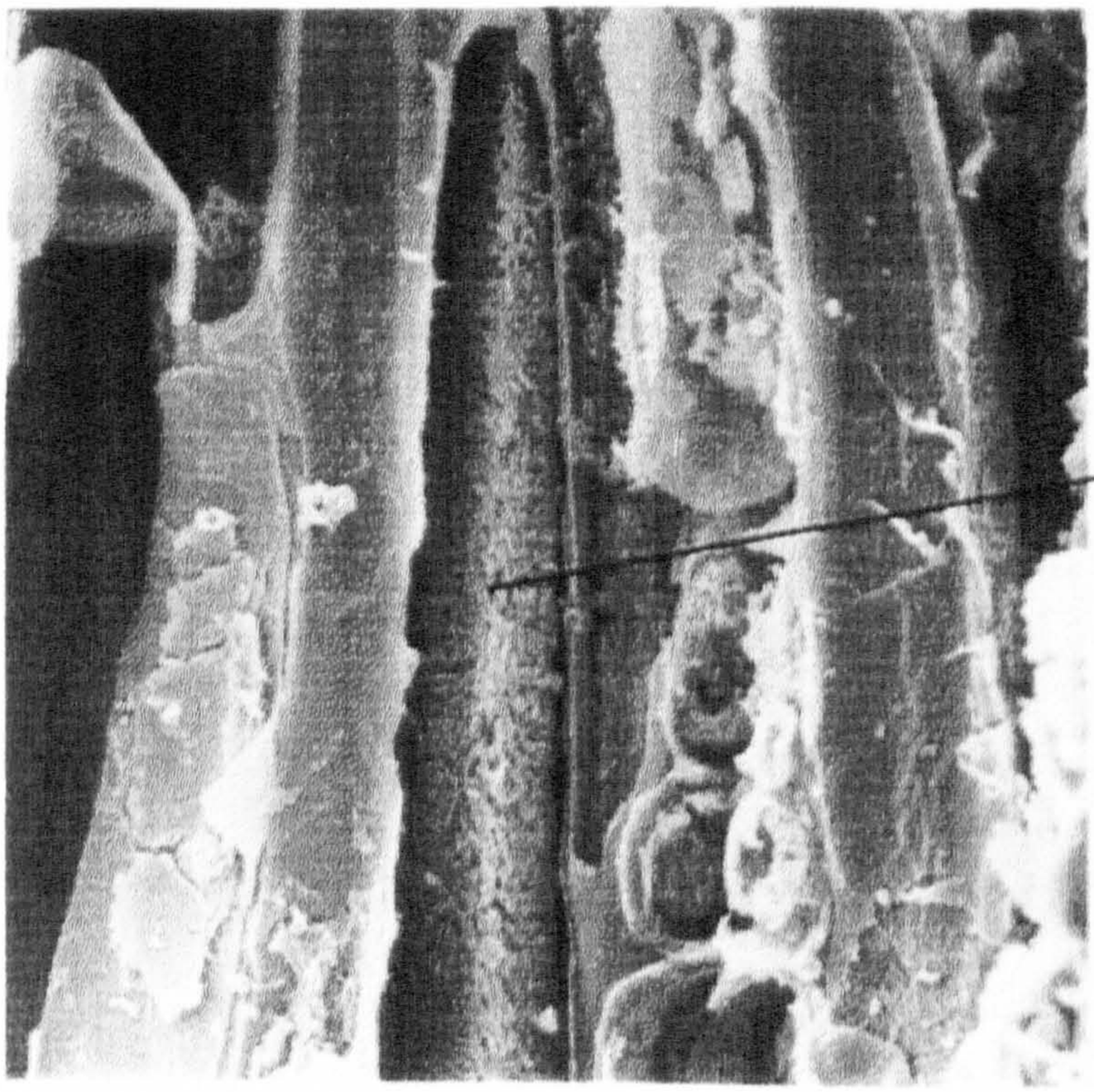


Figure 5.4h Longitudinal view of fibre cell showing detached S2 and S3 layers. (X 1700)

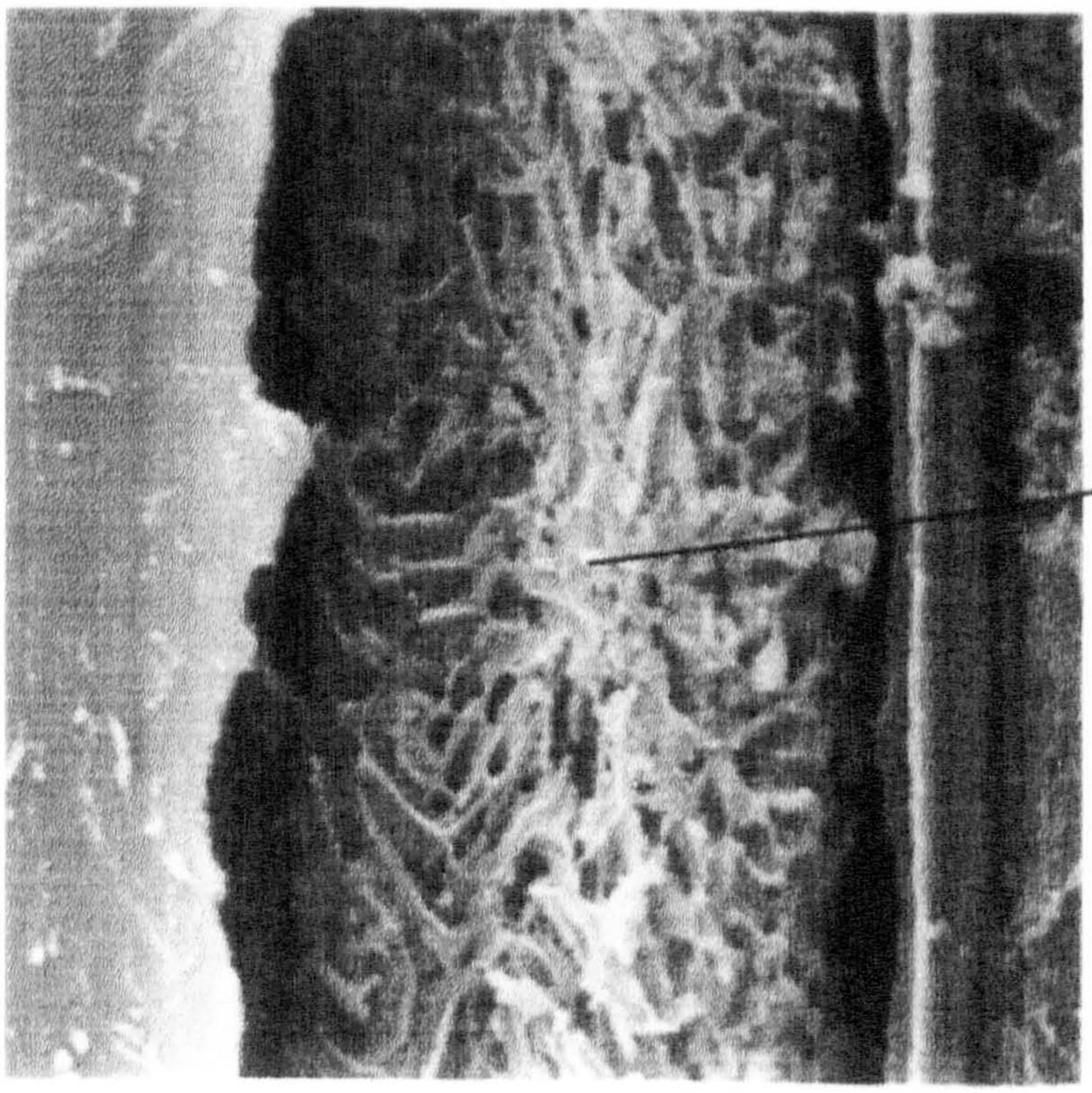


Figure 5.4i Grooves cut into S2 layer of fibre cell-wall by tunnelling bacteria. (X2700)

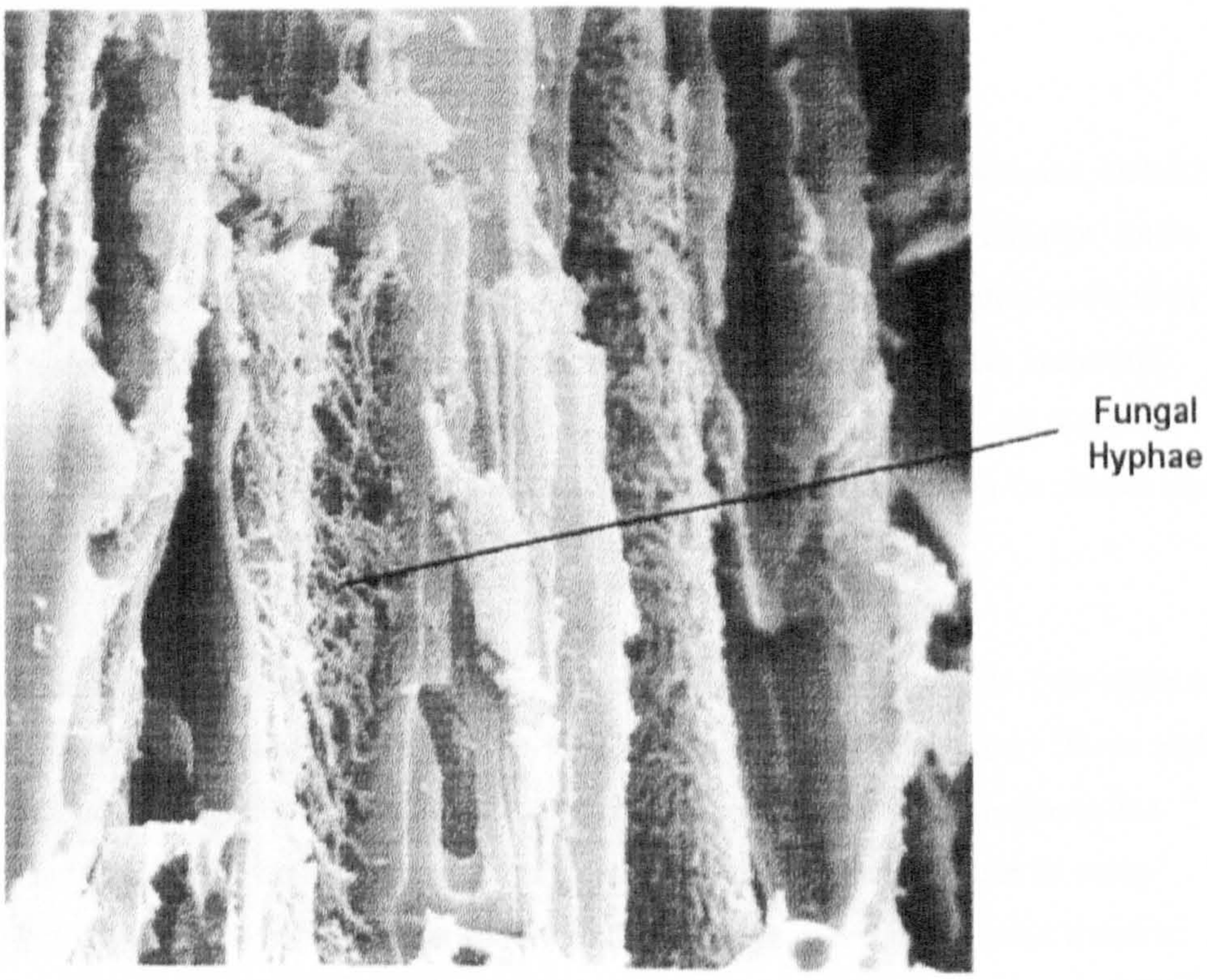


Figure 5.4j Fungal attack on interior of fibre cell-walls. Tangential view. (X 1500)

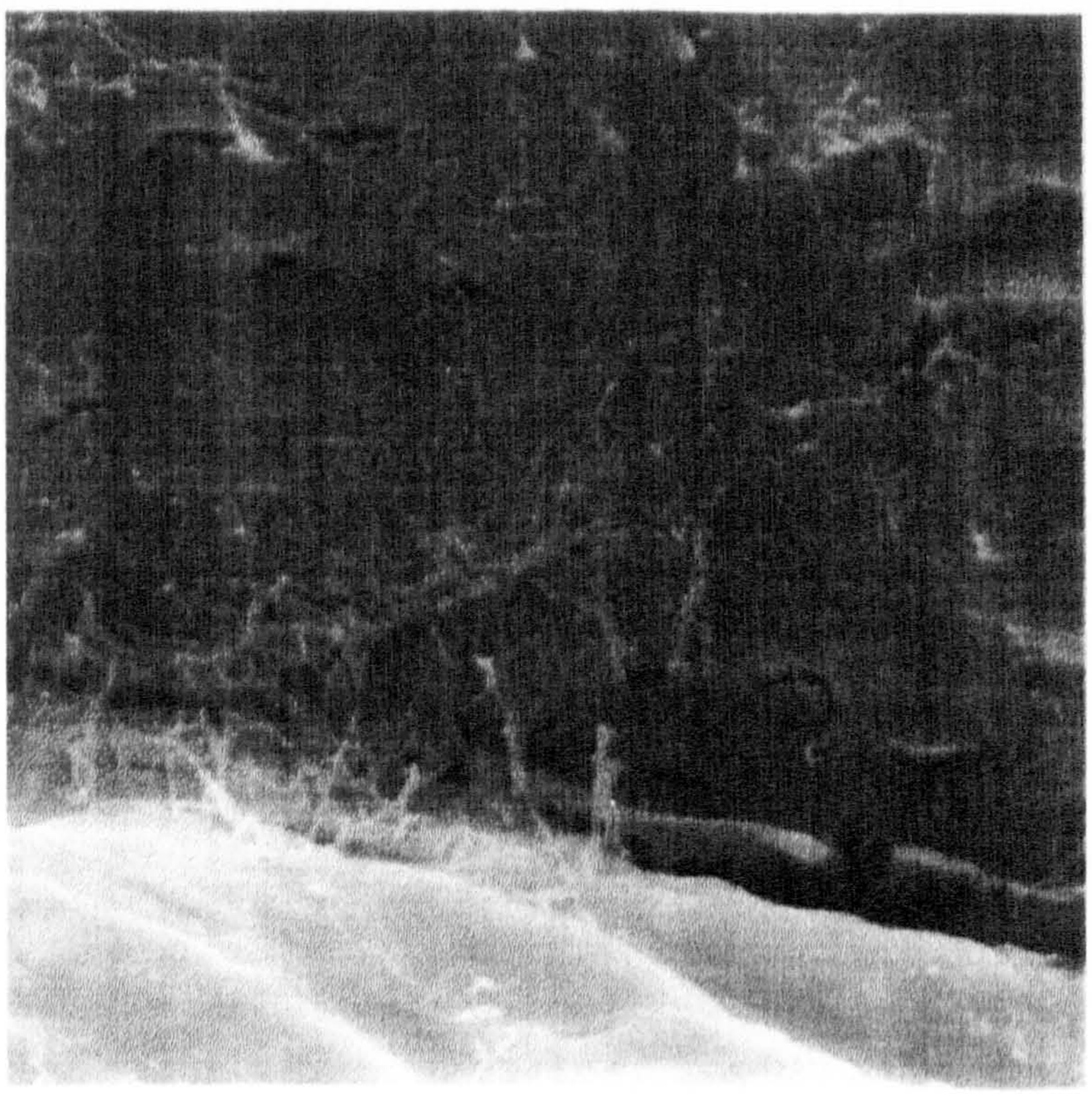


Figure 5.4k Close-up of fungal hyphae attacking lumen surface of fibre cell-wall, or perhaps mucilage. (X3000)

5.3 The Sorption Method: Principles and Previous Research

The sorption characteristics of wood have been measured variously by electrical resistance, dielectric measurements, instrumental techniques (NMR, FTIR, DSC), mercury, membrane diffusion, solute exclusion, and water vapour adsorption gravimetry (sorption method). Detailed critical reviews of these methods can be found in the literature (Stamm 1965, 1971a; Skaar 1954, 1988; Stone and Scallan 1967), and a number of the considerations were summarised in Chapter 3. All of these (except for the gravimetric method) require materials, equipment, and expertise that lie outside those generally available to the conservator.

But there are serious problems with the gravimetric approach, the principle of which is the effect of collapse in restricting the true measurement of resorption values. Mercury porosimetry (Stone and Scallan 1965), non-solvent water content (Tarkow *et al.* 1966), and solute exclusion (Stone and Scallan 1968b; Lin *et al.* 1987; Flournoy *et al.* 1993) all aim at avoiding this problem by using materials that will not cause shrinkage or swelling in the cell walls and secondary order/transient capillary space. All have difficulty in overcoming pressure barriers while trying to achieve diffusion of these alternative materials into smaller capillaries. Electrical methods (resistance, dielectric analysis) experience problems with archaeological woods, largely because of the difficulties measuring wood that is so very far above fibre saturation (Zabel and Morrell 1992; Molinski *et al.* 1991), but also because high ash contents in degraded woods will produce anomalous results due to their bulking effect (Stamm 1971a). Porous plate membrane diffusion methods (Stone and Scallan 1967; Bramhall 1995) have the advantage of being able to control and measure at the highest end of the vapour pressure range, thus making it possible to measure rather than extrapolate to fibre saturation point (0.9999 v.p.). This method is probably still the most accurate for carrying out sorption measurements.

Instrumental techniques are now beginning to take over in the field of moisture determinations in wood. Differential scanning calorimetry (Simpson *et al.* 1991; Skinner 1997), nuclear magnetic resonance (Araujo *et al.* 1992; Cole-Hamilton *et al.* 1995; Menon *et al.* 1987; Skinner 1994), and Fourier transform-infrared spectroscopy (Loudon 1988; Faix *et al.* 1994) have been applied to assessing water form and distribution throughout fresh and degraded woods. Much of this work is in an initial stage, however, and interpretation of the results is complex. There are problems with archaeological material particularly, where high ash contents cause peak broadening and overlap. It will be some time before these techniques are ready to be used as common tests for the sorption properties of wood.

Despite these problems of control and interpretation, the sorption method (gravimetric) continues to be used to provide experimental data for wood sorption (Wadsö 1993b, 1994; Avramidis 1993) and,

for the most part, has been preferred by investigators into the sorption properties of archaeological wood (Barbour and Leney 1982; Hoffmann 1985; Jensen 1996). Thus far, only largely descriptive information and general conclusions have come out of these studies, though Jensen (1997) has used his data to construct an alternative non-destructive, computer-based program for calculating diffusion coefficients for archaeological artefacts undergoing treatment that largely replaces Cook and Grattan's (1991) PEGCON program. At the time of this doctoral research it was not yet possible to use this program to test the validity of the results obtained here.

The results discussed in this chapter will concentrate on determining whether, despite the inherent inaccuracies of the gravimetric method, the simple apparatus designed for this project is able to determine basic differences between wooden artefacts that would affect the choice and type of treatment given to them. Stamm (1971) claimed that FSP varies only slightly with variations in the bulk chemical composition of the wood substance, and it will be interesting to see if this is true with the Roman plank sections. It is likely that the differences he was referring to were the very slight differences existing with species of wood, rather than the rather larger ones experienced during degradation. It will be interesting, also, to see how much FSP values vary with physical properties. (Skaar 1988; Panshin and deZeeuw 1980). Connections between the sorption results and the chemical and physical properties of the samples will also receive discussion in Chapters 6 through 8.

5.4 Experimental Method

Non steady-state diffusion measurements of water vapour sorption were made on the samples listed in Section 5.2.1. By "non steady-state," we are referring to measurements taken of the weight change (moisture content) of a wood sample after a step change in relative vapour pressure (relative humidity, RH). Discrepancies in results exist between these two approaches, and sorption models have arisen in an attempt to accommodate both (Chapter 3). Nevertheless, it is non steady-state measurement that is the standard approach used in the sorption method of measuring diffusivities of wood (Wadsö 1994). The table below summarises the test steps performed for the three curves (initial desorption, resorption, and secondary sorption) measured:

Curve	Test Step (RH %)										
Initial Desorption	(98+)	90%	80%	70%	60%	50%	40%	30%	20%	10%	(0%)
Resorption	(0%)	10%		30%		50%		70%		90%	(98+)
Secondary Desorption	(98+)	90%		70%		50%		30%		10%	(0%)

Table 5.1 **Test steps (RH%) performed and curves measured.**

The accurate construction of the Type II sorption curve requires a minimum of six measured points for equilibrium moisture content. The better quality of the initial desorption curves as a result of using eleven measured points can be seen in the isotherms shown in the results (section 5.6) below.

It is unusual for an initial desorption curve to be measured, i.e., equilibrium moisture contents from the saturated state to the oven-dry. Most studies start from the known point of oven-dry weight, measure initial resorption, and follow with desorption hysteresis. But since the information the conservator needs to obtain about archaeological waterlogged wood pertains to the difference between the original water-saturated state and dimensions and the changes that will occur to the wood if the wood is allowed to dry without bulking (hysteresis), it is important to measure this difference. For this reason, the three curves tabulated above were measured for each of the test samples.

Three-dimensional sorption measurement was chosen over one-dimensional. In one-dimensional sorption, samples are sealed with a wax or resin on four of their six sides in order that flow is in one direction only. In this study, however, minimum interference with samples was a priority (as it often is for the conservator, in order to conserve sample material for multiple analyses) (Section 5.2.2, above). Complete sealing of wood samples against water vapour diffusion is difficult to achieve. Wadsö (1994) discusses the level of error introduced by incomplete sealing. Because of the interference made to surface adhesion by water, complete sealing is still more difficult to achieve in waterlogged samples.

Measurements of water vapour sorption in wood are difficult to carry out to any significant level of accuracy. Too low-tech an approach risks meaningless results and, moreover, involves a great deal of direct monitoring. The brief in this study however, was to investigate methods of analysis that could be carried out by the conservator rather than the specialist. The design of an apparatus for making sorption measurements was part of this brief, and a full description of it is given in 5.5.1, below. Wadsö (1993a and b; 1994) published three papers that describe the design considerations of a much more high-tech instrument. In the design of the apparatus used for this doctoral research, reference was made both to his work and to considerations brought up in conversation with C & I Electronics Ltd. (Salisbury) who produce high-spec sorption chambers for use in scientific research, especially pharmacology. Results from parallel samples run by this company are compared to closely related samples in the present study and have been useful in gauging the relative accuracy of the sorption apparatus described below.

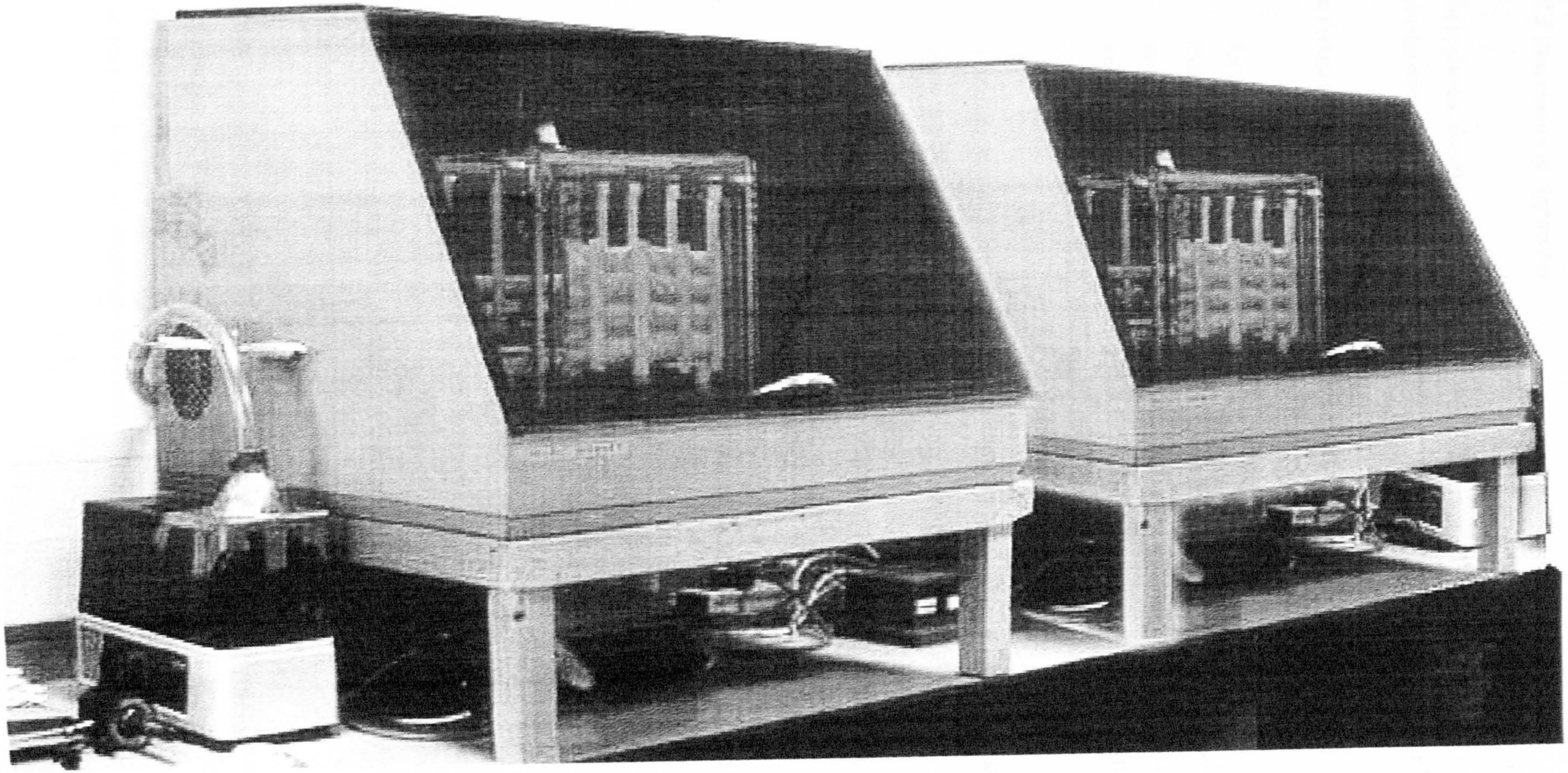


Figure 5.5 The tandem sorption apparatus

5.5 Sorption Measurement Apparatus

5.5.1 Description of Apparatus

The apparatus designed for this project consists, in fact, of two identical apparati running in tandem in order that a higher volume of samples may be run simultaneously (Figure 5.5, previous page).

As shown in Figure 5.6 (next page) each apparatus consists of:

1. An environmental chamber created from a standard perspex dessication chamber (BDH Chemicals) into which inlets (2 cm diameter) were cut for a humidity/temperature monitoring probe (Vaisala HMP 35A); a polyethylene feeder hose leading from an ultrasonic water vapour source; and a purpose-made extension to the balance platform that allowed the balance to remain outside the environmental chamber during the measurement period. (Figure 5.6 below).

2. A Mettler PM480 electronic balance (readability 0.001 g) with RS232 interface; draft shield in place (top panel removed).

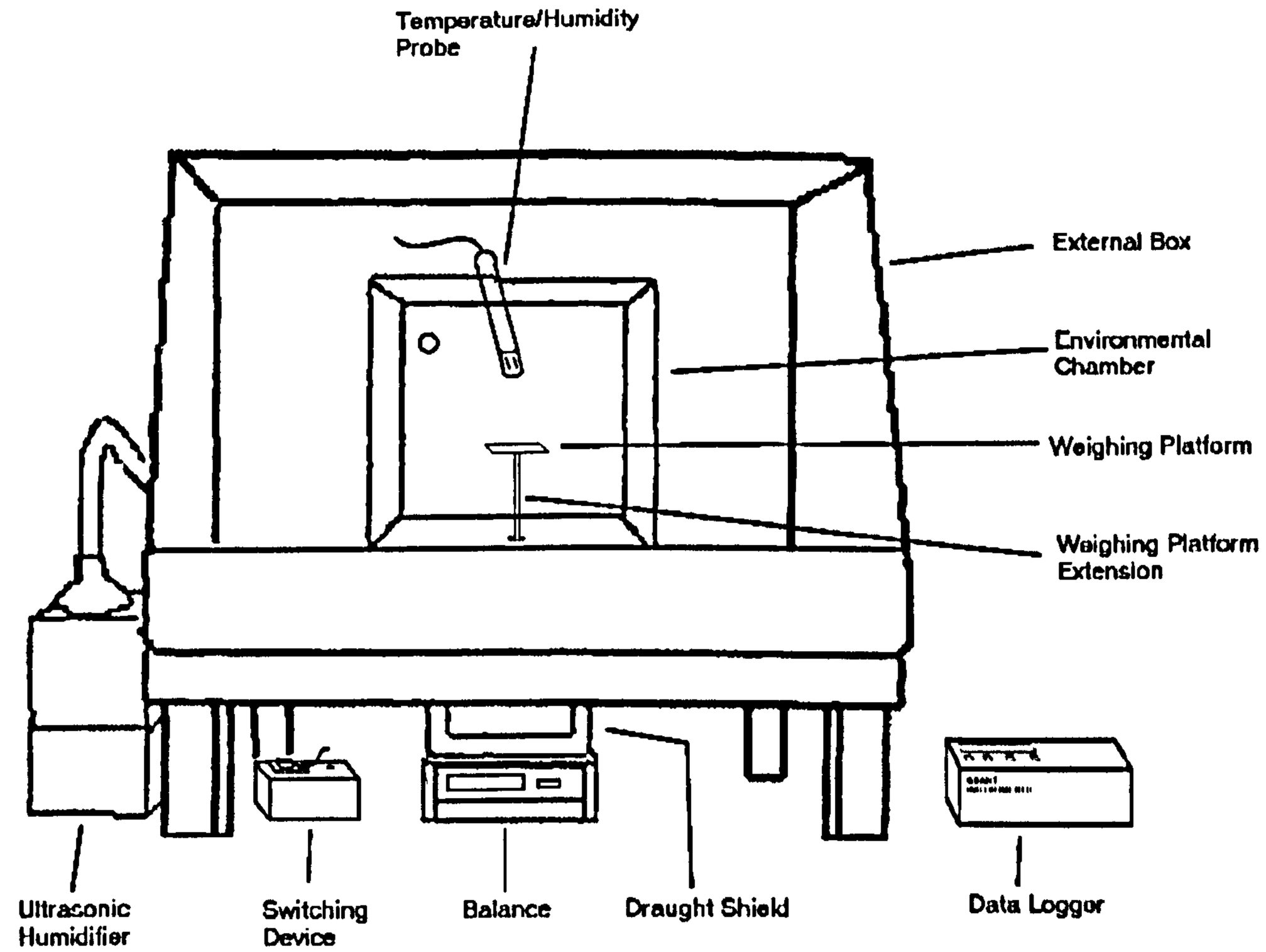
3. A domestic ultrasonic humidifier (PIFCO™ 1074) with deionising cartridge. Silica gel (desiccant) was used in lieu of a de-humidifier.

4. A simple ON/Off relay switching control device (coupling humidifier and datalogger).

4. A Squirrel 1001 Series Temperature and Humidity monitoring (Grant Instruments and Lucien Hatfield, Cambridge), specially adapted to include an I/O port for the balances and the control devices.

The remainder of the apparatus consists of a wooden frame to lift the environmental chamber up so that the balance may lie underneath, and a large case covering the whole in order to buffer environmental changes occurring in the test laboratory. This latter item would not be required where a reasonable tightly-controlled air-conditioned room were available.

All of the constituent parts of the sorption apparatus are equipment common to conservation laboratories, including the Squirrel datalogger. Adaptations to this standard piece of environmental monitoring equipment can be made at relatively small expense and leave it still suitable for re-use as a monitoring device for museum or store environment.



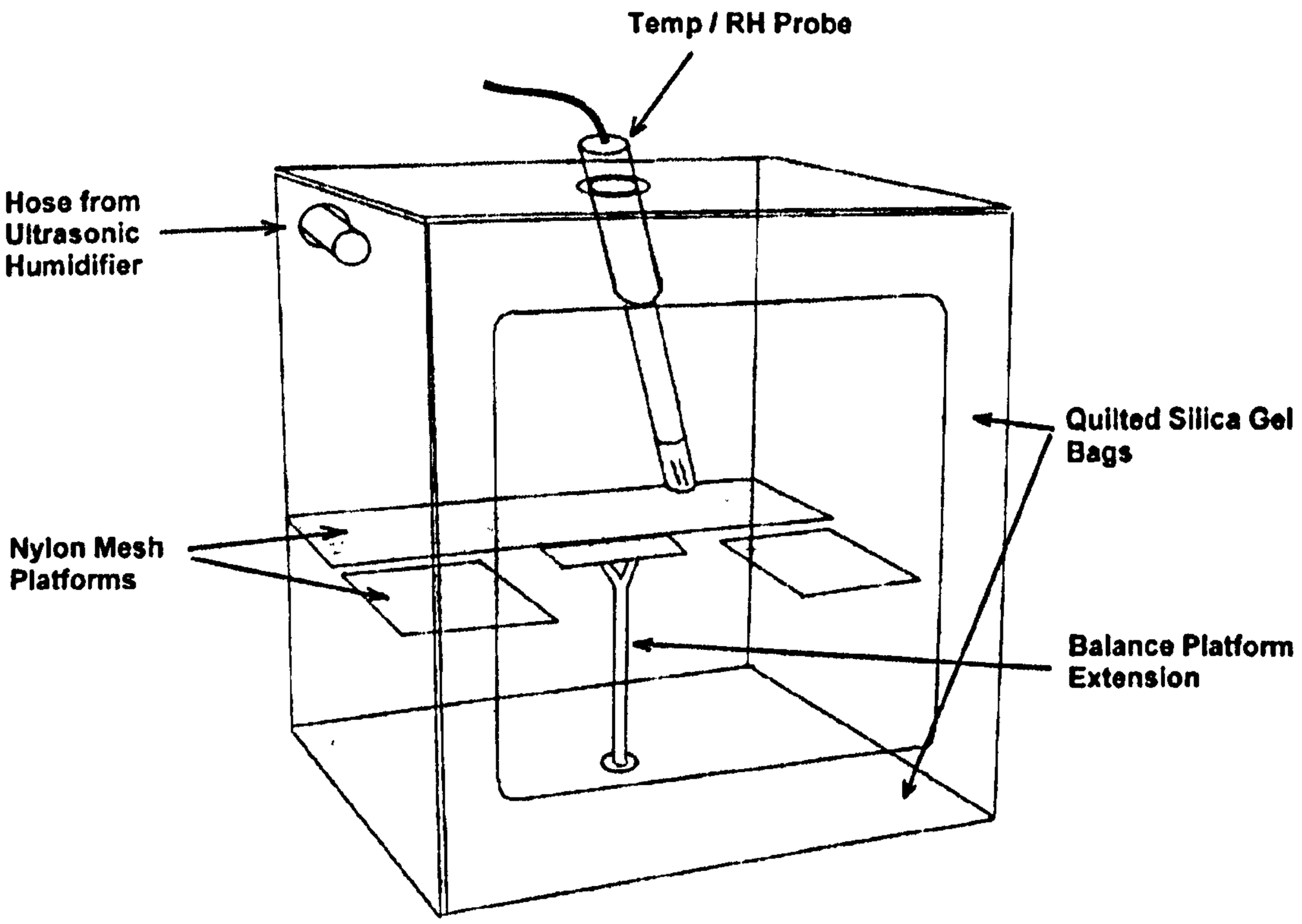


Figure 5.6 **Schematic drawing of sorption apparatus.**

Particular care was taken in the choice of humidity/temperature probes because of their central role both as monitor of equilibrium relative humidity and as 'humidistat' for the control device. The average accuracy (including nonlinearity and repeatability) for the two humidity/temperature probes is: ±2% RH of reading from 0-90% RH; ±3% RH from 90-100% (reduced to 1% and 2% of reading when calibrated to ASTM standards);±0.3°C. Both probes underwent annual recalibration at SIRA NAMAS accredited facility during the course of this study.

Average accuracy for the electronic balances are: repeatability 1.0mg; linearity 2 mg. Taking into account the relative small average sample size (3 g wet wt./ 0.5g dry wt.), it would have been preferable to have utilised a five-decimal-place analytical balance in order to ensure weight data with a lower inherent error. These balances, however, tend to be less stable to environmental stress, thus the air turbulence caused by the humidity input and extremes in vapour pressure would have introduced a level of error that negated this advantage in accuracy (Mettler Technical Support, *pers. comm.* 1994).

5.5.2 Operation and Performance Characteristics

Test sample wafers were laid flat on nylon mesh platforms around three sides inside the chamber. One sample in each chamber sat on the modified balance platform throughout the experiment in order that equilibrium could be accurately determined. The two samples chosen were those with highest initial moisture content in combination with highest density, under the assumption that these samples would take longest to reach equilibrium. All other samples were weighed at intervals of one day to one week depending on the RH step involved. Samples were at all times handled in latex gloves, to ensure that moisture and pollutants from the hands would not affect the results. The control system for humidity was left running during the weighing sessions in order that the samples did not begin to re-equilibrate to another level of humidity. The time taken to complete all measurements was short enough to make such a problem unlikely. During the design of the system, tests were made of the amount of change in weight that could occur during the weighing session as a result of the small amount of drift in humidity that did nevertheless occur. Average calculated drift in weight was less than 1% of reading.

Stable equilibrium conditions were maintained within the environmental test chamber by means of the alternating operation of silica gel desiccant and ultrasonic humidifier. Each humidity step was programmed into the datalogger as its temporary control value, with a plus or minus 0.1% change allowed before the humidifier was switched on or off, as suitable. Once the humidity reached the appropriate level (as measured by the humidity probe located directly above and within a centimetre or two of the sample), the datalogger sent the message to the control device to switch the humidifier off. The presence of silica gel, arranged evenly around the walls and base of the chamber, ensured

that the amount of humidity over-ride was not excessive, and that it was brought down to control conditions relatively quickly. Tests carried out determined its ability to do this within, on average, 15-30 seconds—well within the data logging interval set. The high quality construction of the humidity probes meant that their response time was very quick, and that changes away from control conditions would be recognised and reacted to almost immediately. Figure 5.7 below shows the level to which the control system of the environmental chamber was able to maintain stable humidities. It is clear from this graph that these were only stable to approximately ± 2% RH.

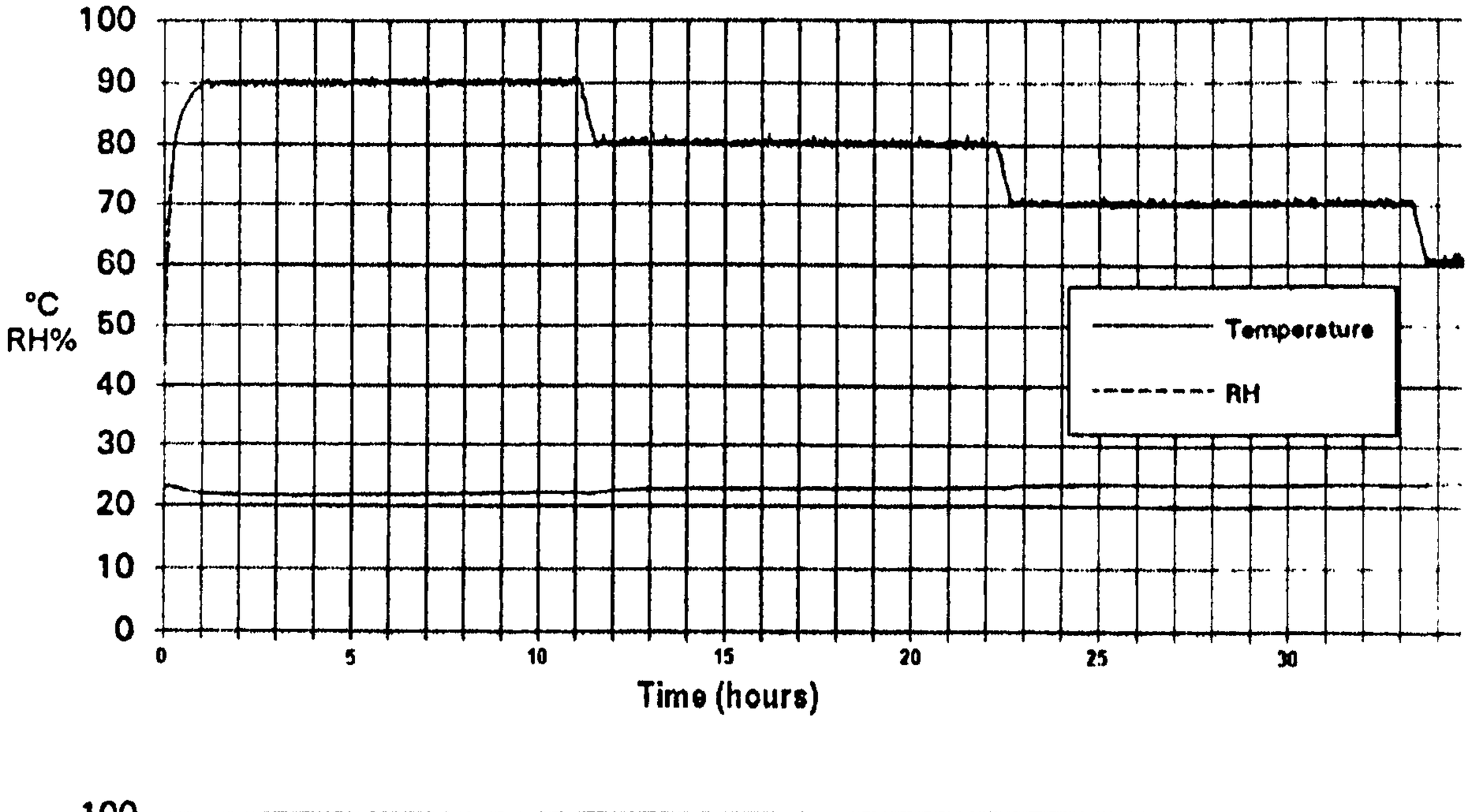


Figure 5.7 **Humidity control at each step of relative humidity.**

The graph also shows some variation in temperature. Though these experiments were not carried out in a temperature-controlled room (which would have been preferred), the buffering effect of the insulated second case (Figure 5.6) was sufficient to keep temperature change down to ± 2°C around

the chosen isotherm temperature of 21°C. Section 5.4.1.3 below discusses the probable effects introduced by the sources of error described in this section.

5.5.3 Sources of Error Affecting Design

Wadsö (1994) gives a detailed critical discussion of the sources of error common to the sorption method of measuring moisture diffusivity of wood. He points out the systematic nature of many of these errors, which means that volume of samples can not make up for them. He also reminds us of the lack of any standard reference material with which to test the accuracy of results. Error analysis of the present apparatus and samples was out of the scope of the present study, but the larger proportion of his considerations were taken into account in the design of the apparatus and the preparation of the test samples (see also 5.2.2; 5.5.1; and 5.5.2 above). Some of these considerations are discussed individually below.

5.5.3.1 Sample specifications

To ensure good measurements where three-dimensional flow has been chosen, it is necessary to ensure that sample thickness is small in comparison to its other dimensions. This will mean that the diffusion coefficient in the main flow direction is the largest and most accurate evaluation of the sorption isotherm using one or other of the current sorption models (Chapter 3). For this reason, samples in wafer form were chosen, following recommendations laid out in Avramidis (1993). Their dimensions were roughly 750mm x 30mm x 1mm, with the largest surface area presented in the transverse plane.

Sample thickness was kept as exact as possible throughout the sample, by means of the micrometer-calibrated diamond-bladed micro-saw used to cut the wafers (section 5.2.2). This was in order that wedging was eliminated as much as possible, since varying thickness will have a relatively large affect on the constancy of the diffusion coefficient that applies throughout the isotherm.

5.5.3.2 Relative humidity

There has been a tradition in sorption studies to use saturated solutions of soluble salts or graduated molar concentrations of sulphuric acid to regulate the controlled relative humidity level of each test step (Stamm 1964; Skaar 1988; Wadsö 1993b). This method has been found to yield consistent and controlled humidity levels in enclosed test chambers. However, there is a high tendency for salts from the saturated solutions to be picked up by moisture vapour and redeposited upon sample surfaces, polluting samples and seriously affecting the accuracy of measurements (Wadsö 1994; UMIST *pers. comm.* 1994). For this reason, a mechanical method of introducing and controlling purified (deionised) water vapour was used in this study.

The single most vulnerable point in the sort of sorption apparatus described in this study is the accuracy of the temperature humidity probes monitoring and controlling humidity within the test chamber. Pragnall (1988) suggests caution when relying on electronic humidity probes under high specification conditions. The best sensor, when correctly calibrated, will only exhibit an accuracy of about ± 2-3% of reading. In addition, sensors may exhibit severe non-linearity at high humidities (above 85% RH) and at low humidities (below 15% RH). A humidity sensor accuracy of ± 2% RH leads to an error of ±0.5°C for the dewpoint, which is very serious in the course of an attempt to measure FSP accurately. Similar errors result from a temperature sensor accuracy of 0.5°C (Pragnall 1993).

The speed with which each RH step change is effected is also important and should be as close to instantaneous as possible, otherwise non-steady-state sorption models can not be applied. Figure 5.7, above, establishes a relatively instantaneous step change for the apparatus used in this study.

Sinusoidal variations in RH are common to sorption testing. Chapter 3 describes the effect they have on the sorption isotherm. Periodic variations of ± 3% RH are not uncommon for even the more sophisticated environmental chamber (Wadsö,1994). There is no question but that such variations were incorporated into the measurements made in this study, and some of the inconsistencies in the sorption curves reported in this study may well be attributable to them. However, Wadsö (1994) calculates that the effect of such variation on sorption measurements is negligible as long as the variation is small in comparison to the step change in RH. This could not really be claimed for all of steps measured in this study. Wadsö, however, goes on to say that the time period of the RH disturbance is more important. As long as the time of disturbance is very much shorter than the time taken to achieve equilibrium at that step, the effect is unlikely to turn up in the measurement. Research by Scott (1994) concurs. The test results shown in Figure 5.7, above, establish that the average period of disturbance with this experimental set-up is very small indeed (something in the range of 15 seconds to a few minutes), compared with equilibrium steps taking a few weeks to a few months. Indeed, over a period of time, a conditioning effect can be observed in the silica gel in the chamber (Cassar and Martin 1994) which lowers the range of variation caused by the over-ride of the humidifier. This is indicated with an arrow in Figure 5.8 below.

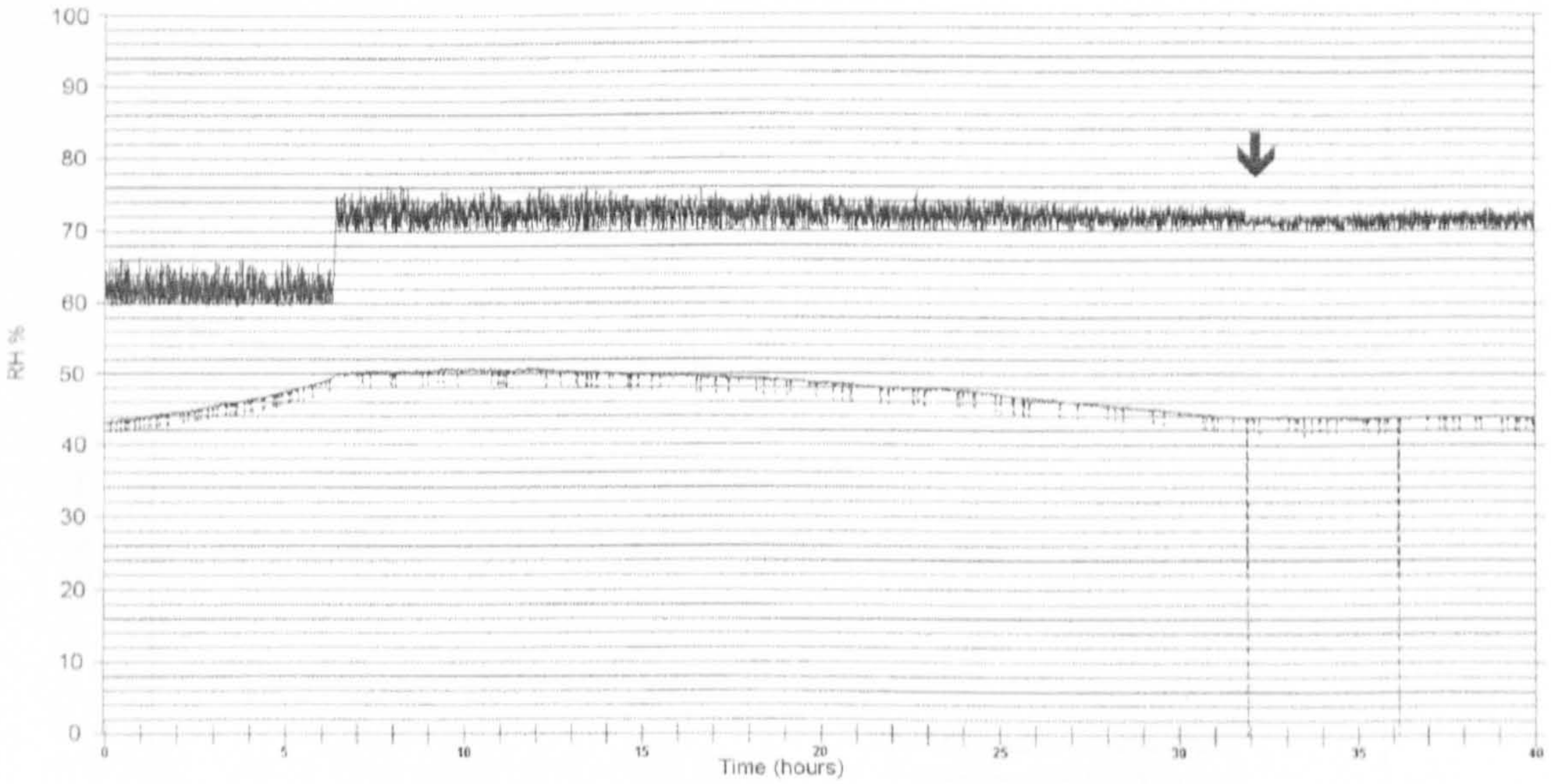


Figure 5.8 Conditioning effect on silica gel during sorption run.

This buffering effect might have been increased had ArtSORB® conditioning paper been used instead of silica gel, since Cassar *et al.* (1994) report a 5-8 times better buffering capacity for the former.

5.5.3.3 Temperature

Temperature was measured at the same interval as humidity (5 minutes). Rapid changes in temperature lead to rapid changes in RH by changing the saturation vapour pressure, and the effect will be registered in changes to equilibrium moisture contents. Temperature changes recorded during the experiment were never sudden (as various of the preceding figures show), and humidity control can be assumed to over-ride any effect they might have had. Humidity measurement, however, will be affected by temperature gradients set up in the chamber. At 20°C, a gradient of 0.1°C produces an error in RH of 0.6% of reading (Pragnall 1988).

Nevertheless, equilibrium moisture contents (EMC) will be affected by temperature also because of its effect on capillary condensation values. The standard value quoted is a decrease in EMC of 1% for each 10°C increase in temperature (Stamm, 1971a). Temperature variation was kept down to ± 2°C by means of the external insulated case that encapsulated each environmental test chamber. The ability of the external case to buffer temperature change is shown in the figure below (Figure 5.9).

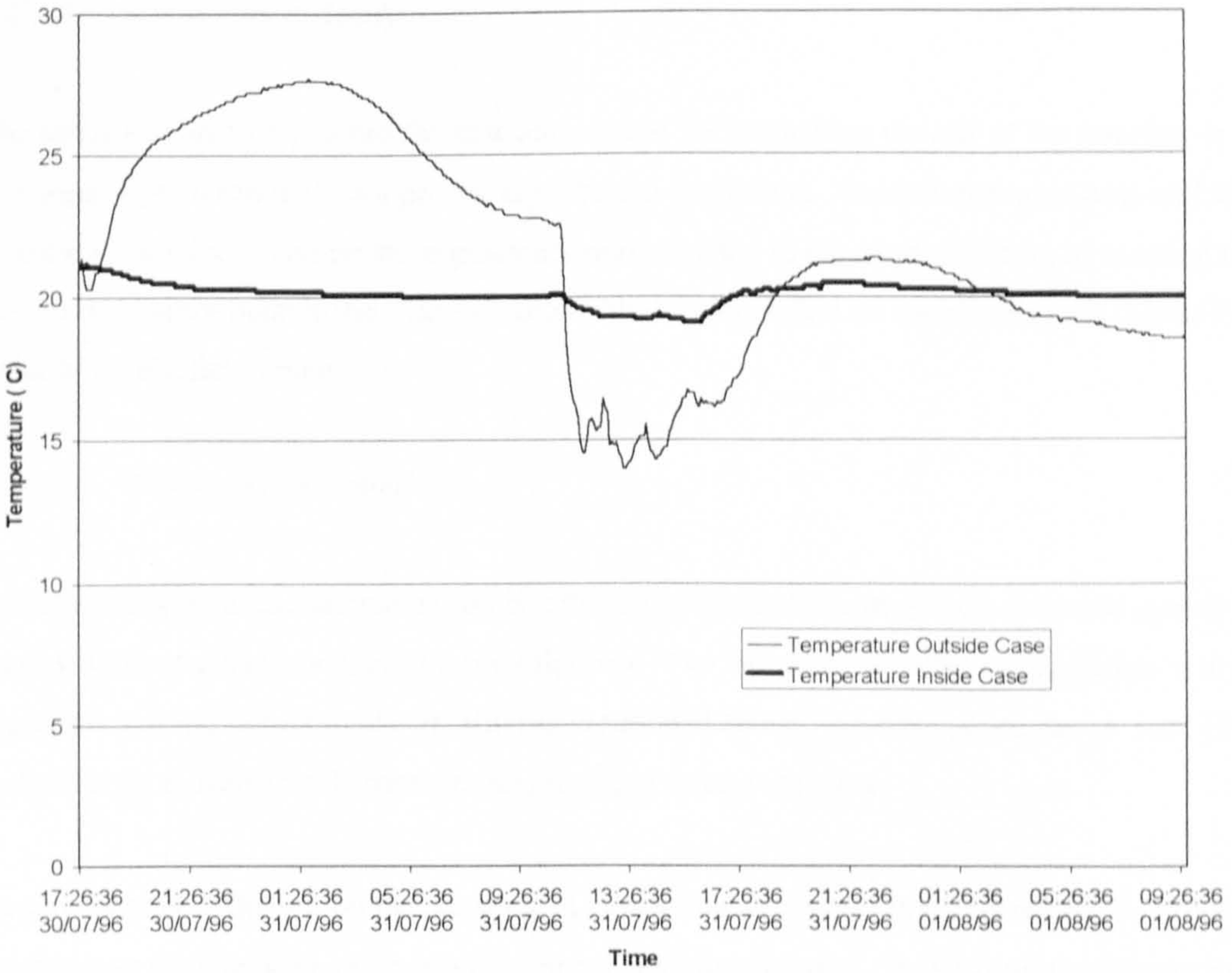


Figure 5.9 **Effect of external insulated case on reducing temperature change.**

The effects of temperature variation were monitored during the tests carried out in this study and were found to have negligible effect on readings. Figure 5.10, below, shows this.

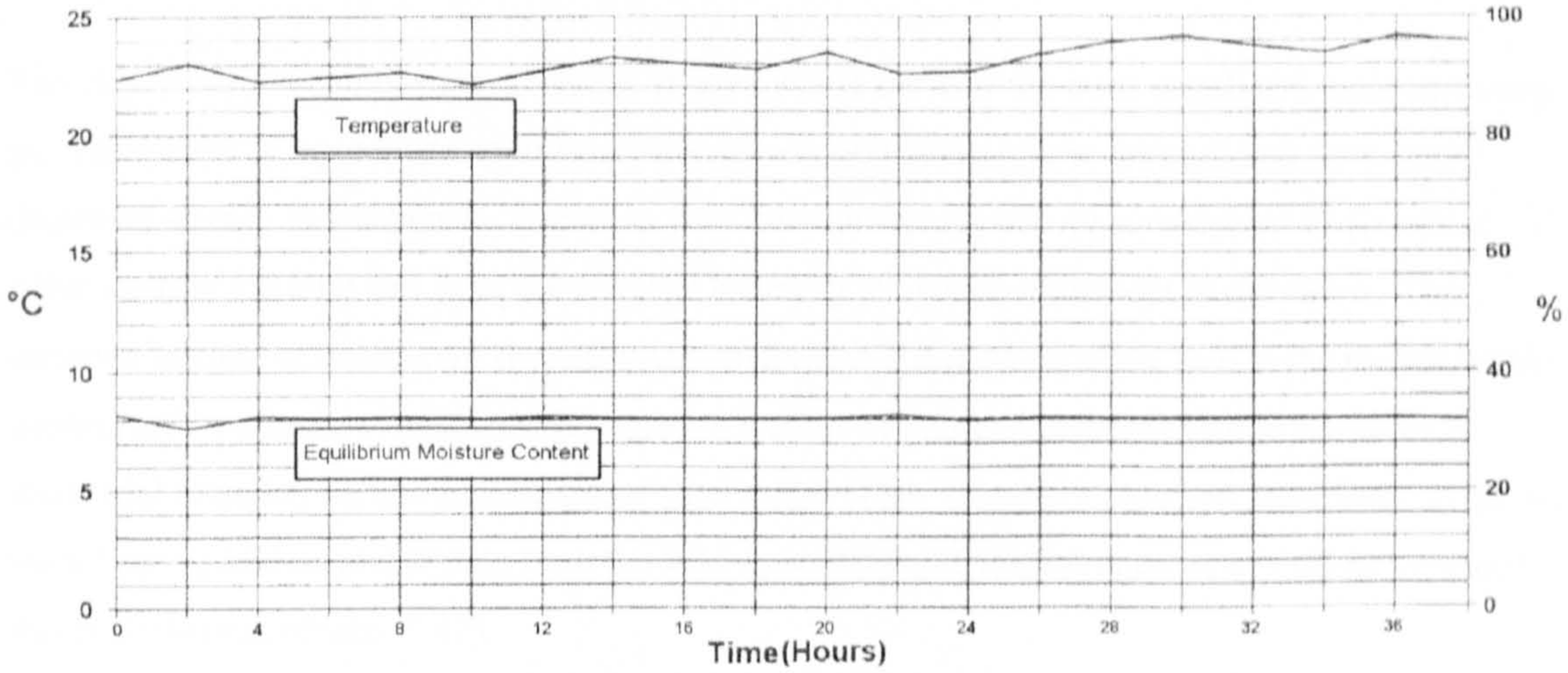


Figure 5.10 **Effect of temperature on equilibrium moisture content.**

5.5.3.4 Air mixing (velocity)

The mixing of air (both within the case and around the immediate vicinity of the samples) is important in order to maintain precise equilibrium conditions. Temperature gradients will also be avoided in this way. Temperature gradients were avoided in the sorption set-up by locating the electronic balance outside the chamber and by the stirring effect on the chamber air caused by the input of humidifier vapour.

5.5.3.5 Weight measurements

Accuracy of weight measurements can be affected by errors of method such as mould growth and the precipitation of salts from conditioning solutions. The latter was avoided by the design of this apparatus and the former by the air stirring mentioned above. Studies carried out by Scott (1994) show that air movements discourage the growth of microorganisms.

An unavoidable influence on the accuracy of weight measurements is that produced by varying air density over the balance pan, caused by vapour pressure changes. By locating the balance outside the chamber and designing a purpose-built weighing platform of nylon mesh only just the size of the samples themselves, it was hoped to minimise this error. Nevertheless, drift crept in over time and had to be factored out of the measurements mathematically.

5.5.3.6 Choice of equilibrium

The choice of final equilibrium weight is an area where perhaps the most significant error can creep in. The effects of incomplete equilibrium on the sorption curve (cyclic desorptions) have been described already in Chapter 3. Failure to wait for equilibrium will raise measured EMC values, while waiting too long will have the effect of lowering the whole remainder of the curve. The common method of waiting for three similar readings will almost certainly lead to the former, while waiting for a perfectly straight line in recorded weight will almost certainly lead to the latter as sinusoidal humidity variations take effect. The graph below (Figure 5.11) shows this latter effect, and the following kinetic plot of data from the high-specification CISORP apparatus (C&I Electronics) shows the former (Figure 5.12).

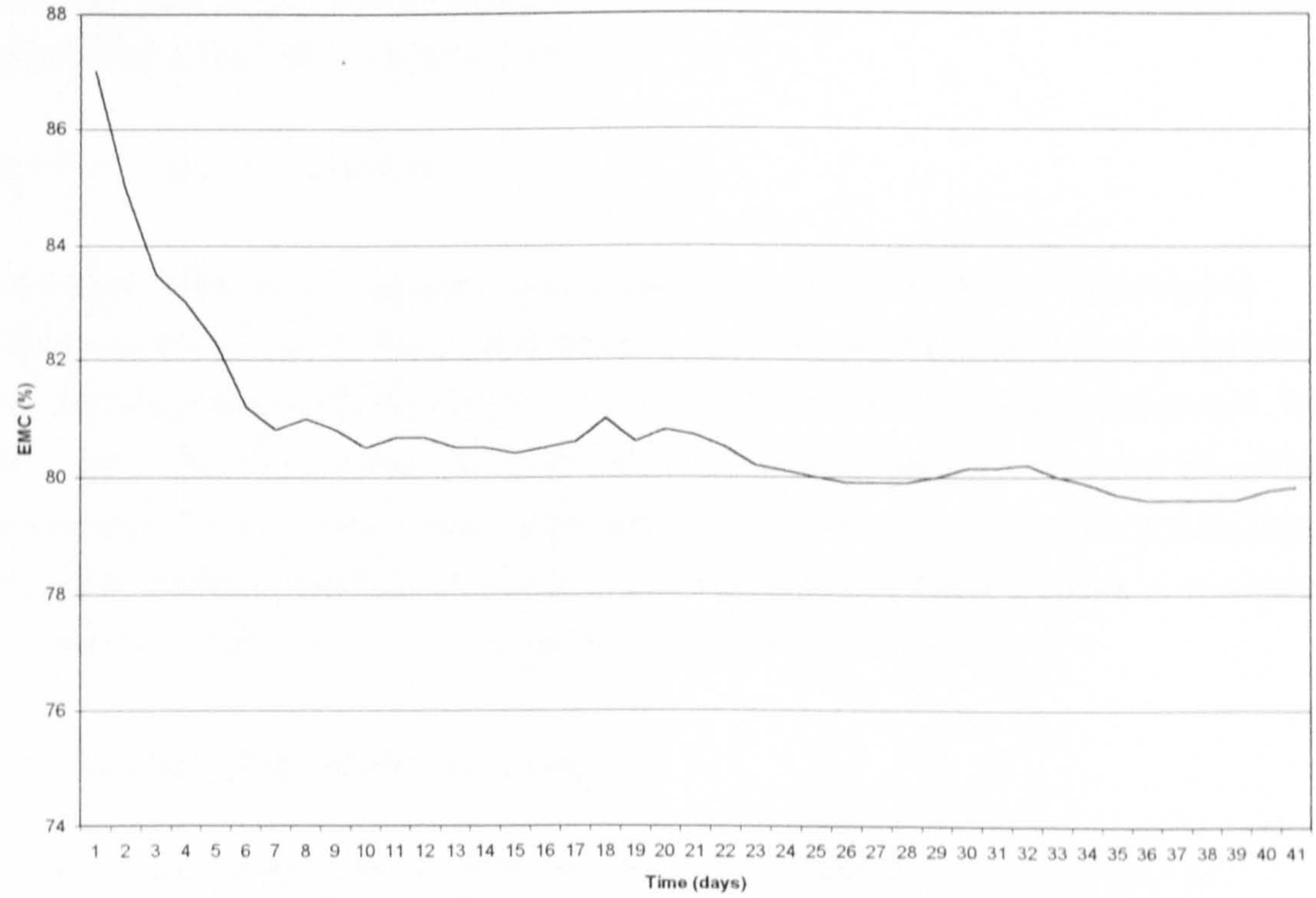


Figure 5.11 **Sinusoidal fluctuations in EMC caused by over assessing time to reach equilibrium.**

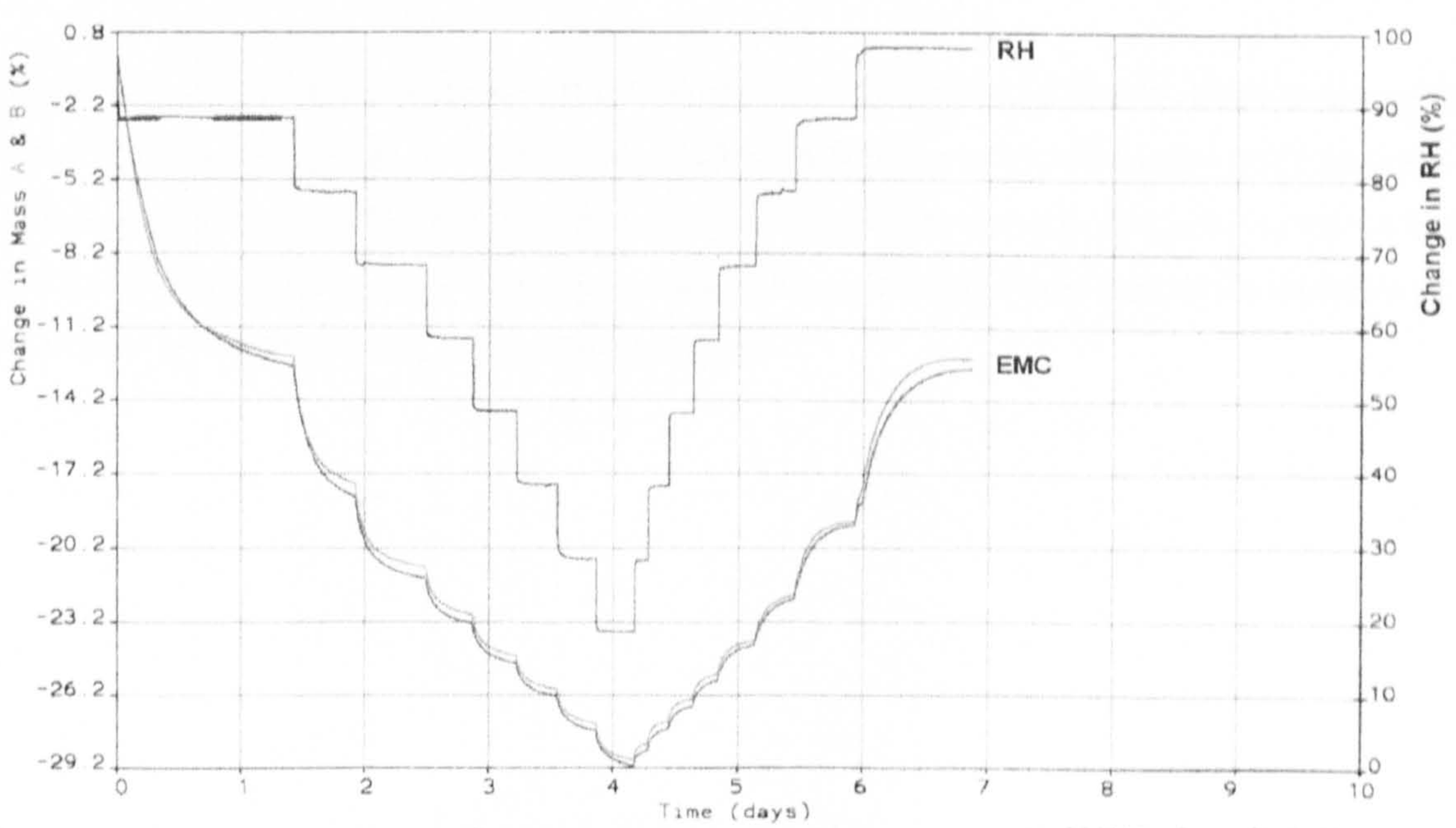


Figure 5.12 **Kinetic plot from CISORP apparatus, showing insufficient time given for equilibration.**

Avramidis (1992) chose to establish equilibrium as the point at which no weight change was observed over 48 hours. Trial tests for the present study established that small changes could occur after this period, even when stable RHs had been achieved. Equilibrium moisture contents were therefore chosen for the current study by regular analysis of weight trends while the trial was running. Multiple

values reported for the curves below (Figures 5.13–5.16) reflect the complexity of choosing any one value to represent EMC at a particular RH.

5.5.3.7 Evaluation of results

Wadsö (1994) gives a very comprehensive review of the limitations of the sorption method for calculating diffusivities in wood, most of which lie with achieving exact thermodynamic conditions. He also reiterates the pitfalls inherent to evaluation of results from experimental sorption data. The literature of sorption modelling also attests to these difficulties (Chapter 3). The model chosen will largely determine the results. What is quite clear is that, for ordinary use (i.e., other than the testing of sorption models), evaluations of sorption data would best be restricted to a slightly more subjective and descriptive appraisal. This is the approach taken in the discussion below.

5.6 Sorption Data Results and Analysis

Sorption isotherms for a selection of the samples tested are reported in Figures 5.13 to 5.16 on the adjoining pages. The sorption curves have been plotted from the final three measured values at equilibrium for each of the steps measured. No data-averaging was carried out, though non-mathematical optimum fit was sought for the curves driven through these points.

Dashed lines on the curves represent what is thought to be the correct orientation of that portion of the curve, where a problem that occurred during experimentation (a power cut) caused a wider spread of final equilibrium values than was consistent with the construction of a Type II sorption curve. A high level of confidence can be given to the upper value shown, since there were signs in the total data set collected that equilibrium was close to being reached.

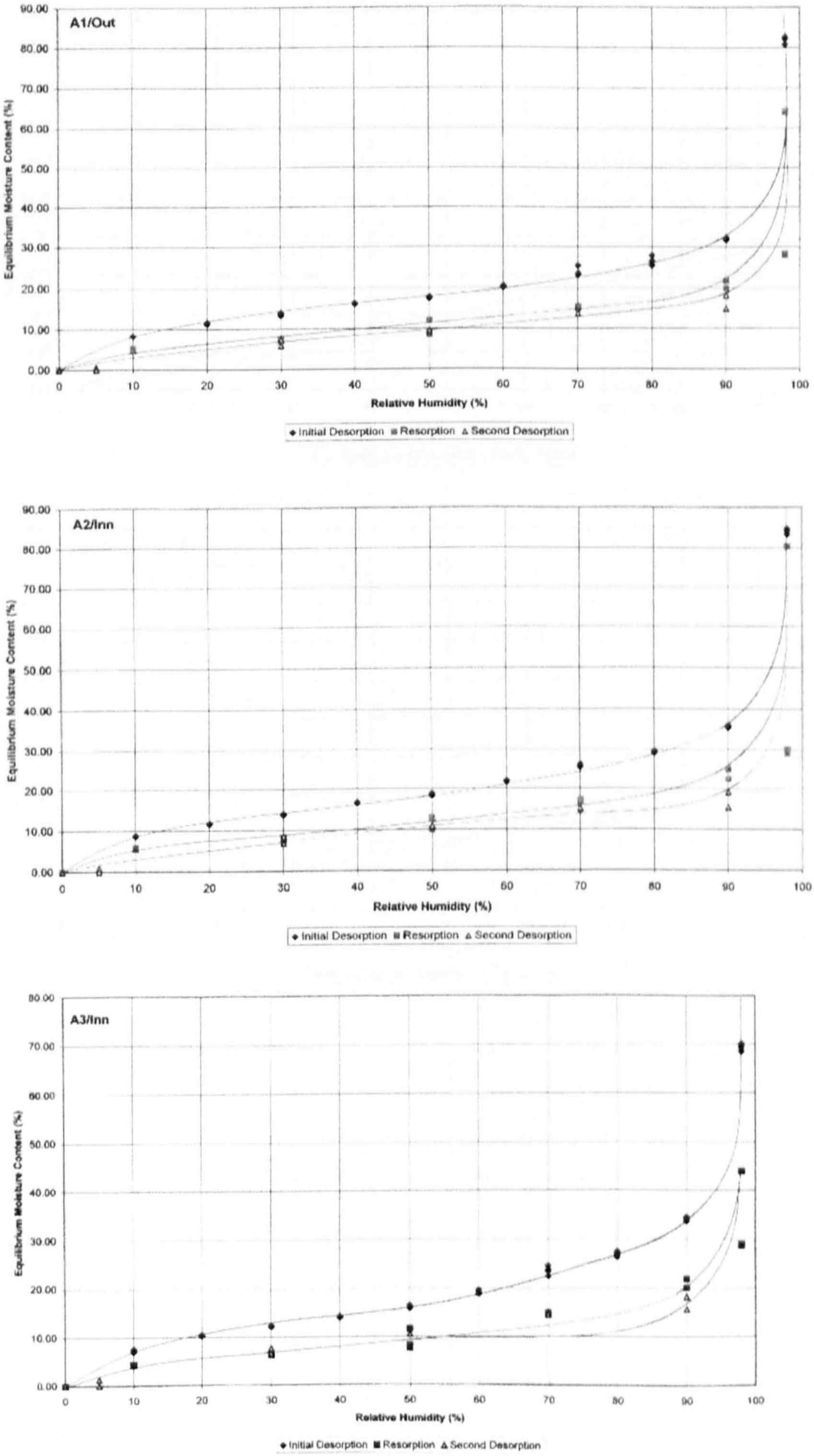
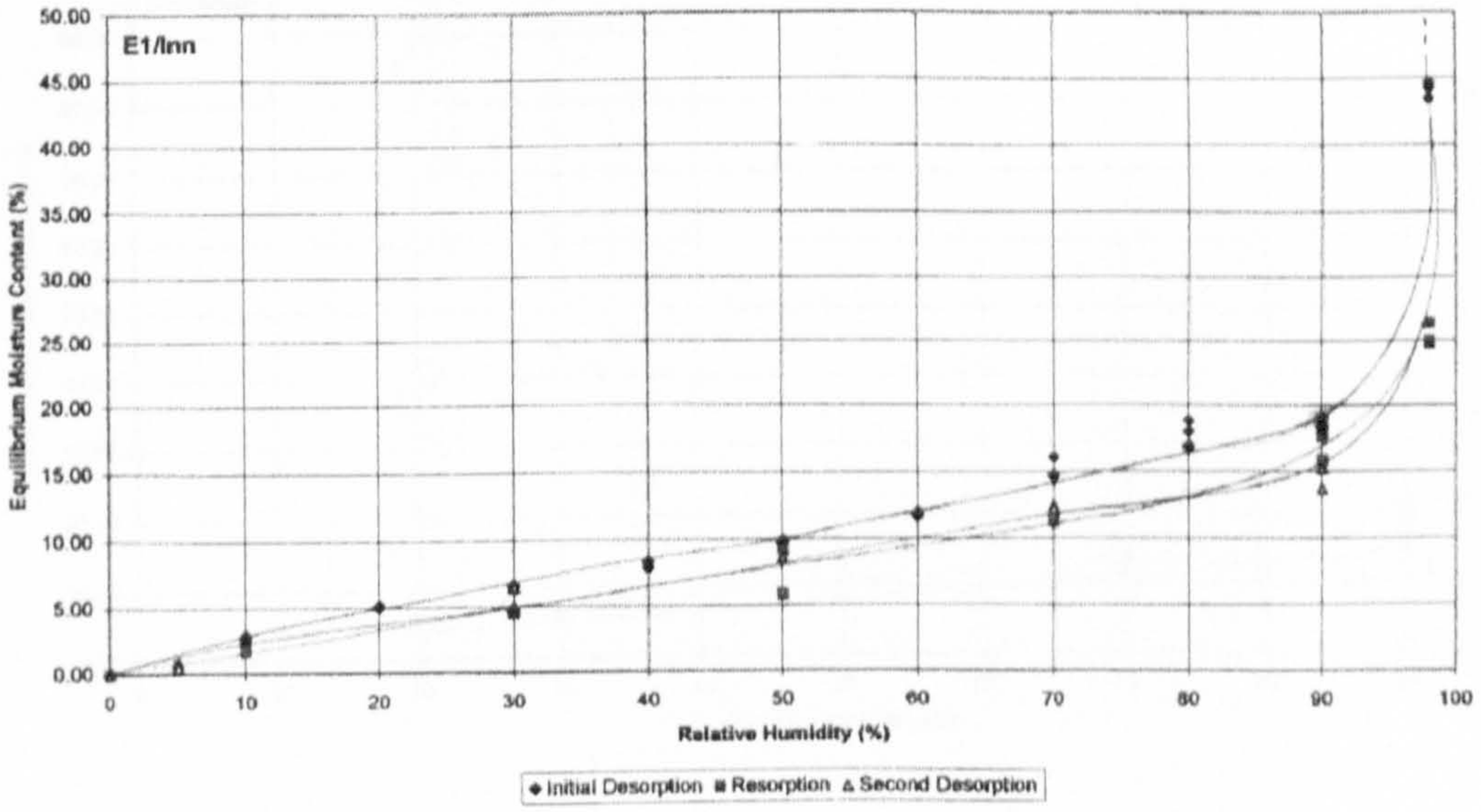
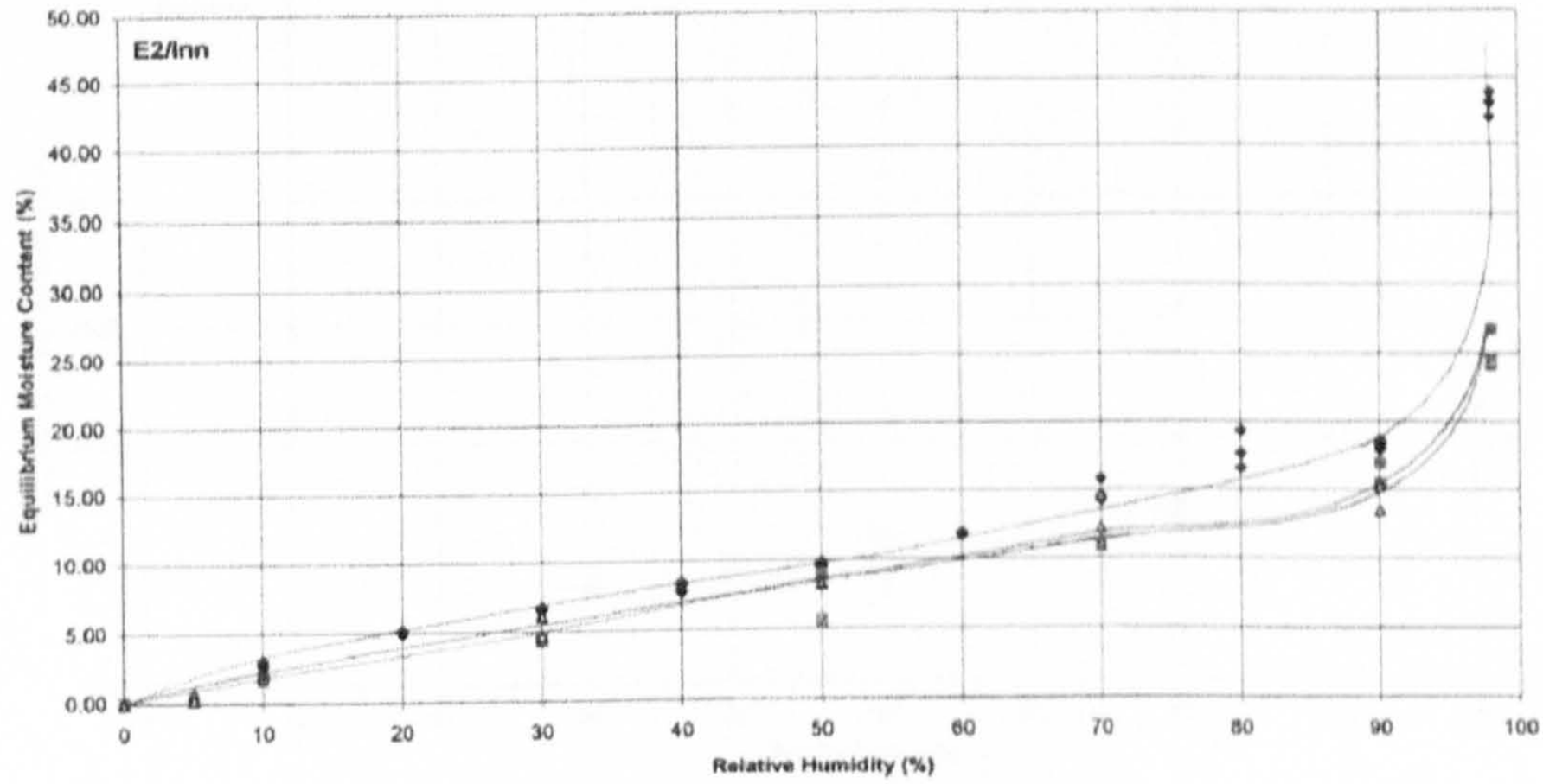


Figure 5.13 **Sorption curves of inner samples compared to outer samples from plank.**





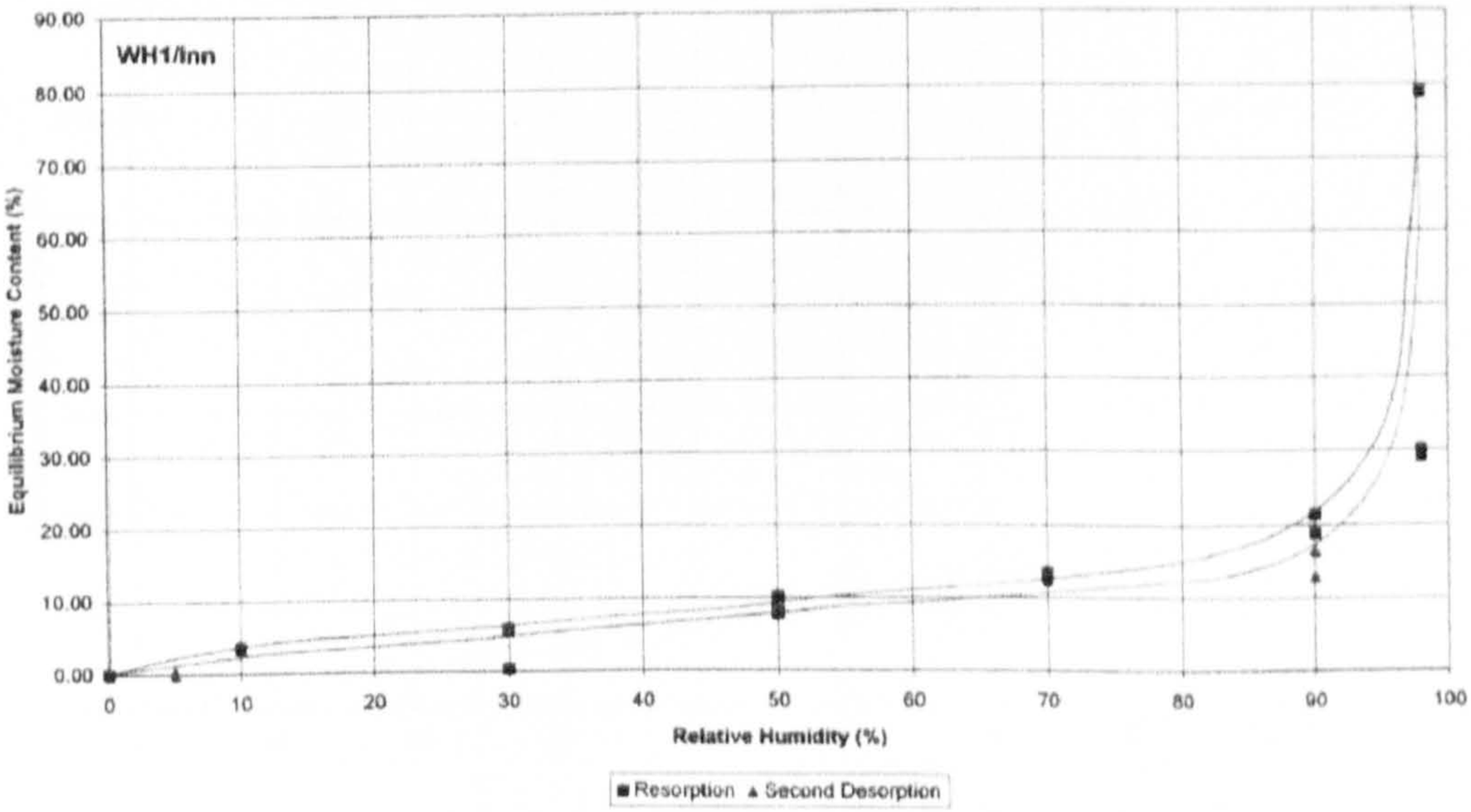
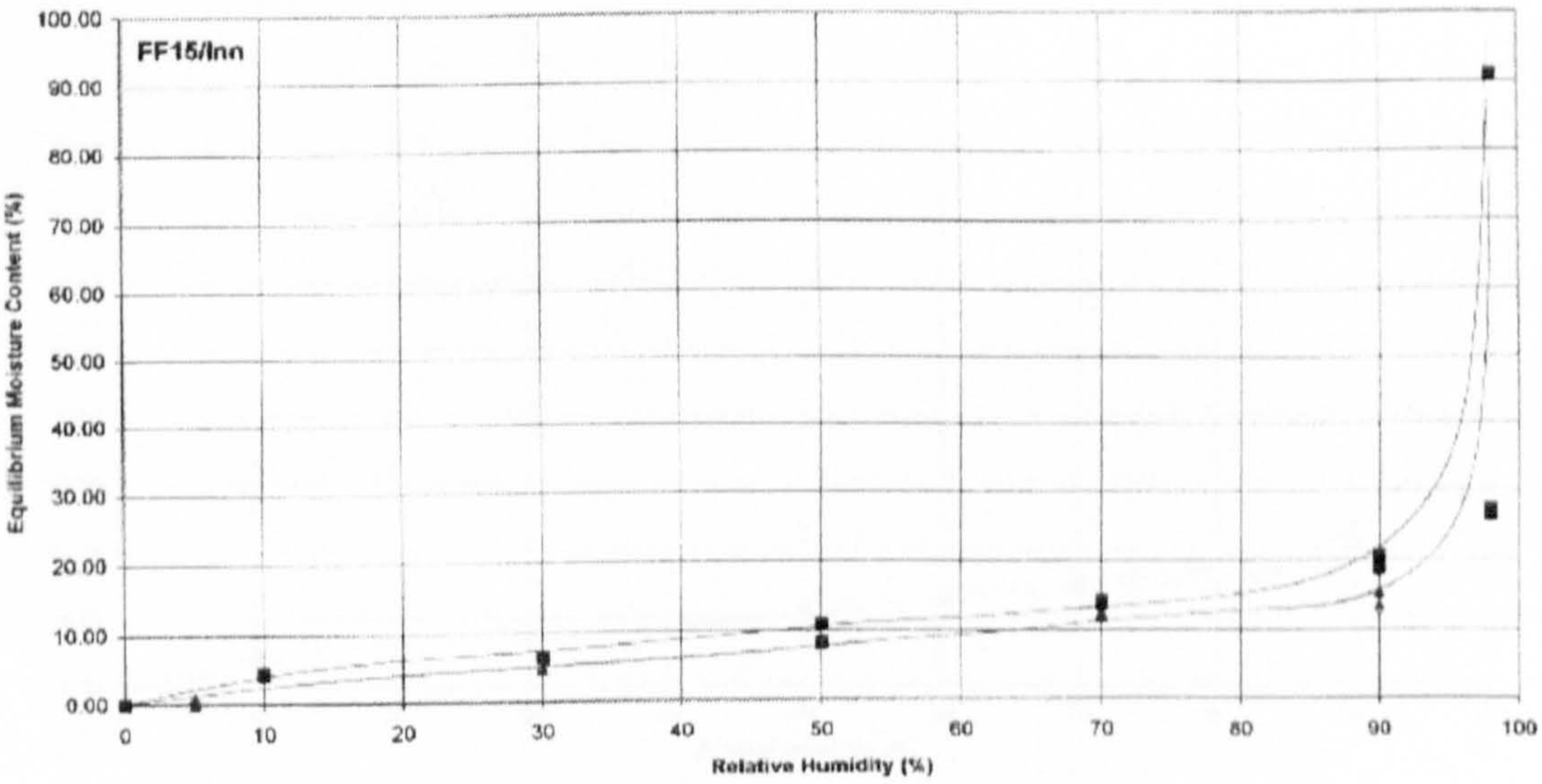
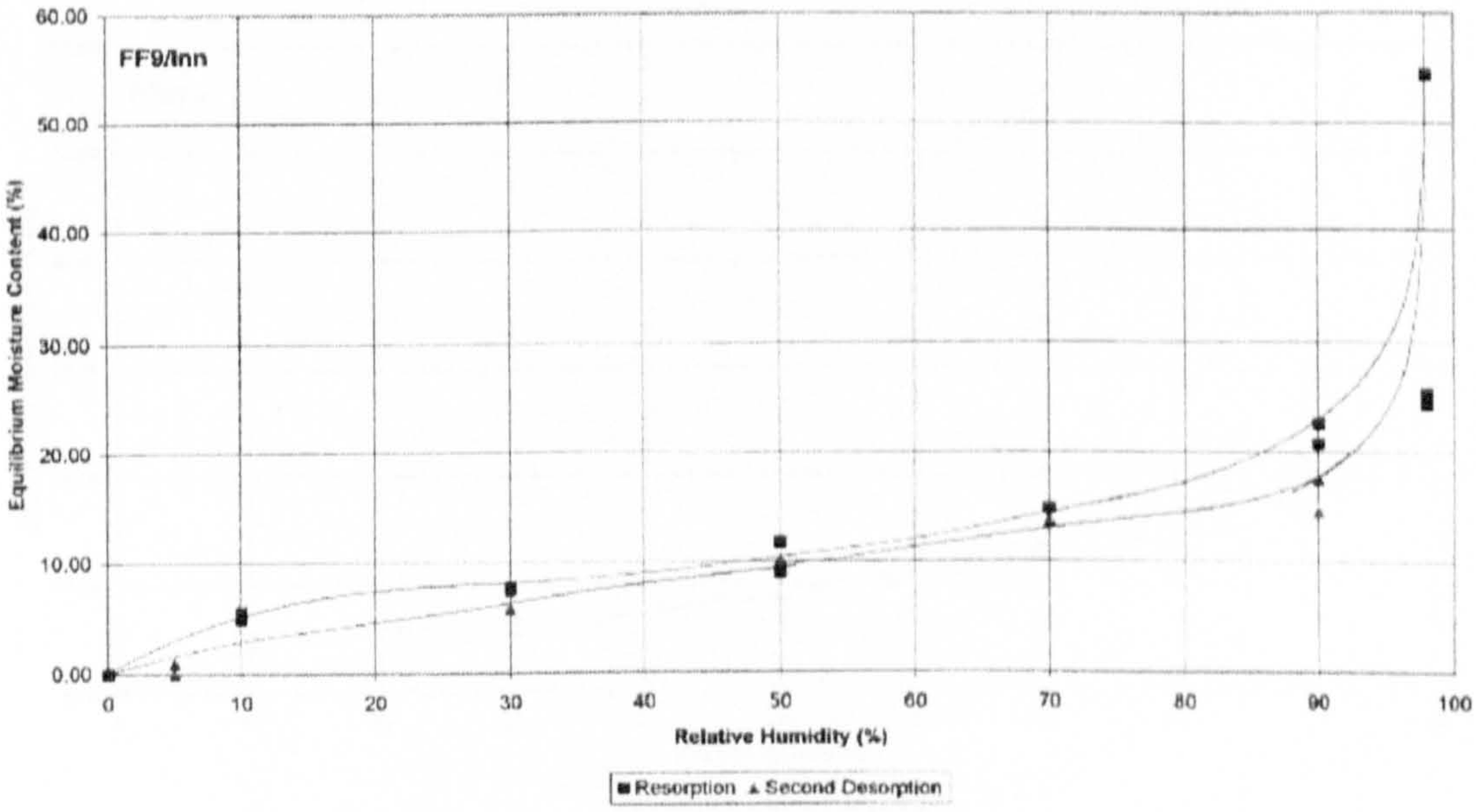


Figure 5.14 **Sorption curves of samples taken from the less-degraded artefacts.**





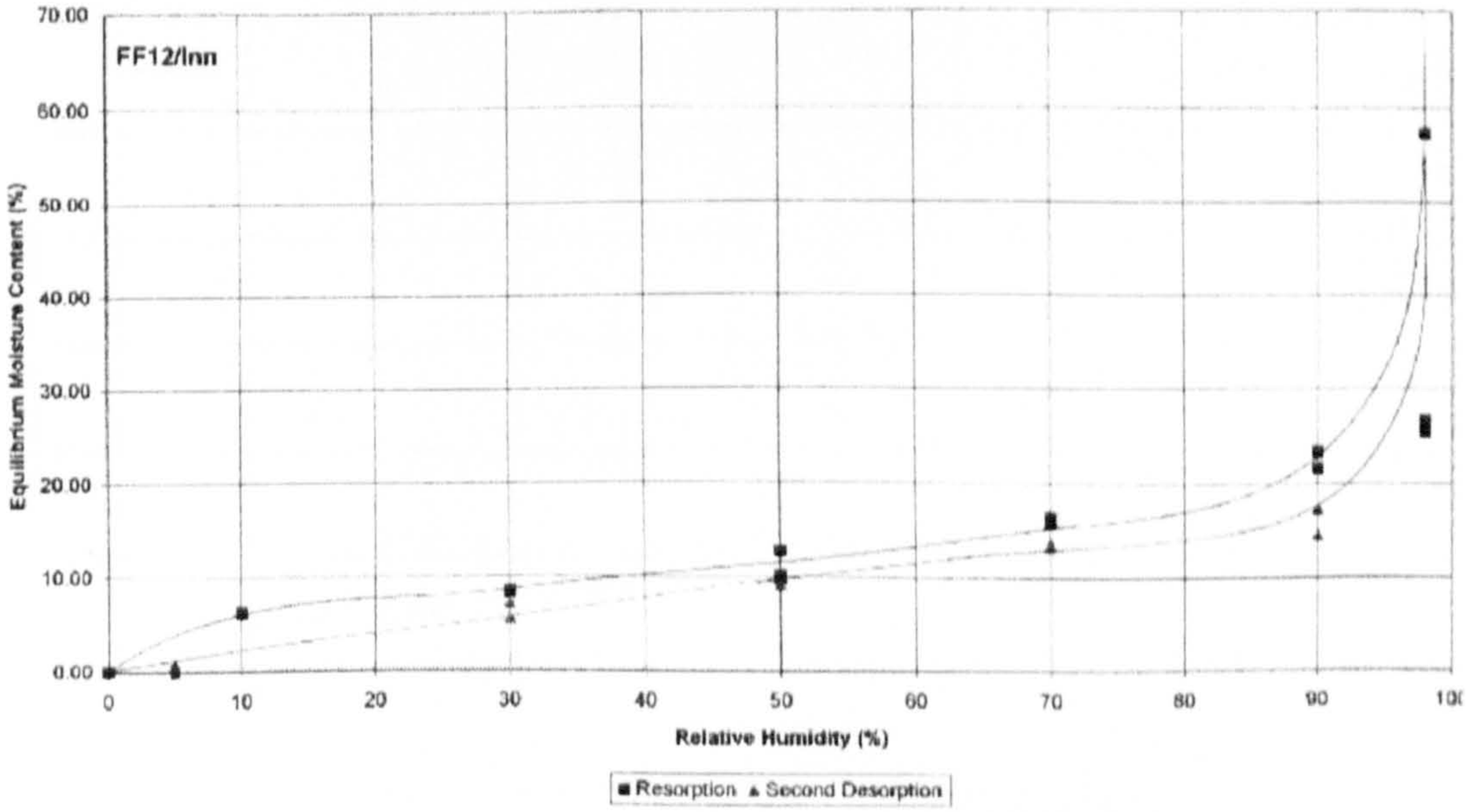
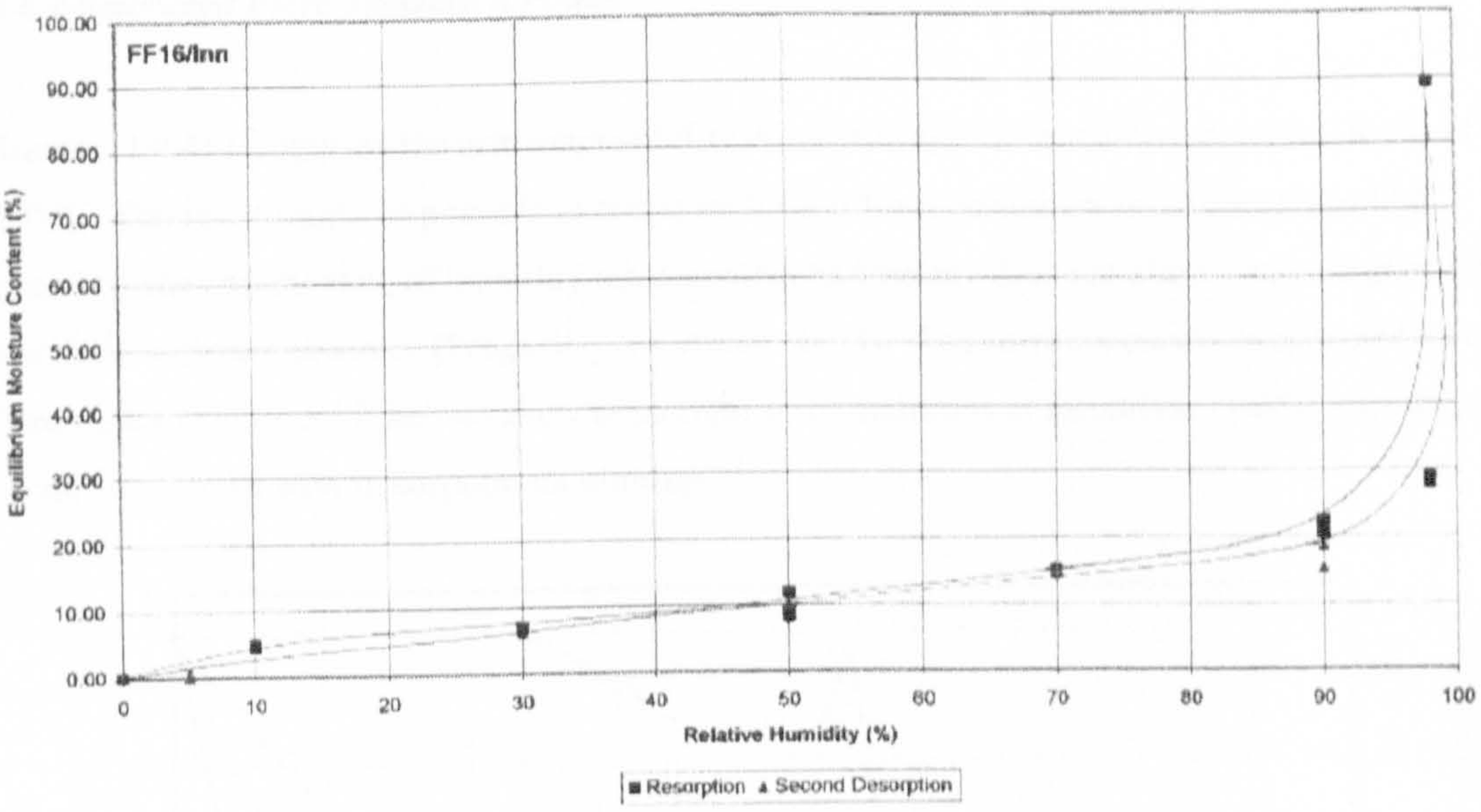
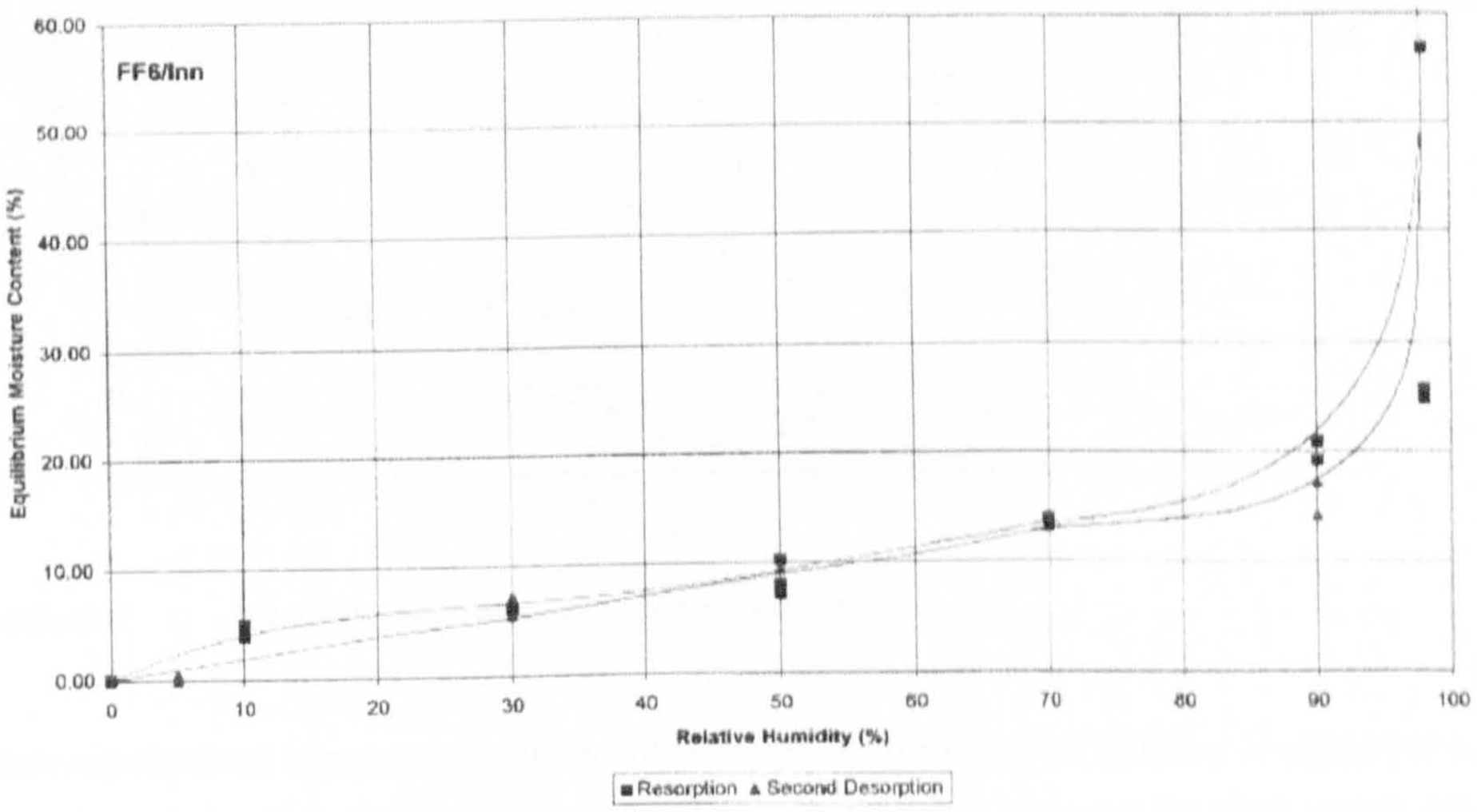


Figure 5.15 **Sorption curves of samples taken from the mid-degraded artefacts.**





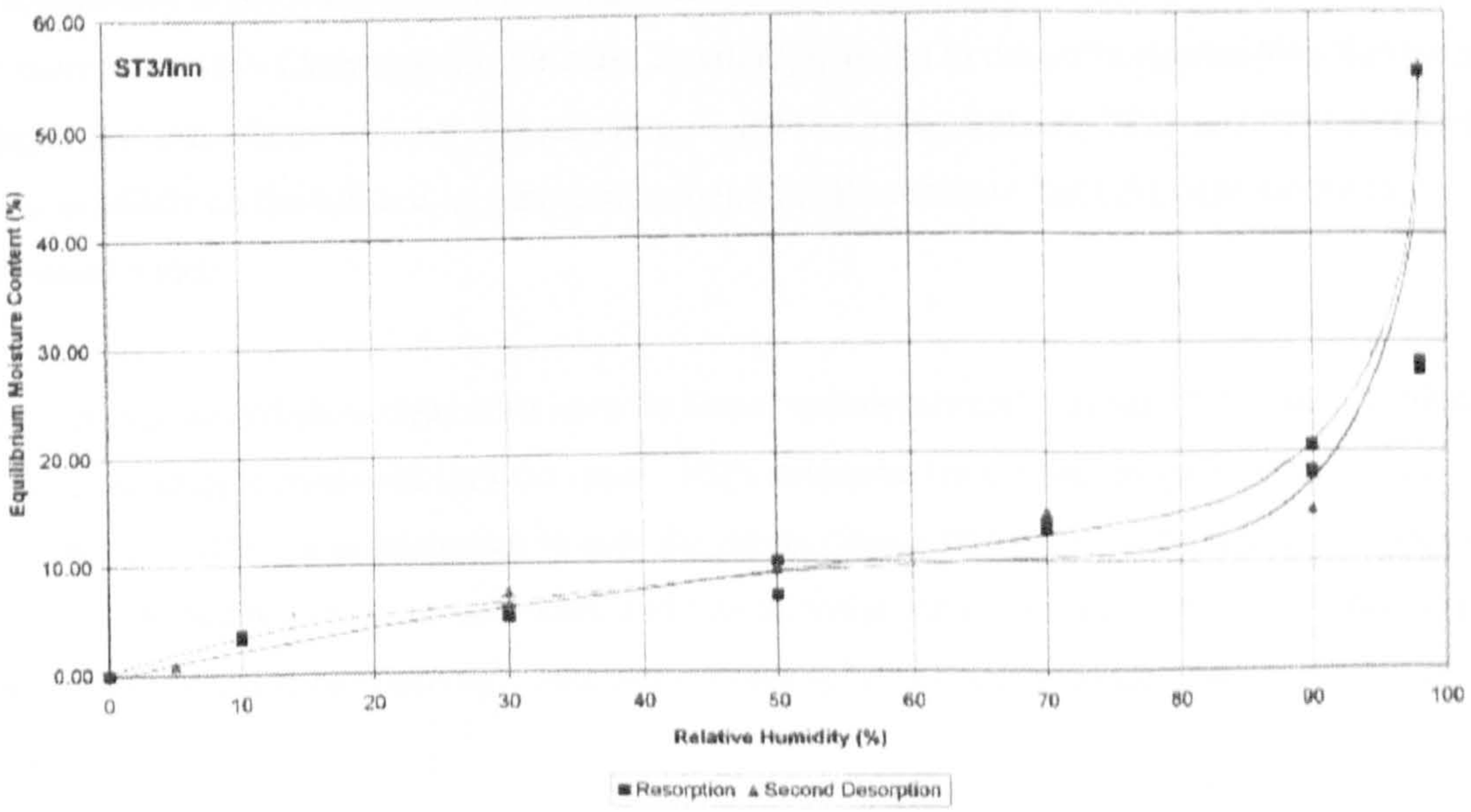


Figure 5.16 **Sorption curves of samples taken from the very-degraded artefacts.**

5.6.1 Estimated Fibre Saturation Points

Stamm (1964) recognised the near-impossibility of measuring FSP at relative humidity levels of 100%. Though it might be possible to create such conditions accurately in an environmental chamber, the current state of humidity measurement technology does not allow us to measure 100% humidity with any accuracy (Pragnall, *pers. comm.* 1995). The sorption curves constructed by C&I Electronics (Figure 5.17, below) show as straight-line conditions at saturation (100%) vapour pressure as are likely to be seen in sorption monitoring.

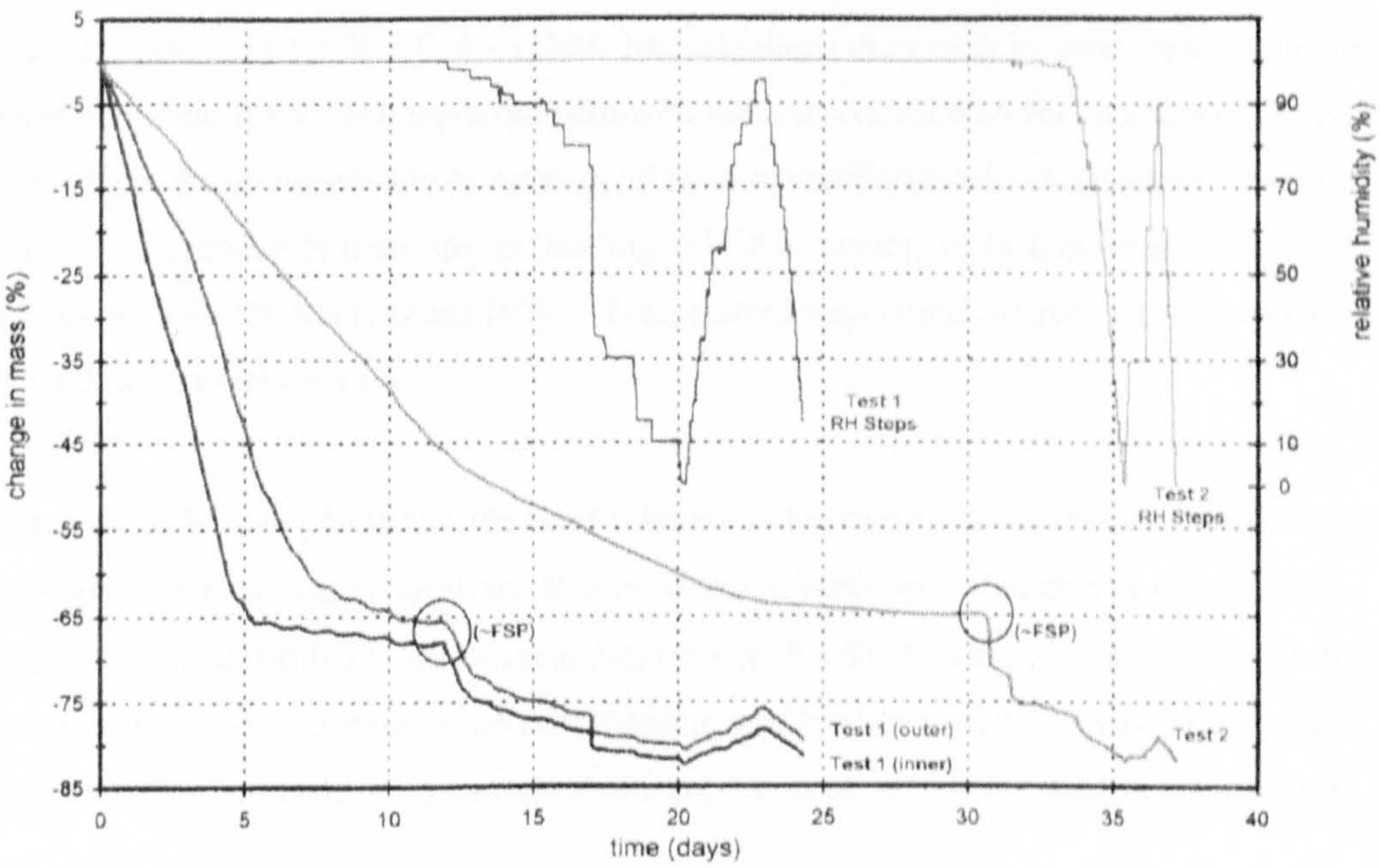


Figure 5.17 Kinetic isotherm measured for sample C4/Inn.

Their experimental apparatus provides totally constant temperature and humidity conditions in a very small control chamber. In all likelihood, the change in mass they measured for plank sample C4/Inn at equilibrium at 100% RH does indeed represent true FSP during initial desorption for that sample, but there is no way of knowing this for sure. Small dips (daily) in the curve approaching this point suggest that some factor or other was affecting results in a cyclic fashion. This may have been vapour pressure effects on the balance, or temperature/humidity fluctuations, but C&I were unable to determine which.

The curves produced show clear differences in slope, with consistently higher EMC values exhibited by the outer sample compared with the inner. FSPs measured for the two samples, however, are very close (within 3-4%). It is interesting to note the abrupt change that occurs at 50% RH, reflecting the important changeover between bulk water and unimolecular water adsorption phases—a change point that has been noted to be relatively consistent between different woods (Skaar 1988; Hartley *et al.* 1992).

The sorption apparatus used for the experiments carried out in this thesis was not designed to the high specifications of C&I's apparatus. In all likelihood, measurements registered for equilibrium at 98% RH represented a humidity significantly higher than this and probably saturation conditions. The humidity probe monitoring conditions registered 100% for a considerable proportion of time. However, because it was impossible to be sure what conditions prevailed, equilibrium moisture content values have been registered at 98%.

The most common approach used to calculate FSP from the sorption isotherm (given the impossibility of measuring it) is extrapolation. Stamm (1971) discusses the advantages and disadvantages of extrapolating curves to 100%. Wadsö (1994) has calculated the probable error value for this method, and rates it as significant. The main problem with the method lies with the fact that the Kelvin equation shows that condensation of water in all sizes of capillaries will cause slight reductions in relative vapour pressure in these spaces, leading to FSP occurring, in fact, at levels much more in accordance with 99.5% RH (Stamm 1971). Temperature fluctuations of even the slightest amount (0.1°C) will also affect the value.

Nevertheless, as Stamm points out, the error inherent in the extrapolation method will have little effect on graphed measures of sorption. It does however, make data collected in this manner unsuitable for calculated fits to sorption models (section 5.6.5). Comfort can be taken from the fact that losses to free and bound water are now thought to take place simultaneously, making the calculation of this point outside the reach of any but the most complex of models (Skaar 1988).

The values for FSP reported for the plank and artefact samples in the tables below were taken directly from measured equilibrium values at 98% RH, with no extrapolation involved. Two extrapolated values (FSP_{EXT}) are reported for the samples E1/Inn (fresh wood) and E2/Inn because it was possible to see from the curves that extrapolation would produce the standard FSP values published for the (undegraded) species (Rijsdijk and Laming 1994). The steepness of the curves recorded for the archaeological samples made it apparent that extrapolation was unlikely to be helpful in these cases. However, because of the more open structure of the degraded woods it seems likely that recorded values represent close to true FSP conditions for this wood.

FSP_{ID} represents FSPs measured during initial desorption (i.e., from waterlogged), while FSP_R represents FSPs measured during resorption from the oven-dry state. Only artefact samples underwent this latter measurement. A third curve of secondary desorption was measured in order that these samples would have hysteresis curves for comparison and calculation.

Sample	E1/ Inn	E2/ Inn	WH1/ Inn	FF15/ Inn	FF9/ Inn	FF12/ Inn	FF16/ Inn	FF6/ Inn	ST3/ Inn
FSP_{ID}	44	43	/	/	/	/	/	/	/
FSP_{R}	26	27	62	89	53	53	88	56	56
FSP_{EXT}	31	32	/	/	/	/	/	/	/

Table 6.2 **FSP values for plank samples.**

Sample	B1/ Inn	B2/ Inn	B3/ Inn	A1/ Out	A2/ Inn	A3/ Inn	C1/ Out	C2/ Inn	C3/ Inn	C4/ Inn	C5/ Inn
FSP_{ID}	68	73	79	78	79	68	75	58	56	59	53
FSP_{R}	48	63	68	61	76	43	77	32	31	29	29
FSP_{EXT}	/	/	/	/	/	/	/	/	/	/	/

Table 6.3 **FSP values for artefact samples.**

The FSP values reported above do not really seem to distinguish the trends we know to exist between these woods of differing levels of degradation. Variation is large between the artefact samples, but the least degraded show very similar FSPs to those of the most degraded artefacts. In the plank, outer and inner samples yield very similar results and there is more variation between the values recorded for the 'B' replicate samples than there is between the end versus middle 'A' samples.

There is no question, however, that values obtained for the fresh and historic oak are very close to published standards, implying that the method used here to determine FSP is not entirely misguided. It is also clear that values measured for the degraded woods are generally and significantly higher than normal values, consistent with reports made for other archaeological woods tested (Barbour and Leney 1982). What is also apparent is that FSP values taken from resorption curves (the standard route of such measurements) quite often yielded results that are much lower (though no more consistent) than those taken from initial desorption from waterlogged material. Certain of those measured were, in fact, very close to the FSP for undegraded oak wood.

The results for archaeological oak woods of varying levels of degradation, collected and summarised by Schniewind (1990) also show little systematic variation. It is unlikely, therefore, that FSP itself as a measure can be used to predict level of loss to cell-wall constituents or be used to complete

calculations of porosity. It appears that these factors can better be appraised by a closer examination of the shape and slope of the entire sorption isotherm.

5.6.2 Shape of Sorption Curves

Examination of the sorption curves in figures 5.14 and 5.16 show that EMC values measured for the degraded archaeological woods are consistently higher than those for the recent undegraded wood, just as Noack (1965), Hoffmann (1981), and Barbour (1983) found with their data. These differences are much more stressed at the higher humidity levels (>70% RH). This is consistent with the fact that the first portion of the curve (Type I Langmuir adsorption) represents the fixed relationship between moisture bonding and cell-wall composition, while the slope of the second portion of the curve depends more on physical conditions in pore spaces (Rijsdijk and Laming 1994). Of course, mass losses to constituents as a result of degradation will also affect this region, because of their effect in reducing the thickness of cell walls, the density etc. The interesting thing is that there ought also to be some change in the slope to the first region of the sorption curve, if constituent ratios have changed, because total numbers of bonding sites ought to have changed along with these changes.

The slopes in each of the three main regions of the sorption isotherm were examined to determine what differences were registered between samples of differing degradation level. Region I represents the monomolecular bound water and covers the range from 10-30% RH; Region II, the polymolecular bound water covering the range from 30-90% RH; and Region III, the capillary free water covering the range above 90% RH (Hartley *et al.* 1992). The information from this examination is summarised below, in Tables 5.4 and 5.5. Numerical data for slope was calculated by dividing the change in EMC (Δy) by the corresponding change in RH (Δx) across the regions described above.

Sample	E1/ Inn	E2/ Inn	WH1/ Inn	FF15/ Inn	FF9/ Inn	FF12/ Inn	FF16/ Inn	FF6/ Inn	ST3/ Inn
Region I	0.15	0.14	0.12	0.12	0.14	0.11	0.12	0.11	0.12
Region II	0.22	0.21	0.26	0.23	0.25	0.25	0.26	0.25	0.25
Region III	0.74	0.98	5.75	7.05	3.18	3.40	6.68	3.59	3.41

Table 5.4 **Range measured within regions of the isotherms for artefact samples.**

Sample	B1/ Inn	B2/ Inn	B3/ Inn	A1/ Out	A2/ Inn	A3/ Inn	C4/ Inn	C4/ Out
Region I	0.12	0.12	0.12	0.14	0.13	0.12	0.14	0.13
Region II	0.25	0.25	0.25	0.24	0.27	0.25	0.24	0.23
Region III	2.76	4.22	4.66	4.24	5.41	4.65	3.93	3.96

Table 5.5 **Range measured within regions of the isotherms for plank samples.**

What this data shows is that this sorption data is disappointing in its inability to show differences in level of constituent loss between samples. The replicate 'B' samples give identical data for the three regions of their isotherms, consistent with good methodology.

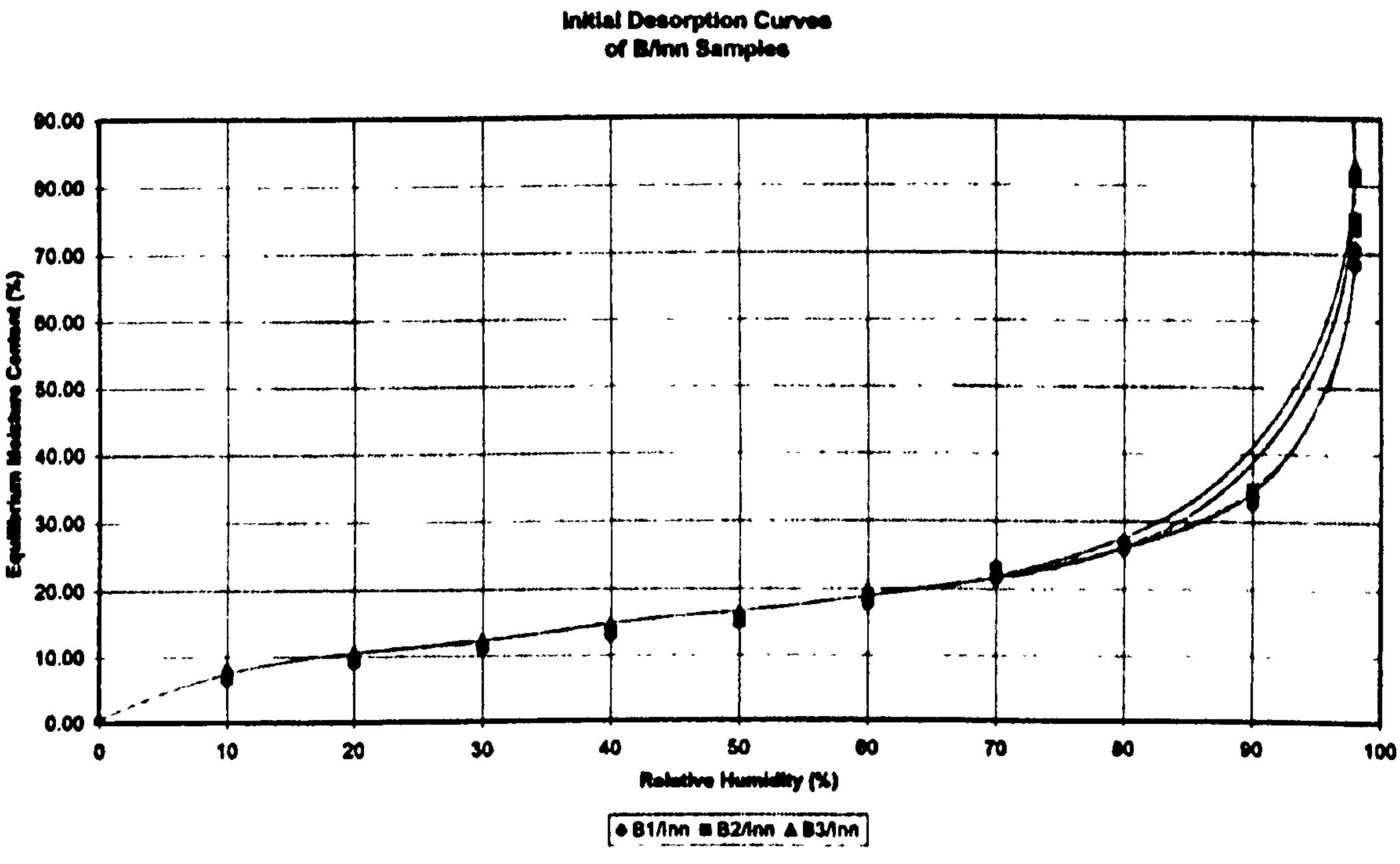


Figure 5.18 **Comparison of initial sorption curves for 'B' samples.**

But the data from the end of plank samples (A1/Out and A3/Inn) is also very close to that of the central plank sample (A2/Inn). The curves recorded for the artefact samples are very flat and featureless, making comparison between zones difficult. Examination of resorption and secondary desorption curves for the plank samples also show this flattening, and the fact that it is absent in the sound recent oak samples is further evidence of the irreversible hysteresis that occurs in degraded samples on drying. It also suggests that, if trends important for interpretation are to be visible, appraisal of sorption data from degraded material should start from its original saturated condition.

In investigating the effects of constituent loss on the shape of the sorption curve, this characteristic of irreversible versus reversible hysteresis becomes significant. These two conditions were defined in Chapter 3. Reversible hysteresis could be thought to be prevalent in degraded wood as well as sound wood if initial desorption and resorption curves coincide below 30% RH, because approximately 30% RH is where completion of unimolecular adsorption is achieved. Differences in curves here (either in height or slope) would suggest that changes in constituent ratios were having an effect on the number of free sites available for bonding in the wood cell walls. There is, in fact, some sign of this in the degraded samples reported here (see Figures 5.15 and 5.16).

As was mentioned in the previous section, approximately 55% RH is the point where irreversible losses to hygroscopicity are registered in both sound and degraded woods, as the permanent loss of sites for polymolecularly bound water takes place. EMCs in this region of the initial desorption curve appear to measure significantly higher in archaeological samples than in undegraded recent samples. And they also measure proportionally lower in this region on the resorption (hysteresis) curve. What also is apparent is that in the more degraded samples there is very little difference between resorption and secondary desorption values, while in the undegraded samples there is slightly more, as if the more degraded the wood is, the more permanent the changes taking place within the cell-wall.

EMCs in the region of 90% RH are similarly of interest. EMC values measured at 90% RH represent the onset of capillary condensation in the fine pores. This is the case for sound recent wood, but Barbour (1983) reported this abrupt increase in slope of the isotherm occurring lower down (at 80% RH) in the degraded woods he measured. When the sorption isotherms of the samples measured in this project are examined, no such decrease in the onset of capillary condensation is recorded, though the slopes recorded for this region are rather steeper in archaeological woods than in recent wood, and in the more degraded archaeological samples in comparison to the better-preserved.

The implication of these basic differences between the curves for degraded wood and those for sound wood (high FSP and more steep hysteresis curves) is that this wood will display much larger movement values in use and much lower dimensional stability (Rijsdijk and Laming 1994) if left untreated.

5.6.3 Comparison with Changes to Constituents Ratios

Limited data are available for the adsorption values of isolated wood components. The composite graph shown below in Figure 5.19 gives a general picture of the differences that exist.

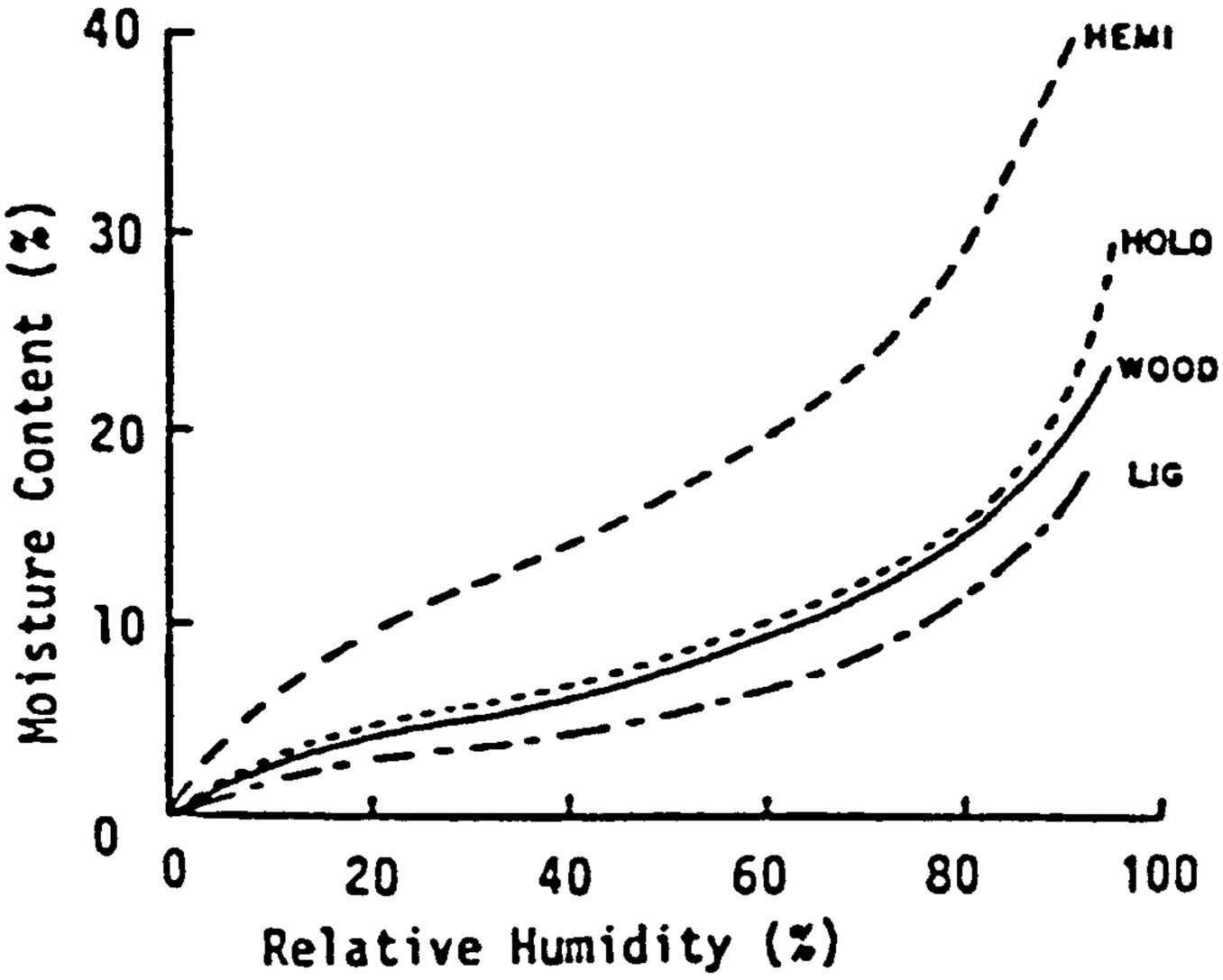


Figure 5.19 **Sorption curves for the three main wood constituents.** **(Rowell, 1990)**

In hardwoods, holocellulose has been found to have considerably higher sorption values than the wood itself. Lignins from hardwoods, however, may have only slightly lower sorption values than the original wood (Stamm 1964) The combined sorption values for the holocellulose and the lignin are often significantly higher than those of the wood itself because of problems in experimentation. In addition, Zabel and Morrell (1992) have noted anomalies in predicted EMC trends arising from preferential attack on amorphous cellulose decreasing the overall moisture-holding capacity of the wood, as well as an absence of change to EMC caused by more uniform removal of constituents. Similarly, alkaline soil conditions, high salt (Rowland *et al.* 1984; Stone and Scallan 1963) or high mineral ash levels (Grethlein 1985) may also affect EMC. Without knowing which of these is the controlling factor in the degradation of an archaeological wood sample, systematic trends can not be drawn between sorption values and changes to bulk constituents.

5.6.4 R/D Ratios

Level of hysteresis should make a useful measure of changes brought about to archaeological woods through degradation. Hysteresis is commonly measured by averaging the ratios of the adsorption to desorption moisture contents at several selected relative humidity points. Results obtained by this method are subject to variation related to the relative vapour pressures at which the ratios are obtained and the limits of accuracy in interpolating moisture contents from the isotherm. Integration methods

combining sorption equations with data calculated for areas under each curve were used by Spalt (1958) to overcome this.

This level of analysis however, relies on choosing between one or other of the available sorption equations (Chapter 3) for this integration, as well as obtaining the physical and fitted constants necessary to complete the calculations. These constants are based on such factors as: calculation of the equilibrium between the fractional humidity and free dissolved water; equilibrium constants of the wood hydrates; equilibrium between the dissolved water and external vapour pressure and between the dissolved water and hydrate water; and the molecular weight of the wood polymers necessary to associate with one molecular weight of water. Spalt (1959) provides these for a selection of hardwoods and softwoods, but not for oak. Certain of them are available in published volumes of physical constants, and Simpson (1973) has carried out the necessary work to provide some others. But the relatively slight research done on oak in comparison to more commercially-valuable timbers (e.g., softwood species, cabinet makers' hardwoods) means that certain of the constants have yet to be measured. Whether these constants can be presumed to apply to degraded wood of the species is another question that has not yet been answered, as far as I know, though the work of Jensen (1997) is certainly aimed in this direction.

Nevertheless, it is quite obvious that accurate, integration corrected, measurement of R/D ratios is, for the time being, out of our grasp. This does not mean that meaningful information can not be obtained by cruder means.

The R/D values presented in Tables 5.6 and 5.7 were calculated by selecting measured values at what can be assumed from previous discussion (section 5.6.3) to be significant equilibrium relative humidities—30%; 50% and 90%—reflecting points of interchange between types of water resident in wood cell walls.

Sample	E1/ Inn	E2/ Inn	WH1/ Inn	FF15/ Inn	FF9/ Inn	FF12/ Inn	FF16/ Inn	FF6/ Inn	ST3/ Inn
30% RH	1.43	1.49	1.04	1.37	1.28	1.51	1.13	1.14	0.91
50% RH	1.05	1.05	1.17	1.36	1.16	1 39	1.20	1.08	1.05
90% RH	1 04	1 06	1.66	1.55	1.56	1.61	1.46	1.47	1.39

Table 5.6 **R/D ratios measured for artefacts.**

Sample	B1/ Inn	B2/ Inn	B3/ Inn	A1/ Out	A2/ Inn	A3/ Inn	C4/ Inn	C4/ Out
30% RH	1.90	1.88	1.94	1.79	1.96	1.88	1.76	1.91
50% RH	1.47	1.42	1.47	1.45	1.53	1.37	1.16	1.21
90% RH	1.59	1.59	1.53	1.46	1.46	1.55	1.21	1.33

Table 5.7 **R/D ratios measured for plank samples.**

A distinct difference shows up between R/D ratio values calculated for degraded archaeological samples in comparison to those for undegraded recent wood. Hysteresis ratios for degraded woods are much decreased in the mid-range (50%). Ratios measured in the low range (30%)—those arising from losses to holocellulose—are also decreased, though to a restricted amount. Ratios measured in the upper range (90%)—arising from physical changes to cell walls—are consistently higher for degraded samples than for those better-preserved.

The latter would appear likely to be the controlling factor affecting the sorption isotherm for degraded waterlogged oak woods.

5.6.5 Calculation of the Void Volume in Wood

An accurate picture of the total void volume present in a sample of wood would be valuable both as a gauge of degradation level and as a means of calculating the maximum possible uptake of bulking chemicals for treatment.

The problems inherent in void volume calculations from data gathered by solvent water sorption techniques have already been thoroughly discussed in Chapter 3 and earlier sections of this chapter (5.3). For more reliable results, data from the sorption isotherm can be applied directly to certain sorption models, more specifically those based on vapour pressure as a driving force (Bramhall 1995). The barriers to making calculations based on sorption models were discussed in section 5.6.4.

Stamm provides the following equation for calculating void volumes directly from FSP values:

$$V_s = 1 - g\left[\left(1/g_w\right) + \left(m_s + m/\rho\right)\right]$$

where: V_s is the solid volume, g is the specific gravity of the wood, and g_w is the cell wall density, m_s is the saturation moisture content, m is the moisture content, and ρ is the density of water.

Equation 5.1 **Calculation of the void volume in wood.** **(Stamm, 1964)**

Since FSP values measured in the present study failed to show consistent relationships with other data measured for these samples (Chapters 6 and 7), and since there is some question about the validity of the average cell-wall density figure of 1.5 g/cm when applied to heavily-degraded woods (see Chapter 6 for discussion), calculation of void volumes was abandoned in favour of other more promising techniques.

5.7 Summary

This chapter has attempted to appraise the value of sorption analysis in providing the conservator with the information he needs (level of degradation, openness of structure to penetration by treatment chemicals, residual hygroscopicity) in order to stabilise archaeological artefacts composed of waterlogged wood.

While the sorption curves produced yielded consistent data for undegraded woods, and the expected trends between archaeological and recent wood, those for degraded woods proved generally unable to show up differences between degraded artefacts. This must be presumed to lie more with the complexity of factors that might influence sorption characteristics in archaeological woods (changes to constituent ratios, ash content, organic residues and physical changes) than to the level of error characteristic to such measurements.

In addition, the sorption method can not be considered a practical one for day-to-day appraisal of archaeological woods. The experiments take a prohibitively long time to carry out (typically 6-12 months per sample). The amount of care and expertise required to yield data specific enough for application to diffusion models suitable for archaeological wood is beyond that which is generally available. Nevertheless, more descriptive data about the relative changes to the holding capacity of woods for differently bound water can be obtained from the results produced using this apparatus.

6 Physical Properties Tests

6.1 Introduction

Determinations of maximum moisture content and density are standard to the appraisal of the physical properties of both modern timbers in use and the condition of archaeological timbers being prepared for treatment. It has been shown that these two measurements are strongly correlated with other important properties, such as wood strength and residual chemical component levels in archaeological wood samples (Hoffmann 1982, Grattan and Mathias 1986; Hedges 1990; Schniewind 1990). Indeed, Hedges (1984) has claimed that where the chemical composition of the wood species under investigation is known, density can be used to estimate the present chemical composition of the archaeological artefact. Barbour (1984) and Jagels (1982) added microscopic examination to the list of standard initial tests for establishing the condition of archaeological wooden artefacts. Both Barbour (1984) and Hoffmann and Jones (1990) showed the potential of fluorescence and polarised light microscopy for providing direct evidence of level of loss to cell-wall constituents.

A number of studies have been carried out to assess the usefulness of moisture content, density, resistance strength, and microscopic examination techniques in establishing an accurate picture of condition in archaeological wood undergoing conservation (Hoffmann 1982; Barbour 1984; Grattan and Mathias 1986; Clarke and Squirrel 1985; Panter and Spriggs 1997; Hoffmann and Jones 1990). All of these workers concluded, to varying degrees, that such measurements were susceptible to high degrees of error and inexactitude, but when studied critically could yield a rough guide to the physical condition of the object—enough to inform the assessment and treatment processes. Despite the problems inherent to density (and to Umax measurements especially), it is claimed that the two have the potential to summarise changes to the chemistry and physical strength of archaeological wood, information that is crucial to predicting the artefact's ability to stand up to drying stresses during treatment.

What the analyses set out in this chapter aim to do is provide further and more systematic appraisal of these techniques for establishing the condition of artefacts and, moreover, to attempt to see whether any direct relation between any of these measurements and wood sorption data can be established. It is sorption data that can tell us what levels of porosity we are dealing with in the object we are attempting to treat. In the process, a rough picture of the relative condition of the test samples will be constructed. Change in condition through the single artefact will be mapped out, and a comparative view of the range of archaeological oak samples that were used in the sorption trials will be built.

6.2 Determination of Moisture Content and Maximum Moisture Content

6.2.1 Principles of Measurement

The actual and maximum water contents give the first impression of the condition of a piece of wood, and thus are the main basis of most classification schemes (Christensen 1970; Jagels 1982; Cook and

Grattan 1991). Hoffmann (1982) established a close link between moisture content and level of deterioration in a piece of wood by providing data that shows the relationship between the volume percentage of cell-wall substance remaining in deteriorated wood, and its maximum water content.

Moisture content determinations are carried out to measure the quantity of free water present in the pore system of a wood. Kollmann and Höckele (1962) made a critical comparison of 15 methods of water content determination applied to several wood species. Four of these methods are covered by ASTM D-2016: titration with water-selective reagent, distillation with water-immiscible solvent, electrical resistance, and oven/vacuum drying. The simplest and most frequently applied method is oven-drying at a standard temperature until constant weight establishes that all free water has evaporated off. Too low a temperature or too short a time fails to reach free water in the innermost pore spaces; too high a temperature or too long in the oven has been observed to cause volatilisation of certain of the cell-wall extractives and may cause fractionation of cellulose (Stamm 1964; Skaar 1988). The TAPPI (T-12) and ASTM standard tests (timber industry measurement standards) control for such errors. These standards are, in fact, designed to measure a quantity known as the *maximum moisture content* (Umax) Maximum moisture content is the maximum amount (%) of water that a wood can hold in its fully-saturated state This is a much more useful measure of the free water in waterlogged samples, as it allows the calculation of the relative percentages of wood volume occupied by cell-wall substance and that made up of void and capillary systems, whereas moisture content will vary depending on the post-excavational storage conditions of the wood. Maximum moisture content determinations thus include an initial step involving vacuum removal of the air present in the void spaces, before weighing, oven drying, and weighing again.

While oven-drying has been the universally-accepted method for determining moisture content, it is slow and destructive. As well, it will give values slightly higher than true moisture content in woods that contain volatile organic extractives (Rijsdijk and Lasing 1994). Though fresh oakwood has considerable levels of these extractives, waterlogged wood has been found to have lost most of its extractive content, and should thus not suffer from this problem. While electrical conductance and resistance methods have been proposed as an alternative (MacLeod *et al* 1994) and are rapid and do not require destruction of the wood, the interpretation of results has tended towards high levels of inaccuracy Generally, these method are limited to use in timbers with moisture contents below 30% (FSP) (Rijsdijk and Lasing 1994)

6.2.2 Problems and Interpretation

Moisture contents reported in the literature can be rather confusing and misleading, since some are calculated as percentage based on waterlogged weight, others on oven-dry weight (Grattan and Mathias 1986). Comparison to the dry wood mass, i.e., the known quantity, is now the standard in wood conservation research as well as in timber science. Archaeological woods from varying contexts have been reported with maximum moisture contents ranging anywhere from 12% to 1000%.

Maximum moisture content (henceforth *Umax*) is meaningless unless related back to the standard for green, unseasoned wood of the same species. Green oakwood (*Quercus robur*) can be expected to have a Umax of 64% thus anything over that percentage may be considered a sign of chemical or physical changes to the wood. Species such as pine have green Umax's of as much as 200%. Because physical (e.g., seasoning shrinkage) and chemical changes to the wood will affect moisture content, the Umax measure is least misleading when taken in context with the density of the sample. This relationship will be investigated in Section 6.3.

The major problem with moisture content determinations is that they are based on gravimetric analysis. Not only is it very difficult to weigh dry samples of wood without instantaneous absorption of moisture, but it is equally difficult to achieve accurate wet weights because of the highly variable amount of water that will tend to cling to sample surfaces (Sjöström 1981). In conjunction with the relatively small sample sizes available for testing (in the perennial juggling between retention of artefact integrity and the needs of science). the resulting highly variable data must be interpreted with general caution.

6.2.3 Experimental

The overall sampling strategy for this body of research has already been described (5.2.1). Moisture content determinations were carried out on transverse-cut sample wafers ranging in original mass from approximately 2-4.5 grams. excepting the *D*-samples from the Roman well plank where the orientation of cut allowed only 0.5 gram samples to be taken. The range of oak artefacts originating from differing contexts were measured, as were samples from the Roman well plank. Sampling recommendations laid out in TAPPI T-11 were followed wherever possible. All weight measurements were made using a four-place Mettler electronic analytical balance.

Procedures laid out in TAPPI T-12 were followed. Initial sample weights were recorded before drawing vacuum, in order that moisture-content levels could be assessed along with maximum moisture contents. Efforts were made to standardise the removal of excess surface water before weighings, by touching one corner to a piece of filter paper for an interval of two seconds. Drying was carried out in a Gallenkamp drying oven, and though it was not fan-assisted, silica gel ensured the thorough removal of all moisture evaporated from the wood samples. Drying took from 24-48 hours to achieve consecutive readings.

Percent moisture content was calculated according to the standard equation:

$$\frac{(WetWeight - OvendryWeight)}{OvendryWeight} \times 100$$

6.2.4 Results and Discussion

SAMPLE	E1/Inn	E2/Inn	A1/Out	A2/Inn	A2/Out	A3/Inn	A3/Out
Cut	*21*	*21*	*1*	*13*	*13*	*27b/out*	*27/in*
Moisture Content %	47	13	436	365	444	441	462
Umax %	83	64	441	365	439	446	462

SAMPLE	C1/Out	C2/Inn	C2/Out	C3/Inn	C3/Out	C4/Inn	C4/Out	C5/Inn	C5/Out
Cut	*4*	*8*	*8*	*12*	*12*	*19*	*19*	*24*	*24*
Moisture Cont. %	450	386	426	372	424	351	407	379	458
Umax %	455	387	430	373	425	353	413	384	464

SAMPLE	B1/Inn	B1/Out	B2/Inn	B2/Out	B3/Inn	B3/Out	D1/Inn	D1/Out	D2/Inn	D2/Out	D3/Inn	D3/Out
Cut	*21*	*21*	*21*	*21*	*21*	*21*	*20*	*20*	*20*	*20*	*20*	*20*
M. C. %	404	475	377	486	373	447	408	537	373	383	430	451
Umax	415	486	383	488	385	456	426	487	379	452	424	445

SAMPLE	WH1 Inn	WH1 Out	FF15 Inn	FF15 Out	FF9 Inn	FF9 Out	FF12 Inn	FF12 Out	FF16 Inn	FF16 Out	FF6 Inn	FF6 Out	ST3 Inn	ST3 Out
M. C. %	/	/	/	/	/	/	/	/	/	/	/	/	/	/
Umax	117	148	322	457	342	721	344	449	361	457	425	880	847	727

Table 6.1 **Moisture content and Umax of Samples**

In Table 1, the artefacts are ordered, lowest inner wood Umax to highest Umax. Consistency within this ordering of the artefacts will be reviewed as the results of other methods of analysis are discussed.

6.2.4.1 Umax and wood classification

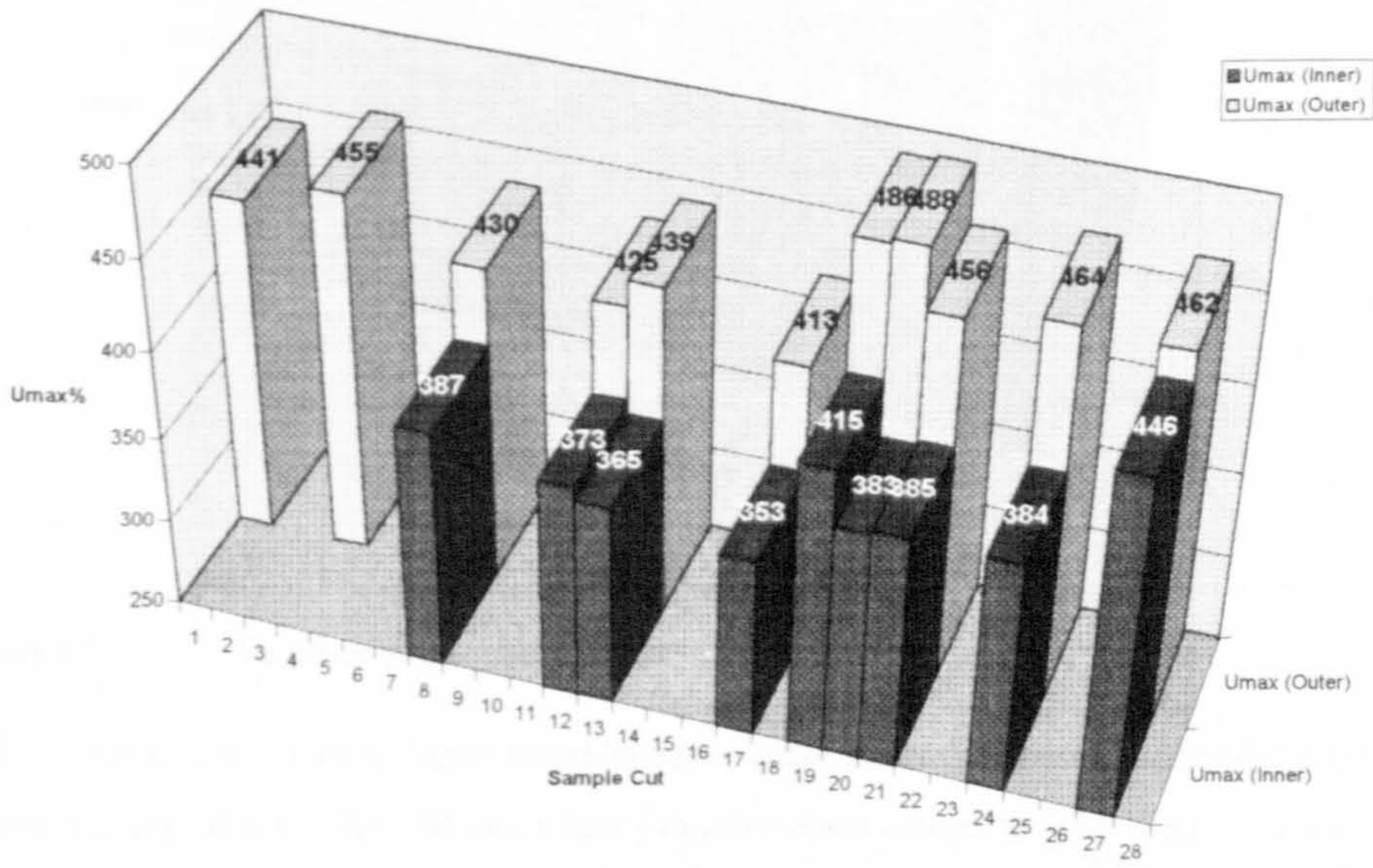


Figure 6.1 Variation in maximum moisture content throughout the Roman plank

Figure 6.1, above, shows that our understanding of the deterioration sequence of the waterlogged wooden artefact holds true, namely that its outer layers will be significantly more deteriorated than its inner core. The Roman well plank analysed in the present study fits into the Umax limits of Christensen's (1970) Class I deterioration level at its outer edges and into Class II in its centre. One end of the artefact seems generally more deteriorated than the other (A3), yet the soundest wood appears to lie somewhere around Cut 19, rather more towards the deteriorated end of the plank but nevertheless reasonably centrally. This information may suggest the orientation of the artefact in the soil, greater deterioration tending to occur to exposed rather than buried surfaces.

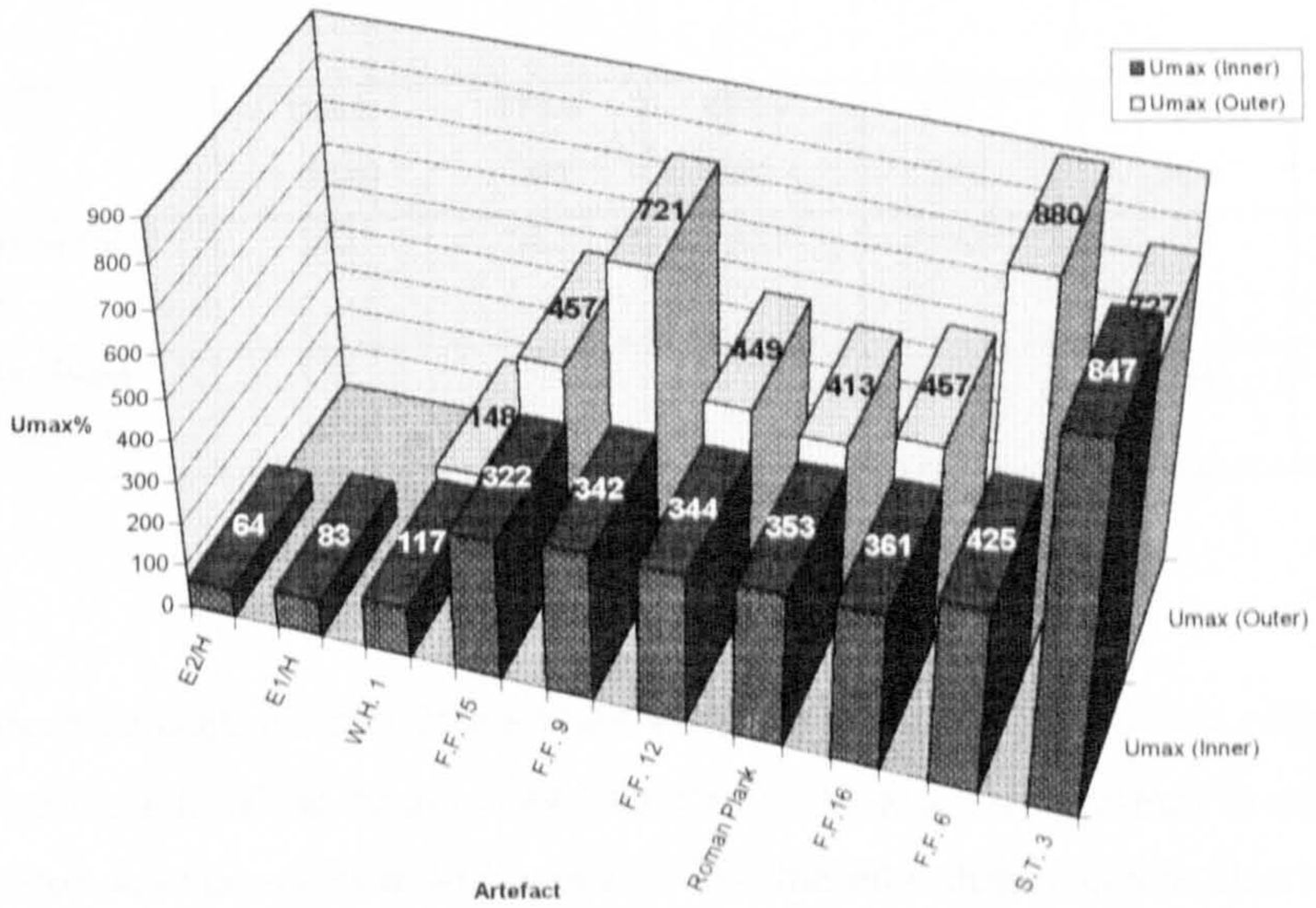


Figure 6.2 Variation in maximum moisture content throughout artefacts

These differences in Umax, inner wood to outer wood, are also observed in the artefacts. All outer wood samples except that of WH1 fit into Class I deterioration category. This suggests that the outer layers of any archaeological wooden artefact, except those in the best of condition (e.g., WH1) would require treatment suitable for very deteriorated, Class I wood, and heavy bulking of these outer layers would have to be carried out accordingly. The larger proportion of inner samples from the range of artefacts tend to group into Class II, with WH1 on one end of the range classified as Class III in deterioration level, and FF6 and ST3 on the other end classified as Class I. Whether other measures can distinguish more precise differences between these Class II samples will be seen in later sections and chapters.

The Umax of outer deteriorated layers can be seen not to vary in any direct fashion with the Umax of the inner layers. Therefore, if the usual practise of taking an average reading from a sample core through the object is followed, there would be a misleading ranking of the artefacts by condition, as can be seen from the average Umax values reported in Table 6.2, below. For example, FF6 would be presumed to fit as well into Class I, despite its very solid, undeteriorated core, as would FF16. These results suggest strongly that increment bore samples rather than the usual adventitious testing of loose surface material may be a requirement for obtaining any meaningful data from this test. As an aid to classifying artefacts for treatment, Umax measurements of both inner and outer wood samples, in conjunction with something like the old pin-probing test could give us a useful idea of the relative proportions of wood in different conditions of deterioration.

SAMPLE	WH1 Inn	FF16 Inn	FF15 Inn	FF12 Inn	FF9 Inn	FF6 Inn	ST3 Inn
Umax from total wood %	100	352	433	453	480	596	731
Umax Av. from data Table 1 %	133	409	390	397	532	653	787

Table 6.2 Comparison of inner and outer wood Umax averages

Umax measurements of outer versus inner wood can be seen to accord well with the drawings taken from cross sections of the samples (see Chapter 5). A great deal of variety in the extent of the deteriorated outer layers, even within one of Christensen's classes, can be clearly seen. This suggests that, despite the large inherent error acknowledged to be associated with this measurement, it can provide a relatively clear picture of the condition of degradation of an artefact, as long as some thought has been put into sampling.

6.2.4.2 Differences between water content and maximum moisture content

Hoffmann (1982) remarks on the possibility of comparing water content with maximum moisture content to reveal incomplete waterlogging and the presence of air in wooden artefacts. The similarity of Umax to moisture content may be a useful indicator of the level of post-excavation stress brought upon the wood, and a predictor for potential problems in its treatment.

The difference between the water content and Umax measured in plank samples proved to be only very slight—at most in the range of 1.5% (see Table 6.3 below). Since this can be presumed to fall well within the error range for such measurements, it might be concluded that the Roman plank was still very thoroughly waterlogged despite the amount of time that had elapsed since its excavation. Initial moisture contents of the other artefacts were not made. It should be noted that Hoffmann (1982) only found large variations between Umax and water content in those of his samples that were in better preservation.

SAMPLE	E1/Inn	E2/Inn	A1/Out	A2/Inn	A2/Out	A3/Inn	A3/Out
Moisture Content%	47	13	436	365	444	441	462
Umax %	83	64	441	365	439	446	462

Table 6.3 Comparison of moisture content to Umax figures in plank samples

6.2.4.3 Reliability of Umax as a measure of deterioration

The significant level of error claimed to be associated with this measure was substantiated by a number of triplicate samples run on both plank and artefacts. Error values ranged from approximately 1.5-6% in

plank samples, with errors as high as 13-20% shown in the 'D' sections where the total sample size was necessarily very restricted.

In general, error values were larger in outer samples and these, too, exhibited less regular trends than those of inner wood. This is most likely associated with the high amount of water held free in the open pores and the difficulty of ensuring that none of it is lost during the weighing process. Such an explanation is further corroborated by the fact that multiple measurements of Umax taken from the range of artefacts showed higher error associated with the more degraded samples.

6.2.4.4 Correlation between Umax results and sorption trends

As reported in Chapter 5, only the most general of correlations was revealed between sorption characteristics and Umax trends in the woods studied. While FSP values measured for degraded woods were in general significantly higher than normal values for undegraded oak wood, regular and consistent differences were not shown between artefacts, reflecting the variety of degradation factors affecting sorption properties. The shape of the isotherms did however reflect Umax data in that the second portion of the isotherm, which illuminates physical conditions extant in pore spaces, showed consistent increase in slope with increase in Umax.

6.3 Determination of Bulk Density and Cell-wall Density

6.3.1 Principles of Measurement

Density is the single most important indicator of strength and chemical integrity in wood. Expressed at its simplest as weight per unit volume, it gives a very clear indication of the drying characteristics of a piece of wood. In general, relatively dense woods such as oak exhibit greater movement under changing moisture contents (Desch, 1981). Density in wood is both a measure of the remaining cell-wall substance and a comment on the proportion of the wood taken up by the pore volume—indeed, this measure may be expressed as the inverse of the pore volume. Very often, the data quoted in the literature is for specific gravity rather than density. This expresses the ratio of the density of the wood to the density of water. This measure is helpful in standardising data for comparison between species. In measuring either of these, it is customary to use oven-dry weight and current volume, as a wood sample's volume, particularly that of waterlogged wood, will vary radically with changes in moisture content (U.S. Forest Products Laboratory, 1989). Above 30% or FSP, however, density has not been found to change with increasing moisture content (U.S. Forest Products Laboratory, 1989). Whether this also holds true for deteriorated archaeological waterlogged woods is a matter for investigation.

Two measures of density are significant to our understanding of the condition of an archaeological wooden artefact: *basic density* and *cell-wall density*. Basic density is the density of the total bulk of the wood and an indicator of its porosity and its remnant strength. Chemical and physical dissolution of the wood will, therefore, affect this measure. Basic density of undeteriorated *Quercus robur* generally falls in the region of 0.63 g/cm^3 (Fengel and Wegener 1984). Cell-wall density, in contrast, is the density of

the cell-wall matrix itself. Cell-wall density varies little between most undeteriorated woods, and is given as an average value of 1.5 g/cm^3 (Rijsdijk and Laming 1994).

Changes to the relative proportions of cell-wall constituents as a consequence of deterioration could be expected to have a noticeable effect on cell-wall density. Barbour's (1984) results, however, apparently showed no significant change to cell-wall density with increasing deterioration. No more recent work has followed to test this conclusion, and without further appraisal it has since been incorporated into a number of methods for the estimation of condition in waterlogged archaeological wood, e.g., PEGCON and density from Umax calculations. It is difficult to envisage a theoretical construct that could support such a statement, in view of the severe and unequal losses to cell-wall polymers that are recorded in chemical analysis of this type of wood. Schniewind (1990), however, seems to acknowledge the probability of change to this measurement. Changes to cell-wall density will receive new appraisal in this chapter.

As mentioned above, density can be calculated from water content where, for one reason or another, the single measurement only is possible. Grattan and Mathias (1986) produce the standard equation for this from the wood-science literature. The equation is based on two assumptions, the first, complete saturation before measurement (i.e., Umax), and the second, a standard unchanging value for cell-wall density. The problem with the second of these assumptions has already been discussed. Nevertheless, relationships between basic density and maximum moisture content will also be tested, and attempts made to use this for appraisal of the results from resistance strength measurements.

6.3.2 Problems with Interpretation

No single, standard method has been developed for determining the density (bulk or cell-wall) of wood. This is because sample size, form, and regularity vary greatly, depending on the circumstances governing their collection, e.g., increment boring, micro-samples, etc. Stamm (1964) describes in detail five methods of measuring density in wood: micrometry of a perfect parallelepiped, water buoyancy displacement, picnometric method, maximum moisture content, and mercury dilatometry. Mention has also been made in the literature of X-radiography as a method (Panshin and de Zeeuw, 1980). The small size and irregular dimensions of archaeological samples commonly available make water buoyancy and picnometric methods those in most common use. Maximum moisture content calculations are less commonly used, since error quoted for this method is in the range of 5% even for sound modern specimens (Stamm 1964).

Accurate and consistent density data are difficult to obtain without very standardised procedures, and become even more difficult when testing deteriorated material such as archaeological wood. Temperature of both wood and water must be constant at the specified standard temperature, and oven-dry weights and volumes must be quoted at some specified moisture content. Some very basic difficulties arise with density measurements of wood, both because of the moisture it contains and because of the inaccessibility of a proportion of its void space. Partly as a result of this, and partly

because of the inherent variation within wood species, a coefficient of variation of about 10 % is considered suitable for describing the variability of density within a single species (U.S. Forest Products Laboratory, 1989).

Because density measurements are gravimetric and rely on accuracy with both wet and dry weighings, they suffer from the same tendency to high error that maximum moisture content does. Additional error will be introduced if the wood sample has originated from an object that has experienced crushing or drying collapse. While density is expected to vary with mass loss during deterioration, increased mineral (ash) content will interfere with this relationship and introduce error (unreliable trends) into evaluation of the density results for the more-deteriorated woods. Further problems arise if density measurements are made on samples that have not undergone full saturation. As with moisture content, density measurements are largely meaningless unless they can be compared against standard values for the species of wood under study.

6.3.3 Experimental

Density measurements were carried out on 1-2 grams of material cut from the test material removed from the artefacts. The picnometric method was chosen over others because of its lesser tendency towards error with small irregular sample material. Stamm's (1964) method and recommendations were followed. Temperature of both wood and water during the measurements was maintained at 23°C. Moisture content quoted for dry weights was assumed to be effectively 0%, as samples were cooled over silica gel and not allowed to re-equilibrate to ambient humidity before weighing. Results are listed in Tables 6.4 and 6.5.

Cell-wall density was calculated using:

$$R_g = \frac{W_d}{W_0 - (W_1 - W_s)} \qquad \textit{(Stamm 1964)}$$

where: W_d is the dry weight, W_0 is the weight of water in the picnometer, and W_1 is the weight of the picnometer, water and wood; and W_s is the weight of the original saturated wood..

Basic density (R_g) figures were obtained by the following calculation:

R_g = *Oven dry weight / waterlogged volume*

from data provided by picnometric measurements.

Density values calculated from maximum moisture content (Umax) used the formula:

$$R_g = \left(\frac{U\max}{100} + \frac{1}{1.5} \right)^{-1} \qquad \textit{(Schniewind 1990)}$$

6.3.4 Results and Discussion

SAMPLE	E1/Inn	E2/Inn	A1/Out	A2/Inn	A2/Out	A3/Inn	A3/Out
Cut	*21*	*21*	*1*	*13*	*13*	*27b/out*	*27/in*
Bulk D. g/cm^3 *	0.672	0.740	0.223	0.235	0.200	0.189	0.199
Bulk D. Umax *	0.668	0.765	0.197	0.231	0.198	0.195	0.189
Cell-wall Density *	1.500	1.480	1.469	1.334	1.308	1.260	1.363

SAMPLE	C1/Out	C2/Inn	C2/Out	C3/Inn	C3/Out	C4/Inn	C4/Out	C5/Inn	C5/Out
Cut	*4*	*8*	*8*	*12*	*12*	*19*	*19*	*24*	*24*
Bulk D. *	0.196	0.214	0.196	0.232	0.204	0.236	0.211	0.227	0.186
Bulk D. Umax *	0.192	0.220	0.201	0.227	0.203	0.238	0.208	0.222	0.189
Cell-wall Density*	1.324	1.269	1.267	1.337	1.306	1.303	1.323	1.337	1.277

Table 6.4 **Density values for plank samples**

SAMPLE	B1/Inn	B1/Out	B2/Inn	B2/Out	B3/Inn	B3/Out	D1/Inn	D1/Out	D2/Inn	D2/Out	D3/Inn	D3/Out
Cut	*21*	*21*	*21*	*21*	*21*	*21*	*20*	*20*	*20*	*20*	*20*	*20*
Bulk D.*	0.196	0.181	0.214	0.189	0.224	0.194	0.191	0.183	0.228	0.194	0.203	0.194
Umax D.	0.208	0.181	0.223	0.180	0.221	0.191	0.203	0.181	0.223	0.194	0.203	0.195
Cell-wall Density	1.231	1.305	1.258	1.354	1.324	1.310	1.228	1.306	1.338	1.299	1.298	1.294

SAMPLE	WH1 Inn	WH1 Out	FF15 Inn	FF15 Out	FF9 Inn	FF9 Out	FF12 Inn	FF12 Out	FF16 Inn	FF16 Out	FF6 Inn	FF6 Out	ST3 Inn	ST3 Out
Bulk D.	0.550	0.460	0.256	0.191	0.246	0.127	0.243	0.194	0.237	0.191	0.204	0.105	0.110	0.126
Bulk D. Umax	0.544	0.466	0.248	0.191	0.245	0.127	0.244	0.194	0.234	0.191	0.204	0.106	0.109	0.126
Cell-wall Density	1.456	1.391	1.314	1.294	1.325	1.266	1.312	1.300	1.334	1.299	1.303	1.259	1.268	1.269

Table 6.5 **Density Measurements for Wood Samples**

6.3.4.1 *Trends in bulk density results*

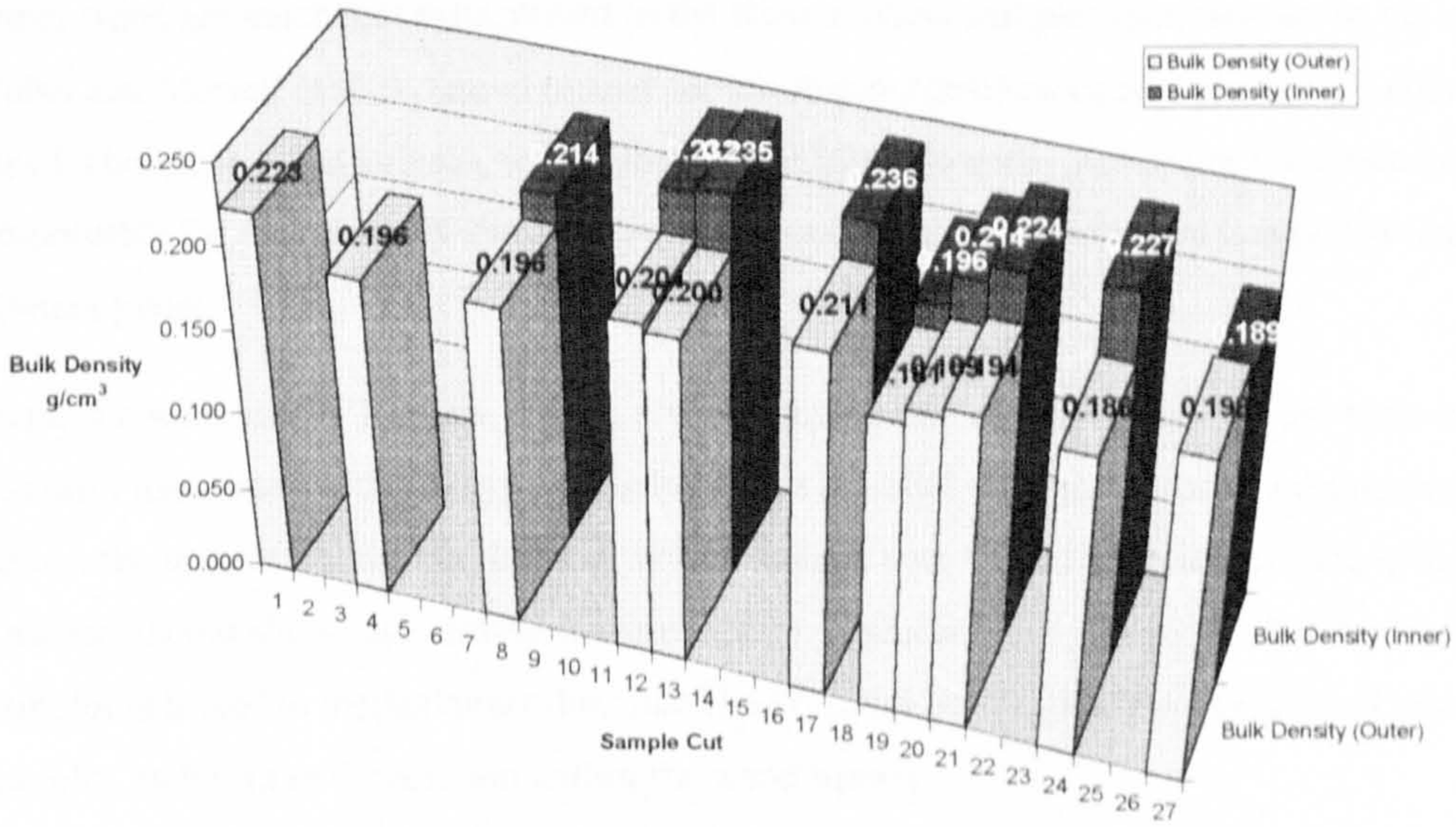


Figure 6.3 **Bulk density values throughout Roman plank**

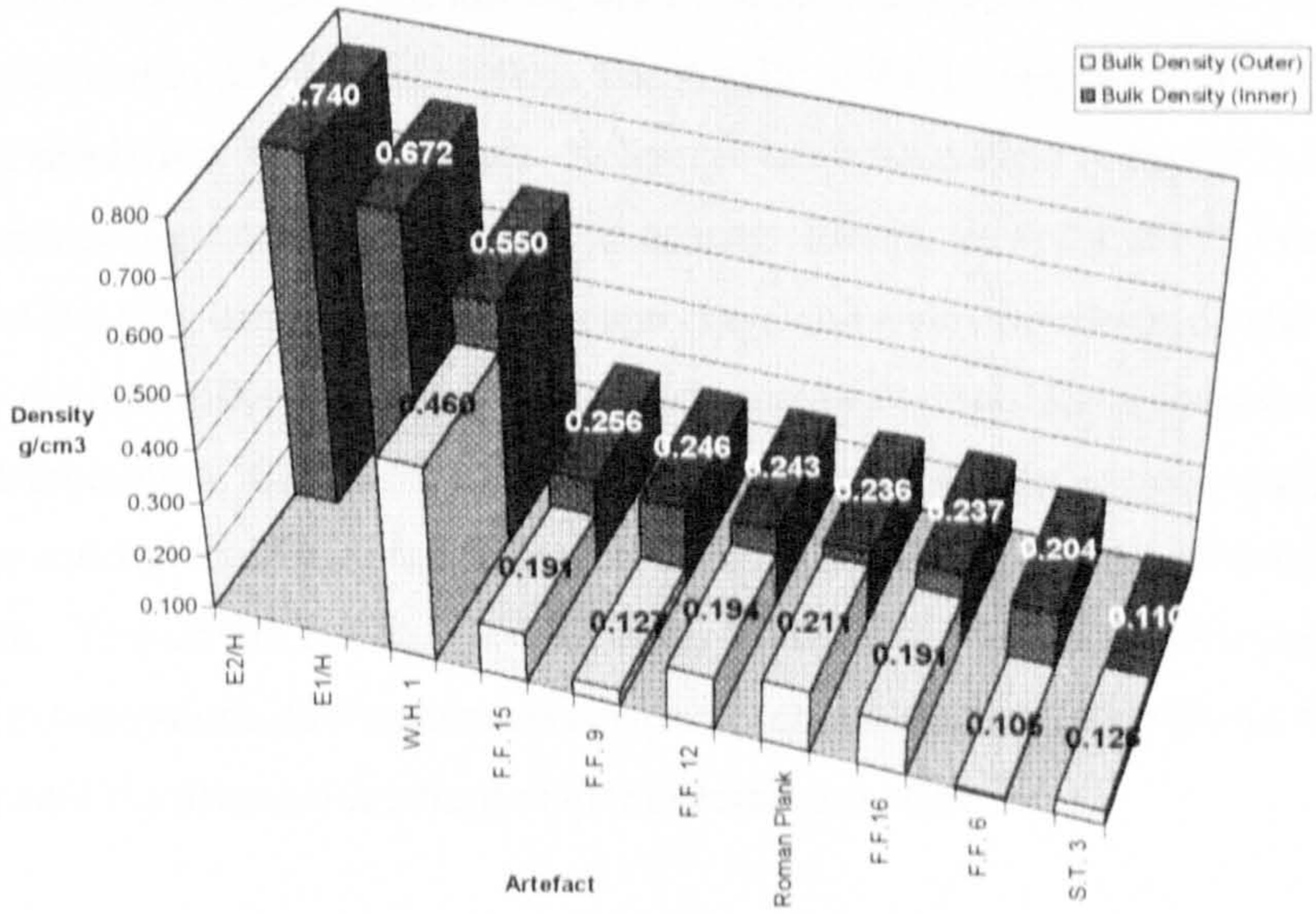


Figure 6.4 **Bulk density values for artefacts**

Results for the bulk density of the Roman plank show roughly the expected trend, with density rising slightly towards the centre of the plank and tapering off toward the more deteriorated edges (Table 6.4; Figure 6.3). This trend occurs also in the third dimension ('D' samples) revealing, as with Umax results, that one side of the plank seems slightly more deteriorated than the other. Outer wood densities are in general significantly lower than inner wood densities, but the tendency towards elevated error in the more deteriorated samples noted already with Umax, appears again here. This is not

surprising, as density measurements also rely heavily on gravimetric accuracy, which is difficult in saturated wood samples. In addition, the effects of elevated ash content characteristic of more degraded wood must be presumed to show their effects here. Differences between density losses in outer wood and inner wood are much less exaggerated in the Roman plank samples than they are in the other artefacts. Zabel and Morrell (1992) remind us that certain microorganisms cause substantial weight loss without much change in wood volume, while others cause losses to both. Actions of these latter might be responsible for the relatively similar density losses shown by sapwood and heartwood samples in the Roman plank.

Replicate samples ('B'), again, did not produce results that concur closely. If this were entirely due to the error associated with this type of analysis, it is doubtful whether the other samples would have shown the regular trends that they did, or that sample cuts 12 and 13, lying in close association with one another, should show such similar density figures. It seems likely, therefore, that the error in these samples is linked to methodology that, like Umax, relies on weight measurements of saturated wood samples, rather than to variation within the wood tissues.

Results from the artefacts (Table 6.5; Figure 6.4) match up well with those for Umax, and thus agree with the relationships charted in Hoffmann (1982) and Grattan and Mathias (1986). The higher bulk density of the historic oak compared to that of the fresh oak is expected, in that it will have been very thoroughly seasoned and have thus lost significant volume compared to weight. These results also agree with those reported in Schniewind (1990). The density of WH1 suggests that this artefact has not deteriorated much from its original state. Reference to its ash content (Chapter 7) does not provide reason for suspecting that this has affected its density. Results for FF9 and FF6 establish with certainty the presence of a very hard inner core, in conjunction with a very deteriorated outer layer. ST3, again, shows very minimal difference between outer and inner layers, and that is consistent with its very advanced deterioration. Comparison of the values for inner and outer samples suggest that deterioration of these two zones proceed together, though at differing rates, while the whole artefact is undergoing deterioration. To a certain extent, this contradicts Hoffmann and Jones' (1990) suggestions, made from microscopic observations, that deterioration virtually completes dissolution of one set of cells before moving forward the deterioration front onto undeteriorated cells.

6.3.4.2 Reliability of bulk density as a measure of deterioration

The relationships revealed by these data suggest that density is perhaps a slightly more useful measure of the condition of waterlogged wood than is Umax. While differences in zonation show up with consistency in both measures, density appears to show a slightly lesser tendency towards gross error, e.g., as evidenced by the 'B' triplicate samples.

Basic densities of plank samples show reductions in density to approximately 30-35% of that normal for oak of this species. Basic densities of artefacts range from approximately 17% to 87% of that normal for oak. Schniewind's (1990) results for a range of archaeological artefacts of *Quercus robur* show a similar spread, but since he compared density results with age rather than Umax, it is not possible to see

whether any consistent correlation between water content and density change can be established from such tests. Neither Hoffmann (1982) nor Hoffmann and Jones (1990) report density with their figures for Umax and chemical analyses. As a result, it is not possible at this point to say with certainty that an artefact's residual density could be predicted from the single measure of Umax.

6.3.4.3 Bulk density calculated from Umax

This can be tested by looking at how closely Umax-calculated bulk density figures match those of measured bulk density.

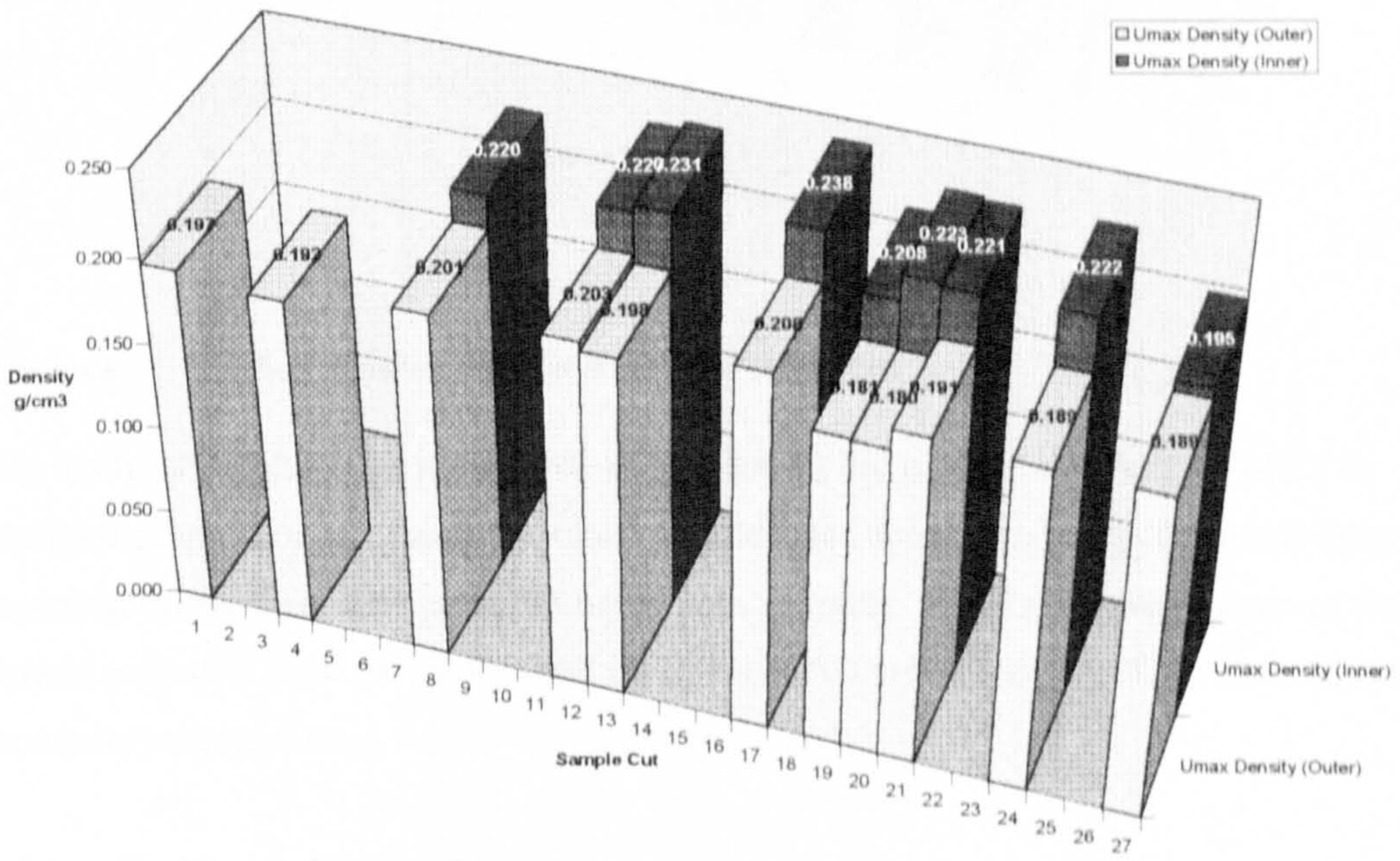


Figure 6.5 Bulk density calculated from Umax (Roman plank samples)

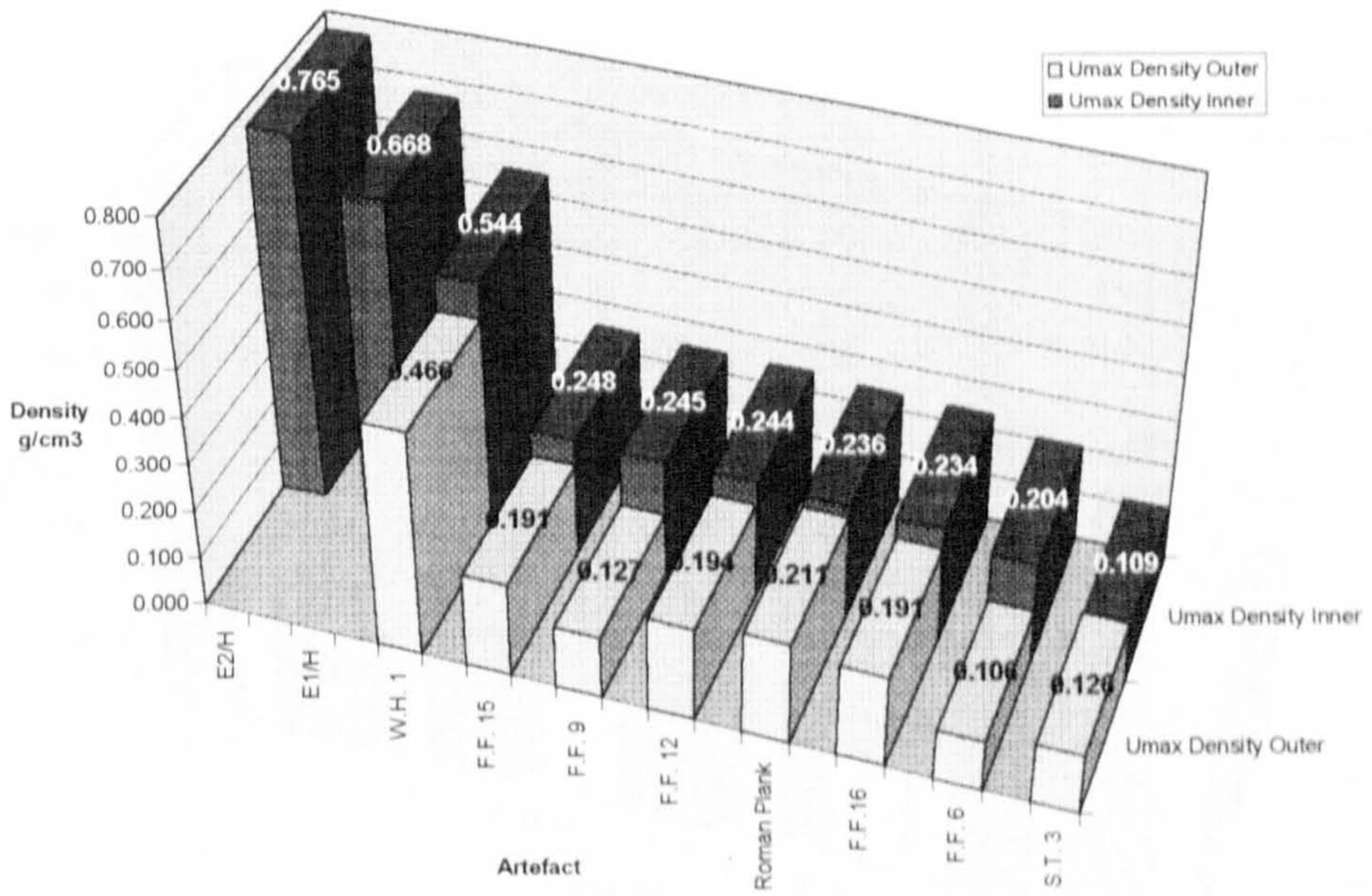


Figure 6.6 **Bulk density calculated from Umax (Artefacts)**

The results above show that basic trends in bulk density are repeated relatively faithfully in Umax-calculated results. Though results from calculated density are generally slightly lower than measured values, most differences fall well within 2% error. Results for better-preserved wood samples deviate more than those for the less well preserved, an occurrence for which it is difficult to find a satisfactory explanation.

6.3.4.4 Trends in cell-wall density

Results for cell-wall density, as shown in the charts below (Figures 6.7 & 6.8), are significantly changed from the average value of 1.5 quoted for all wood species. They range from between 1.480 g/cm^3 for the dry historic wood (E2/H) down to 1.268g/cm^3 for the wood from the Sweet Track (ST3).

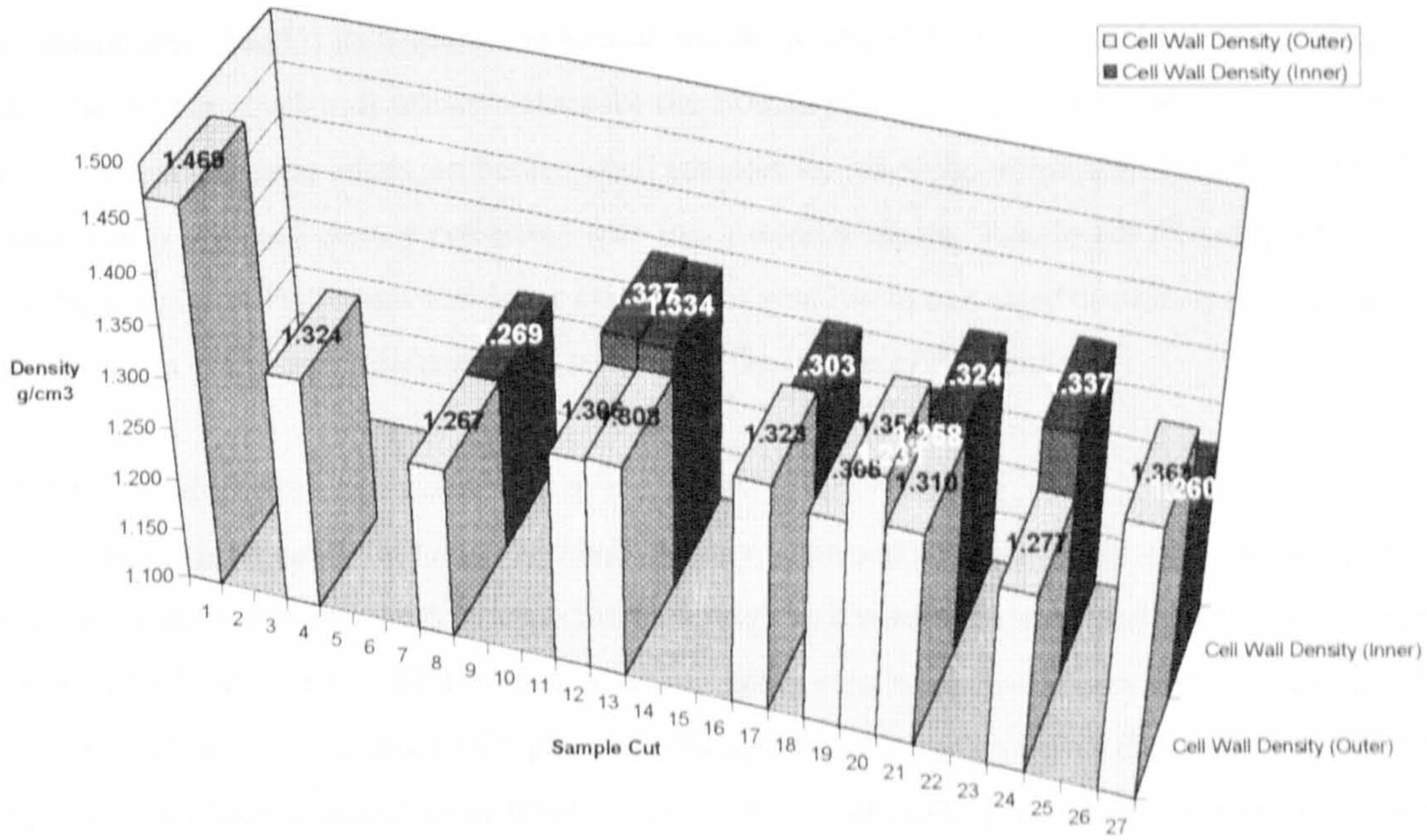


Figure 6.7 **Cell-wall density values throughout Roman plank**

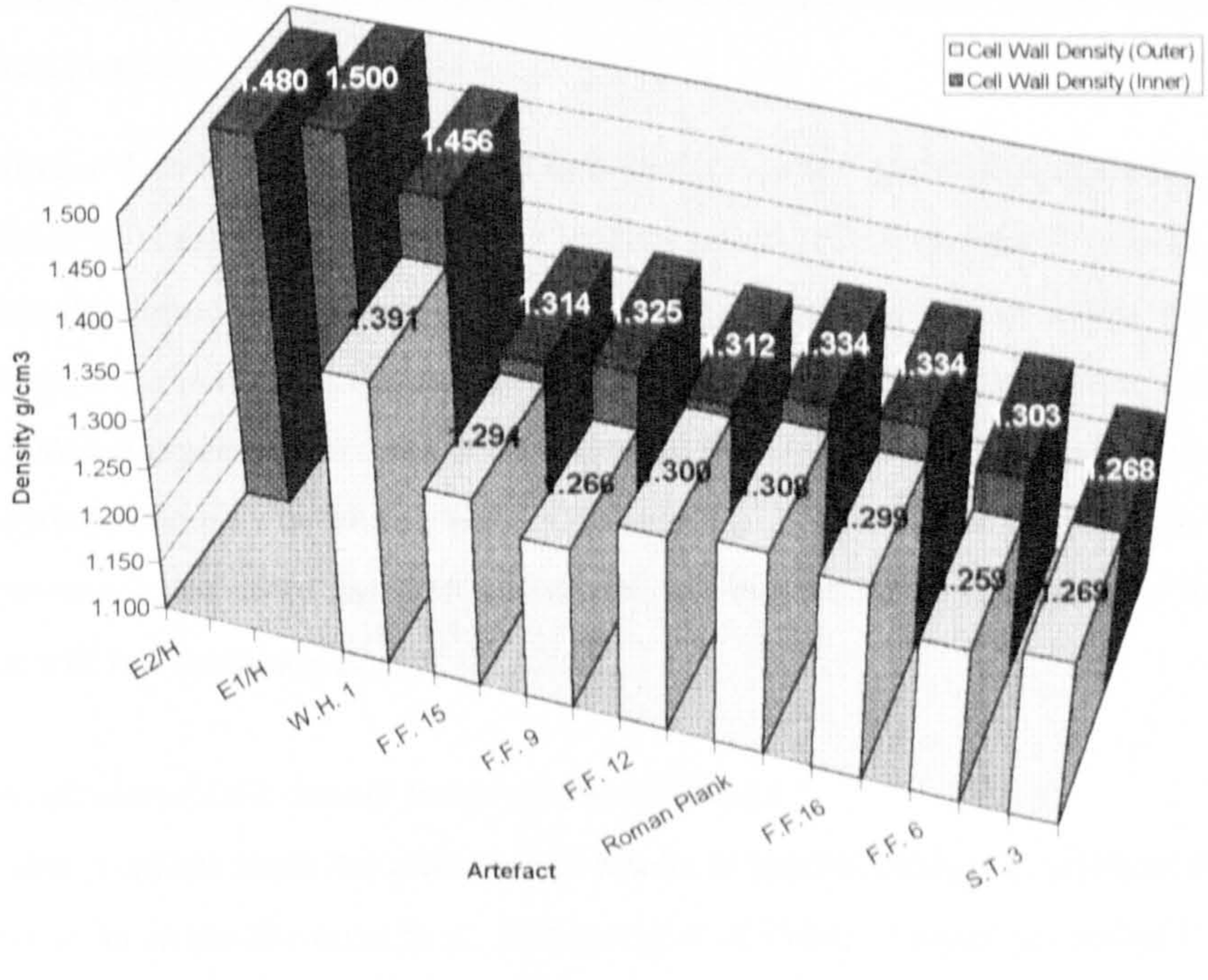


Figure 6.8 **Cell-wall density values for artefacts**

There can be no question that this loss to cell-wall density of up to 16% is significant and probably reflects figures for loss to constituents. Indeed, results reported in Chapter 7 supports this. Losses to cell-wall constituents for ST3 were measured to be 45% and for E2/Inn were 1.4%. The majority of the other artefacts showed losses to cell-wall density of close to 10% where their measured loss to constituents was in the region of 38%. The best-preserved of the archaeological waterlogged samples,

WH1, showed a much-reduced loss of only 3% in cell-wall density that matched well with an 11% loss to constituents. Trends throughout the Roman plank are consistent with both these observations and with Umax data. Cell-wall density values for the Roman plank are generally higher in the plank's centre than at the outer edges, and outer wood samples for all of the woods tested show a generally larger loss to cell-wall density compared with inner wood samples. Results for ST3 support the statement made by Hoffmann and Jones (1990), that zonality in oak wood appears to disappear by the time Umax is 900% and bulk density is reduced to the region of 0.1g/cm^3.

6.3.4.5 Reliability of cell-wall density as a measure of deterioration

As with the data reported for Umax and bulk density, sapwood samples do not show reliable trends, and errors with these sections could be expected to be high as a result of higher and more variable quantities of mineral ash (see 7.3.1). 'D' samples, however, show very consistent results that reflect those of previous analyses. The centre of the plank shows significantly higher cell-wall density than the outer edges, one of which appears in much better condition than the other, perhaps (as mentioned earlier) because of its orientation relative to exposure before burial. Sapwood samples show almost identical losses in cell-wall density. What is interesting is that the dry oak now reveals the small amount of deterioration not shown by bulk density data, where the years of seasoning effects coupled with loss to constituents have resulted in a wood that has undergone shrinkage and thus an increase to its bulk density. This would suggest that cell-wall density is a measure that can reflect quite small changes within or between artefacts.

Though less extreme than losses experienced in bulk density, these figures showing reductions to cell-wall density cannot be considered insignificant. Barbour's own results showed 7% losses, on average. Presumably since this figure is close to the 5% error that might be expected for certain methods of measuring density, it led to his conclusion that no change to cell-wall density could be assumed. Schniewind (1990) anticipates reduction in cell-wall density with degradative loss of carbohydrates from the lignocarbohydrate complex of the cell wall. Grattan (1987) points out, however, that once the cell wall becomes severely eaten away, the internal volume will begin to decrease again and the fibre saturation point will fall correspondingly.

6.3.4.6 Umax-calculated bulk density from experimental data

Schniewind is also sceptical about the relevance of results of level of change to cell-wall density that have appeared thus far in the literature (e.g., Tanaguchi *et al.* 1986). Though accepting the results as meaningful, he does not feel that they would have much effect on, for example, calculations of basic density from Umax. When Umax-calculated density data is recalculated using experimental cell-wall density data from the present study, differences in the values for the resulting basic density were 2%-3%, and all were less than those calculated with the average value of 1.5. Furthermore, results for better-preserved wood samples deviated less than those for the less well preserved, and thus perhaps better reflect our understanding of variables affecting density (e.g., elevated ash content).

However, results from both of these methods can not be considered to be significantly different if estimated levels of error associated with the measurement of Umax and density are taken into account. And since the entire reason behind Umax-calculated bulk density is that it obviates the need for a second measurement, it is difficult to state that accurate cell-wall density figures are helpful in this case.

SAMPLE	WH1 Inn	FF15 Inn	FF9 Inn	FF12 Inn	FF16 Inn	FF6 Inn	ST3 Inn
Umax-calculated Bulk density[1]	0.466	0.191	0.127	0.194	0.191	0.106	0.126
Umax-calculated Bulk density[2]	0.455	0.187	0.125	0.190	0.187	0.104	0.124

Table 6.6 Comparison of Umax-calculated bulk density from measured[2] vs. standard[1] values

6.3.4.7 Correlation between density results and sorption trends

As already discussed in section 6.2.4.4, direct correlation between sorption values such as FSP and density values is not possible. The increase in slope of the second portion of the isotherm which was shown to accompany increased degradation would naturally apply particularly to density results since bulk losses to cell wall constituents have a radical effect on the physical condition of the pore spaces. Discussion in Chapter 5 reiterated the problems associated with use of average cell-wall density values to calculate void volumes.

6.4 Physical Resistance Measurements

6.4.1 Principles of Resistance Strength Measurements

The measurement of mechanical properties is an alternative approach to the assessment of deterioration level in archaeological wood. In modern timbers, the object of such tests is to acquire information on the working qualities of the wood and the amount of moisture held within the tissues; in waterlogged archaeological woods, however, such tests prove themselves by what they can tell about the chemical deterioration of the wood, losses to density, and the artefact's ability to support its own weight in handling. Any appraisal of strength in archaeological material can only be useful where related to other measures of deterioration. Zabel and Morrell (1992) report measurable changes to mechanical properties before the wood has exceeded a 5% loss of constituents. Though the effects of decay on wood strength have been intensively studied for recent timbers (Zabel and Morrell 1992) and for dry context archaeological timbers (Schniewind, 1990), very little data exist on strength values for waterlogged woods. And methods suitable for tackling such deteriorated material tend to be so variable as to make direct comparison of results between studies difficult.

The strength property most sensitive to small variations in decay is toughness or resistance to impact loading (Wilcox, 1978). Reduction in toughness or hardness is a very good gauge of the early stages of

degradation (Zabel and Morrell 1992). This is, coincidentally, also the least destructive of the available methods for evaluating strength in archaeological wood. Two measurement approaches of this strength property have been reported in the archaeological wood conservation literature: the Pilodyn (Clarke and Squirrell 1985) and the Sibert Decay Detecting Drill (Panter and Spriggs 1997). Kazankaya *et al.* (1985) also reported on a related method, though not in detail. All three methods proved relatively reliable in showing a linear relationship between hardness and maximum moisture content, and some correlation between hardness and density over a range of waterlogged samples in different states of degradation. (Figure 2.18)

The Sibert resistance drill was chosen over the others for the present study because of its ability to provide information on variation in deterioration throughout a timber rather than the generalised deterioration value given by the Pilodyn. Although classed as a destructive method of analysis, the damage caused to the surface of the object by the penetration of the drill pin is minimal.

The Sibert Drill produces a graphic representation of the rate of penetration into the wood of a 200 mm-long high-speed probe under constant pressure. The amount of resistance encountered in each centimetre is recorded as a series of lines drawn onto plotting paper on a rotating drum (Panter and Spriggs 1997). It works on the principal of the resistance of wood to an applied load, this load being applied at a known rate (rather than the shock resistance measured by the Pilodyn). This is akin to the impact bending test used in timber analysis. It measures, however, the fracture surface area (the edges of the pin) created by a constant energy source, rather than the amount of energy required to produce a constant fracture. The resistance is dependent on the anatomy of the wood sample, the nature and length of its fibres, its relative density and moisture content, and the type and amount of it extractives (e.g., ash). Of these, direction of sampling and moisture content in particular have been found to influence depth of pin penetration in modern timbers. With waterlogged material, however, moisture content is less influential, except in marginally-deteriorated samples (Schniewind 1990). Since orientation is important, direction of sampling must be stated for results to be meaningful.

The main drawback to the Sibert Resistance Drill is in quantifying its data. Though original developmental research produced an equation correlating average number of bands per centimetre and bulk density, this relationship could not be established in tests carried out on waterlogged timbers (Gabby 1993; Panter and Spriggs 1997). Nevertheless, its traced profiles yielded clear views of sequential levels of resistance progressing through an artefact/timber.

6.4.2 Problems with Interpretation

Getting meaningful results from strength testing of archaeological waterlogged woods is very difficult. Uneven decay is recognised to affect results (Zabel and Morrell 1992). Pockets of degradation produce failure zones that can magnify strength losses in small areas of the cell-wall or wood tissues. In addition, when only smaller specimens are available for testing, accuracy has been found to be variable.

Measures of toughness (e.g., impact resistance) are, however, the most reliable of the strength measures with such sample material, and the values attained are comparable.

It is not unusual for archaeological woods to show significantly lower strength properties than recent wood, without any accompanying reduction in density (Schniewind, 1990; Kommert 1981). This seems particularly the case with the more highly deteriorated oak woods. Kommert suggested that this implied deterioration without mass loss. Schniewind's (1990) data collected for maximum crushing strength, static bending strength and stiffness of waterlogged wood illustrated that strength losses appear not to be directly proportional to mass losses, though cell-wall density figures indicate that degradation of the quality of the remaining substance (e.g., lignin) is taking place. Zabel and Morrell (1992) believe elevated ash contents to be partially responsible for this, and also cite decay mechanisms such as brown-rots and soft-rots, which have the tendency to create relatively large strength losses before much loss in mass has taken place. More completely degraded wood tends to show little difference in the degree of strength loss resulting from different mechanisms of polysaccharide dissolution. Certain very high levels of impact bending strength reported for archaeological timbers are thought to be due to increases in plasticity related to changes to the loss of crystalline cell-wall constituents in relation to amorphous plastic ones (Hoffmann, 1986; Jagels *et al.* 1988). Average residual impact bending strength of archaeological waterlogged wood tends to lie in the region of 68%.

6.4.3 Experimental

Test drillings using the Sibert Resistance Drill were carried out on a limited subsection of sequential samples from the Roman well plank and from each of the individual archaeological artefacts from Flag Fen and Somerset Levels. Samples chosen from the well plank were those from whom sufficient material remained to produce meaningful results from drilling. Sample size was on average 15 cm (length, sapwood to pith) by 3 cm (depth, thickness of plank) by 2-3 cm (width, along plank). Artefact samples comprised whole remains of the artefact. Samples were clamped lightly in a table mounted vice, only enough to prevent slippage during the drilling process. All samples were tested in the water-saturated condition. Measurements were taken in triplicate from the three principle orientations of wood (see Figure 6.9, following page).

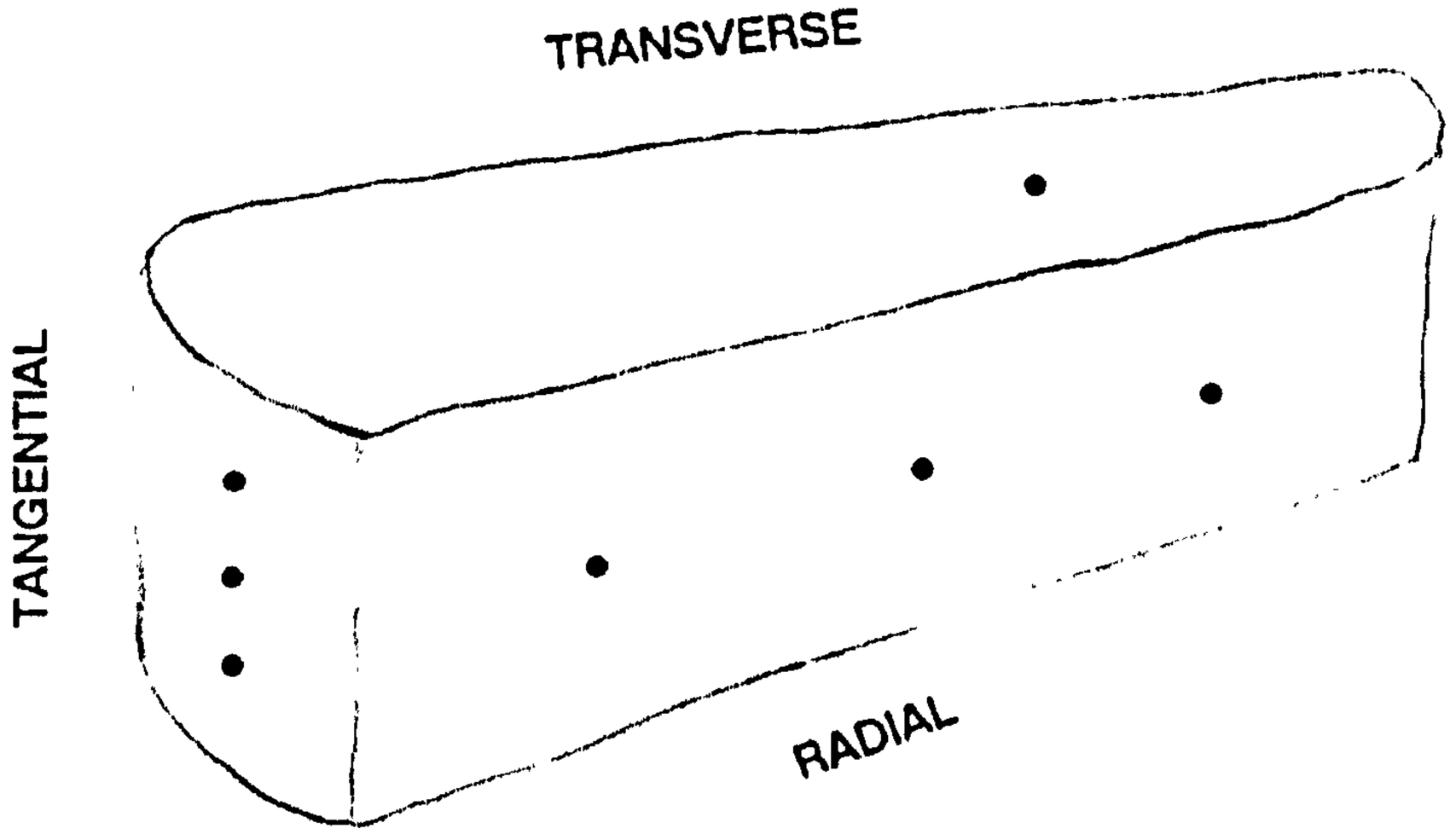


Figure 6.9 **Orientation of drillings taken from artefacts**

Results tabulated in Table 6.8 originate from radial measures only, as the data for this best avoided problems of large error introduced by wood structure, and also showed most clearly the change in resistance between outer layers of the artefact and inner core material. Results express averages obtained from the triplicate measurements. Average lines per centimetre were obtained, where possible, by counting the number of lines in each centimetre division of the plotting paper and averaging the results. Areas considered to represent outer and inner layers of the artefact are differentiated on the tracings in Figure 6.10. Where lines per centimetre became particularly sparse, average lines per centimetre was calculated from the average slope of the line.

Bulk density for each of the samples was calculated from the data from drill tracings using the following equation:

$$D = \frac{\sqrt[3]{B_{cm} + 0.1}}{10.855}$$ *(after Gabby 1993)*

where: ***D*** **is the density in g/cm^3, And** B_{cm} **is the number of bands per centimetre.**

6.4.4 Results and Discussion

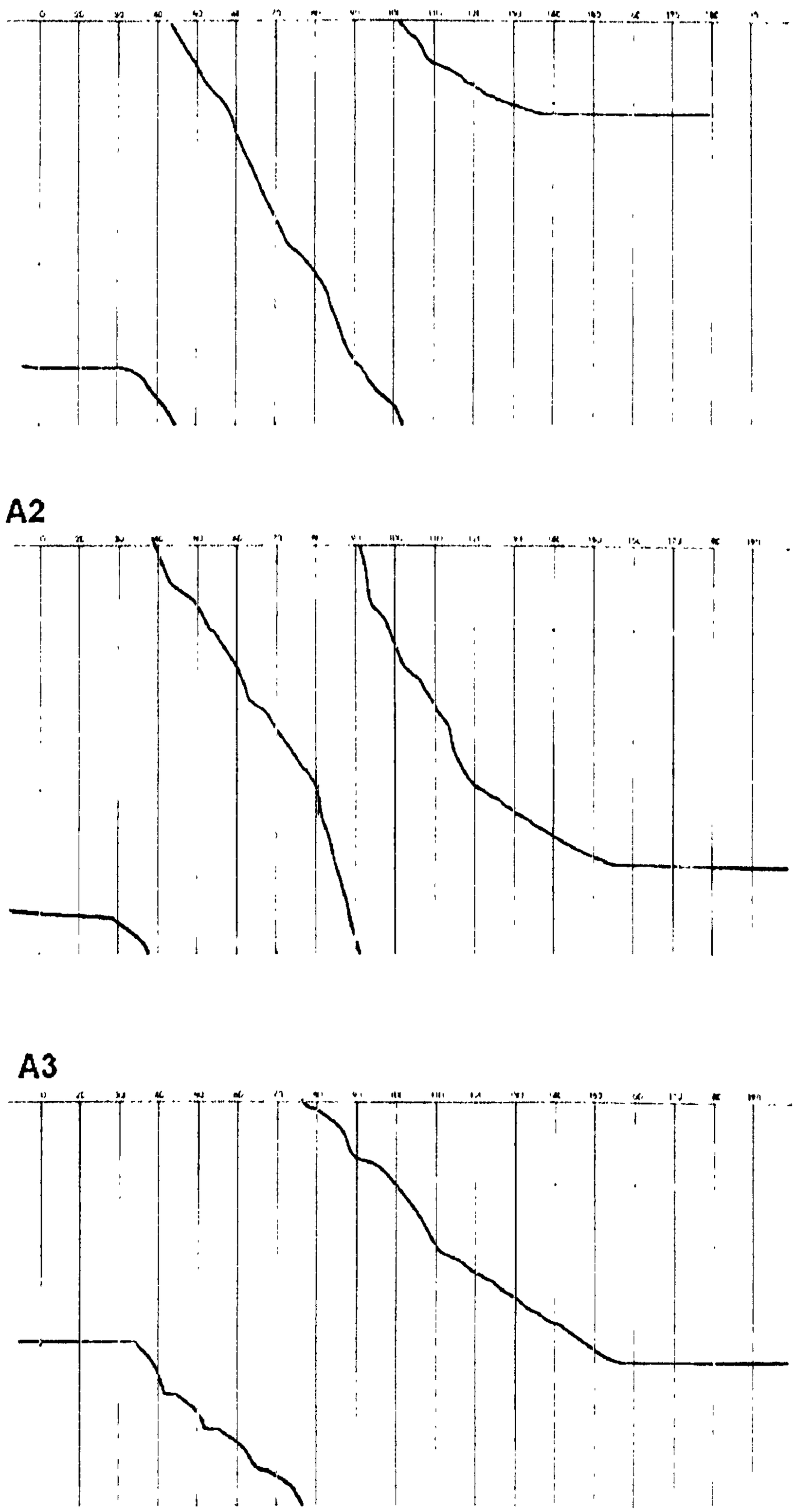
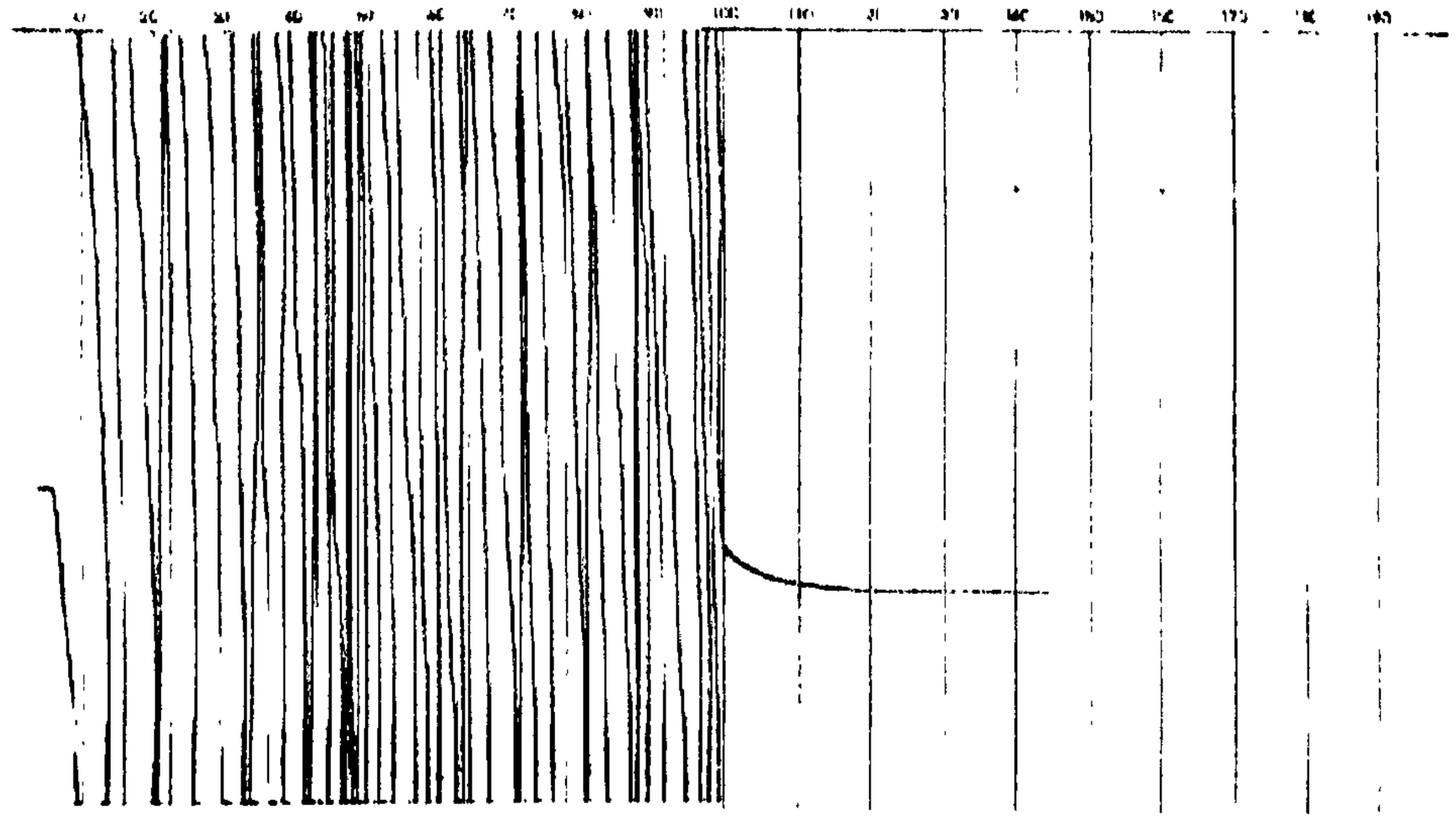
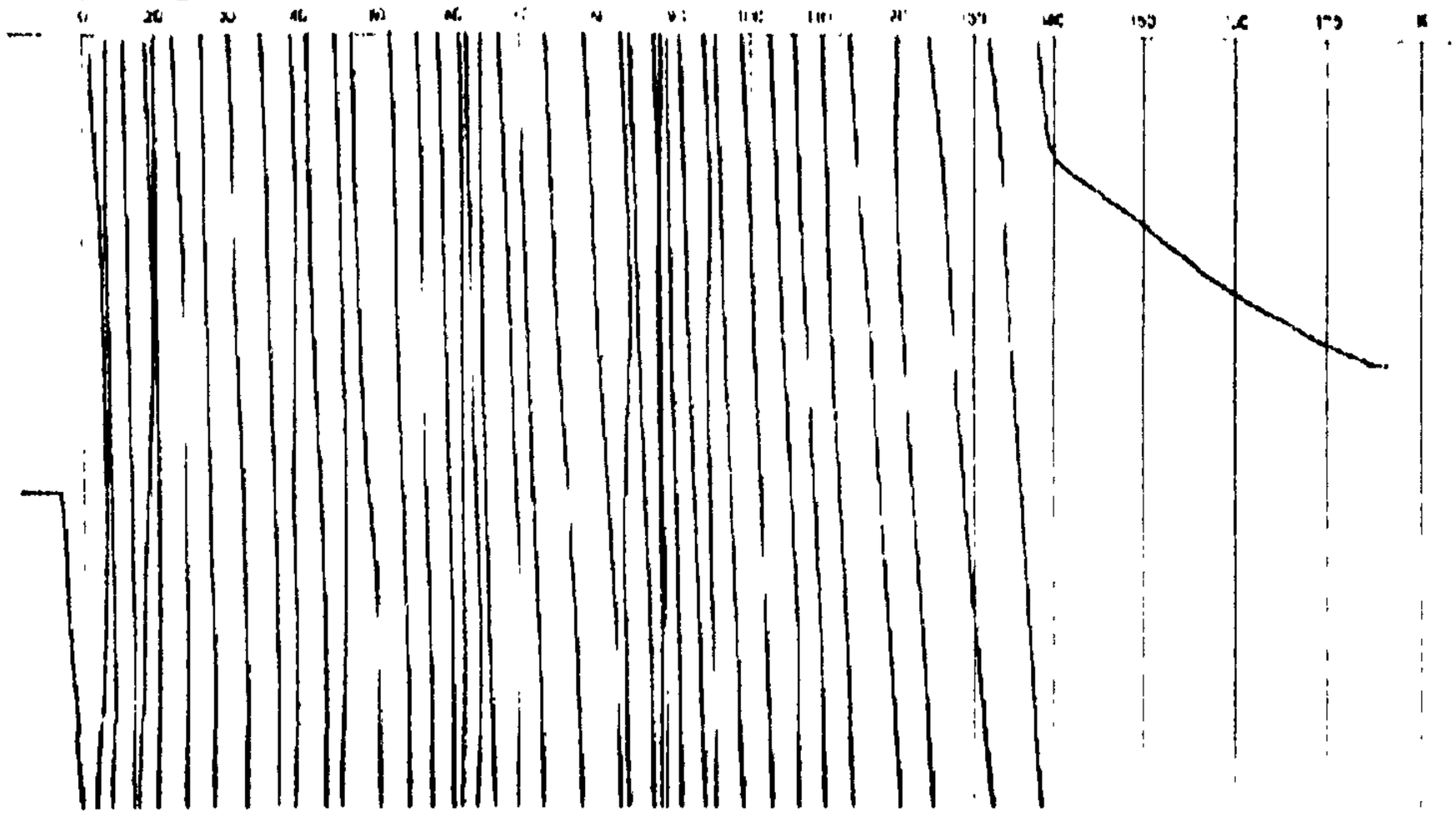


Figure 6.10 **Sibert drill tracings from ends and centre of Roman plank**

E1 (Radial)



E1 (Longitudinal)



WH1

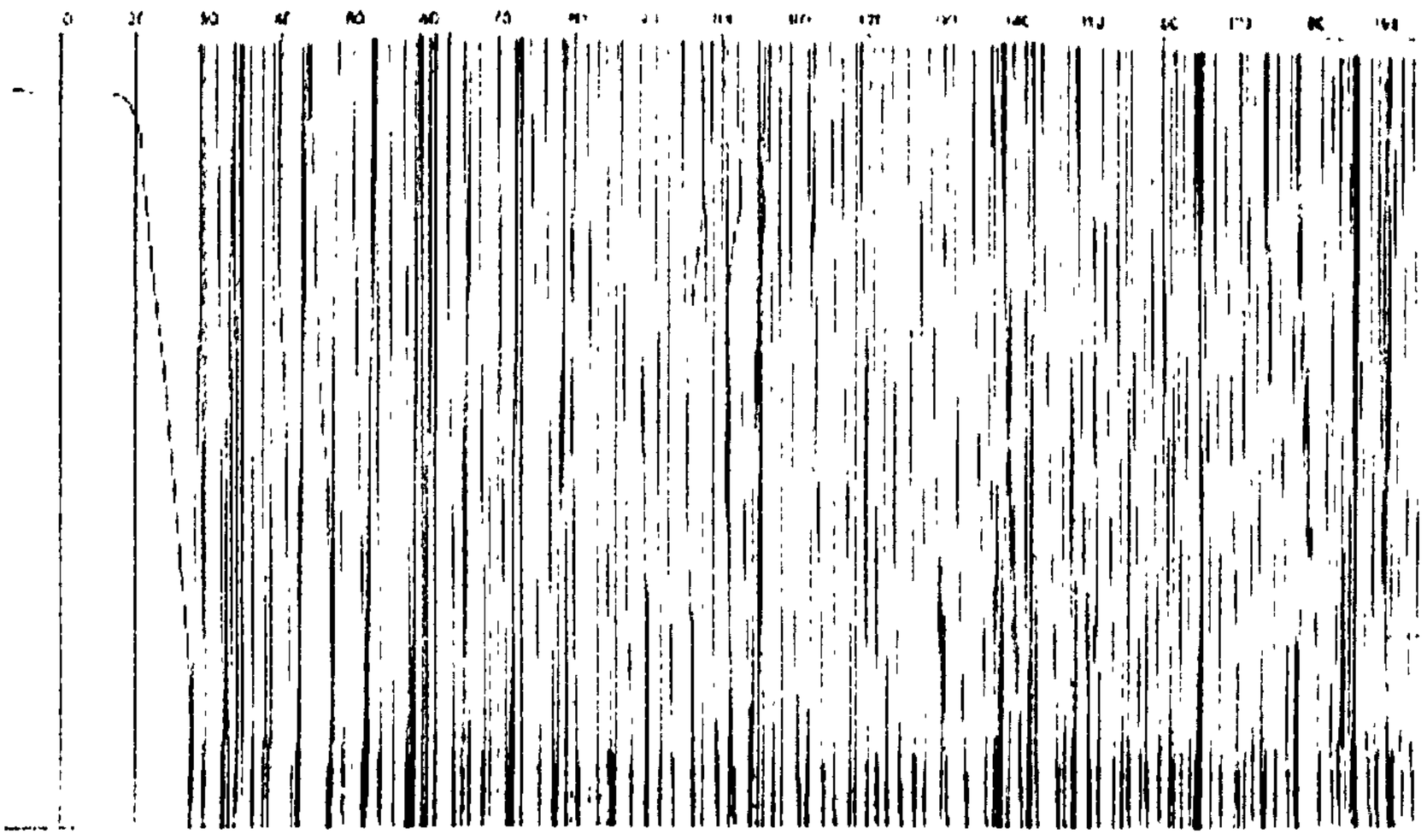
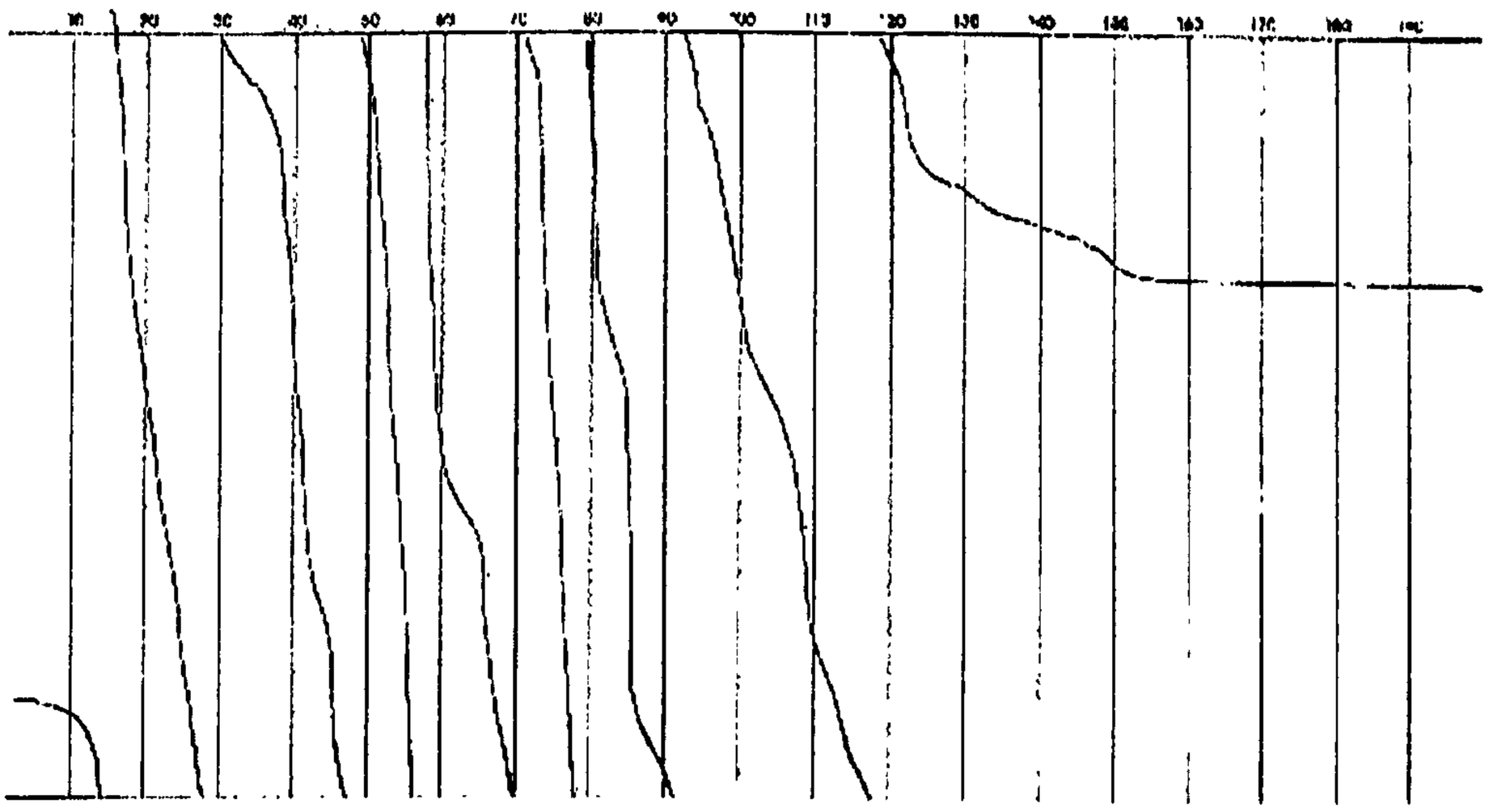
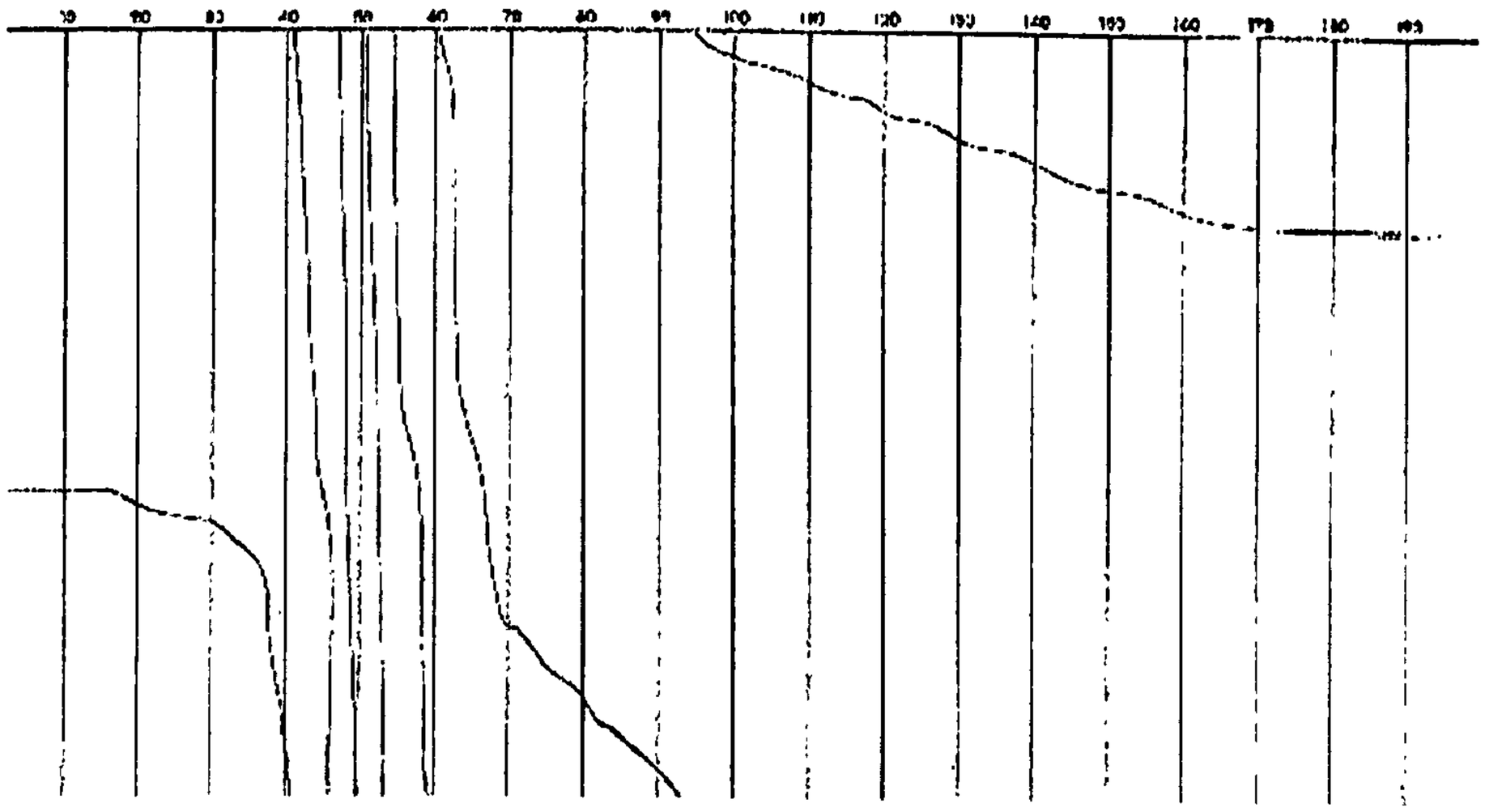


Figure 6.11 **Sibert drill tracings from fresh oak and WH1**

FF15



FF9



FF12

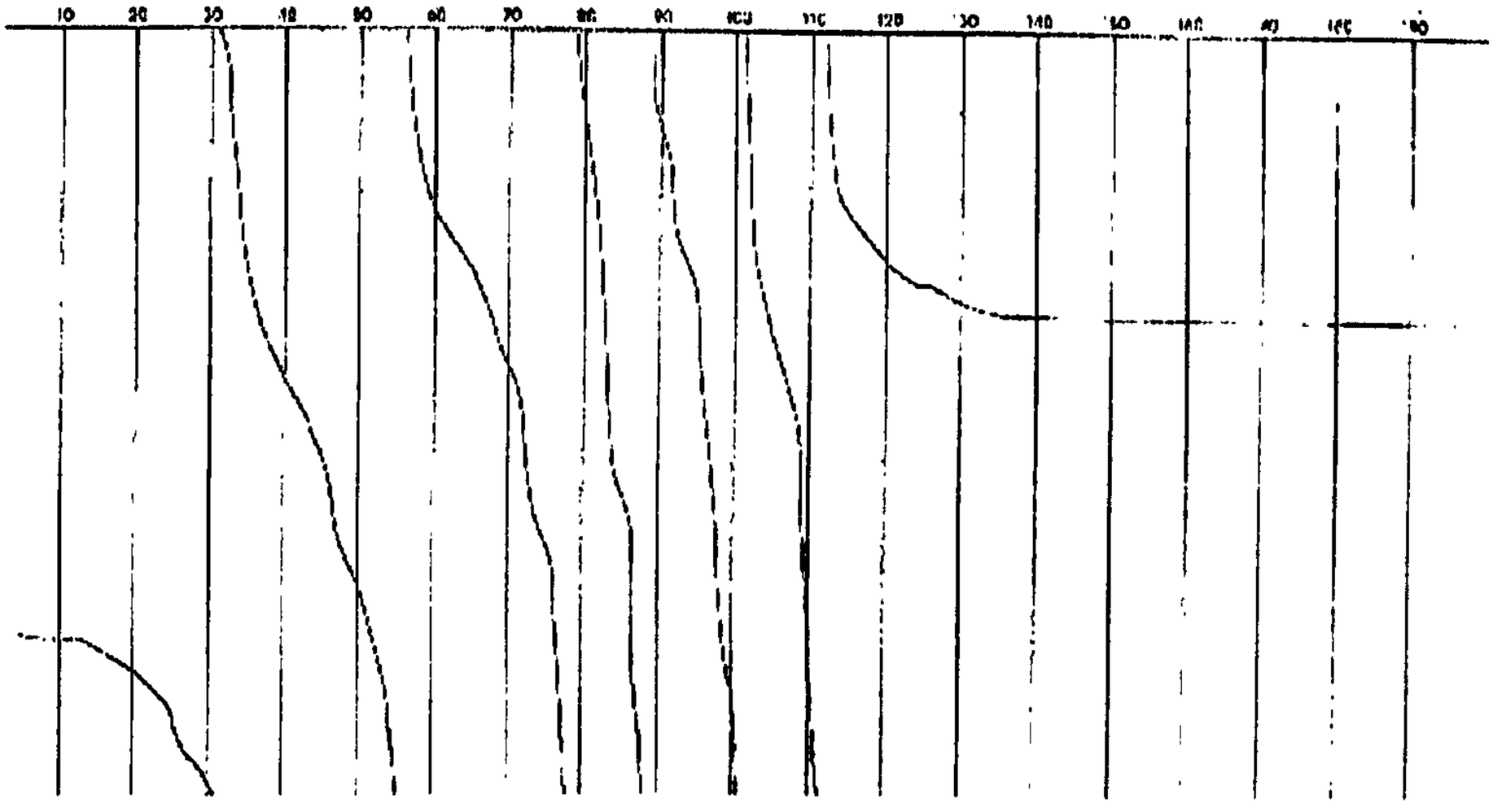


Figure 6.12 **Sibert drill tracings from less deteriorated artefacts**

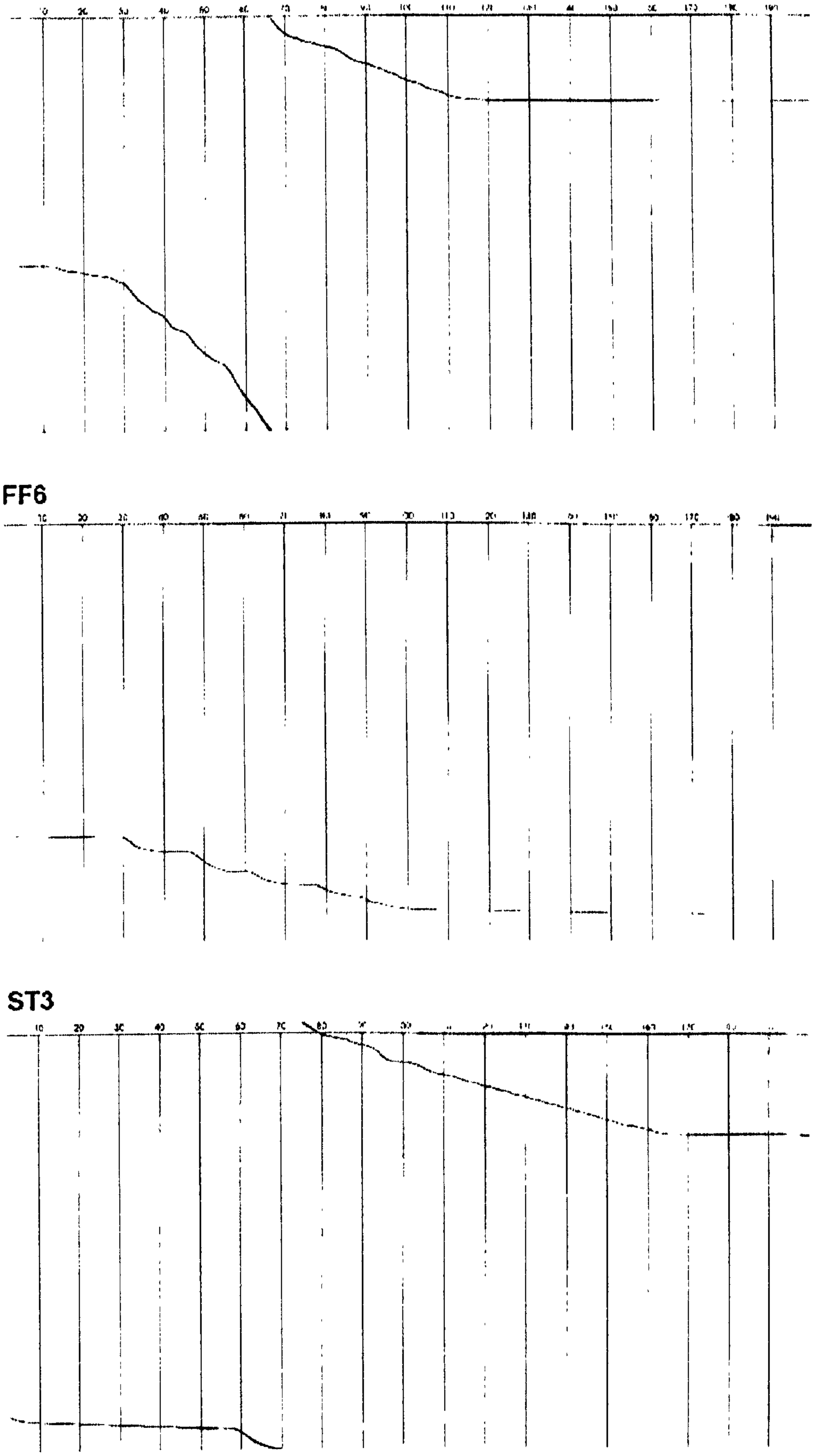


Figure 6.13 **Sibert drill tracings from more deteriorated artefacts**

6.4.4.1 Trends with resistance measurements

SAMPLE	E1/Inn	C1/Out	C2/Out	C2/Inn	C3/Out	C3/Inn
Cut	Fresh	*4*	*8*	*8*	*12*	*12*
Impact Resistance (Av. Lines/cm)	*4.6713*	*0.2659*	*0.0702*	*0.1486*	*0.1818*	*0.1066*
Bulk Density (Calculated)	*0.1632*	*0.0684*	*0.0472*	*0.0580*	*0.0614*	*0.0529*

SAMPLE	C4/Out	C4/Inn	B1/Out	B1/Inn	A3/Out	A3/Inn
Cut	*19*	*19*	*21*	*21*	*27*	*27*
Impact Resistance (Av. Lines/cm)	*0.0333*	*0.1594*	*/*	*0.1667*	*/*	*0.0865*
Bulk Density (Calculated)	*0.0389*	*0.0592*	*/*	*0.0599*	*/*	*0.0500*

Table 6.8 **Impact resistance and calculated density values for test samples**

SAMPLE	WH1 Out	WH1 Inn	FF15 Out	FF15 Inn	FF9 Out	FF9 Inn
Cut	out	inn	out	inn	out	inn
Impact Resist. (Av Lines/cm)	0.9730	7.0000	0.3831	1.034	0.6974	2.2227
Bulk Density (Calculated)	0.1005	0.1854	0.0761	0.1024	0.0909	0.1294

SAMPLE	FF12 Out	FF12 Inn	FF16 Out	FF16 Inn	FF6 Out	FF6 Inn	ST3 Out	ST3 Inn
Cut	out	inn	Out	inn	out	inn	out	inn
Impact Resist. (Lines/cm)	0.2119	0.7044	0.0392	0.0727	0.0244	0.0625	0.0290	0.0290
Bulk Density (Calculated)	0.0641	0.0912	0.0405	0.0477	0.0359	0.0453	0.0375	0.0375

Table 6.8 con't **Impact resistance and calculated density values for test samples**

Impact resistance values for samples from the Roman plank follow the trends set up with Umax and density relatively closely. Central areas of the plank show graduated higher resistance values compared to areas towards the outer edges. Outer samples show significantly lower resistance than inner samples. The most noticeable anomalous result is with the outer section of sample C1. Though situated at one of the deteriorated ends of the plank, and composed largely of sapwood, this sample shows much higher resistance than any of the other plank samples. Chemical constituents data for this sample may allow Kommert's (1981) explanation to be adopted, since this sample shows relatively similar levels of polysaccharides to some of the more central and presumably less deteriorated samples. High resistance values for this sample can also be explained by increased ash content (7.3.1), as Zabel and Morrell suggested (1992), and which is not inconsistent with accepted trends between deterioration and elevated ash content (Hoffmann, 1982).

Either of these explanations, strength loss without associated mass loss, or elevated ash content, might be the reason for the exceptionally high resistance value of the Wood Hall oak—approximately 150% of that measured for fresh oak. But neither seems to explain the relatively low values measured for FF15, though its levels of hot-water extractives are significantly higher than those for sample FF9, suggesting a certain amount of increased deterioration (section 7.3.1).

The potential for error showing up as a result of unevenness of degradation is particularly noticeable in the tracing for FF6, where wavelike ripples in the resistance plotted by the drill seem likely to correspond to Zabel and Morrell's experience of the failure zones produced by pockets of degradation. The size of sample of Roman plank undergoing testing was comparatively small, which may explain some of the variability in results (Zabel and Morrell 1992), more particularly in the trend experienced with second and third drillings along the artefacts that showed fewer number and shallower lines compared to the first tracing, despite being located further from the artefacts' ends.

Trends within the other artefacts show very consistent likeness to Umax and density results. Contrasts in density between inner wood and outer wood, especially strong in samples FF6 and FF9, also show up in impact resistance values. Total lack of differentiation between inner and outer regions in ST3 are borne out by impact resistance data as well.

Residual impact resistance strength of the samples tested ranges from 0.62% to 149%. This does not accord well with Schniewind's statement that 68% is the region within which residual impact resistance strength for archaeological waterlogged wood tends to lie.

6.4.4.2 Physical resistance as a measure of deterioration

It appears clear from comparisons of graphic and quantified data from the Sibert Drill tests that the value of this technique lies mostly in the information contained in the probe tracings. Figure 6.10 quite clearly shows how easily trends between samples show up on the plotted measurements from tests. The relative depth of deteriorated outer layer versus core is obviously similar for all samples. So too is the relative extent of strength deterioration in these woods. As with many techniques adopted from the

timber industry, however, the method is not well suited to quantifying the deterioration at the lower end of the scale typical of much waterlogged archaeological material.

It is obvious from the calculated bulk density data in Table 6.8 that the equation provided by Gabby (1993) does not work for deteriorated archaeological woods, as already stated by Panter and Spriggs (1997). Values for the woods in the present study are almost an order of magnitude lower than the measured figures for bulk density. It is not clear from the literature how Gabby chose his constant of 10.855, thus it is not possible to speculate on the source of the problem with this equation.

Whereas Zabel and Morrell (1992) comment on the necessity of making moisture-content corrections for each reading from resistance testers such as the Pilodyn and presumably the Sibert Drill, they do not mention either how to make these corrections or in which direction they need to be made. Therefore it was not possible to make such corrections with the results from the present study. Gabby's equation relating density to resistance would no doubt be improved by incorporation of Umax into the algorithm.

6.4.4.3 Correlation between resistance results and sorption trends

As a descriptive technique for determining degradation in archaeological woods, resistance strength measurements echo well the information given by sorption data for the same wood. Generalised increase in EMC values accompanying increased mass losses and the increase in slope of the second portion of the isotherm are matched well by decreased resistance figures for degraded woods. Differences between zonal areas in the wood are also reflected in data from both types of measurement.

6.5 Polarising Microscopy Study

6.5.1 Principles of Polarising Microscopy Studies of Wood

Polarised light microscopy has established itself as a useful tool in the examination of wood ultrastructure (Côté 1965; Kollman and Côté 1968; Panshin and de Zeeuw 1980; Fengel and Wegener 1984; Diaz-Vaz *et al.* 1991). Its usefulness in the study of archaeological waterlogged woods has been established by Hoffmann and Jones (1990) and Blanchette *et al.* (1990). While commonly known as a technique for examining mineral and metal sections, it can usefully be used in the study of biological polymers as well, because of their natural birefringence. *Birefringence* is a characteristic of materials whose refractive index varies with direction. It tends to arise from anisotropy within the material, more particularly crystalline anisotropy, molecular orientation, or strain. It becomes most useful in the examination of degraded wood because of its ability to reveal the degree of residual orientation of cellulose in wood fibrils. Under polarised light, sound tissue shows bright birefringence as a result of the crystalline arrangement of cellulose chain molecules in the cell walls. Polarised light also aids the delineation of diagnostic signs through its ability to improve contrast. Though a number of instrumental analytical techniques and transmission electron microscopy may have proved more precise at defining degree of crystallinity present in wood material (Stamm 1964; Bednar and Fengel 1974; Blanchette *et al.* 1990; Daniel 1994; Newman and Hemmingson 1990; Passialis 1997), the advantage of polarised

light microscopy is in the simplicity of the technique, requiring no special staining or coating steps, that brings it well within the range of the average working conservator, and makes it an easy adjunct to the species identification activity common to the investigation stage in the conservation process of this material.

6.5.2 Experimental

Samples were taken from each of the macroscopically-discernible zones of degradation in the wooden artefacts. Small centimetre-square cubes from each of the artefacts were prepared by soaking in a solution of 15% PEG 400/30% PEG 4000 for one month, in order that cells of the very deteriorated woods might not fracture during freeze-sectioning nor crumble on cutting. Experiments carried out by Young (1985) established that the presence of polyethylene glycols does not influence the level of residual crystallinity of the wood.

After this preparation, the samples were sectioned to 15 μm thickness using a cryostat thin-sectioning stage, non-vacuum freeze-dried within the cryostat chamber, fixed with DPX mounting agent, and mounted onto glass slides for examination. Transverse sections were chosen over other orientations of wood structure because they have, in general, been found to be the most diagnostic for level and type of deterioration—they best allow examination of cell-wall microstructure and layering (Hoffmann and Jones 1990). Sample thickness was kept standard, following the recommendations of Kollman and Côté (1968) and Young and Wainwright (1982), because relative birefringence will be influenced by sample thickness and the level of light able to get through.

6.5.3 Results and Discussion

The photomicrographs shown in Figure 6.14 on the following page establish the usefulness of this method of appraisal for determining level of degradation in archaeological wood. They have been ordered by increasing level of degradation, and accompanying relative loss of crystalinity to cell walls.

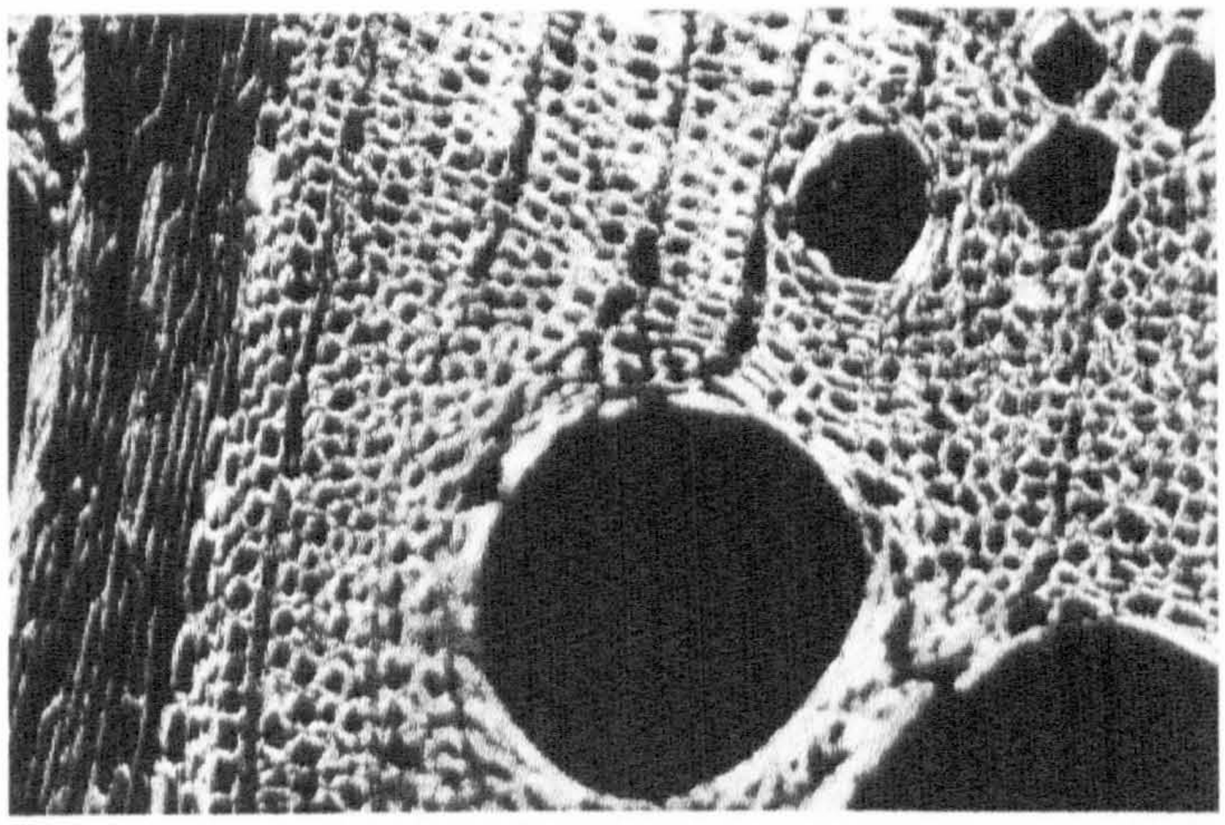


Figure 6.14a Photomicrograph of FF15 under polarised light (X 30)

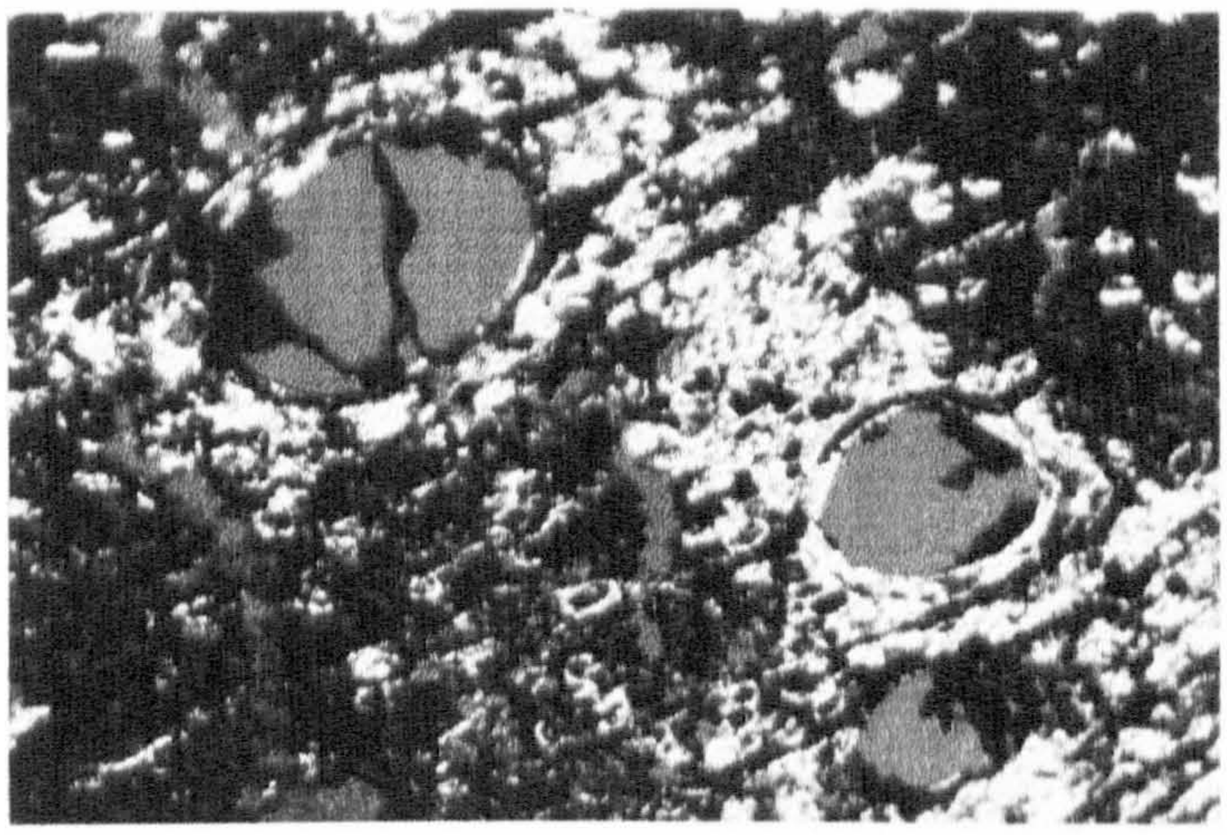


Figure 6.14b Photomicrograph of FF9 under polarised light (X 25)

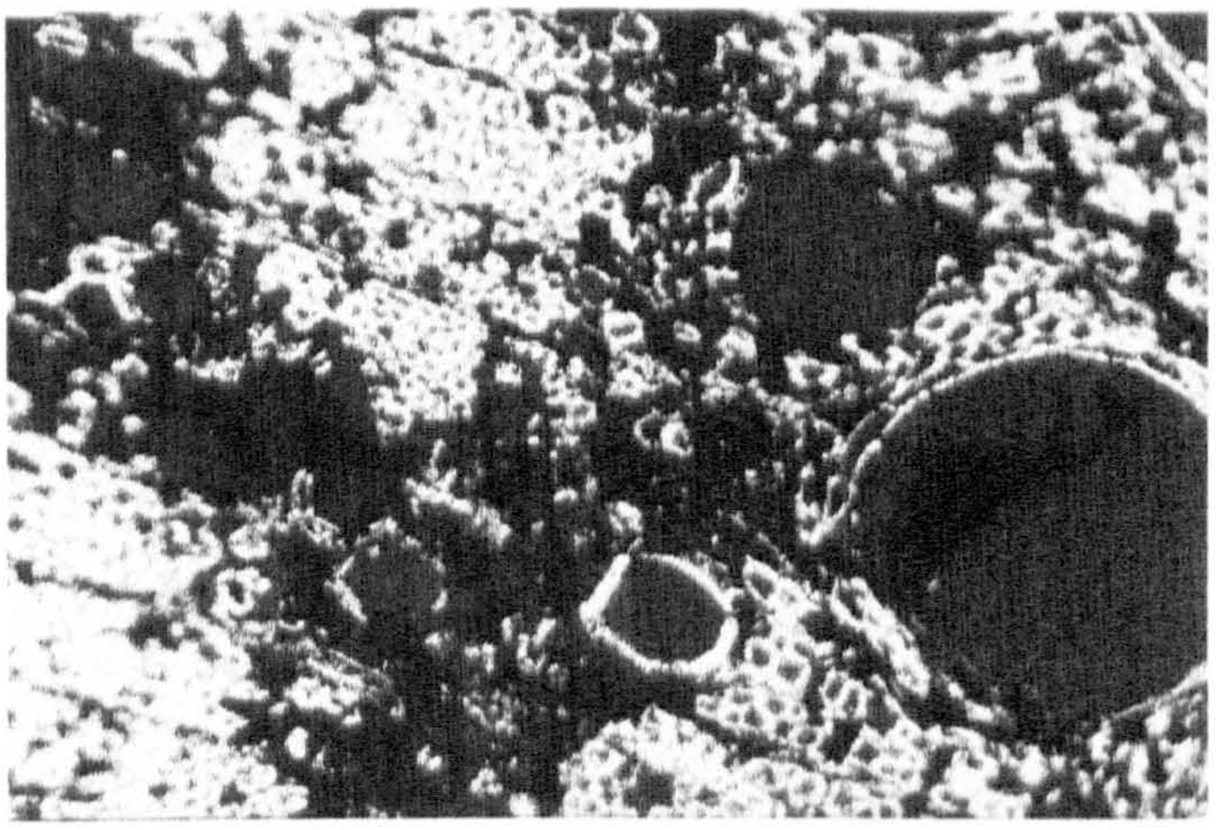


Figure 6.14c Photomicrograph of FF12 under polarised light (X 30)

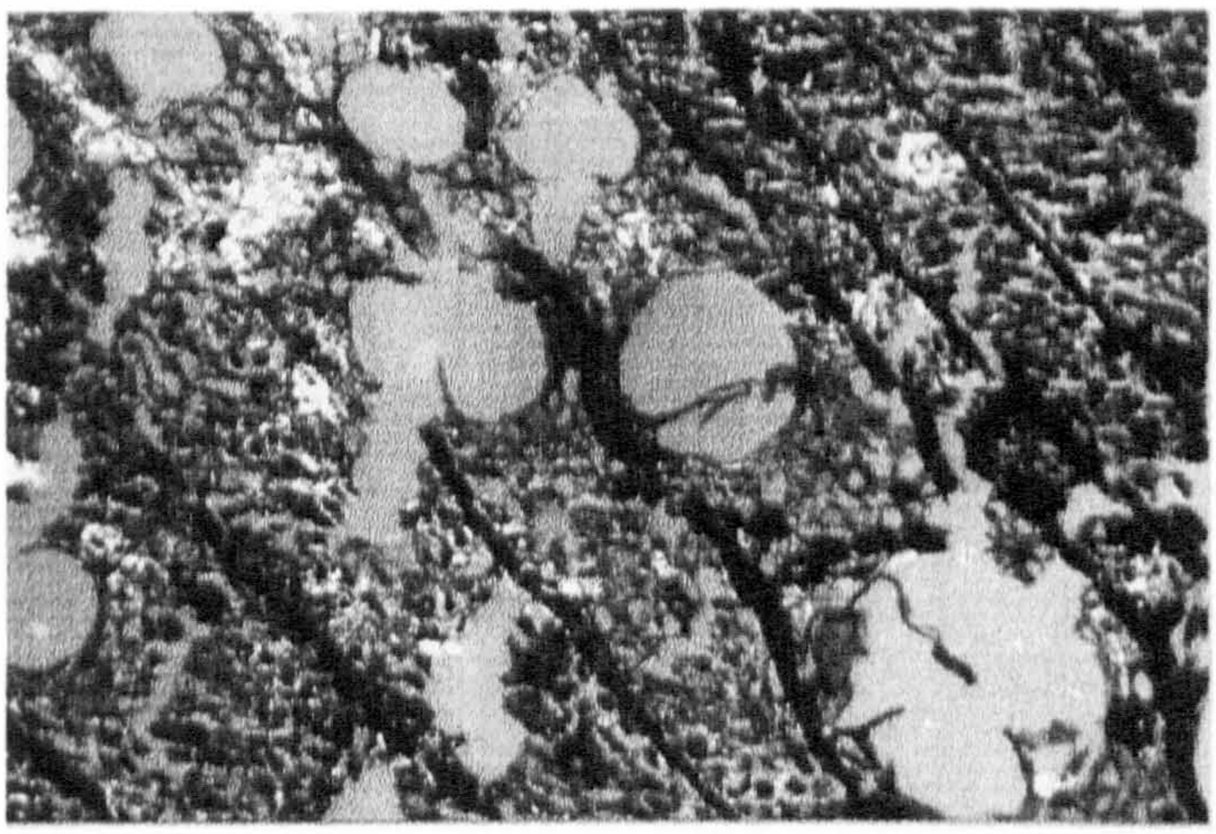


Figure 6.14d Photomicrograph of FF16 under polarised light (X 20)

Figure 6.14e Photomicrograph of FF6 under polarised light (X 20)

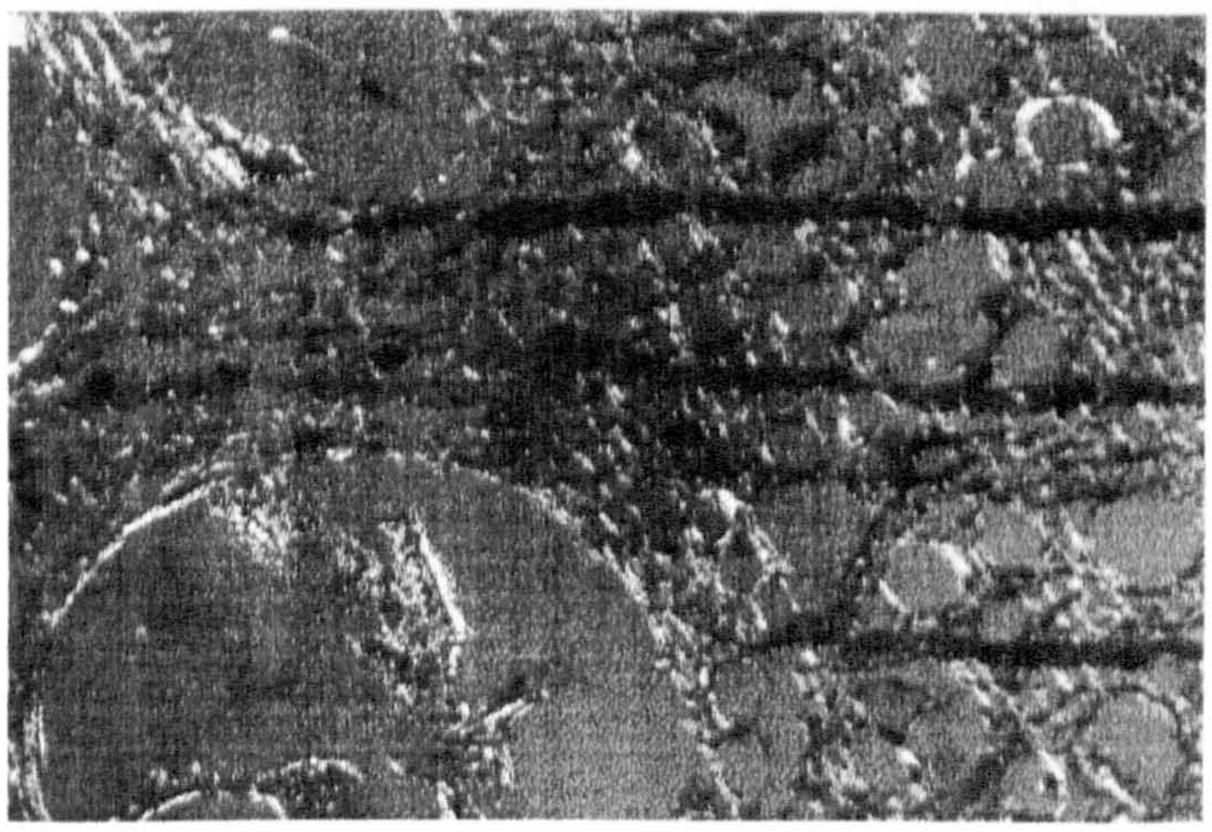


Figure 6.14f Photomicrograph of ST3 under polarised light (X 50)

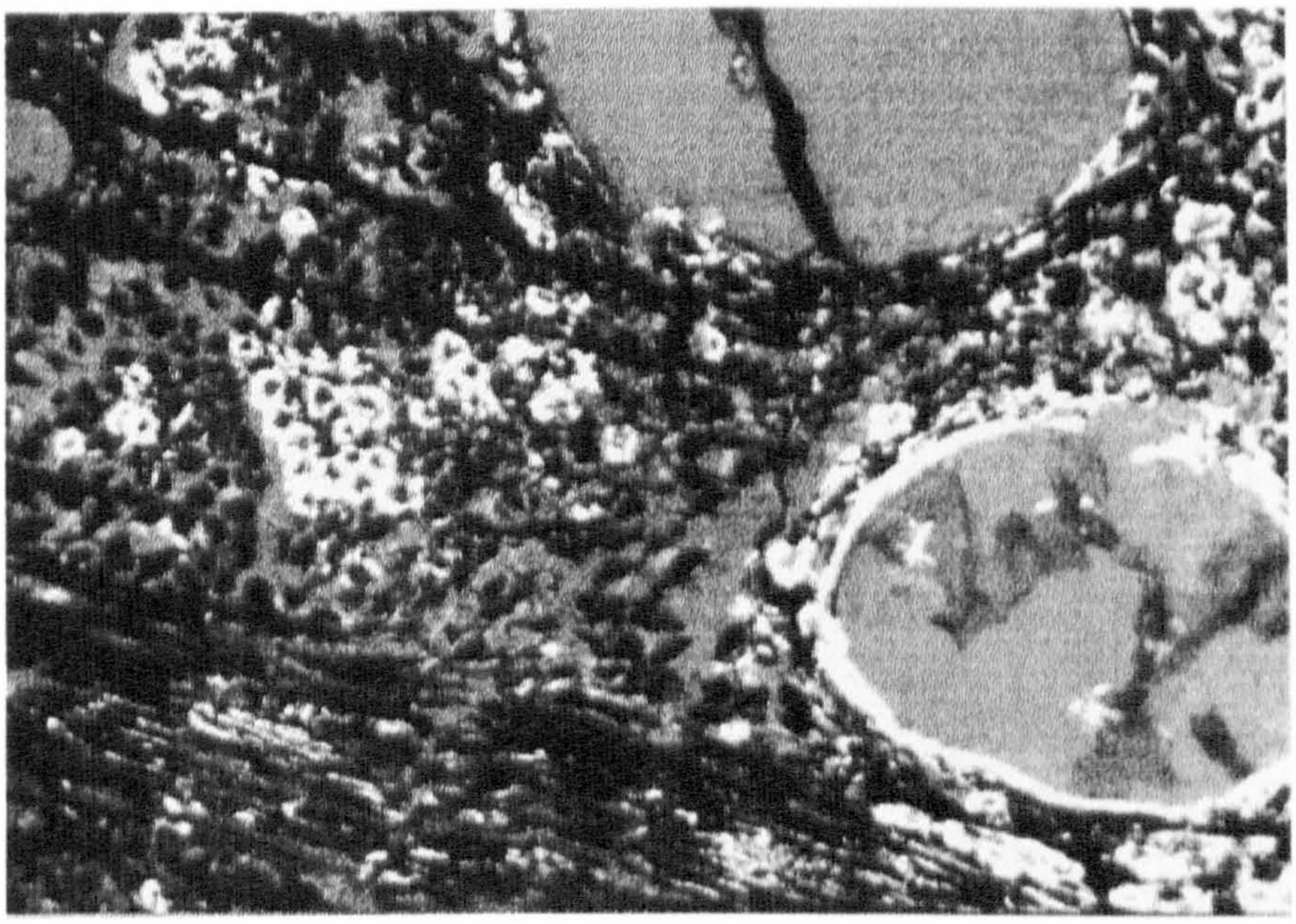


Figure 6.14g Photomicrograph of A1 (outer edge of plank) under polarised light (X 50)

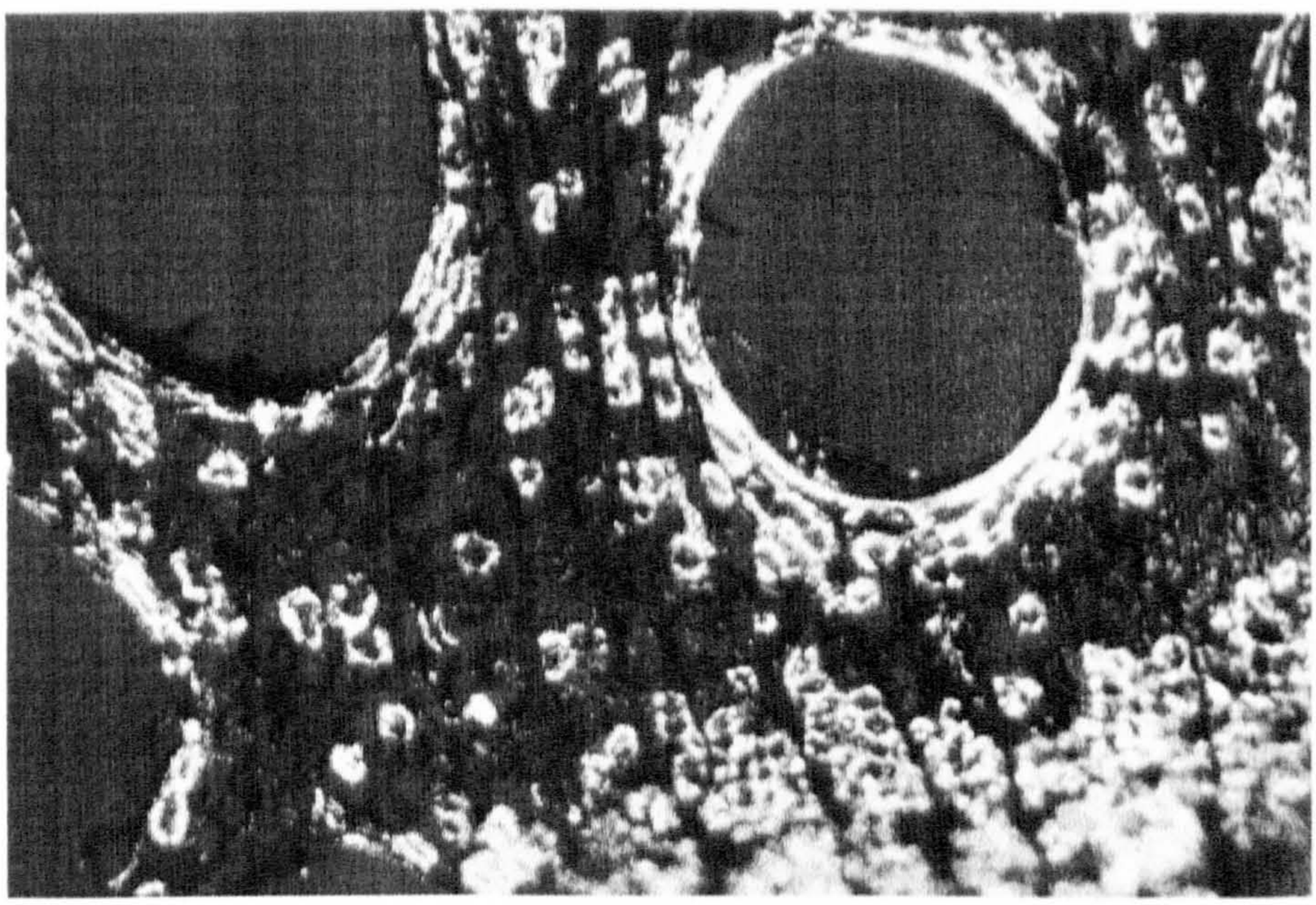


Figure 6.14h Photomicrograph of C4 (inner section of plank) under polarised light (X 50)

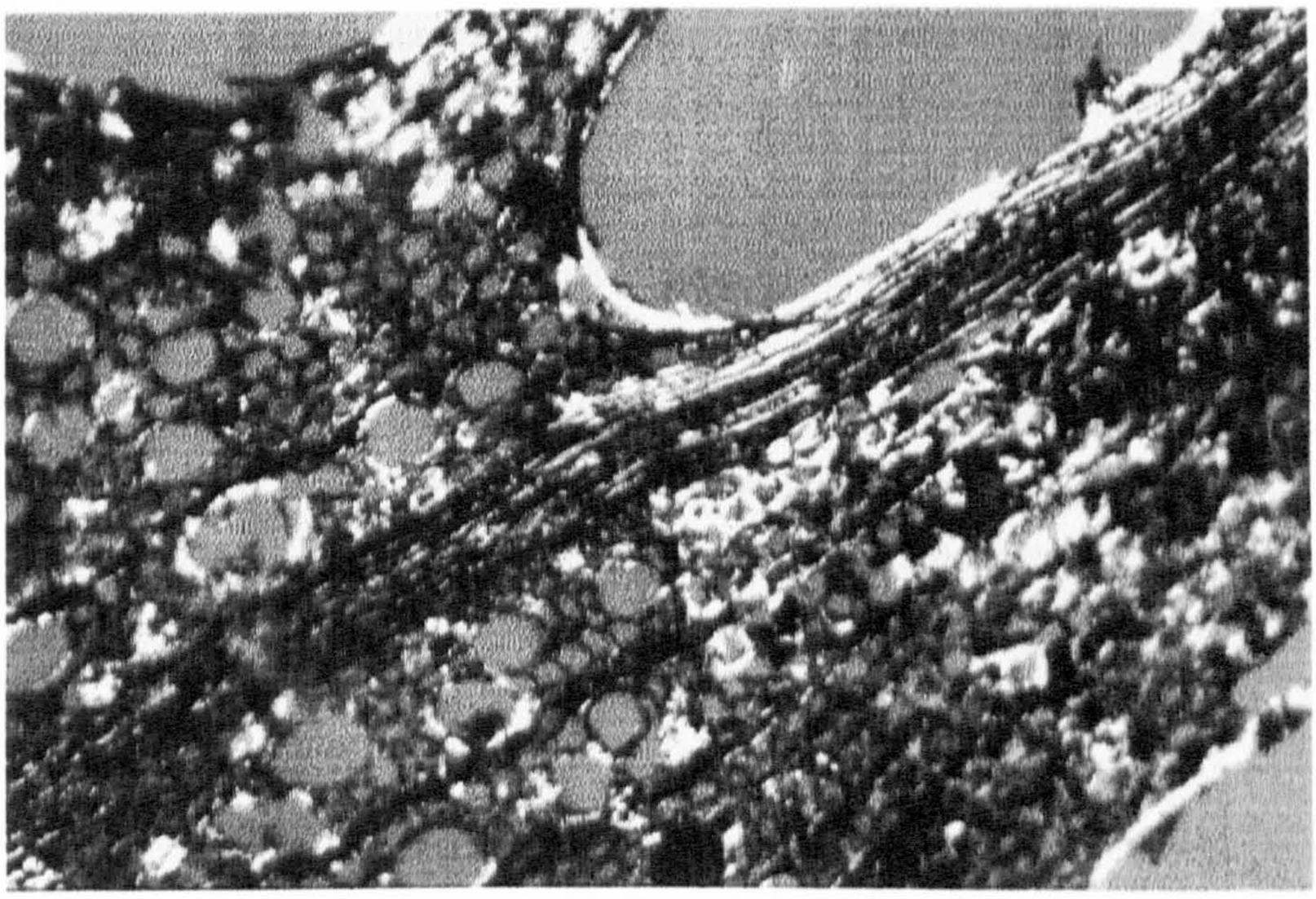


Figure 6.14i Photomicrograph of A3-Inn (degraded end of plank) under polarised light (X 50)

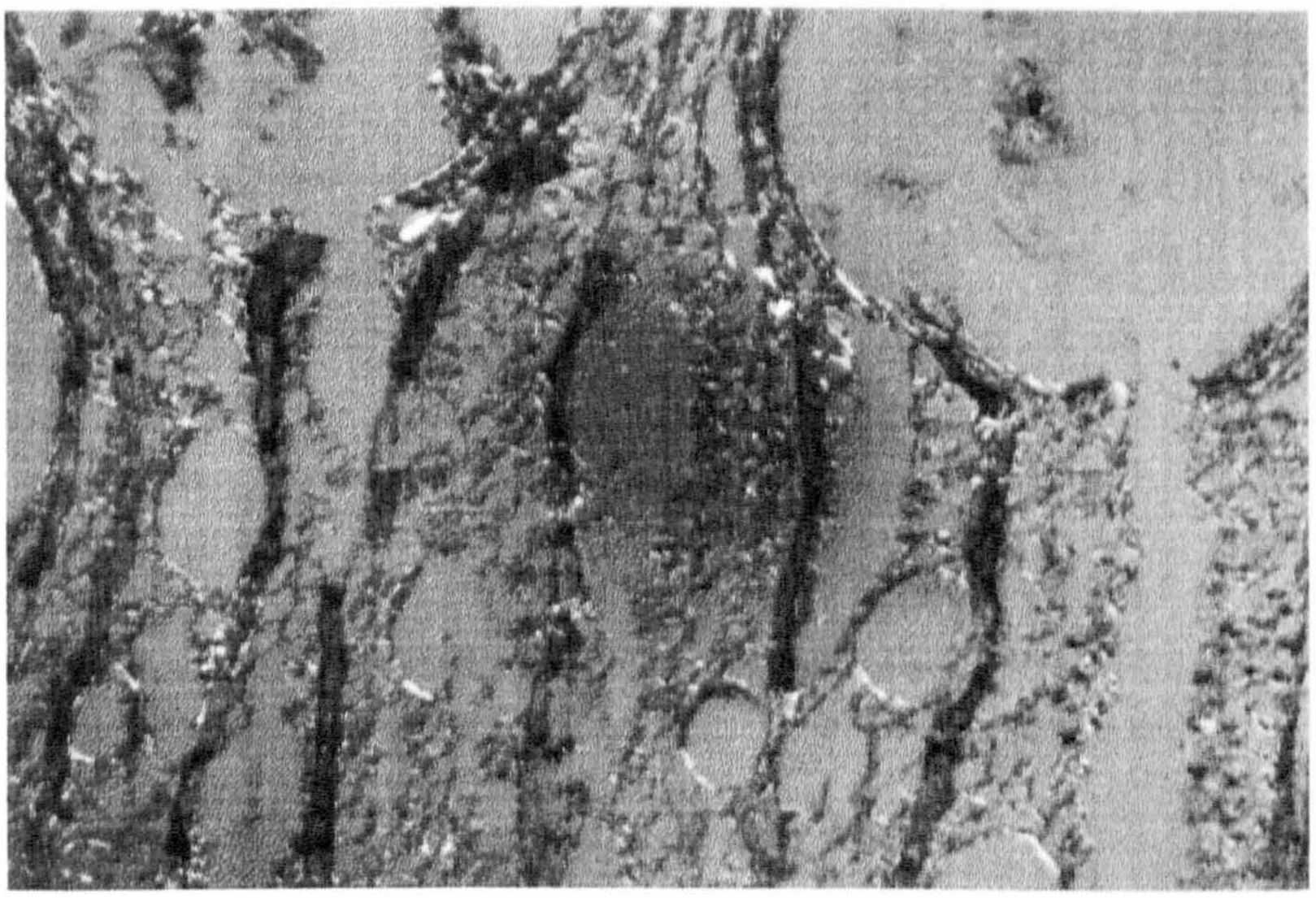


Figure 6.14j Photomicrograph of A3/Out (sapwood from end of plank) under polarised light (X 50)

Rapid appraisal of the sample sections shows a clear correspondence between increased degradation, as evidenced by changes to Umax cell-wall density and loss to constituents discussed in earlier sections, and decreases to the level of crystallinity. Regular trends are observed.

Further analysis of these results by image-processing techniques could establish relative crystallinity indices (defined as the proportion of the crystalline and amorphous regions of wood) for each of the samples. Using X-ray diffraction, comparing selective X-ray diffraction patterns (crystalline) and indefinite X-ray diffraction patterns (amorphous), rather than polarising microscopy, Passialis (1997) determined that the crystallinity index of samples of waterlogged archaeological woods (including *Quercus robur)* may be reduced by as much as 3 times. Cursory examination of the results shown here indicate similar levels of loss, indeed the more degraded samples FF6 and ST3 can be seen to have lost virtually all of their crystalline material. Comparison of these results with those for residual cellulose, reported in Chapter 7, show close concordance. In these samples, less than 30% of the cellulose remains, and since we can expect this figure to be artificially inflated by larger-molecular-weight degradation products of lignin (7.3.3), crystalline content of these samples is very probably considerably lower. Barbour and Lency (1985) report the presence of small amounts of crystalline cellulose remaining attached in thin continuous sheets to the lignin skeleton in wood deteriorated to below a bulk density of 0.1 g/cm^3 . These findings are confirmed by the faint remnants of crystallinity visible in the middle lamella remnants visible in the photomicrographs shown in Figure 6.14.

Time did not permit testing whether this method of examination was capable of showing up very minor differences in level of degradation (e.g., by taking sections throughout the plank), but the results from FF9, FF12, and FF16 do appear to show the ordered decrease in crystallinity indicated by other tests, though these samples are not very dissimilar in relative preservation.

Hoffmann and Jones' (1990) and Blanchette's (1990) investigation of the structural changes in degraded woods as shown by microscopy went much deeper, making observations on the order of dissolution of cells within the wood structure; intactness, leaching of constituents and delignification of the middle lamella; presence of bacterial erosion trough versus soft-rot chain cavity degradation; and relative intactness of pit membranes (significant to increased water permeation and FSP). While there is no doubt that such level of examination yields data important to the understanding of the condition of the artefact, the results reported here show that the working conservator would be able to get enough data for his purposes just from a general look at thin sections from artefacts—perhaps from the same samples taken for species identification.

6.6 Summary

The results from the physical tests methods examined in this chapter underline the weakness of such tests as single indicators of the physical and chemical condition of the wood substance of archaeological artefacts. Umax, bulk density and cell wall density were reliable at showing general trends between artefacts, and results between these three measures proved by-and-large consistent. They were also

capable of exposing zonal variation within artefacts. But high levels of error associated with the gravimetric nature of such measures tended to produce anomalous results, more particularly with the more degraded samples.

The importance of representative sampling was emphasised by the way in which homogenised samples of inner and outer wood did not produce data which reflect the true physical condition of the samples when compared to values obtained from inner and outer samples separately. In addition, one measure did not commute into another with any accuracy as shown by results from resistance measurements and density. The more descriptive results from the Sibert Drill tracings and polarised microscopy appear to yield more detailed and useful information about the chemical and physical condition of archaeological wood.

The ability of the data from the physical tests examined in this chapter to reflect chemical changes of archaeological woods in any significant detail will be examined in the next chapter.

7 Bulk Constituent Analysis

7.1 Introduction

It was Hoffmann (1982) who first suggested that it was worth investigating whether the degradation that most archaeological woods have undergone could be traced to changes in their chemical constitution. Once such information was available, conclusions about the sort and degree of modification of the wood could be drawn and the response of wooden artefacts to drying treatments predicted.

The chemical analysis he was referring to, and carried out, was a type of bulk constituent analysis already standardised by the wood-science and timber-manufacturing communities, involving gravimetric analysis of solubilised residues from various graded chemical digestion tests. Hoffmann found the results of analysing archaeological timbers to be variable and their interpretation to be difficult. Grattan and Mathias' (1987) later appraisal of this technique's use as a generalisable method in the selection, design and evaluation of treatments, concluded that, though it was perhaps too time-consuming to prove generally applicable to the conservator, results could reveal trends meaningful for diagnostic purposes. In addition it proved a more accurate and reliable method of defining degree of degradation than either Umax or density measurements in isolation. Bednar and Fengel (1974); Fengel (1976); Fengel and Wegener (1988); Kim (1990); and Passialis (1997) also reported results from the analysis of archaeological waterlogged woods.

The advantage of chemical analysis over the more descriptive approach is that the information obtained is numerical and easier to classify, and compared to other simpler methods such as measurement of water content or probing with pins, the results ought to give much greater insight into chemical preservation of the artefact and be far more reliable (Grattan and Mathias 1986). The main disadvantages of bulk chemical analysis—sample size and time requirements (as much as five days to process one sample)—are not dealt with in any constructive fashion in the literature. Zabel and Morrell (1992), however, reported on a less time-consuming chromatographic quantification of the major sugars, glucan, zylan, and mannan.

This chapter will investigate the usefulness of bulk constituent analysis as a technique for illuminating the preservation condition of waterlogged archaeological wooden artefacts. Because of the time and resource commitment involved with this type of analysis, it will be necessary to determine whether it can give an adequate absolute chemical characterisation of archaeological wood or whether, rather, it is only capable of providing a rough guide to wood preservation. More significantly, results will be appraised for their ability to illuminate the sorption relations within archaeological material, e.g., as a predictor relating loss in cell-wall substance and shrinkage, such as produced by Grattan and Mathias (1987).

7.2 Bulk Chemical Analysis by Preferential Solubilisation

7.2.1 Principles of Measurement

The chemical composition of sound fresh wood varies remarkably little within a single species and therefore for each species there are approximate standard values. The degradation that most archaeological wood has undergone should therefore be traceable through changes to its chemical composition (Figure 7.1). The aim of chemical analysis is to separate and determine quantitatively the chemical constituents of the wood. The main chemical constituents of wood are, in broad categories:

1. the macromolecular cell-wall components: cellulose, hemicellulose, lignin, and minor polymeric substances such as starch, pectins and a small amount of protein; and

2. the minor low-molecular-weight compounds: extractives such as aromatics, tannins; terpenes; aliphatic acids, esters of glycerol, fats, oils, waxes; inorganics such as magnesium, calcium and potassium salts, and also iron; including the mineral substances.

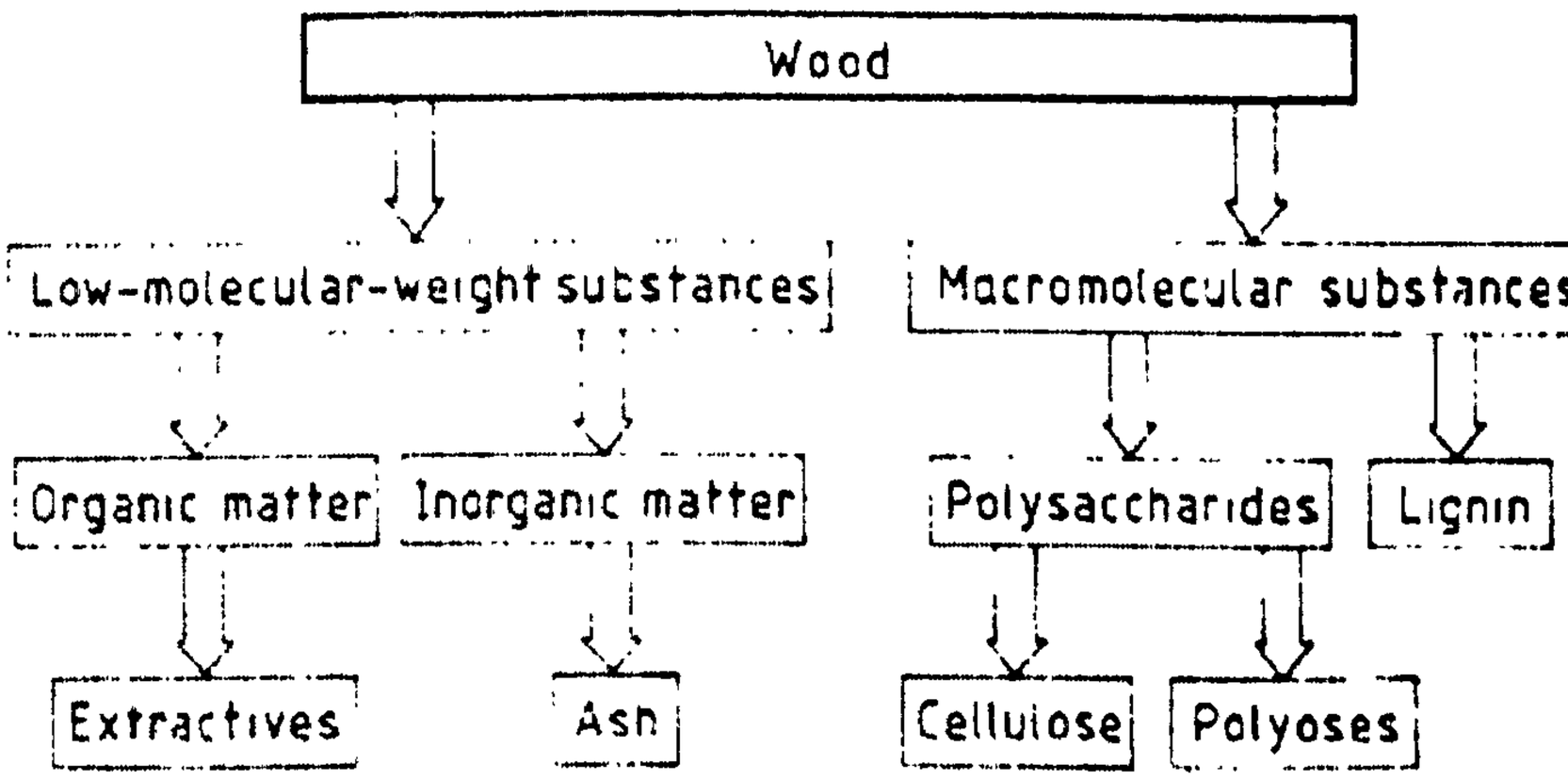


Figure 7.1 **General scheme of the chemical wood components** **(Sjöström, 1981)**

Quantitative changes in structural components during decay can be monitored by comparing gravimetric data of individual components with original values for that wood. The chemical components of wood are separated from the milled and dried wood, using a variety of chemical reagents and solvent extraction procedures. Sjöström (1981) describes four alternative pathways for wood solubility analysis. Fengel and Wegener (1984) give a particularly useful guide to these procedures, more especially those laid out as TAPPI (Technical Association of Pulp and Paper Industry) standards. Grattan and Mathias (1986) recommended the use of ASTM (American Society for Testing and Materials) standards instead, because of their relative ease of application and greatly reduced sample requirements. Results from the two systems have been found to be very similar (Grattan and Mathias 1986). Hoffmann's (1982) detailed practical recommendations for both application and interpretation of wet chemical solubility analysis are of immense aid to the study of archaeological material.

Since bulk constituent analysis is so very time- and sample-consuming, it can only be thought worthwhile if it can provide generalisable trends when interpreted with other simpler measurements such as maximum moisture content, density, and ash content. Hedges (1990) has attempted to correlate

mathematically, changes in density to specific changes to wood mass. Since this relation is based on the assumption that lignin is not lost during the degradation process, the conclusions must be treated with a certain amount of caution and it must be assumed that a number of sources of error affect the interpretation of his results. The meaningfulness of this equation will be investigated in this chapter, in addition to correlations between chemical constituent ratios and changes to fibre saturation point.

7.2.2 Problems and Interpretation

The main problem associated with bulk chemical constituent analysis of wood arises from the difficulty of carrying out accurate gravimetric measurements on small samples (Zabel and Morrell 1992; Sjöström 1981). In the tests outlined in the next section, the potential for errors arising from sample-handling and the weighing of awkward filter crucibles are very high. Even variations in the method and the particle size to which the sample is ground can affect the outcome of analysis (Browning 1967; Wallace and Johnson 1993). Samples are usually oven-dried before analysis so that moisture is removed from the equation. But oven-drying itself is problematic because of the potential evaporation of volatile organics from the wood (Skaar 1988). The drying is also rarely complete because of the appreciable vapour pressure that may build up within the drying oven (unless it is particularly efficiently fan-assisted), or unless a vacuum oven is used.

Sample selection in archaeological material must be carried out carefully, not only because of the variation in constituents between cell tissue types but, more importantly, because substantial decay gradients occur over even small areas of wood. The decay contributed by microorganisms may mean selective attack of specific cell types and the storage of certain breakdown products (e.g. sugars and polyphenols) in the wood, thus artificially raising cell-wall component values (Zabel and Morrell 1992). A test for elevated protein content can show whether the presence of fungi is artificially raising polysaccharide levels in the wood analysis.

Hedges *et al.* (1985) give the degradation order of wood as: hemicelluloses, α-cellulose, pectin, and then first syringyl lignin units, followed by ρ-Hydroxyl and vanillyl lignin units, an order based on their natural resistance to chemical and biological degradation. In general, deterioration in archaeological woods has been observed to affect the holocellulose fractions more than the lignin. Hoffmann and Jones (1990) gave a more complex picture of the changes to polymer fraction ratios which is observable in the results of the present study. They point out that the lignin middle lamella skeleton left in wood that is most severely degraded also contains some cellulose in crystalline form that has been protected by the relatively higher amount of extractives encrusting this area. They claim that this structure stays intact until its specific gravity/density (Rg) decreases to 0.1g/cm3. Trends in constituent losses do not appear to increase with the age of the sample in any regular fashion, suggesting that a combination of the chemistry of burial environment and exposure to microorganisms influence the degradation process.

Since solubility analyses yield their results through the sequential stripping-off of chemical components (hence *preferential solubility*), problems of interpretation can be expected to arise where the processes

used have failed to remove from the residue all of the component being measured. Because of the extreme structural and chemical complexity of wood, contamination of residues and losses to the desired isolate are common. Hoffmann points out (1982) that in carrying out chemical analysis on wood, we are attempting to make the impossible possible: to separate wood components quantitatively. None of the methods available is 100% successful. Either the fraction to be determined is not pure, or losses must be accepted to produce a pure component. Crawford (1981), in comparing various of the methods for isolating lignins from wood, remarks on the particular difficulty of removing all of the carbohydrate fraction from around wood lignin. Holocellulose determinations by NaOH solubility are particularly affected by this problem. Errors of 2-5% are expected even for modern undeteriorated woods (Hoffmann 1983; Grattan and Mathias 1986). Degradation of structural polymers typically increases their solubility in acid and base solutions, which may mean erroneously low values in carbohydrate determinations in waterlogged archaeological material (Hedges 1990). Klason lignin determination—the method common to both TAPPI and ASTM methods—has been found to produce degradation in lignin end products which may artificially inflate lignin losses (Zabel and Morrell 1992). So the problem can work either way. DHP (dehydrogenation polymerisate) analysis and MWL (solvent extracted milled wood lignin) are the preferred methods for critical lignin studies, since they are able to be totally specific in stripping the carbohydrates from lignin without degradation of the residual lignin. These methods, however, require too much expertise to be suitable for general use.

The issue of contribution to mass loss by lignins as well as carbohydrates is thus put into question. We should anticipate losses to lignins as well as to carbohydrates because of the microorganisms involved in archaeological wood degradation (Chapter 2) and because of the published results of studies using more chemically-specific instrumental analysis methods (Borgin *et al.* 1975b; Hatcher 1988; Wilson *et al.* 1993). The results discussed below will assess the significance of lignin degradation to the total degradation patterns in archaeological wood and challenge the assumption that lignin deterioration does not begin until the carbohydrates are almost entirely gone from the wood. Relationships based on these assumptions—such as Hedges (1990) above, density from Umax calculations (Chapter 6), and those underlying PEGCON—will have to be reappraised.

7.2.3 Experimental

Chemical analysis of the main constituents of wood was carried out on prepared samples of ground wood flour made from 1-2 gram cuts (wet) taken from the Roman well plank and from other artefacts used in this study. Sample sections were first freeze-dried to reduce error associated with oven-drying (as explained above) and thermal decomposition observed at temperatures above 80°C (Grant and Macnaughlain 1968). Milling was carried out using an agate ball and sample chamber in conjunction with a powder-milling machine. This was done to avoid possible contamination of the flour with inorganic fragments from the surface of the metal mill (Wallace and Johnson 1993). The flour was reduced by milling to an average 20-mesh particle size, the size recommended to insure a representative sample in relatively small (0.50g) sample aliquot size for assay (Wallace and Johnson 1993). Fines were

included despite published concerns that they may interfere with analysis by clogging fine filters or by passing through coarse filters (TAPPI, 1975). Removing fines from archaeological wood samples would involve removing a disproportionate amount of the more severely-degraded material. After preliminary tests, filters were chosen that could accommodate fines without producing erroneous results. Until analysed, samples were stored over silica gel to prevent uptake of moisture, and under refrigeration to discourage microorganisms and protect from light.

Wood flour samples were then subjected to the standard test series for bulk chemical analysis of wood, with choices being made between certain of the TAPPI and ASTM standards, depending on reported relative effectiveness with archaeological material (Hoffmann 1982; Grattan and Mathias 1986; Panter *pers. Comm.* 1996). Determinations were made for each constituent by subtracting the residue weight after digestion from the residue weight before digestion. Material removed by the digestion is converted to percent determinations for that material.

Following is a list of the chemical analyses carried out on wood flour:

1. *Moisture content determination* (TAPPI standard-T12): was carried out on a selection of the ground samples in order to determine whether it was necessary to correct for moisture in the subsequent determinations. This was not found necessary, as a result of the preparation and storage methods used with the samples.

2. *Hot water solubles* (TAPPI standard-T207): Water soluble extractives were determined after extracting with boiling distilled water. Starch, tannins, gums, short chain sugars, proteins and inorganic salts present in the wood would be removed by this means. Cold water extractive determination was not carried out because this process can be assumed already to have taken place in the burial environment.

3. *Alcohol/benzene solubles* (TAPPI standard-T204): Extractives such as waxes, fats, resins, oils and tannins were determined after extraction, using an ethanol benzene mixture. This test was carried out on only a small selection of the samples, to determine whether it is needed in work with archaeological material. Certain researchers believe that most of these materials have already undergone deterioration sufficient to make them soluble by hot water extraction (Panter *pers. comm.* 1996). As I did not carry out this last extraction, it can be presumed that as much as 0.4% of these components could make up part of the following determinations, most likely contributing to the holocellulose fraction (according to figures for fresh oak published by Fengel and Wegener 1984). Results from pyrolysis gas chromatography mass spectroscopy (Chapter 8) do not appear to suggest that these substances make any significant contribution to constituent proportions in archaeological wood.

4. *Hemicellulose determination* (Hungate 1938): Extractive-free wood produced from previous extractions was digested with dilute (5%) sulphuric acid to determine hemicellulose content. This determination will also include breakdown products of the polyose form.

5. *Cellulose determination* (TAPPI standard-T222): All remaining carbohydrates (celluloses) were removed by digestion with concentrated sulphuric acid (72%), yielding a cellulose determination.

6. *Lignin determination* (TAPPI standard-T222): Acid insoluble or *Klason* lignin was determined as the residue after the previous extraction. This residue can be assumed also to contain a significant proportion of the mineral ash present in the original wood sample, and thus must be corrected for. This method is acknowledged to remove as much as 3-5% of original lignin, even in sound modern woods (TAPPI).

7. *Ash content* (ASTM D1102-56): As it is extremely difficult to carry out this test with accuracy on the residue from the previous determinations, ash content was determined on a separate sample as the residue remaining after ignition at 600°C. This gives the mineral content as oxides. Comparing ash contents obtained by this method with the few samples that underwent ashing after lignin determination established that this determination represented the ash remaining in the wood to be within 2%.

Chemical tests were carried out sequentially on each wood sample following the order given in the flow chart (Figure 7.2) on the following page.

Because of shortage of time, double determinations were carried out on only one sample. Results from this showed reasonably good agreement (within 2%). In these types of determinations, potential for error is very high, therefore it would be safer to treat figures generated by such tests with a level of scepticism.

Results are listed in Tables 7.1 and 7.2. In the case where the sum of the determined constituents is less than 100%, this discrepancy reflects the presence in the wood of soluble degradation products of carbohydrates or acid-soluble lignin fragments that are not retained on the filters used in the analysis.

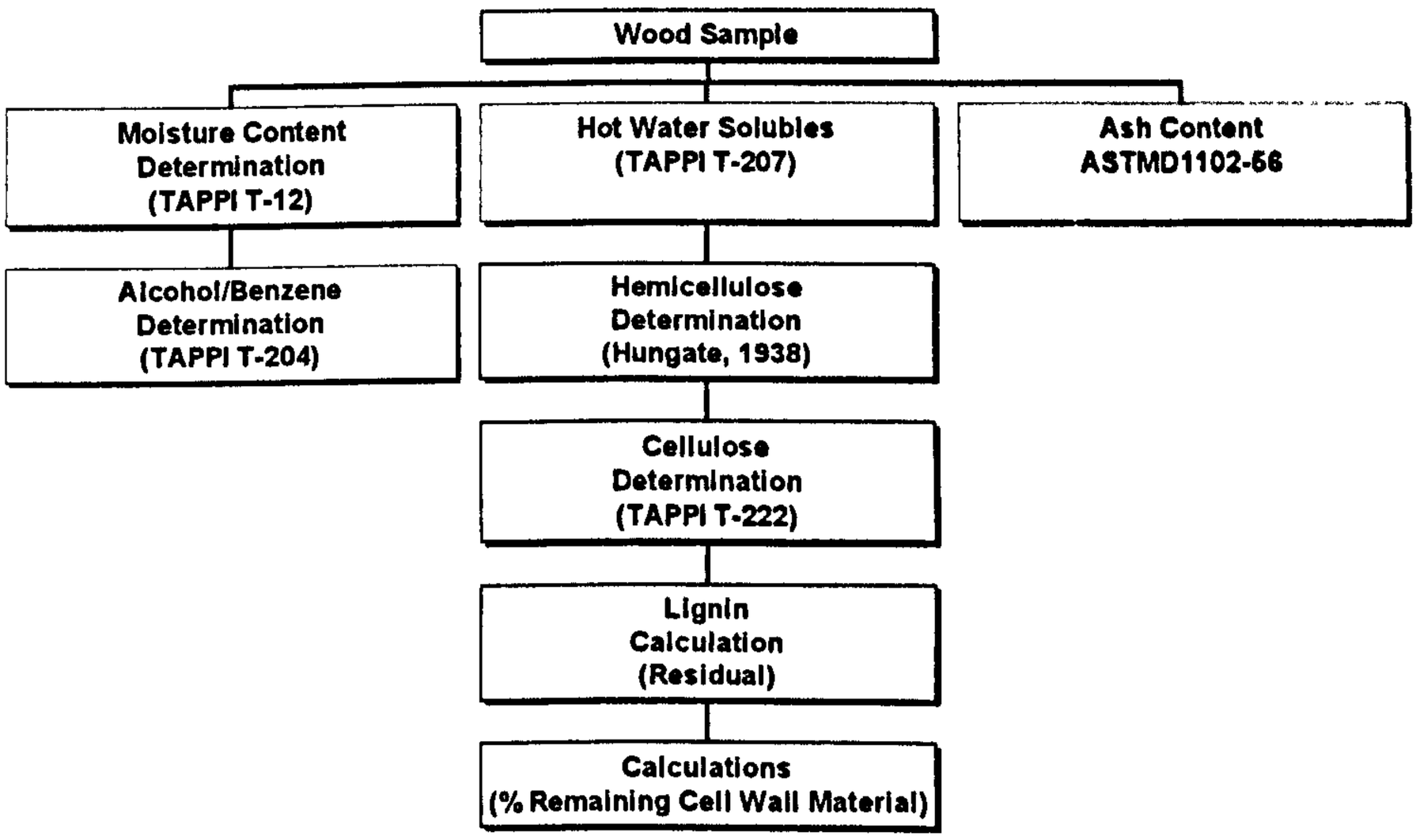


Figure 7.2 **Flow chart of sequence of chemical tests carried out on wood samples**

7.3 Results from Bulk Chemical Analysis

7.3.1 Mass Normalised Yields

Results in Table 7.1 and 7.2 below have been recalculated to express component percentages as mass normalised yields, in other words as percentages of the original amount of wood substance present in fresh wood of that species. Both Grattan and Mathias (1987) and Hedges (1990) argue that this yields data that more truly express material losses to the wood, and avoid the confusion produced by individual constituent determinations that may produce values far in excess of the original values for that species.

Mass normalised yields are calculated indirectly by multiplying component percentages by the proportion of cell-wall material that remains, a value based on estimated original wood density. Thus,

$$\%LWS = 100\left(1 - {}^{1}/_{F}\right)$$ (after *Grattan and Mathias 1996*)

where: *%LWS* is the percent loss in wood substance, and *F* is the ratio of the final to the original weight percentage of lignin.

And % LWS can be calculated by the following:

$$\%LWS = \frac{R_{gn} - R_{g}}{R_{gn}} \times 100$$ (*Grattan and Mathias 1996*)

where: *%LWS* is the percent loss in wood substance, R_g is the bulk density of the sample, and R_{gn} is the standard bulk density for green wood of that species.

This equation relies on the assumption that lignin is not lost (to any significant extent) during deterioration.

Sample	% Water Sol Extractives.	% Hemi-cellulose	% Cellulose	% Lig &Ash Residue	% Lignin	% Ash
A1/Out	5.36	10.52	23.03	21.84	17.50	4.34
C1/Out	6.06	9.99	18.26	24.90	21.03	3.87
C2/Out	7.27	10.70	13.88	27.36	23.59	3.77
C2/Inn	3.13	5.85	15.24	27.01	24.48	2.54
C3/Out	9.09	11.43	14.38	24.76	21.07	3.69
C3/Inn	4.76	7.59	19.21	29.73	26.78	2.95
A2/Out	7.83	7.74	21.09	22.78	19.21	3.57
A2/Inn	11.08	10.41	21.50	18.47	15.54	2.93
C4/Out	9.54	8.77	10.54	31.21	27.69	3.52
C4/Inn	8.84	10.72	19.39	22.56	19.69	2.87
C5/Out	6.56	6.71	7.70	31.51	27.93	3.58
C5/Inn	7.23	9.76	16.87	27.12	23.64	3.48
A3/Out	8.24	10.91	8.67	23.09	19.25	3.85
A3/Inn	5.21	11.62	10.89	22.29	19.23	3.06
D1/Out	/	/	/	/	/	/
D1/Inn	/	/	/	/	/	/
D2/Out	/	/	/	/	/	/
D2/Inn	8.67	10.22	18.30	23.86	21.01	2.85
D3/Out	/	/	/	/	/	/
D3/Inn	5.57	11.73	15.92	26.39	21.11	5.28
Fresh Wood (E1/Inn)	12.20	16.401	41.10	30.89	29.60	1.29

Table 7.1 **Mass normalised yields for sections across Roman plank**

Sample	% Water Sol Extractives	% Hemi-cellulose	% Cellulose	%Lig & Ash Residue	% Lignin	% Ash
E1/Inn (Fresh Wood)	12.20	16.40	41.10	30.89	29.60	1.29
E2/Inn	15.23	20.96	33.98	28.43	28.23	0.20
FF16/Out	9.71	12.85	13.66	22.71	17.50	5.21
FF16/Inn	11.70	11.93	19.41	18.55	14.95	3.60
FF15/Out	11.04	/	/	/	/	/
FF15/Inn	5.05	15.99	25.83	15.88	13.89	1.99
FF12/Out	6.57	/	/	/	/	/
FF12/Inn	6.53	15.39	21.26	18.78	16.43	2.34
FF9/Out	/	/	/	/	/	/
FF9/Inn	6.95	16.08	22.99	16.11	12.49	3.62
FF6/Out	/	/	/	/	/	/
FF6/Inn	6.21	13.86	12.99	26.60	22.87	3.72
WH1/Out	/	/	/	/	/	5.58
WH1/Inn	11.99	23.09	45.16	8.49	6.61	1.88
ST3/Out	/	/	/	/	/	1.45
ST3/Inn	5.39	5.20	14.52	29.68	28.47	1.22

Table 7.2 **Mass normalised yields for artefacts**

7.3.2 General Trends in Water-Solubles and Carbohydrates

From the work of other researchers (Hoffmann 1982; Hedges 1990; Passialis 1997) it is clear that we should expect consistent and accelerated decreases to carbohydrates with increased degradation of the samples. We might also expect the same of water-soluble extractives, since we could expect all of this material to have been removed earlier in the burial environment. Trends exhibited by solubility analyses carried out in the present study, however, do not always present so clear an interpretation.

Hot water extractives can be seen in Figure 7.3 to increase towards the inner, less-deteriorated parts of the plank, though still reduced from values measured for sound recent oakwood. This suggests some other cause than augmentation of these extractives by low-molecular-weight degradation products from cellulose or lignin, unless for some reason these types of extractives are less firmly bound into the wood structure than the native hot-water extractives of sound wood. If this were true, hot and cold water extractives produced by degradation could be expected to leach out of the degraded areas of wood

relatively quickly. Sapwood values are also often higher than heartwood values. Another explanation for this might be a contribution to water soluble extractives from soluble inorganic salts that have made their way into the more porous outer layers of the woods. This possibility is further supported by results in outer samples from the artefacts and inner wood from certain of the more-deteriorated artefacts (Figure 7.4). When these results are compared with particularly high ash contents, as in sample FF16, this explanation seems even more likely.

The range of loss to components in artefacts in comparison to sound oak can be seen in Figure 7.4.

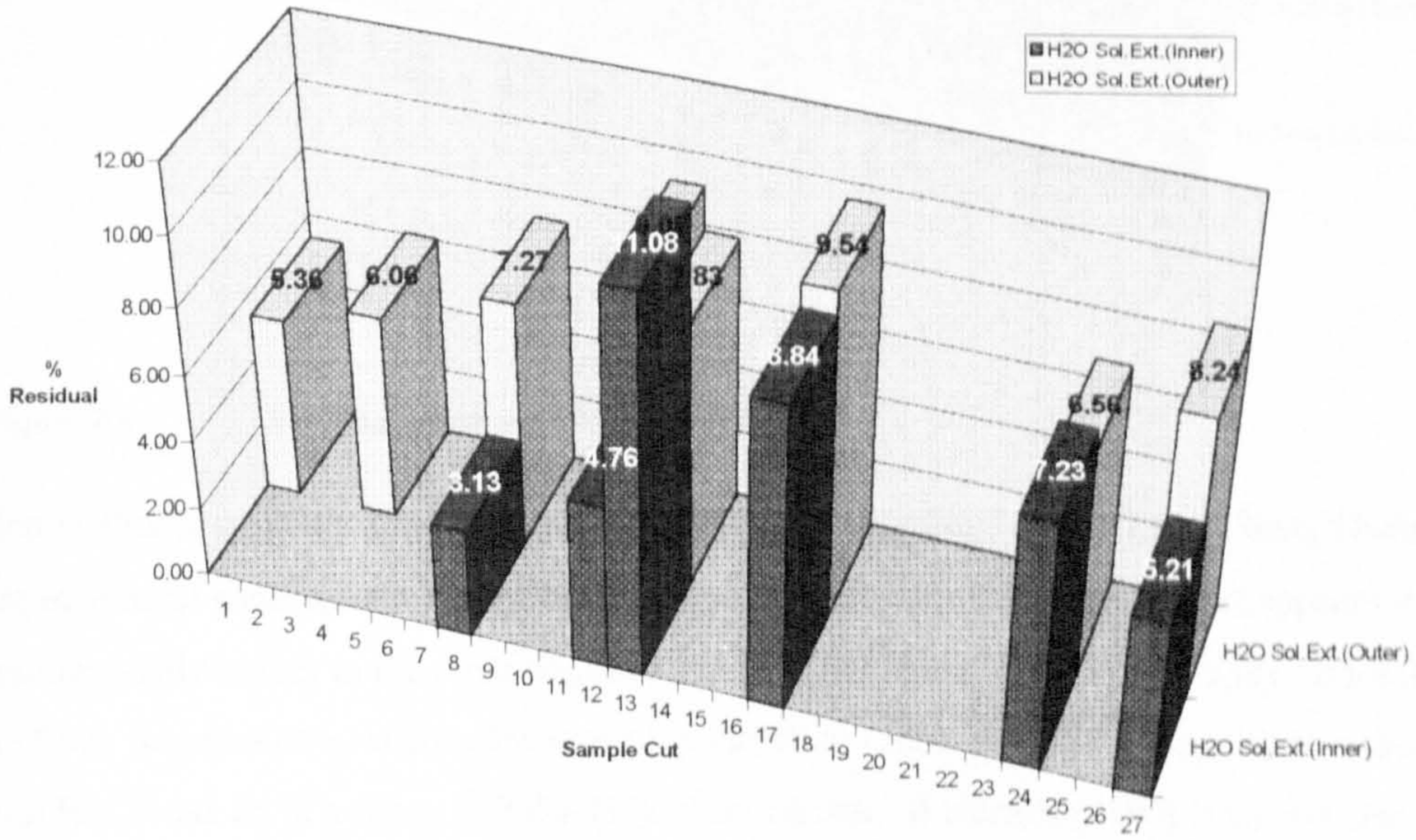


Figure 7.3 **Residual water solubles measured in samples taken throughout Roman plank**

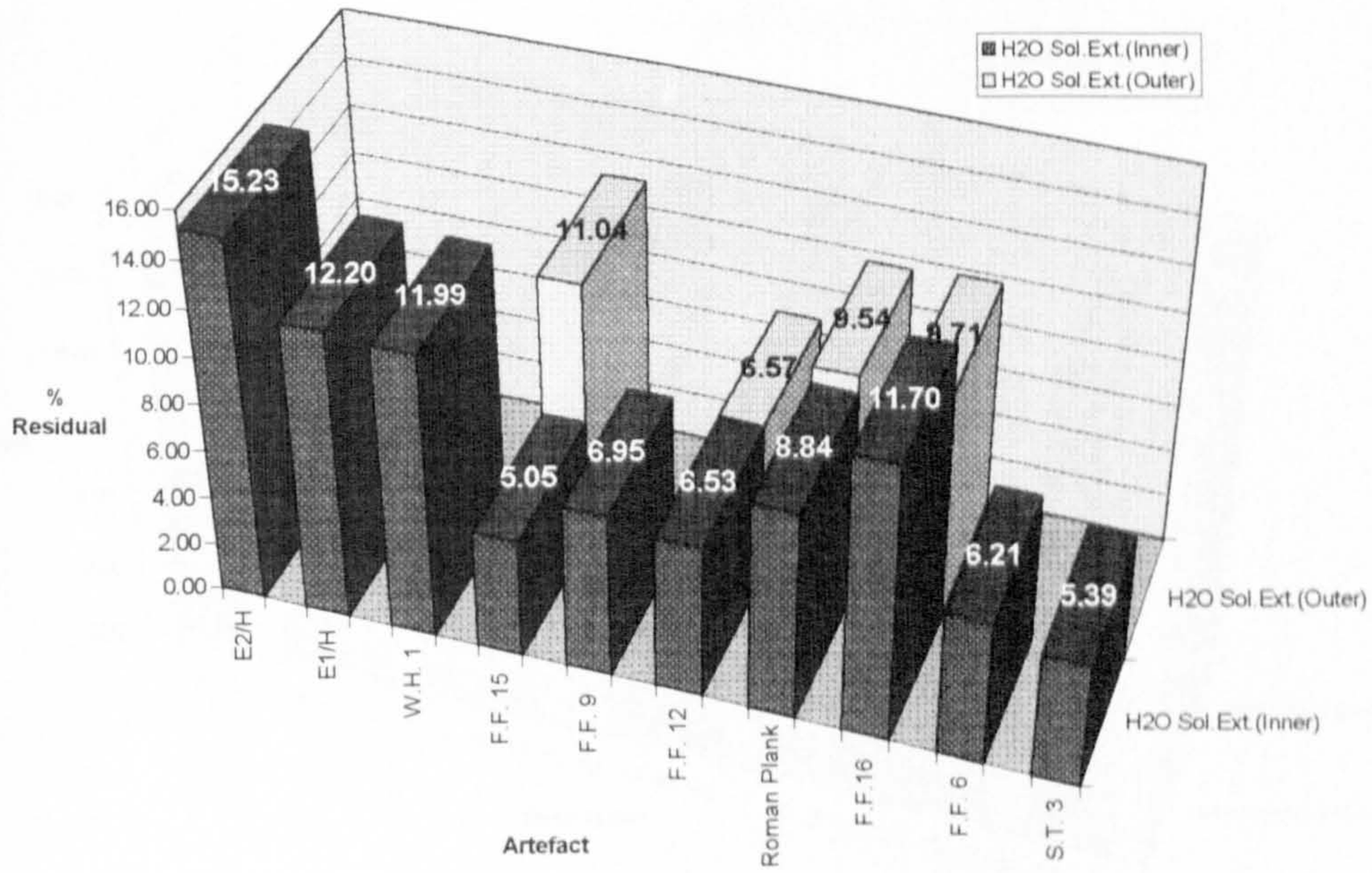


Figure 7.4 **Residual water solubles in artefacts**

Hemicellulose contents also show inconsistent trends (Figures 7.5 and 7.6). Though heartwood values are in general significantly higher than sapwood values, hemicellulose content appears to be systematically higher in the more degraded areas of the plank. This is especially noticeable in sample A3/Out. Samples of isolated outer layers compared to inner core ("D" Samples) also show this trend. Residual levels lie in a range of 36%-71% of sound oak. If Hedges (1990) is correct that hemicellulose undergoes almost complete dissolution before cellulose is affected, the levels ought to be much lower. It seems likely that a certain contribution to these values is being made by cellulose degradation products. And where hemicellulose contents exceed those for sound modern oak, this explanation would seem the only one possible. Hemicellulose levels in artefacts show more regular trends than do those from plank samples (Figures 7.5 and 7.6). Elevated levels in sample FF9 and FF6 are indicative of the good preservation in the core of these artefacts, shown up previously in Umax and density figures.

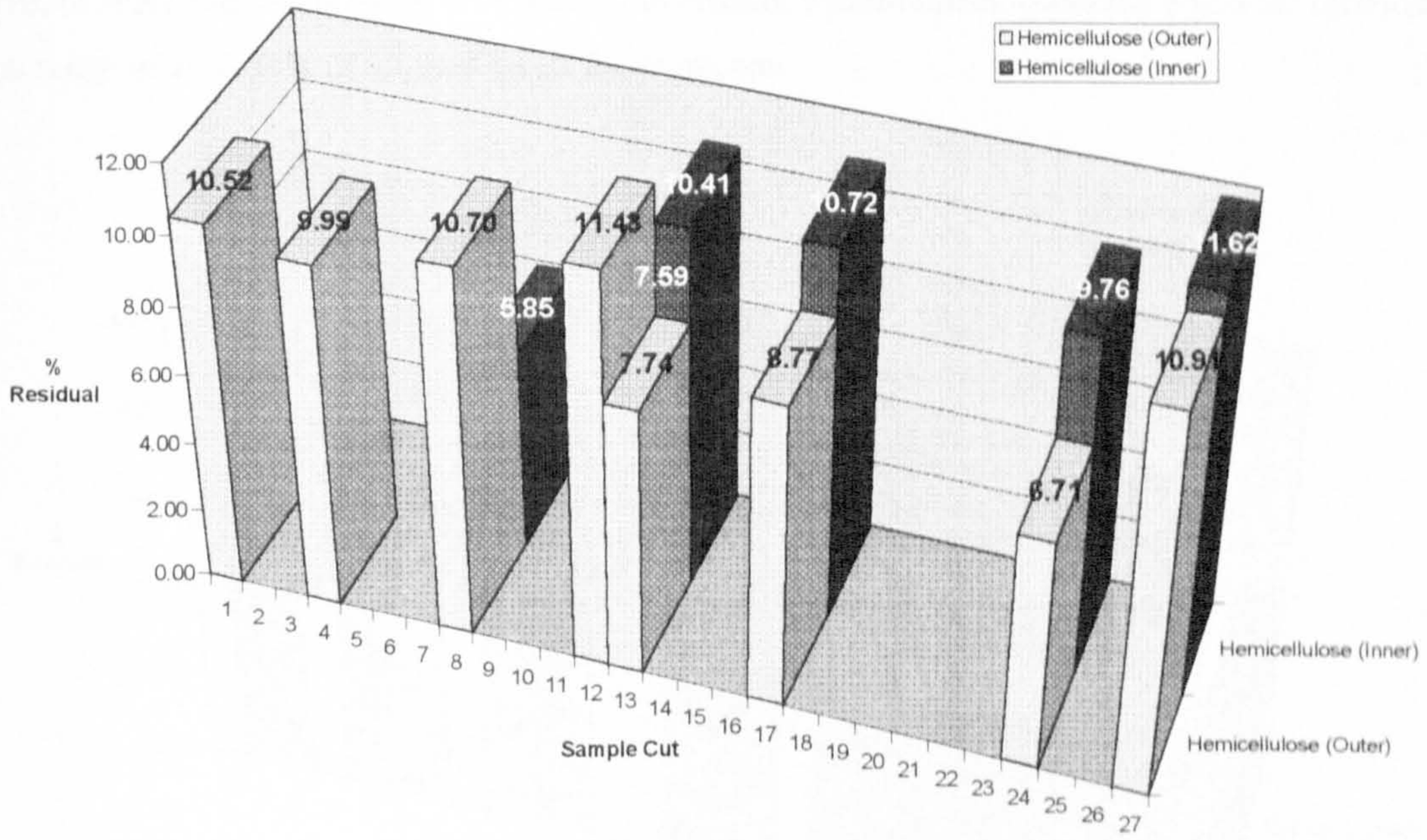


Figure 7.5 **Residual hemicellulose throughout Roman plank**

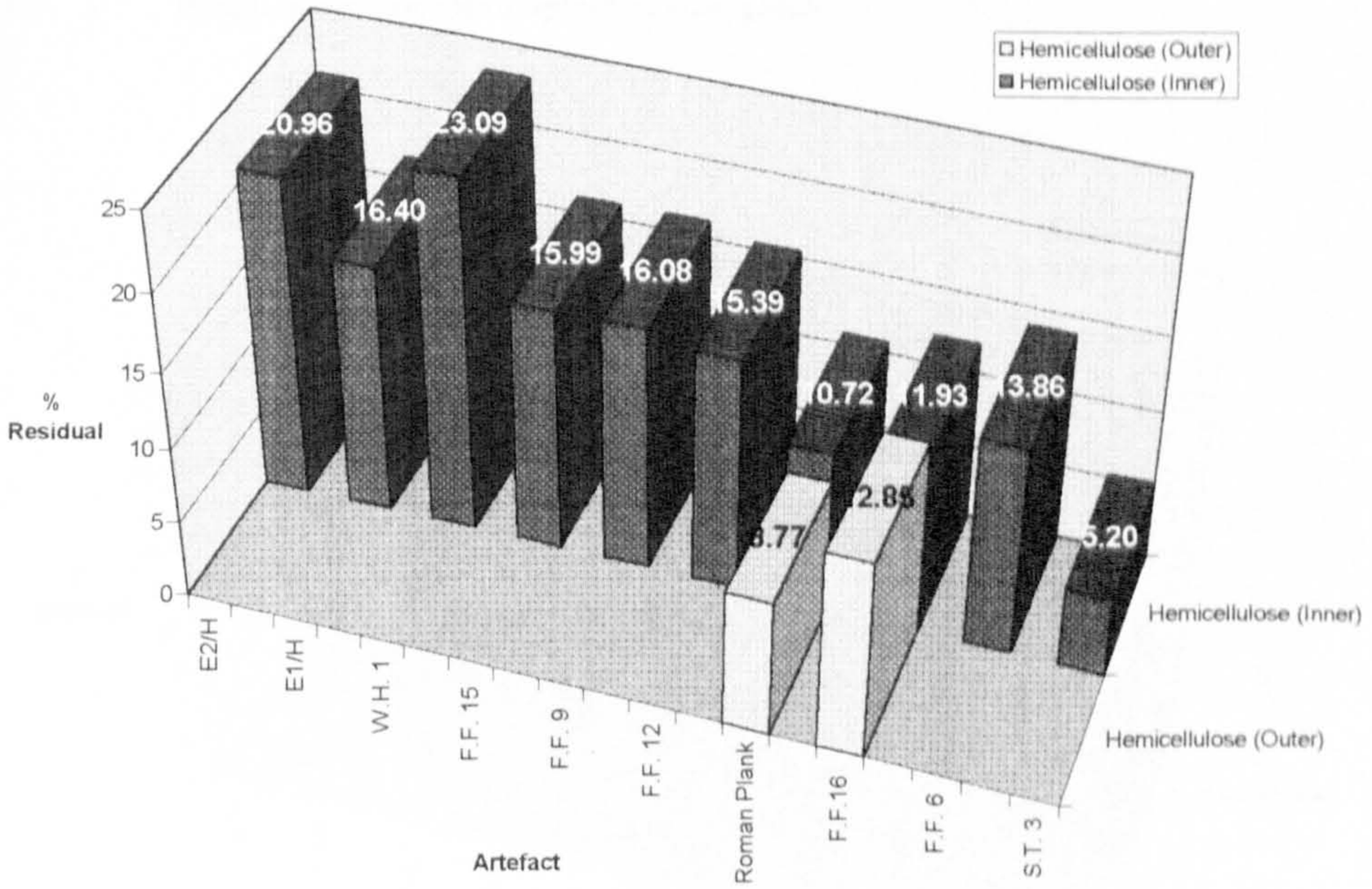


Figure 7.6 **Residual hemicellulose in artefacts**

The cellulose levels that have been recorded make much more consistent reading and follow the expected trends, with gradually decreasing levels towards outer edges of the plank and generally lower levels in sapwood than in heartwood (Figure 7.7). The particularly high level measured for sample A1/Out, though surprising, helps explain the comparatively high bulk density measured for this sample. Cellulose contents for artefacts also show very consistent trends, decreasing with increasing moisture content, and significantly reduced in outer wood compared to inner wood (Figure 7.8). The elevated

level of WH1/Inn seems likely to be a factor of error in measurement. Residual levels for cellulose lie in the range of 19%-56% of original levels for sound oak.

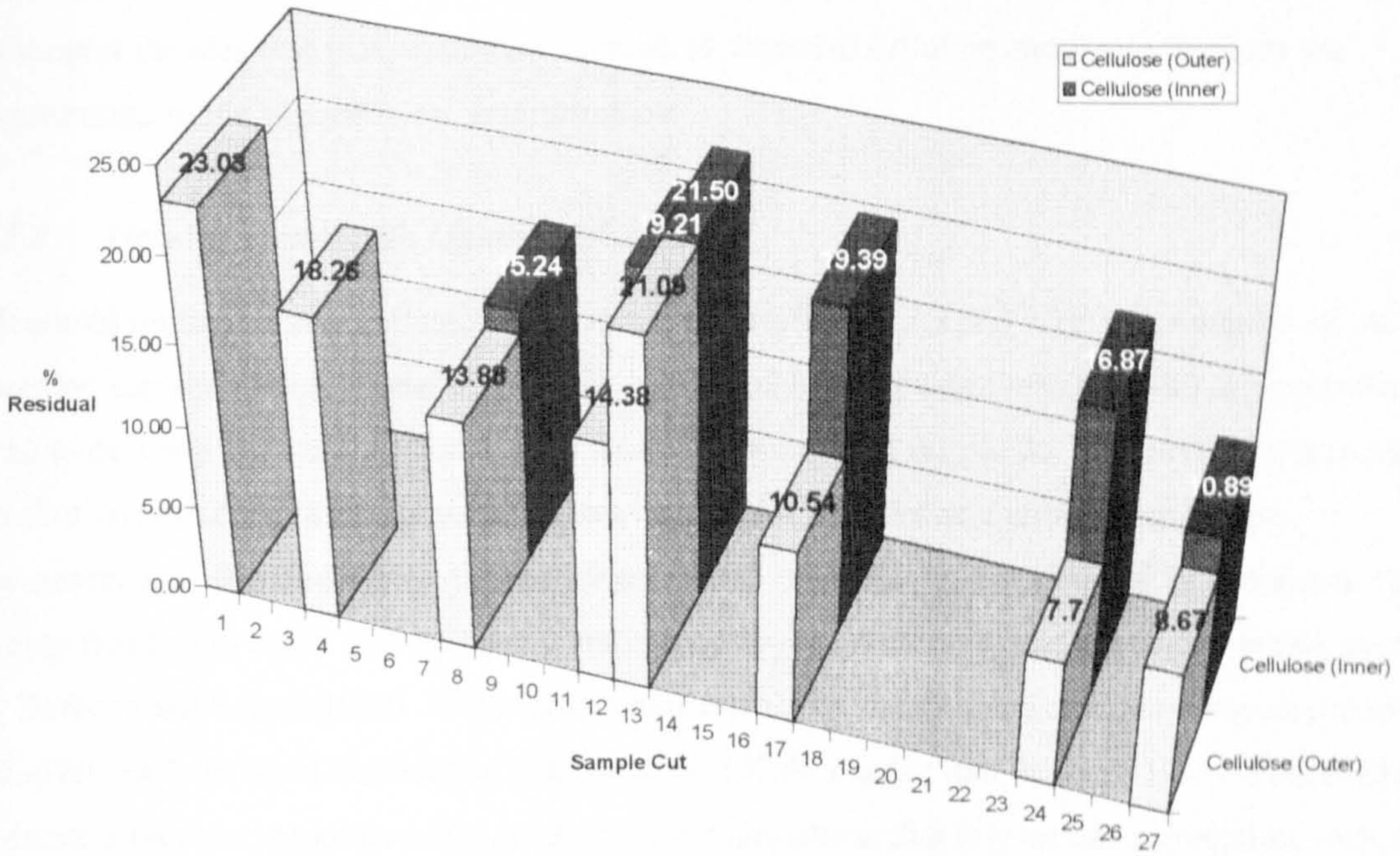


Figure 7.7 **Residual cellulose throughout Roman plank**

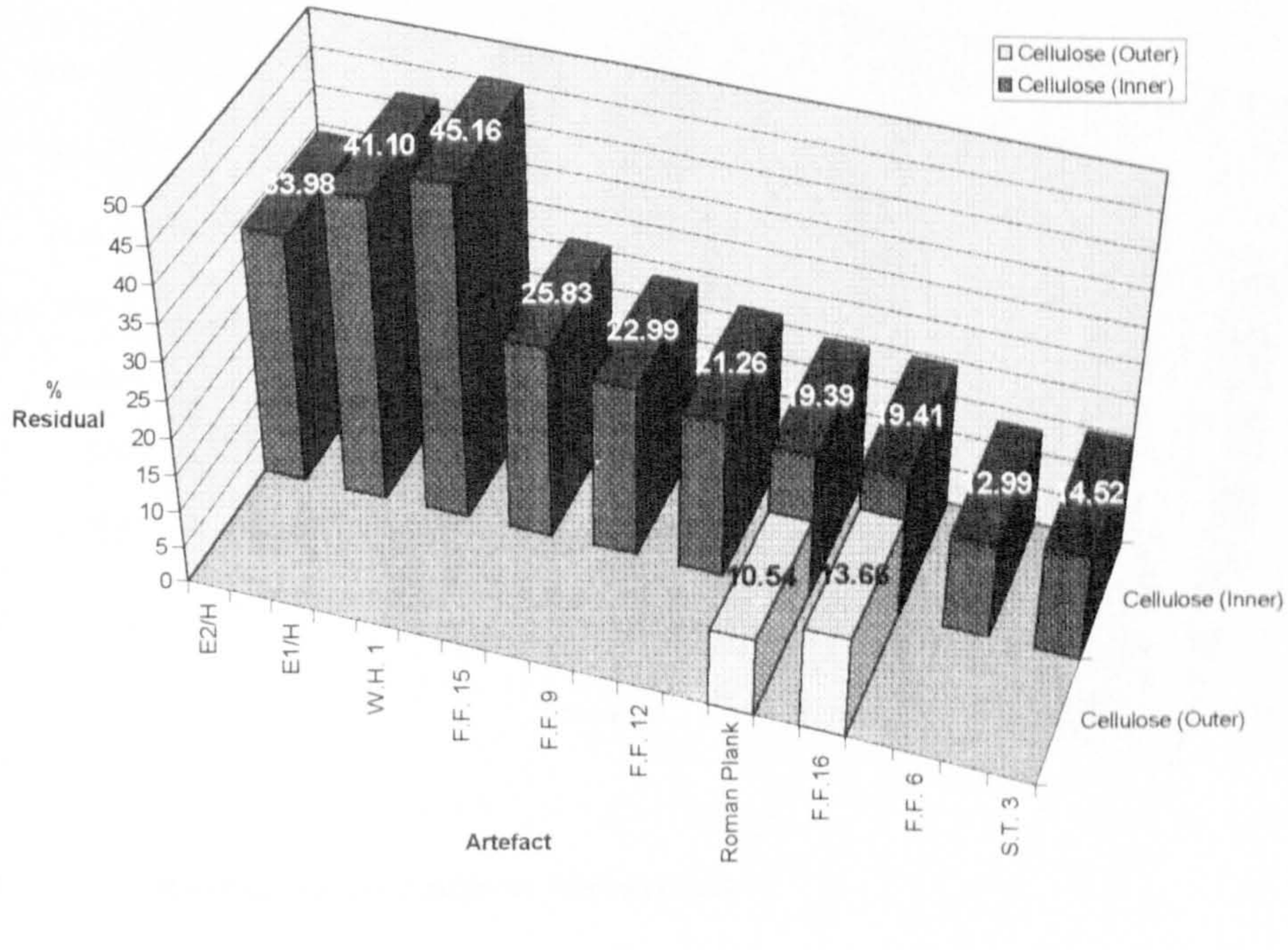


Figure 7.8 **Residual cellulose in artefacts**

Hoffmann (1982) felt that his data showed hemicelluloses and celluloses were removed during wood degradation in the same proportions as they exist in sound wood. The data from the present study does not support this conclusion. Hemicellulose/cellulose ratios calculated for fresh wood produce a figure of approximately 0.4. Our more degraded wood samples show rather elevated ratio values, suggesting

generally higher measured levels of residual hemicellulose than cellulose. These results disagree with everything we know of the relative vulnerability to degradation reactions of these two constituents. Since levels are as high as and sometimes higher than proportions present in sound wood, it would seem to support the idea that that significant amounts of degraded cellulose and lignin fractions are contributing to the hemicellulose determination.

7.3.3 General Trends with Lignins and Ash

Measured lignin contents are much more inconsistent (Figures 7.9 and 7.10). In a number of the samples, sapwood levels appear higher than heartwood levels, though levels in both can generally be seen to decrease toward the outer more-deteriorated portions of the plank. This may indicate a high level of error in correcting this value for ash content, i.e., multiplying error values for two measurements. Residual lignin content ranges from 53%-94% of original levels for sound oak. This argues that loss to lignin may be significant in waterlogged archaeological material, contrary to claims by Barbour and Leney (1982). Other researchers have noted measurable changes in lignin occurring relatively early in wood degradation (Borgin *et al.* 1975b; Fischer and Schmidt 1983). This would indicate a need for reappraisal of a number of the calculations that rely on this assumption, including that for mass normalised yield.

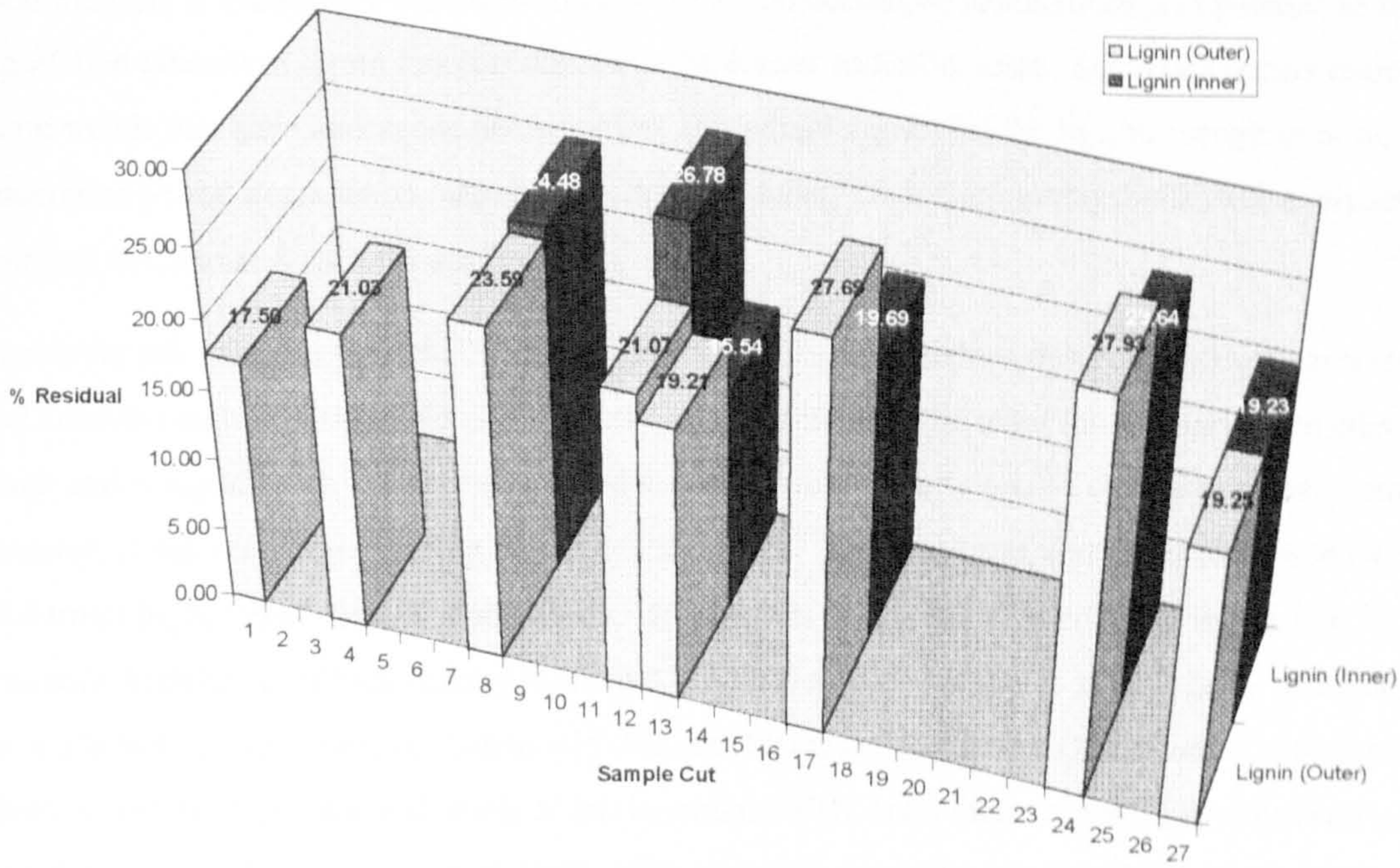


Figure 7.9 Residual lignin throughout Roman plank

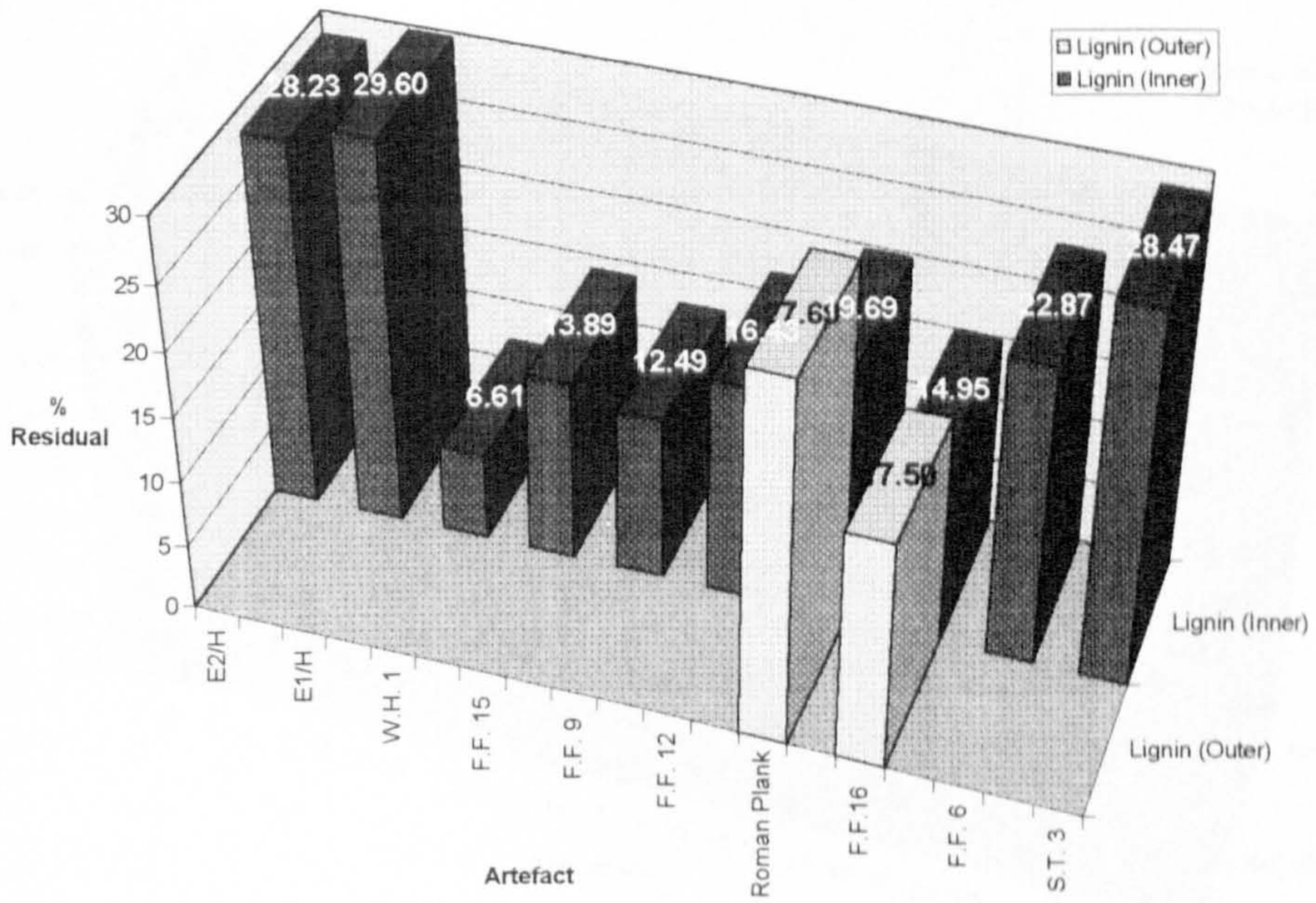


Figure 7.10 **Residual lignin in artefacts**

Trends in lignin content measured for the artefacts are very difficult to interpret, arguing incomplete removal of either cellulose or ash. Faix *et al.* (1994) report between 3%-8% carbohydrate present in their analysis of chemically-separated lignins. From holocellulose calculations it is possible to see that a significant amount of lignin has contributed to the earlier solubility tests. Since this occurs mainly in those woods that have undergone deterioration, this would argue that the lignin, though present, has undergone partial degradation into shorter chain products. Data from pyrolysis-GC/MS analyses reported in Chapter 8 partially confirm this.

Trends for ash content (Figures 7.11 and 7.12) follow the relationships observed by Hoffmann (1982) and Grattan and Mathias (1986). Ash content increases toward the outer more-deteriorated edges of the plank and is significantly higher in sapwood samples than in heartwood. Total range in ash content however, is not very large, varying between 2.5%-4.3%. This, however, translates to between 8.5 and 14.4 times higher than values for sound oak. High levels of ash can be seen to be responsible for the unusually high levels of bulk density measured for outer sapwood samples in the plank. Ash contents in these artefacts are relatively consistent with the conclusions of Hoffmann (1982) and Grattan and Mathias (1987). Very elevated levels of ash in sample WH1 are a factor of burial environment rather than deterioration level (Caple *et al.* 1997). The only surprise is the very low level of ash apparently present in the Sweet Track wood. As bulk density figures show, this wood is severely deteriorated. The question is whether levels of ash could become reduced again once the structure of the wood is opened up so much by deterioration that it is unable to bind minerals.

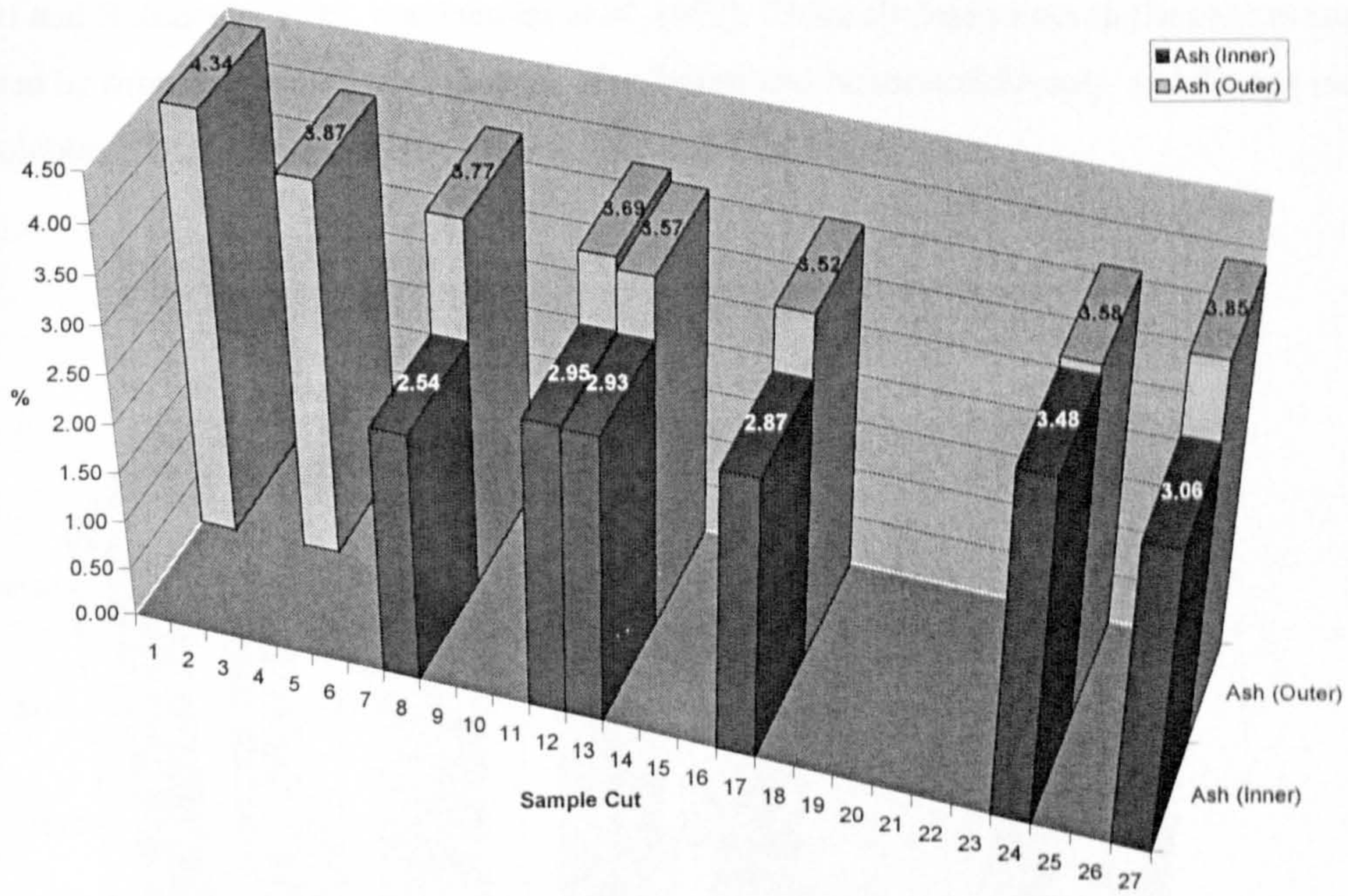


Figure 7.11 **Ash content of samples taken throughout Roman plank**

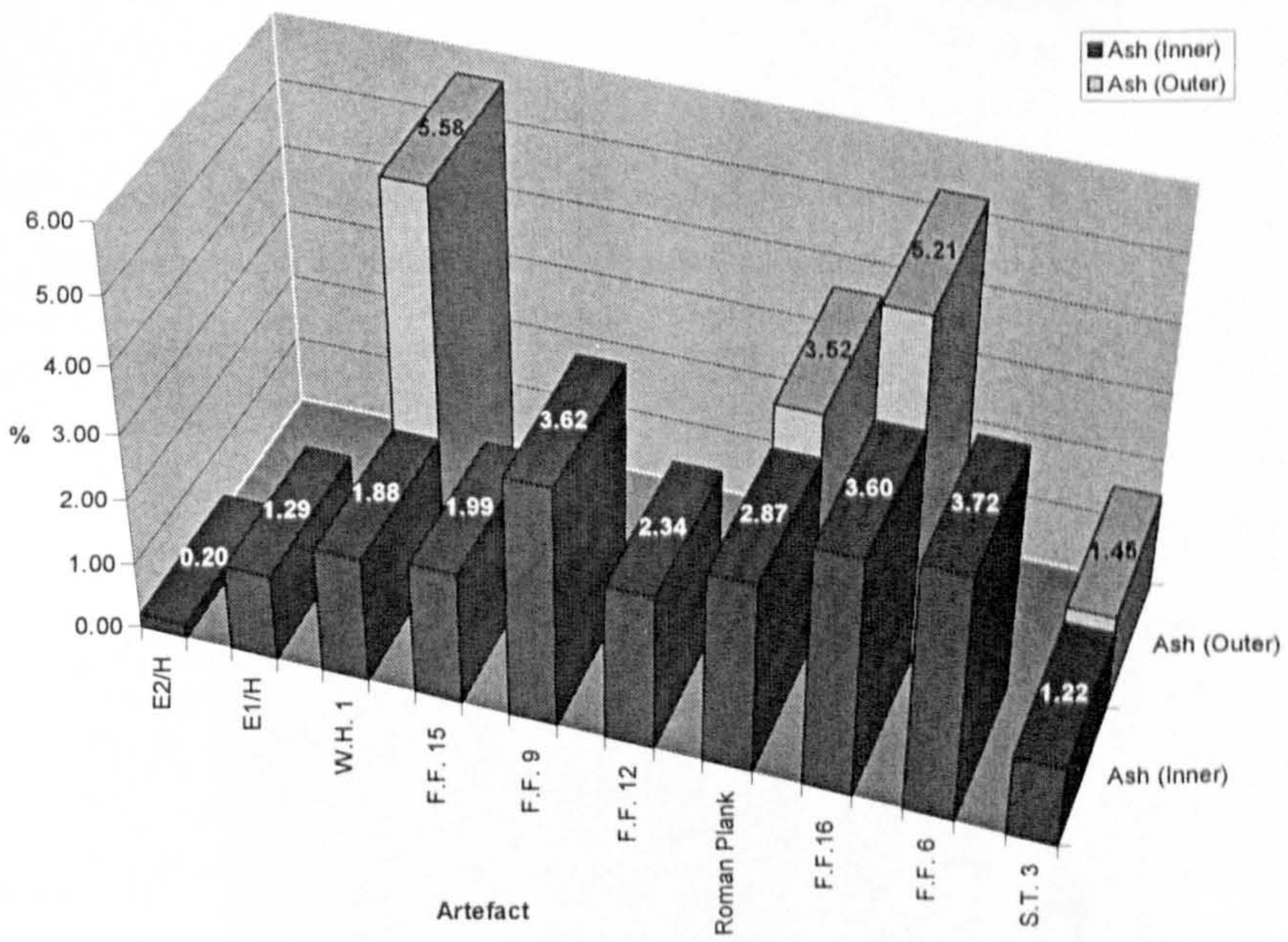


Figure 7.12 **Ash content of artefacts**

7.3.4 Holocellulose/Lignin Ratios

Various indices have been used in wood degradation studies to summarise chemical changes in a way that allows comparison between samples. Crystallinity index has already been mentioned (Chapter 6) and guaiacyl/syringyl ratios will be discussed in Chapter 8. Because of our understanding of the standard degradation path of wood, namely loss of polysaccharides before lignins, the cellulose/lignin ratio is common to most degradation studies, regardless of the method of analysis used

(Galletti and Boccherini 1995; Stankiewicz *et al.* 1997). Holocellulose values in the present study were calculated by summing constituent fractions of cellulose and hemicellulose only, and did not include water solubles. They are reported in Figures 7.13 and 7.14 below.

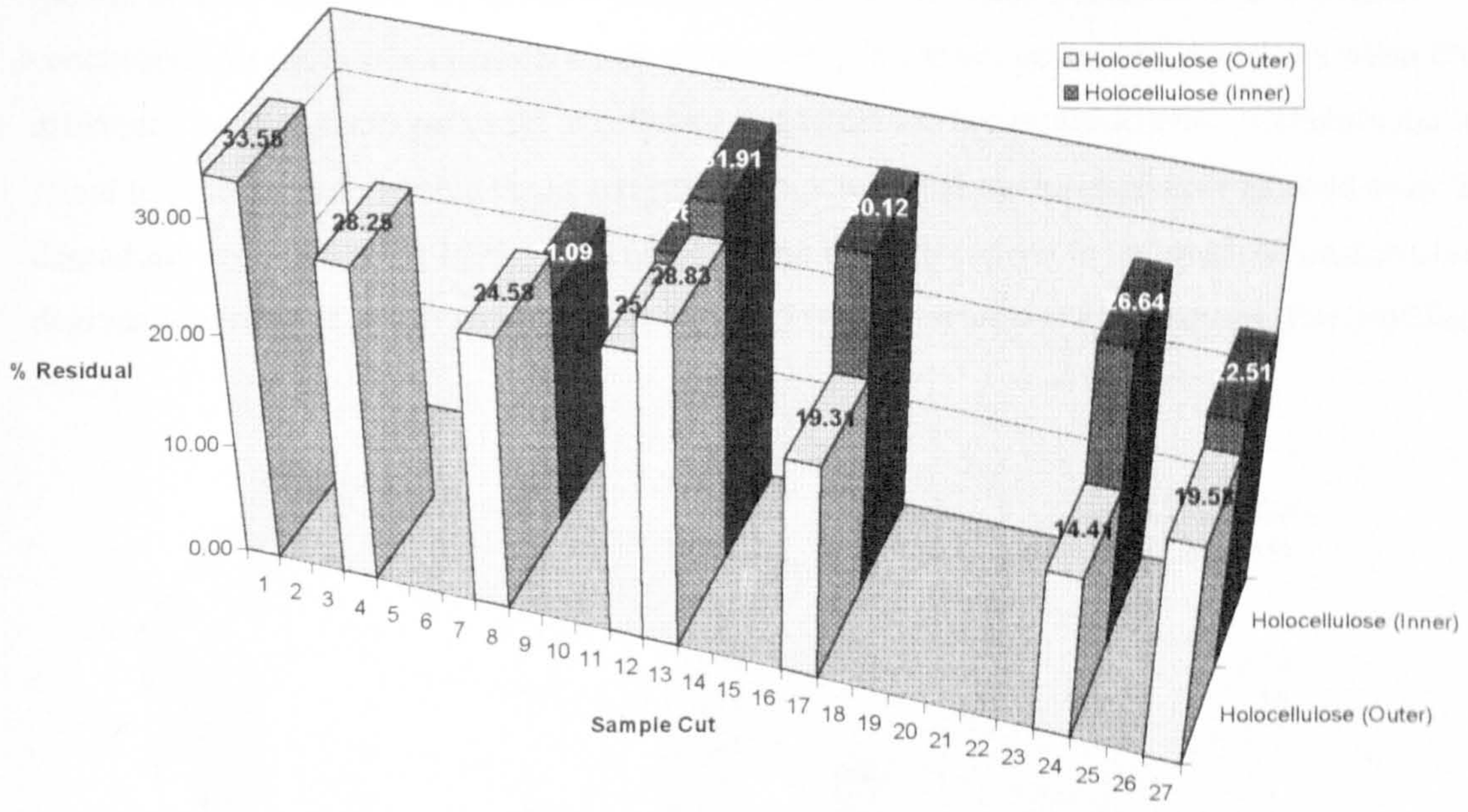


Figure 7.13 **Residual holocellulose content throughout Roman plank**

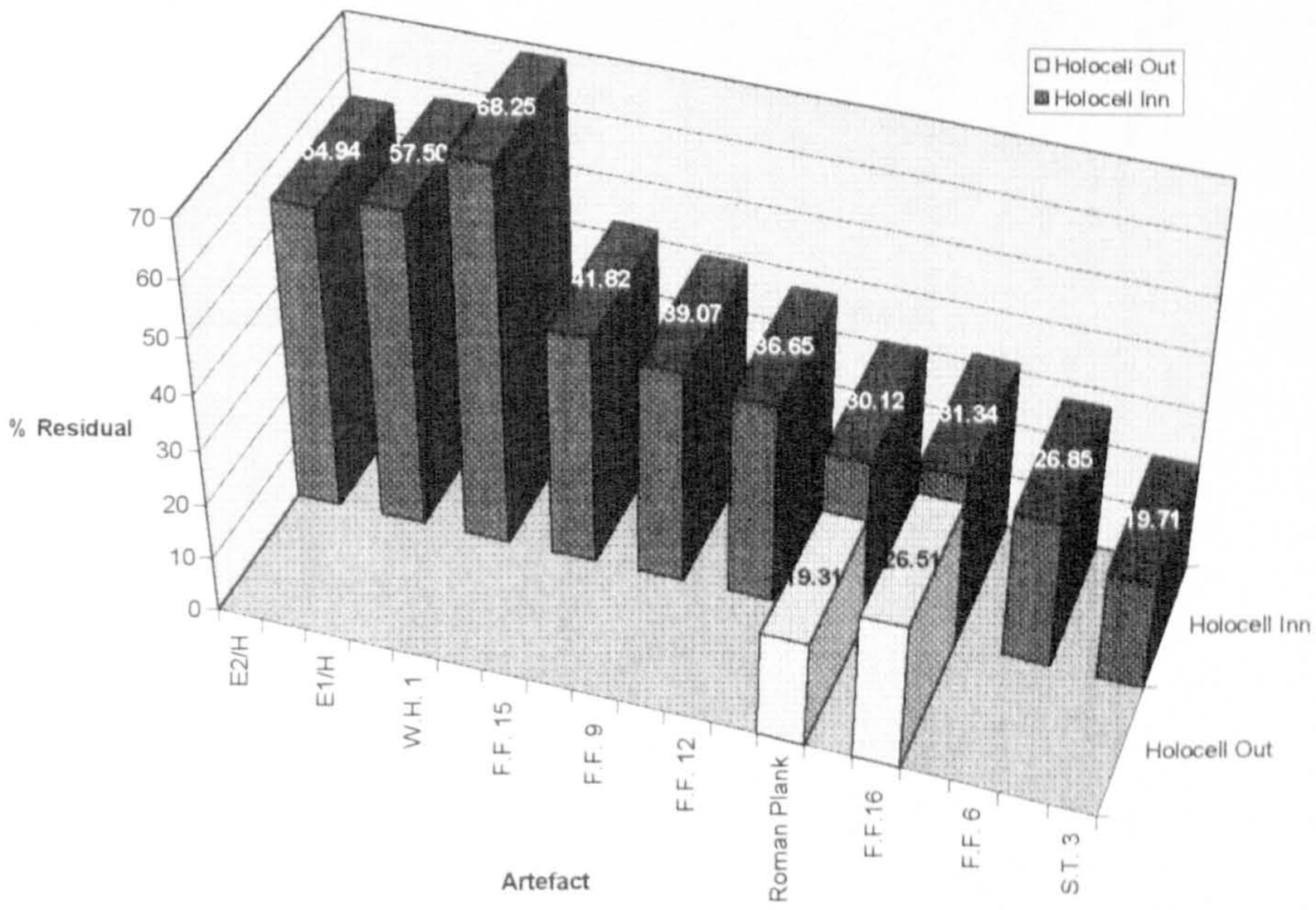


Figure 7.14 **Residual holocellulose in artefacts**

Because of the irregularity of the lignin results reported here, any attempt to summarise the results from bulk constituent analysis into a single index for degradation—the holocellulose/lignin ratio—is unlikely to achieve any level of success. As can be seen from Figures 7.15 and 7.16 below, holocellulose/lignin ratios for many of the more degraded wood samples are significantly higher than those for fresh (E1/Inn) and recent dry wood (E2/Inn). This suggests that no great level of confidence can be placed in the use of these figures in any absolute comparative sense with other published data or to draw conclusions for the design of conservation treatments. This is not necessarily surprising when the difference in degradative pathways of cellulose and lignin are taken into account. Cellulose has been found to decompose to soluble liquid and gaseous products that can be leached or diffused away from degrading wood (Ambrose 1990). In contrast, lignin tends to convert to intermediate products on degradation, some of which remain in the degraded wood as relocated aggregations (Ruel and Barnaud 1985).

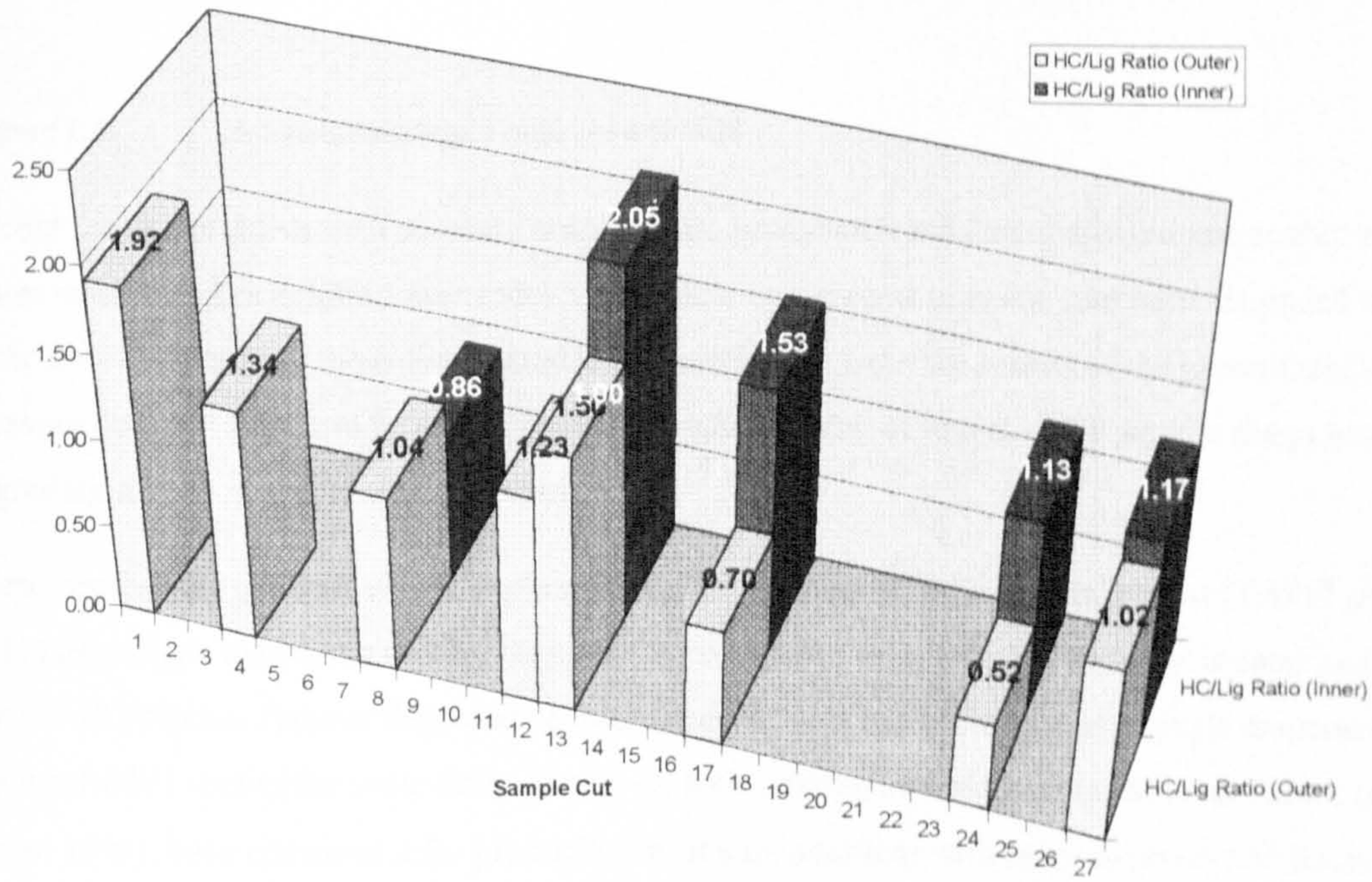


Figure 7.15 **Holocellulose/lignin ratios throughout Roman plank**

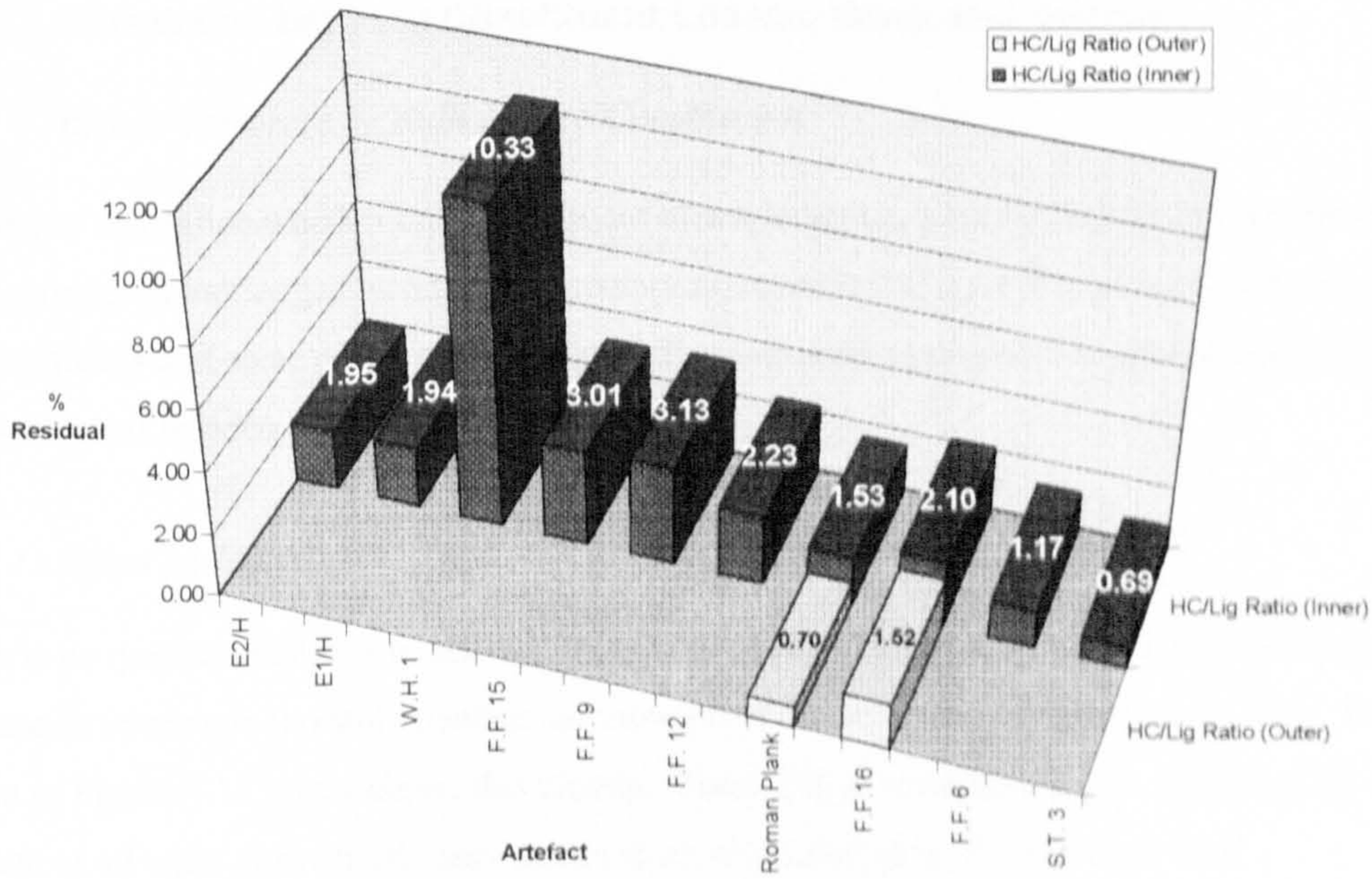


Figure 7.16 Holocellulose/lignin ratios in artefacts

Except for this problem with absolute index values, predicted trends are displayed reasonably well. Outer wood samples exhibit lower index values than inner wood samples, and more degraded woods show lower values than those less degraded. Nevertheless, from the results of the present study, this measure does not appear to be as useful as the single measure of loss to cellulose as a diagnostic for degradation level in archaeological material.

These results may go some way to explain the failure of the 1% NaOH solubility test (TAPPI standard-T212) as a single diagnostic tool for degradation in archaeological wood. This test is supposed to remove all polyoses and any degraded cellulose present, and has been used as a single diagnostic tool in modern timber studies for some time. However, both Grattan and Mathias (1986) and Panter (*pers. comm.* 1996), have criticised it for producing results inconsistent with other analyses and because microscopic investigations have shown losses to holocellulose proportions in degraded woods.

7.4 Correlation between Constituent Losses, Umax and Density

7.4.1 Effects Produced by Bulk Loss to Constituents

In order to determine whether bulk constituent measurement is a useful tool for the assessment of archaeological waterlogged wood, it is necessary to examine the level of correlation between bulk losses to constituents and some of the simpler diagnostic tools used commonly to appraise degradation level in archaeological wooden artefacts.

7.4.1.1 Effect on Umax

There is no question that loss to cell-wall polymers in degraded woods is directly connected to an increase in maximum moisture content, as shown first in the results of Hoffmann (1982). The graph shown in Figure 7.17 below shows this clearly. Total loss to constituents was calculated by subtracting the sum of all mass normalised constituent values, excluding ash, from one hundred.

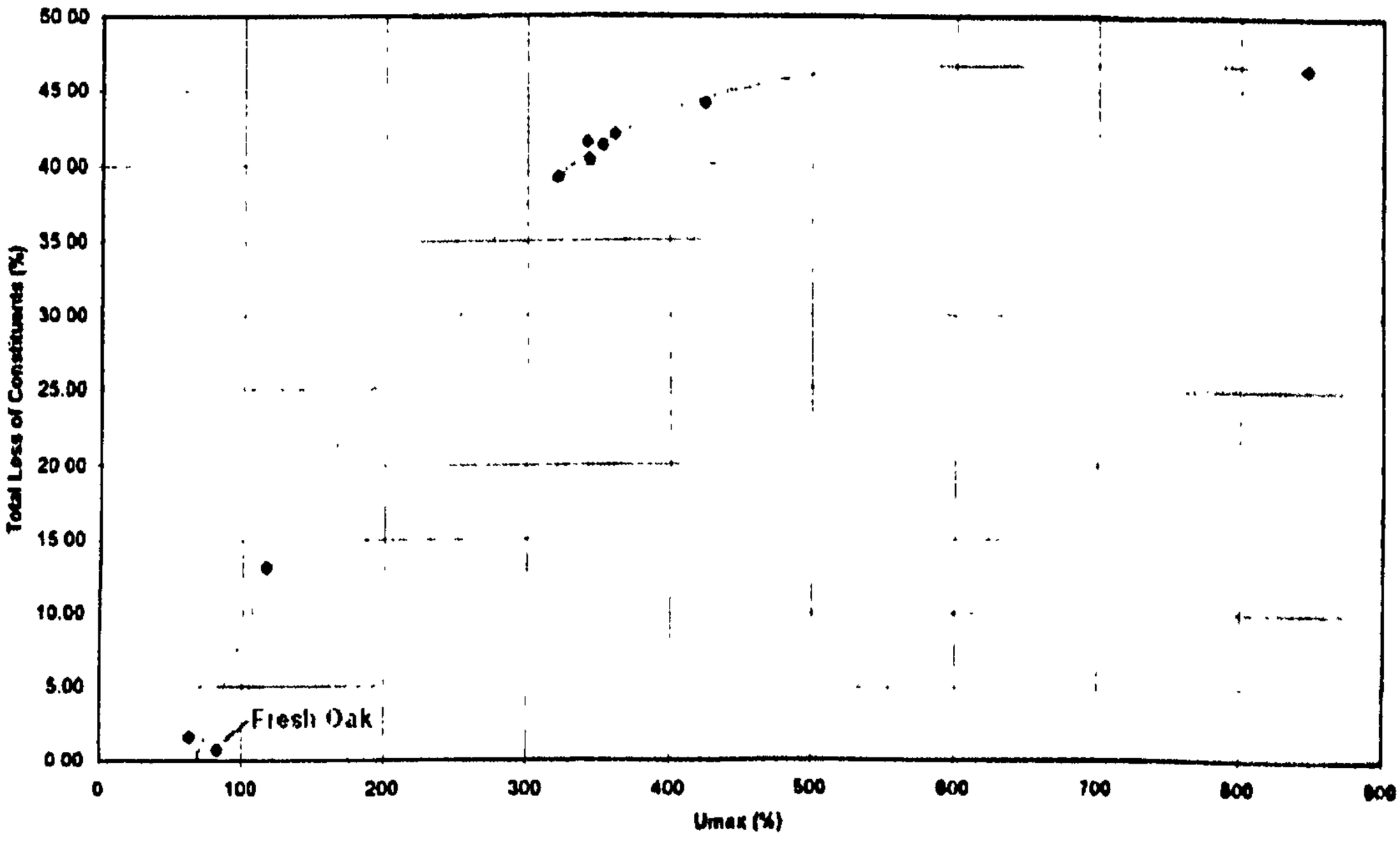


Figure 7.17 Total loss to constituents related to Umax

But the slope is not identical to Hoffmann's (a straight line), therefore the predictive value of such data is put in question. The level of increase to Umax per unit loss to constituents is relatively small at the lower levels of degradation, and very large once a certain amount of the chemical components have been lost from the wood. This argues that total losses to wood through degradation are more significant than losses to the carbohydrate fractions alone. It also argues that increases to moisture content are primarily related to a general opening up of physical space within wood structure rather than any change to relative number of bonding sites (see also section 7.6 below).

7.4.1.2 Effect on bulk density

As expected, bulk density figures decrease along with losses to cell-wall constituents (Figure 7.18. below).

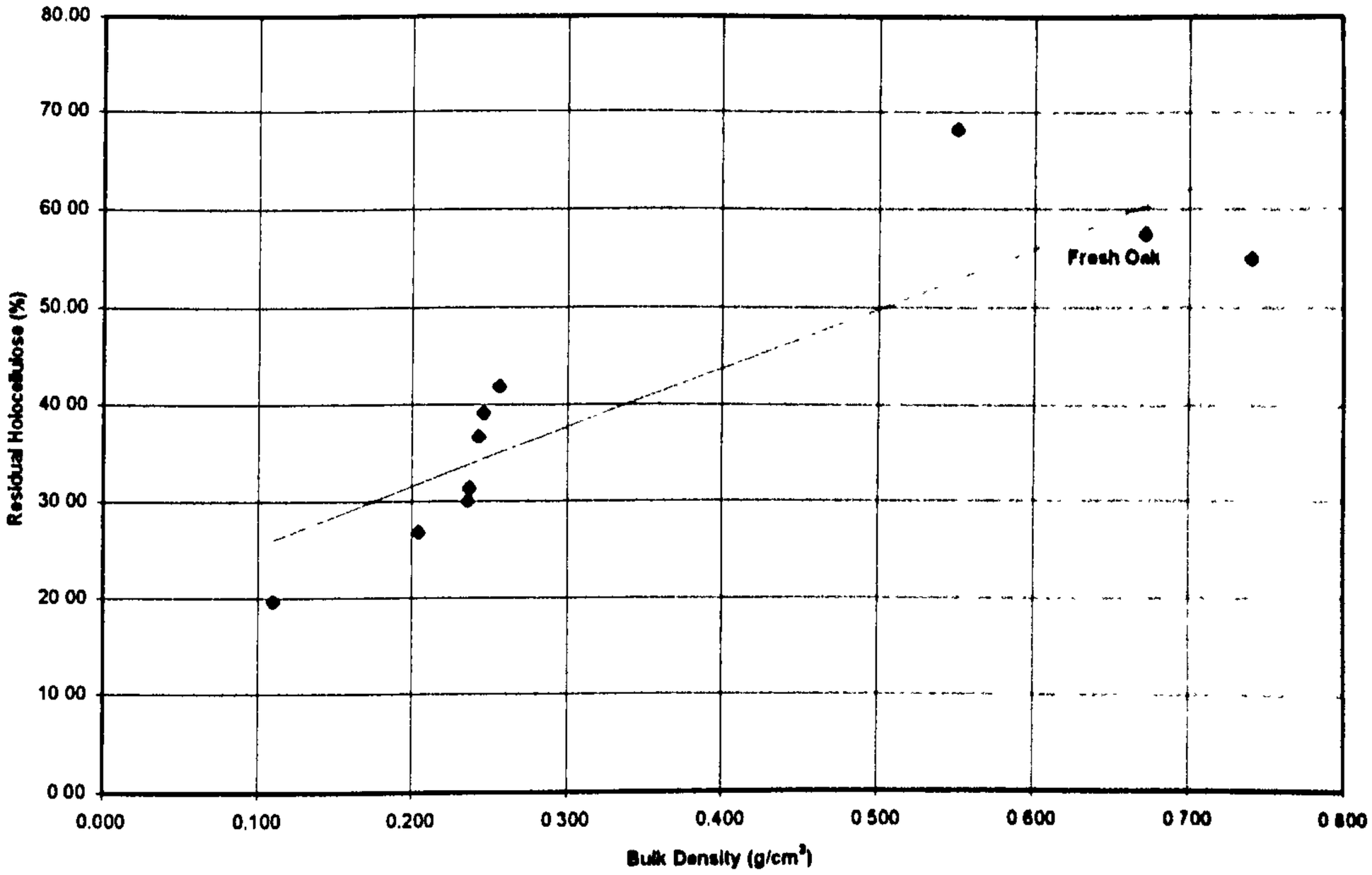


Figure 7.18 Residual holocellulose related to bulk density

Basic densities of artefacts range from approximately 17% to 87% of that normal for oak in conjunction with total losses to constituents ranging from 1.6% to 46%. This correlation of results accords well with data for *Quercus robur* published in Schniewind (1990). By the point at which bulk density has reduced to 0.1g/cm^3 (Hoffmann and Jones 1990), as with samples FF6 and ST3, more than half of original cellulose contents has been lost. Though it appears that, after a certain level of deterioration, zonality disappears (as shown by samples A3/Inn and ST3), it seems that this does not necessarily begin until the sample shows moisture contents of 700% and above and density losses of 80%.

The graph above (Figure 7.18) shows that relatively large changes to density appear to be associated with relatively negligible changes to total loss of constituents; despite the contribution made by elevated ash levels. This does not appear to be explainable by our knowledge of wood chemistry and degradation patterns, unless the contribution of cellulose to overall density is much less than that of lignin. This means that either we can not rely on the single measure of bulk density to make assumptions about residual levels of cell-wall polymers (e.g., for conservation treatment design), or that unacceptable levels of error are prone to creep into bulk constituent analyses. Considering the level of variables known to affect these results, this is not unexpected.

7.4.1.3 Effect on cell-wall density

Reduced overall levels of cell-wall constituents ought to be reflected in values recorded for cell-wall density. Losses of carbohydrates from the ligno-cellulose structure of the cell wall, while leaving this structure largely intact (as evidence from microscopy studies has shown), could be predicted to leave a residual substance with lower mass per unit volume than that of the original cell-wall substance. Channelling of cell walls by soft rot and bacteria, and losses to pit membranes, would predict the same.

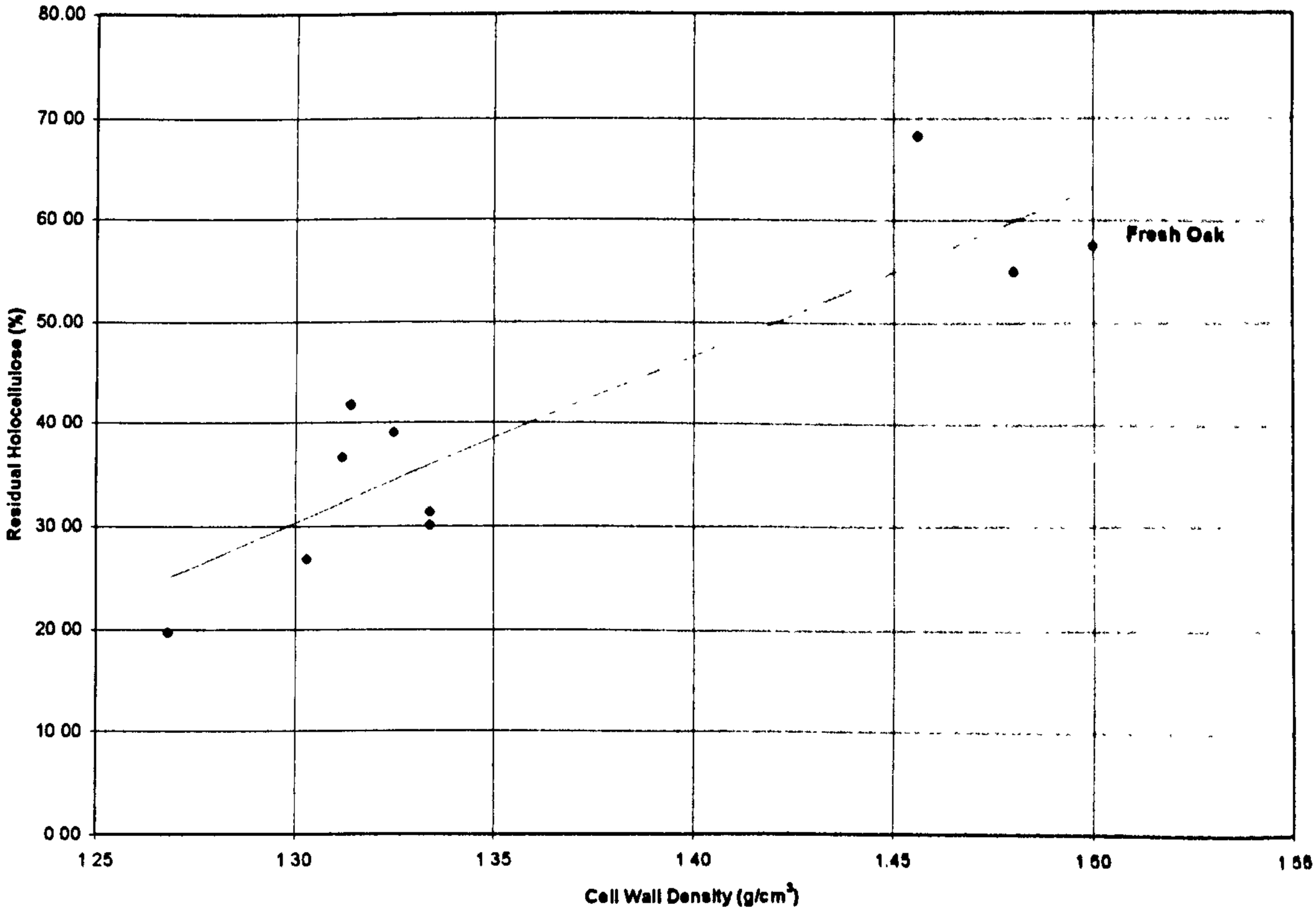
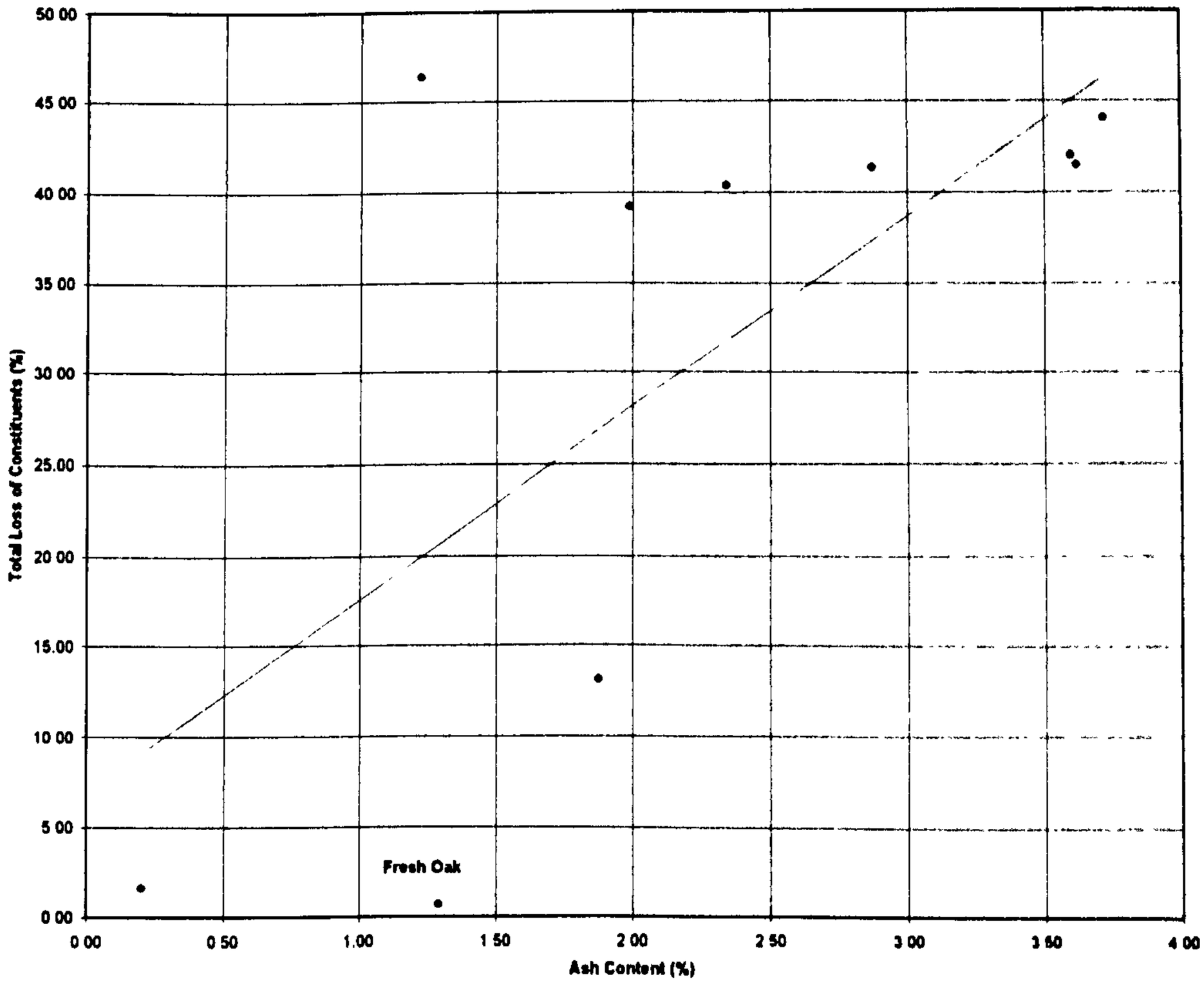


Figure 7.19 Residual holocellulose related to cell-wall density

In the samples measured in the present study, losses to cell-wall constituents are mirrored by losses in cell-wall density (Figure 7.19). Variations shown are not large and the majority of the change to cell-wall density appears to have taken place by the point at which 40% of constituents have been lost; bulk density is reduced to 38% of original values, and Umax is up in the region of 325%. After this point, changes to cell-wall density are negligible until the very uppermost levels of degradation have been reached (as with sample ST3). This may argue for carbohydrate losses being the most significant to affect cell-wall density, but it is questionable whether any more direct correlation can be reached.



7.4.2 Effects Produced by Elevated Ash Levels

The relationship between elevated ash levels and Umax and density have already been discussed (section 7.3.3). Its increase in line with losses to cell-wall constituents appears in Figure 7.20.

Figure 7.20 Ash content in relation to loss of constituents

The clearest indication of the close relation of level of ash to level of bulk constituent loss may be seen in the results for sample ST3, where ash content drops away, back almost to levels characteristic of fresh wood. It was suggested earlier in this chapter that this might be the result of a generally opened-up structure in this highly degraded wood. Yet results published by Hoffmann and Jones (1990) reported an ash content of 10.6% for a wood almost as thoroughly degraded, going by density, residual holocellulose, and Umax. This suggests that ash content can not always be depended on to perform as an accurate indicator of degradation in wood. Comparison of ash content values for this sample with its bulk density values do, however, go some way to explain anomalous density results. Here elevated ash contents in outer wood samples can be seen to explain the artificially high density values measured for this sample over its inner wood sample.

7.5 Correlation between Ash Content, Density, and Resistance Strength

We have been told that strength in wood is directly correlated to moisture content (Chapter 1). We also know that losses to cellulose, the main structural polymer of wood, will affect strength values. Losses to cellulose have been shown to be reflected in density changes. A final variable to affect strength in wood is level of mineral ash present. We have seen its effect on density in section 7.4.2 above. While elevated ash content will tend to cause reductions to tensile strength values, it will also tend to cause elevation of resistance strength values.

As discussed already in Chapter 6 (section 6.4.4.1), ash content proved to be a useful measure to explain some of the unexpected results in resistance strength. Samples C1/Out and WH1/Out, which exhibited higher-than-expected resistance values, also measured unexpectedly high ash content. It seems probable that this measure makes a good co-diagnostic measure for degradation in conjunction with one or more of the other available measures.

7.6 Correlation Between Constituent Loss and Sorption Results

Degradation of cell-wall constituents leads to losses of material from the cell wall matrix, affecting the physical structure and thus also affecting the permeability of the wood to water. Hoffman (1982) related losses to holocellulose directly to increases in water content, and Grattan (1987) related them to increases in the fibre saturation point— up to more than 60% in degraded woods. This increase was attributed to increases in internal cell wall volume, allowing more water to fill this space as degradation proceeds (Ambrose 1990). Internal volumes of the wood can be expected to decrease, however, after the cell wall becomes highly diminished of constituents, which goes some way to explaining certain observed lower values for fibre saturation point measured in very degraded woods (5.6.1), and some of the anomalies observed in the slopes of their sorption isotherms (5.6.2).

Changes to chemical constituent ratios in wood can be expected to be reflected indirectly in the upper portions of the sorption curve where physical changes are registered, and directly in lower portions of the sorption curve where changes to number of available sorption sites are registered.

As already remarked in Chapters 5 and 6, bulk losses to constituents were certainly registered in the increased slope of the upper portions of the sorption curves measured for the degraded archaeological woods. Samples measuring higher total constituent loss measured correspondingly higher slope in this region, by-and-large. Reduced thickness of cell walls and reduced overall density must be the major factor driving this trend.

Changes to the initial portion of the sorption curve, attributable directly to changes in constituent ratios, was not for the most part observed in the results from this study. Very small differences were observable in the slope in this region between degraded and undegraded samples, with more degraded samples exhibiting very slightly steeper slope than undegraded. This suggests some small increase to total number of sorption sites in the wood, but much less than the large increases in hygroscopicity observed by conservators in this material would have suggested. This leads us to conclude that these increases in

hygroscopicity may be more a factor of increases to internal surface area in the wood, than to any net increase in free sorption sites. Since losses to carbohydrates can be expected to reduce numbers of sorption sites, while increases in smaller carbohydrate and lignin breakdown products can be expected to increase numbers of sorption sites, it is perhaps not surprising that the affect of constituent changes on this area of the sorption curve is less than might have been expected.

This means that measures of constituent loss in archaeological wood will always only be a general gauge of changes to its sorption properties.

7.7 Summary

It should be clear from the discussion in this chapter and the previous one that no single standard measure commonly used for degradation assessment in archaeological wood is going to prove reliable as a diagnostic tool. Hoffmann (1982) expressed similar (though less detailed) reservations about the use of bulk chemical analysis for the characterisation of degraded woods. Grattan and Mathias (1987) concluded that this type of analysis is not usually worth the effort, unless large batches of wood are to be treated, and furthermore, that its results must be interpreted as guides rather than absolute indications of the residual constituent levels in wood.

These reservations are reflected in the fact that very little evidence exists for conservators making use of the data from chemical analysis in designing treatments for waterlogged wood. They have not, for example, attempted to treat the major holocellulose and lignin components as separate problems, or to devise chemical treatments according to their relative proportion in degraded wood. This disregard of chemical differences has been possible because for many years the standard procedure for wood treatment involved total water replacement and impregnation of the artefact with waxy, crystalline, or polymer solids. More recent work, aimed at defining the chemical properties of water-degraded wood for conservation purposes, (Cook and Grattan 1985; Hoffmann 1985; Young and Wainwright 1982; Ambrose 1990) has not yet led to greater attention to the treatment of lignin as well as depleted cellulose. The major problems that have arisen with new treatments aimed at stabilising individual cell-wall chemicals alone have been discussed in Chapter 4. These methods also tend to contravene basic conservation ethics, and the efforts required to avoid coping with the water element usually involve expensive or undesirable amounts of organic solvents.

Yet what other simple tool is available for the diagnosis of degradation in waterlogged wood by the conservator? And why, since results from these simple tools discussed in Chapters 6 and 7 appear to show consistent and reasoned trends, can the conservator not rely on them as absolute predictors for component levels, drying behaviour, or permeability in archaeological wood? These are questions which I feel are in need of some concentrated critical appraisal.

The basic question underlying this research project has been whether it is possible to devise a method that is both non-technical and inexpensive (in terms of time, equipment, and materials) for the working archaeological conservator to find out what he needs to know about a piece of deteriorated wood in order

to assess how to treat it. Ideally, we would go right to source and attempt to obtain information about the sorption characteristics of the wood. But Chapter 5 has shown how complex and time-consuming this type of data can be to collect. So we look for another predictor that can provide this information indirectly and is more easily accessible to the conservator. This predictor will have to yield information on residual levels of carbohydrate (holocellulose) in the wood because these losses affect the wood-water relations and the drying behaviour of waterlogged wooden artefacts.

Conservators have a number of apparently easy methods of obtaining information about holocellulose content—indirect measures such as bulk density, cell-wall density, and water content, and TAPPI/ASTM standard preferential solubilisation tests for polysaccharides. But, as discussed in earlier chapters, each of these has its drawbacks. The TAPPI/ASTM measure of holocellulose content is accurate enough for new wood, but becomes increasingly inaccurate the more deteriorated a piece of wood is. This is principally because deteriorated wood not only experiences losses to holocellulose but also undergoes a number of other chemical changes in the process (e.g., increase in mineral content, fractionation of lignin, etc.). Unfortunately, the TAPPI/ASTM tests pick up these products as well and therefore yield corrupted measures of constituent contents. The other three measures (water content, bulk density and cell-wall density) are even less satisfactory, since they are at best indirect measures of holocellulose content, and also include a substantial degree of error (Sections 6.2.2; 6.3.2; 7.2.2). They, like the TAPPI/ASTM tests, are also affected by other chemical processes associated with wood deterioration.

Nevertheless, it is sometimes argued that these are adequate measures for the conservator to use, on the grounds that each of them appears to show a clear correlation with the degree of deterioration as measured by water content. This can be seen in Figures 6.4, 6.8, and 7.13. In each graph, the horizontal axis ranks our 10 wood-samples according to their deterioration as measured by water content, while the vertical axis shows the bulk density (Figure 6.4), cell-wall density (Figure 6.8), and residual holocellulose (Figure 7.13). In each case, one can observe a clear positive or negative association between the indirect measure of constituents loss on the vertical axis and the degree of deterioration as measured by Umax on the horizontal axis. It might be thought that using these measures the conservator could simply read off the cellulose content corresponding to the given measure, and choose the treatment accordingly, for example, making use of a program such as PEGCON.

However, there are serious arguments against this approach. For one thing, although one obtains a clear correlation between the measures on the vertical axis and a *ranking* of samples according to deterioration, it is not so clear precisely what measure on the vertical axis one would obtain for a given absolute *level* of deterioration in a sample. For another, these graphs show that the relationship is not a perfect one: the ten data-points make up a scatter (effectively), not a straight line, and thus it seems likely that the apparently simple relationship between, say, bulk density and Umax is perturbed by one or more of the following: measurement error, stochastic error within the sample, and/or movements in

underlying variable(s) that *also* systematically affect one or both of bulk density and water content. Furthermore, it is not even clear that the relationship between each of the variables on the vertical axis and the degree of deterioration on the horizontal axis is linear at all—rather than, for example, exponential, logarithmic, or inverted-U-shaped.

In order to develop a reliable diagnostic for the residual holocellulose content in a given piece of wood, it would be necessary for a researcher to obtain an accurate measure of the holocellulose content, as well as of bulk density, cell-wall density, Umax, and preferably all the other variables that are thought to affect (or to be associated with) residual holocellulose content, for a very large sample of pieces of wood (several hundred at least). With a sufficiently large sample, the researcher could then construct a multiple linear regression model something akin to the following form:

$$Y = \alpha + \beta_1 X_1 + \beta_2 X_2 + \beta_3 X_3 + \ldots + r$$

where Y = accurate measure of holocellulose content or mass loss to constituents

X_1 = bulk density

X_2 = cell-wall density

X_3 = residual holocellulose

α = constant term

β_1 = estimated coefficient on X_1 (i.e. size of change in degree of deterioration with a 1-unit change in bulk density)

β_2 = estimated coefficient on X_2 (i.e. size of change in degree of deterioration with a 1-unit change in cell-wall density)

β_3 = estimated coefficient on X_3 (i.e. size of change in degree of deterioration with a 1-unit change in residual holocellulose)

r = error term.

If one obtained statistically significant coefficients on X_1, X_2, and X_3, as well as a statistically significant estimate of α, then one would have an equation into which a practising conservator could plug her/his measures for bulk density, cell-wall density, and residual holocellulose for a given piece of wood, and simply calculate an accurate measure of holocellulose content.

However, there are a number of problems with this approach. First, and probably most important, judging from the experience of the present study, collecting information on all the variables necessary for a sample of several hundred pieces of wood in order to estimate such a multiple linear regression equation would be prohibitively costly in terms of time and resources, and is unlikely ever to be carried out. Moreover, it may prove impossible to obtain data on a number of variables that the theory of wood science suggests probably affect cellulose content (e.g., iron take-up, etc.), thus even if an equation were estimated it might well contain sources of systematic error. Furthermore, even though our scatter plots suggest that there *is* a clear relationship between these variables and true cellulose content or wood deterioration, the regression analysis might show that once we control for other variables this apparent clear relationship disappears. Therefore, although it would be of intellectual interest to find out how good these various 'low-tech' measures are as predictors of holocellulose content or wood deterioration, it is a very costly approach that might, in the end, might yield an equation that was seriously inaccurate,

or even one that was not useable at all. Certainly, in the present state of our knowledge, without the requisite large data set having been collected and the requisite statistical analyses having been carried out, these apparently low-tech approaches to assessing holocellulose content or wood deterioration, and thereby sorption characteristics, are seriously flawed: they measure the desired variable only indirectly, they are systematically perturbed by other chemical processes we know to be associated with wood deterioration, they do not control for other variables, and they contain large sources of error (both measurement error and, possibly, stochastic error).

Given these severe drawbacks, there is an urgent need for alternative diagnostic tools that can be used by the practising conservator as a more accurate and reliable measure of cellulose content. An array of such diagnostic tools does in fact exist, and a selection of the more accessible ones will be discussed in the next chapter. Although apparently much 'higher-tech,' the techniques of instrumental analysis discussed in that chapter (Elemental analysis, FTIR, and Py-GC/MS) have many advantages, both logistical and scientific, for the practising conservator. I will argue that these tools are, in the end, much less expensive than the array of indirect measures discussed above, because they require much lower levels of lab technical knowledge, time and materials, and that their results are much more accessible to conservation use because of the more precise and accurate information they yield.

8 Instrumental Analysis

8.1 Introduction

Instrumental analysis is a term sometimes used to describe the range of techniques for chemical analysis that involve harnessing the interaction of radiant energy with matter to obtain information about the structure of materials. The nature and concentration of elements and compounds present in a substance can be obtained by this approach. High-energy radiant sources are used to study inorganic materials, where they measure the relative amounts of energy emitted by the atoms excited in the substance. Organic materials, however, tend to decompose when subjected to the high energies necessary for such excitation. Therefore, the majority of instrumental techniques suitable for the study of organic materials such as wood centre around absorbance measurements, which reveal the characteristic wavelengths and intensities of radiation absorbed by a substance. Often, too, these techniques concentrate on the molecular rather than the atomic structure of substances; which can make them particularly useful in the study of complex biopolymers.

A number of instrumental analysis techniques have shown their value in the characterisation of wood. Much of the literature published up to now has concentrated on identification and clarification of wood constituents. Instrumental techniques found useful in these studies have included nitrobenzene and permanganate oxidation (Iiyama *et al.* 1988); acid hydrolysis/HPLC (Walters and Hedges 1988); CuO (Sarkanen and Ludwig 1971; Hedges and Ertel 1982); solid state ^{13}C, ^{31}P, and ^{1} H-NMR (Faix *et al.* 1994; Saiz-Jiminez *et al.* 1987); FTIR (Pastorova, *et al.* 1994; Faix *et al.* 1994); and pyrolysis gas chromatography mass spectrometry (Boon *et al.* 1987; Faix *et al.* 1990; Obst 1983; Pouwels *et al.* 1987). Degradation studies have largely concentrated on fossil woods and aerobic fungal degraded wood (Saiz-Jimenez and de Leeuw 1984, 1986; Van Smeeridijk and Boon 1987; Stankiewicz *et al.* 1997). A much smaller number of studies have concentrated on the identification of diagenetic markers in archaeological wood (Borgin *et al.* 1975a and b; Hedges *et al.* 1985; Saiz-Jimenez and de Leeuw 1986; Hatcher *et al.* 1988, 1989b; Lewis and Yamamoto 1990; Wilson *et al.* 1993; Camarero *et al.* 1994; Faix *et al.* 1994; Nelson *et al.* 1995; van Bergen *et al.* 1995). Only one paper discusses chemical changes that might effect moisture sorption within wood (Faix *et al.* 1994).

Many of these analysis techniques lie right outside the range accessible to the archaeological conservator in his everyday work, either because of cost or the expertise required both to run the analysis and to interpret the results from it. Three techniques that the present study believes have potential for diagnostic use in wood conservation are discussed in this chapter. These are: elemental analysis (CHN), Fourier transform infrared spectroscopy (FTIR), and pyrolysis-gas chromatography/mass spectroscopy (Py-GC/MS). The results from analyses of the woods under study in this thesis will be discussed, and the potential of the techniques for archaeological degradation studies examined. Where possible, evidence for the link between degradation level and sorption characteristics will be revealed.

Discussion will concentrate on the insights and conclusions that the non-specialist can obtain from the data yielded by such analytical techniques.

8.2 Elemental Analysis of Wood Flour

8.2.1 Principles and Previous Research

In elemental analysis, samples are combusted in a stream of oxygen until all organic components are burnt to carbon dioxide, water vapour and nitrogen oxide. After excess oxygen removal, these compounds are separated in a column before passing to a thermal conductivity detector. Blanks are analysed simultaneously to allow the mass of the gasses to be calculated from the areas under the respective peaks on a graphical trace generated by the detector. Results are usually expressed as percent carbon, hydrogen, and nitrogen, with oxygen calculated as the difference left after ash and water contents are taken into account.

Elemental analysis is a rapid and relatively inexpensive method for wood characterisation and degradation studies. Sample size required is less than a milligram, and results allow for immediate superficial appraisal. The four elemental concentrations can be combined to calculate the absolute quantities of constituents present in a sample. Plotting of ratios of these elements (e.g., in the form of a van Krevelen plot) will reveal compositional shifts indicative of preferential loss to certain of the sample material's constituents. Published results from elemental analysis show changes to the main wood constituents of degraded and undegraded woods (Hedges *et al* 1984, 1985; Hedges 1990; Waite and King 1980; Wilson *et al.* 1993; Nelson *et al.* 1995). Preferential preservation of lignins over polysaccharides is clearly shown as well.

This technique has also proved a useful adjunct in the clarification of the results from other analyses (Nelson *et al.* 1995). Nitrogen contents can be examined to determine the presence of proteins, an indication of fungal degradation (Nelson *et al.* 1995), and increased levels have been used as a general diagenetic marker for degradation in wood (Waite and King 1980; Zabel and Morrell 1995).

8.2.2 Experimental

Three samples of wood flour of approximately equal weight (2.3 mg) were subjected to elemental analysis. Samples from the outer regions of the Roman plank were compared to those of the central region, and samples from each of slightly-degraded, medium-degraded, and highly-degraded artefacts were also analysed to examine the usefulness of this technique as a degradation marker. Nitrogen, hydrogen, and total carbon content were determined, using a Carlo Erba Strumentazione Analyser. Results are usually expressed as percent carbon, hydrogen, and nitrogen, with oxygen calculable as the difference left after ash content is taken into account.

8.2.3 Results and Discussion

Results for triplicate analyses of sample C3/Out provided weight percentages as given in the table below. Weight percentage of oxygen was calculated from the difference remaining after ash and moisture content were taken into account.

		Carbon	Hydrogen	Nitrogen	Oxygen
Analysis 1	**Wt Percent**	64.14	1.31	2.29	28.57
	Carbon Ratio	1	0.25	0.03	/
Analysis 2	**Wt Percent**	55.65	1.41	2.00	37.25
	Carbon Ratio	1	0.30	0.03	
Analysis 3	**Wt Percent**	70.14	1.30	2.58	22.29
	Carbon Ratio	1	0.22	0.03	/

Table 8.1 Elemental analysis of a sample from the Roman well plank

Sample	Carbon	Hydrogen	Nitrogen	Oxygen
E1/nn	46.94	6.46	0.11	45.20
A1/nn	47.61	5.82	0.86	41.37
A2/nn	47.80	6.10	1.01	42.16
A3/nn	46.56	5.95	0.95	43.48
WH1/nn	45.43	6.33	0.21	46.15
FF12/nn	47.55	5.54	0.37	44.20
ST3/nn	51.73	5.79	0.39	40.87

Table 8.2 Elemental analysis of samples from the artefacts

As the results above show, lower hydrogen and oxygen contents (in relation to carbon content) are exhibited as degradation progresses, and they are considerably lower than those from undegraded fresh oakwood. According to Hedges *et al.* (1985), this shift corresponds to preferential carbohydrate loss. Nelson *et al.* (1995) and Wilson *et al.* (1993) also observed these changes in dry-site archaeological woods. Weight percentages of organic carbon can be seen to increase along with degradation in the sample results above. This, too, is consistent with the results of Nelson *et al.* (1995). The raised nitrogen levels (as calculated in ratio with organic carbon contents) found in the degraded samples above are characteristic of raised protein content, and argue for a significant contribution to degradation by aerobic pathways (Waite and King 1980). This firmly establishes the usefulness of this technique to produce diagenetic markers for archaeological wood.

The technique might be extended usefully to determine the average elemental composition of the organic material that is being removed or added. Where there is reason for suspicion that fungal degradation has artificially contributed to holocellulose fractions measured in wood samples, raised nitrogen levels might be a quicker way to test this than glucosamine determinations of chitin (Zabel and Morrell, 1992).

8.3 Fourier Transform Infrared Spectroscopy Analysis

8.3.1 Principles

In the technique of infrared spectroscopy, radiation from an infra-red source is divided in a spectrometer into two equivalent beams. One passes through the sample cell and the other through a reference cell. The two beams are then recombined and focused on a monochromator slit where the component wavelengths of the spectrum are separated out, finally to fall on a detector that emits electrical signals that can be amplified and recorded (Skoog and Leary 1992).

The difference in the absorption between sample and reference cells gives rise to the absorption spectrum. This is expressed as a series of dark lines appearing in the spectrum at those wavelengths where the light has been absorbed. Molecules give rise to bands rather than to sharp spectral lines, each band extending over a considerable range of wavelengths and frequently superimposed with a fine structure of separate lines. The absorption bands of the infrared spectra each correspond to a particular change in the vibrational state of a molecule, and each line in the band corresponds to a change in the rotational state (Laidler 1978). The characteristic absorptions of most of the organic functional groups are known. Characteristic changes to the spectra also allow the chemical environment around hydrogen bonds to be identified. The complete spectrum with its selective absorption bands will be very complicated and, particularly in the fingerprint region from 1400 to 990 cm^{-1}, will be unique to the substance under study. The intensity of the peaks is governed by the number of molecules in the sample, among other things, but this technique cannot be thought to be truly quantitative without rather complex corrections for peak overlap, scattering and absorption by the other materials involved in the technique (Skoog and Leery 1992).

IR spectroscopy is particularly good at picking up the presence and extent of hydrogen bonding. The hydrogen bonding within an organic molecule leads to a shift to lower frequencies within an absorption band and an intensification of the band (Laidler 1980). This should mean that the relative proportions of free –OH groups on the molecule (very important to sorption characteristics) can be identified by this analysis. Studies have been carried out that focus on the information about moisture given by FTIR spectra, but the interpretation of spectra for this sort of information is very difficult (because, says Loudon (1988), of the masking of bands by the very wide absorbance of water itself), still in relatively early stages and thus outside the bounds of the remit for this thesis (see section 8.1).

FTIR is a very rapid technique, whose equipment costs are relatively inexpensive, indeed more within reach for the archaeological conservator than scanning electron microscopy. The sample size required is

also suitably small, typically in the range of one milligram. Its main disadvantage is the high level of peak broadening and overlap introduced by complex and degraded sample material.

8.3.2 Previous Research into Archaeological and Degraded Wood

Hergert (1971) summarised the results of a comprehensive study of wood chemicals, more specifically the lignins, by FTIR. Crook *et al.* (1965) were some of the earliest to investigate degradation of wood using FTIR. They described oxidative effects visible in increased C=O vibrations in the FTIR spectra of aged woods. Wayman *et al.* (1971) investigated two ancient woods with this technique, providing some of the first markers for degradation. Fengel (1991) discussed the comparative effectiveness of FTIR and a number of other techniques of instrumental analysis for describing chemical and biological degradation in aged woods. Kim (1990) provided the most comprehensive study to date of markers for degradation revealed by FTIR analysis of waterlogged archaeological woods. Wilson *et al.* (1993) provided comparative spectra of a range of differently-degraded samples from shipwreck timbers. Faix *et al.* (1994) revealed the trend towards a generalised increase in hydroxyl groups in degraded lignins.

A certain amount of literature exists dealing specifically with FTIR in conjunction with the solving of conservation problems. Kirillov and Mikolajchuk (1990) studied the IR spectra, constructing cellulose/lignin ratios from peak areas in order to characterise degradation in archaeological waterlogged woods. They produced a number of statistical methods for use with this technique to reduce errors brought in by peak overlap, and found a close straight-line correlation between FTIR data and results from bulk constituent analysis. Mills-Reid *et al.* (1984) carried out quantitative incremental analyses of timbers from a waterlogged shipwreck in order to follow the progress of diffusion of polyethylene glycols into large structural blocks of wood. They modelled the potential of this technique for studies relevant to archaeological conservation and its ability to yield meaningful results to non-specialist workers. They did not, however, feel that it could be used easily for accurate quantitative work. Baker and von Endt (1988) discussed the advantages of FTIR microspectrophotometry for the non-destructive examination of works of art and other valuable artefacts where the removal of sample material is impossible.

8.3.3 Experimental Method and Materials

Small sub-samples from wood flours prepared by the methods described in Chapter 7 were taken from the archaeological and fresh woods that are the focus of this thesis, and ground further with an agate mortar and pestle. Between 0.9 and 1.0 mg of the ground sample was mixed by grinding with approximately 75 mg of spectroscopic-grade potassium bromide and pelletised in a SpectraTech Qwik Handi-Press. Every attempt was made to standardise the sample size used for analysis, in order that peak intensities should be more comparable. Spectra were measured on a Bomem MB50 FTIR spectrometer and processed using Win-Bomem Easy software.

Identification of peaks of interest for comparison was made by reference to the literature listed above.

8.3.4 Results and Discussion

The discussion here confines itself to a selection of the inner sections of the artefacts analysed in this study. No attempt was made to quantify peak areas or calculate such indices as holocellulose/lignin ratios.

Results from FTIR analyses were largely clear and unambiguous. Good reproducibility can be seen in the spectra shown in Figure 8.1 below—and much better congruence than displayed in results from bulk constituent analysis.

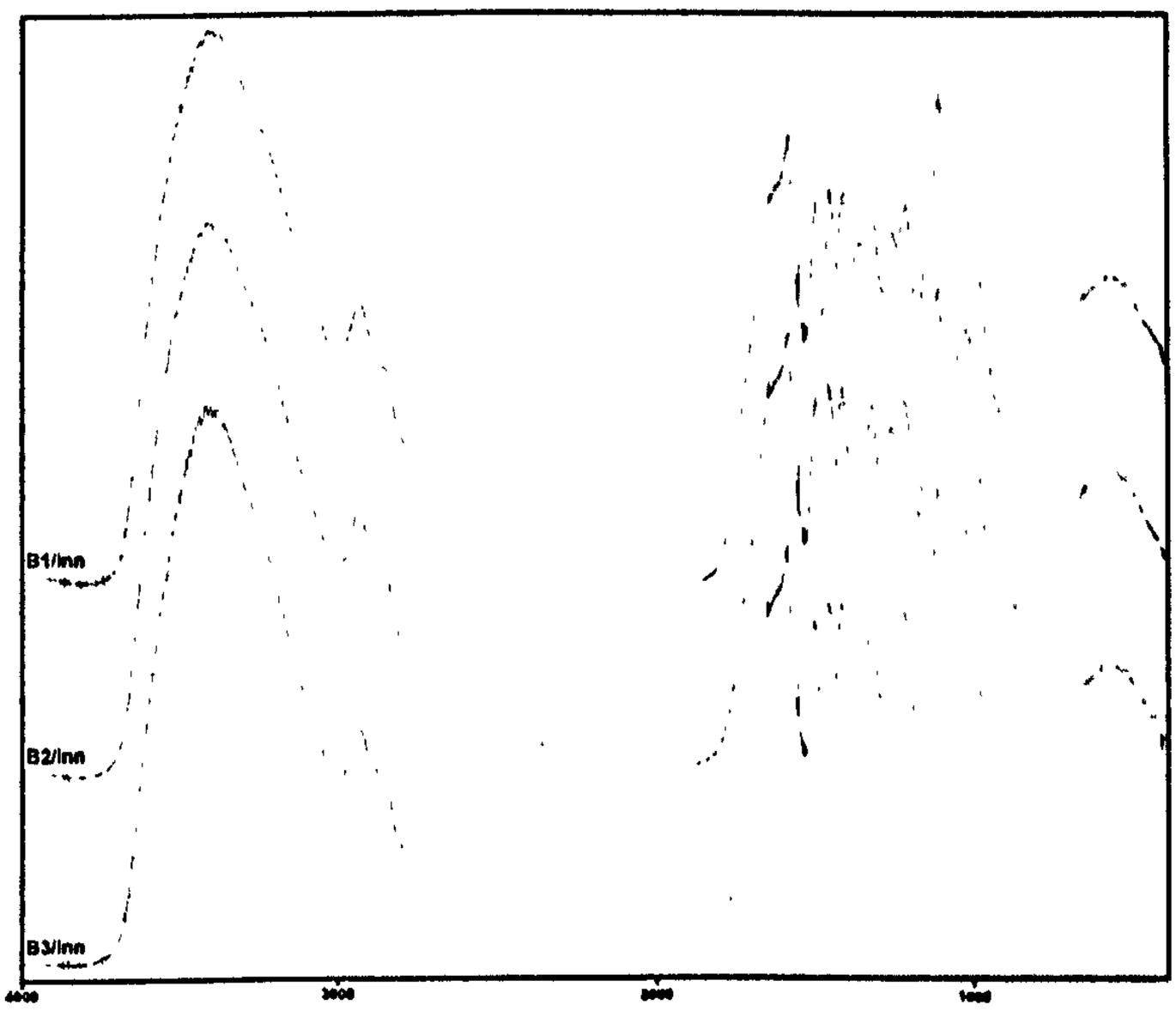


Figure 8.1 Reproducibility in FTIR spectra

8.3.4.1 Band assignments and diagenetic markers for wood degradation

The table below summarises the approximate band assignments characteristic of wood and certain of its diagenetic markers. In general, the bands in the 1200-1600 cm^{-1} region and the those in the 1700-1750 cm^{-1} region arise primarily from lignins. Bands in the 1100-1200 cm^{-1} region arise from cellulose. Hemicellulose is represented by the band at 1730 cm^{-1}. A small peak at 896 cm^{-1} arises from the lower-molecular-weight carbohydrates (Wilson *et al.* 1993). References given in the table below refer to sources provided in the literature on degraded wood, rather than to the original identification of the band.

Band cm $^{-1}$	Origin
1730	Hemicellulose (Kim 1990)
1720	Brown-rot decay marker (Kim 1990)
1700; 1715	Oxidised lignin (Crooke *et al.* 1965; Borgin *et al.* 1975b)
1600	Lignin (Hergert 1971)
1590; 1270	Degraded guaiacyls (Fengel 1991)
1510	Lignin (Hergert 1971)
1270	Lignin (Hergert 1971)
1220; 1320	Syringyl (Fengel 1991)
1225	Guaiacyl (Fengel 1991)
1120	Degraded syringyls (Wilson *et al.* 1993)
1110; 1060; 1040	Cellulose (Kim 1990)
1050	Degraded Cellulose (Kim 1990)
896	Anchiomeric carbohydrates (Wilson *et al.* 1993)

Table 8.3 **Band assignments for FTIR traces of degraded wood**

Labelled FTIR Spectra comparing fresh to degraded wood in conjunction with spectra of pure samples of cellulose and isolated lignin are shown below for reference.

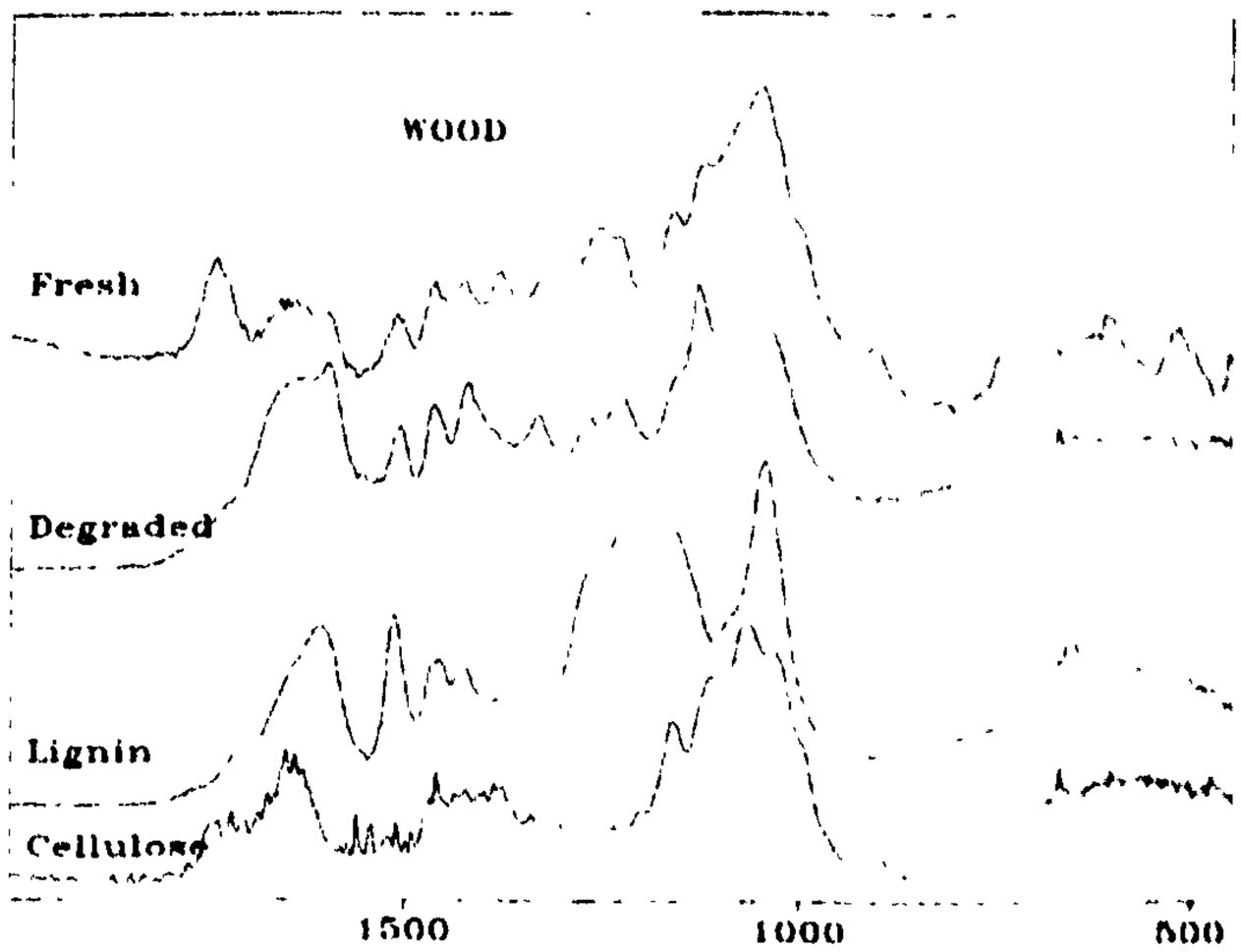


Figure 8.2 **FTIR spectra of fresh wood, degraded wood, cellulose, and lignin**

There are roughly seven markers to watch for in the interpretation of FTIR spectra for signs of chemical changes to degraded archaeological waterlogged woods. These are summarised below.

1. Decrease in intensity of band at 1730 cm $^{-1}$ due to losses in hemicellulose (Kim 1990).

2. Emergence of single band at 1050 cm $^{-1}$, replacing the three cellulose bands 1110 cm $^{-1}$, 1060 cm $^{-1}$, 1040 cm $^{-1}$ (Kim 1990).

3. Relative increase in intensity of lignin bands 1600 cm $^{-1}$, 1510 cm $^{-1}$, and 1270 cm $^{-1}$ due to losses in carbohydrates (Kim 1990).

4. Relative decrease in intensity of 1220 cm $^{-1}$;1320 cm $^{-1}$ due to preferential syringyl loss; also to arising of new band at 1120 cm $^{-1}$ (Wilson *et al.* 1993).

5. Bands at 1590; 1270 indicating degradation of guaiacyls (Fengel 1991).

6. Arising of band at 1720 cm $^{-1}$ as a result of aerobic fungal decay (Kim 1990).

7. Increase to bands at 1700 and 1715 due to oxidation of lignins (Crooke *et al.* 1965; Wayman 1971; Borgin *et al.* 1975b)

Detailed information about the vibrational and rotational perturbations to specific functional groups from which arise the bands listed above are well covered by the literature (Crook *et al.* 1965; Hergert 1971; Fengel 1991; Wilson *et al.* 1993; Faix *et al.* 1994), and therefore not discussed here.

8.3.4.2 FTIR spectra of degraded woods

The FTIR spectra that follow in Figures 8.3 through 8.6 show the results produced by analyses of a series of samples from the degraded and undegraded woods that have made up this study.

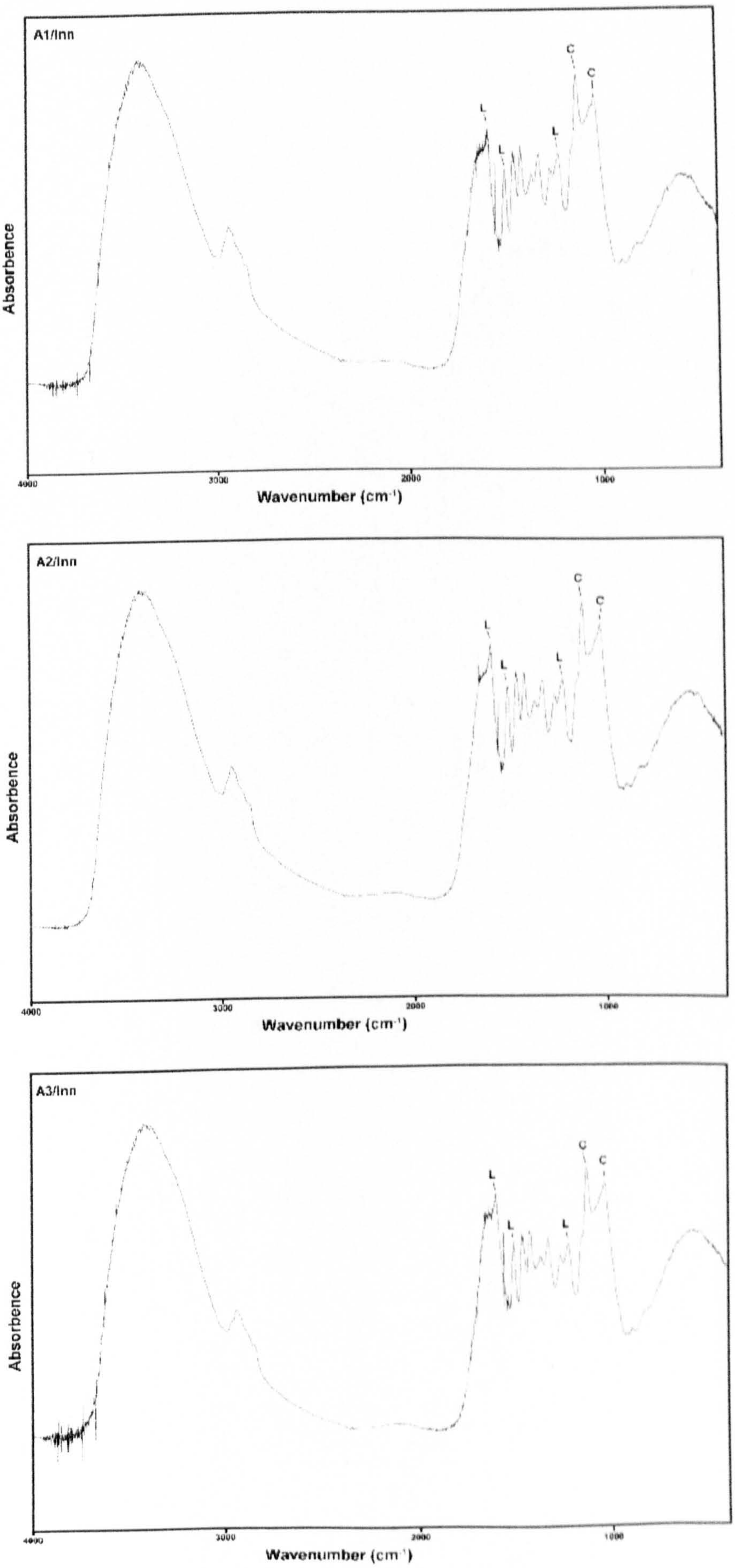


Figure 8.3 **FTIR spectra from sections from ends and centre of Roman plank**

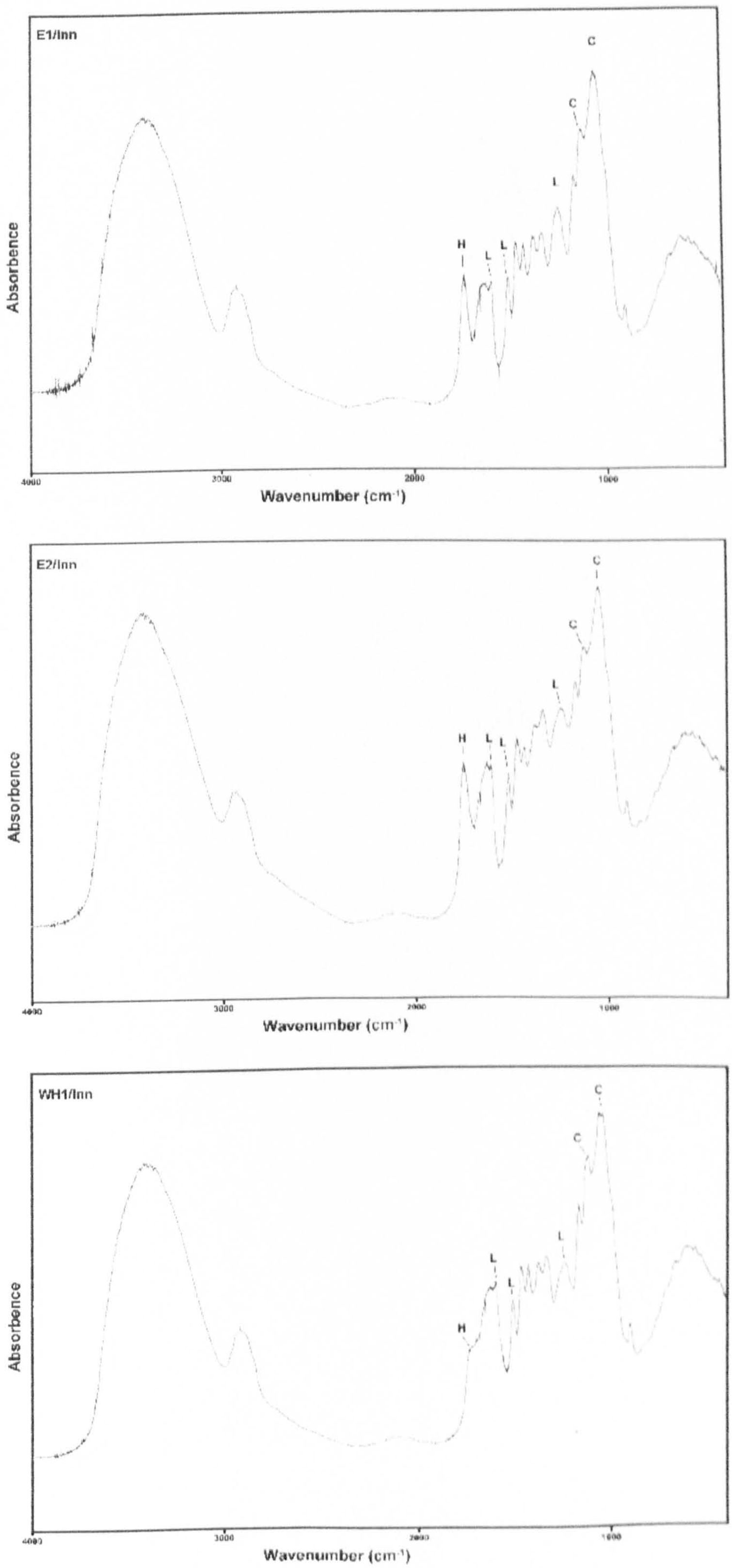


Figure 8.4 FTIR spectra from fresh oak, dry archaeological wood, and WH1

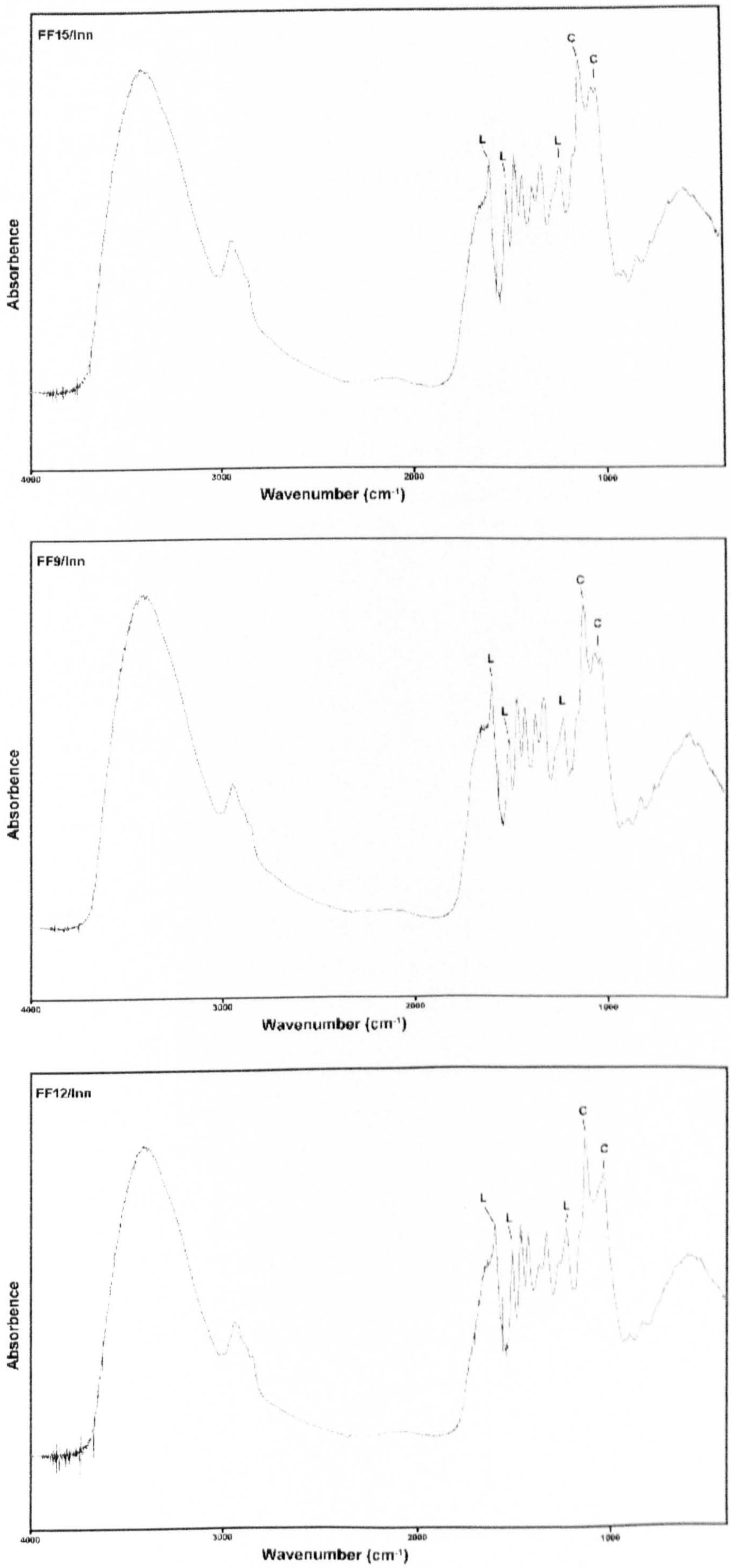


Figure 8.5 **FTIR spectra from less deteriorated artefacts**

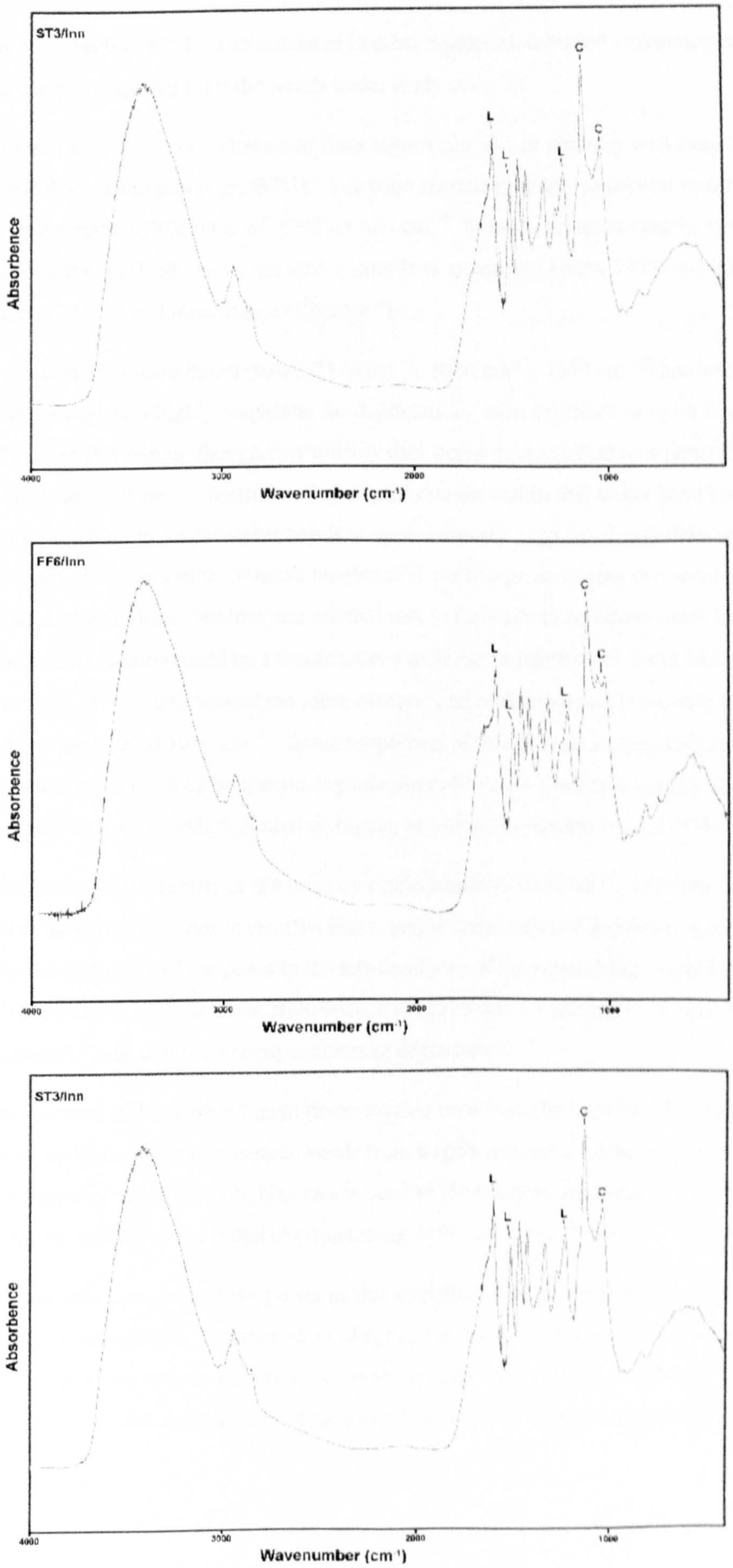


Figure 8.6 **FTIR spectra from more deteriorated artefacts**

8.3.4.3 Trends revealed by spectra

Trends listed in Section 8.3.4.1 and discussed in other studies of degraded archaeological wood are clearly visible in the spectra from the woods under study here.

Hemicellulose (band 1730 cm^{-1}) begins to show significant loss in intensity with even the less degraded of the archaeological samples (e.g., WH1). The band representing low molecular weight anchiomeric (linkage) carbohydrates (Wilson *et al.* 1993) at 896 cm^{-1} follows this trend closely, and both can be seen to be almost entirely absent by the time a sample is measuring Umax 300% and has lost approximately 25% of its holocellulose (Chapter 7).

The changes to the cellulose bands (bands 1110 cm^{-1}, 1060 cm^{-1}, 1040 cm^{-1}) are somewhat more complicated, though still highly diagnostic for degradation. Less degraded samples (e.g., WH1) display separate bands in this region, though very quickly they begin to be masked by a generally broader peak with a maxima at 1050 cm^{-1}. Distinctive bands still remain within this larger band during the process of increasing degradation, in particular bands at approximately 1125 cm^{-1} and 1030 cm^{-1}. There are definable trends observable in the relative heights of these two peaks during the process of increasing degradation. Losses to hemicellulose and relative loss in intensity of cellulose bands in relation to lignin bands appears to be accompanied by a simultaneous increase in intensity of band 1125 cm^{-1} relative to the band at 1030 cm^{-1}, until toward the more extreme end of degradation two bands show up in the place of the single band at 1030 cm^{-1}. Some proportion of this change seems likely to be associated with the gradual build-up of carbohydrate degradation products in the wood sample, though the peak at 1125 cm^{-1} may well arise from degraded syringyls, as argued by Wilson *et al.* (1993).

The relative increase in intensity of the primary lignin bands at 1600 cm^{-1}, 1510 cm^{-1}, and 1270 cm^{-1} in relation to the cellulose bands is clearly visible, and is progressive as degradation level increases. Changes to the intensities of the peaks to the left-hand side of the lignin band range (1590; 1510 cm^{-1}; 1270 cm^{-1}) in relation to those at the right-hand end (1220 cm^{-1};1320 cm^{-1}) clearly reflect changes to syringyl/guaiacyl ratios that accompany increasing degradation.

No sign can be seen of the aerobic fungal decay marker mentioned by Kim (1990), though this marker has appeared in degraded archaeological woods from largely anaerobic contexts. It is difficult to tell whether any signs of oxidation of lignins can be seen in the samples analysed, since bands 1700 and 1715 are largely masked by the broad band spanning 1600 cm^{-1} to 1730 cm^{-1}.

The discussion above emphasises the power of this analytical tool to reveal diagenetic information about archaeological wood samples. Interpretation of spectra is not difficult once the significant markers are known. It is easy to see that results from such post-analysis interpretation could be summarised into a system that could be used to categorise wooden artefacts about to undergo conservation treatment.

8.4 Analytical Pyrolysis Study

8.4.1 Principles

Pyrolysis is the thermal fission of a sample material, in the absence of oxygen, into molecules of lower mass. In analytical pyrolysis, a small sample, typically less than 1 mg of finely-ground solid material, is heated on a wire or in a quartz tube to a rising temperature schedule in excess of 200°C until high temperature decomposition occurs, releasing volatile compounds. These compounds are then often separated by gas chromatography prior to analysis by mass spectroscopy. The pool of fragments that is detected provides a fingerprint characteristic of the sample in terms of both fragment nature and relative distribution. Small sample size is not only an advantage of this technique for archaeological use, but is a requisite to avoid temperature gradients within the sample bulk. A typical trace from a wood sample contains 50-100 individual peaks, each corresponding to a product typical of one of the major or minor constituents of wood. Furans and carbonyl compounds are produced from polysaccharides such as cellulose and hemicellulose, and phenols from lignins (Table 8.4). Lignin-derived products are particularly diagnostic as they tend to retain the methoxylation pattern (i.e., the arrangement of $-OCH_3$ around the benzene ring) of the parent structural units, guaiacyl and syringyl, and "carry diagenetic information on their side chains" (Saiz-Jiminez and de Leeuw, 1984).

Various variations in both sample degradation method and method of detection have been employed, e.g, Curie-point; filament pyrolysers; chemical ionisation; direct total ion current and offline flame ionisation detection. Galletti and Bocchini (1995) claim that the advantage of filament pyrolysers (used in the present study) over Curie-point systems is that relatively larger amounts of sample can be analysed, allowing a higher degree of reproducibility with dishomogeneous materials such as wood Unfortunately, the differences between these methods, the specific sensitivities of different detectors used, and changes to coil between sample runs, will have a significant effect on results, more particularly on elution times of pyrolysis products. This tends to make comparison of pyrograms of different origin difficult. For this reason, designation of pyrolysis product by retention time or scan number is considered much less meaningful (van Bergen, *pers. Comm.* 1997) than identification made by *m/z* number.

Perhaps the great advantage of pyrolysis over other degradation techniques is that sample digestion is not required prior to analysis. This reduces the likelihood of artefacts being introduced from chemical digestion. Though fresh wood may undergo pre-analysis extraction with dichloromethane/methanol to remove resinous compounds (extractives) that would otherwise yield merged peaks, waterlogged wood does not appear to require this extraction process, since most of these have been lost through degradation and leaching in the burial environment (note absence of peaks after scan no. 3300 in Figures 8.8-8.11) Diaz-Vaz *et al.* (1991) has also reported no serious interference caused by the presence of PEG in wood samples analysed by Py-GC/MS, thus widening its applicability to post-treatment diagnostic studies Galletti and Bocchini (1995) point out its ability to show up protein markers (e.g., 4-methylphenol, indole, and 3-methylindole), indicators of aerobic degradation pathways.

Pyrolysis-gas chromatography/mass spectroscopy is a very precise and extremely broadly-based technique for the recognition of wood constituents. Analysis throughput is quick and data generated are in digital format, thus readily accessible to statistical analysis and pattern recognition treatments. Its main quoted disadvantage is that it does not provide true quantitative yields. This means that Py-GC/MS data cannot be compared on an absolute scale with techniques such as gravimetric analysis. Quantification of yields from Py-GC/MS is occasionally carried out, more particularly to construct polysaccharide/lignin or guaiacyl/syringyl ratios (Stankewiccz *et al.* 1997). Quantification of such complex pyrograms does indeed require special care. Merged peaks, differential response times, and various other factors decided by the performance of the coil can mean that absolute yields for particular products are unreliable. For example, it has been found that less than 20% of original lignin is represented by the lignin pyrolysates present in a chromatogram. This is, however, a much higher yield than by other methods such as nitrobenzene oxidation (Galletti and Boccherini 1995). Recent papers quoting ratios constructed from the sums of the areas of the chromatographic peaks assigned to the relevant pyrolysis fragments are, however, considered to have given reproducable and comparative results for deterioration studies (Galletti and Boccherini 1995; Stankiewicz *et al.* 1997).

Since, as Obst (1993) points out, no method or combination of methods is available that unambiguously provides quantitative analysis of the chemical components of cell walls because of the difficulty in isolating pure lignocellulose fractions, perhaps the aim for quantitative results needs to be re-examined It is arguable that the clear relative intensity yields of a Py-GC/MS trace can provide much less ambiguous markers for degradation level in complex materials such as waterlogged archaeological wood. And though the cost of such an analytical facility may be appear to be out of reach of the conservator of this material, the lack of preparation, speed of results, and relative ease of interpretation could make the cost per sample a worthwhile investment.

8.4.2 Existing Research into Archaeological and Degraded Wood

Pyrolysis-gas chromatography/mass spectroscopy is by now one of the most widely used methods for characterising degraded woods from natural environments (Wilson *et al.* 1993; Diaz-Vaz *et al.* 1991; Faix *et al.* 1987). Galletti and Boccherini (1995) reviewed the advantages of the pyrolysis technique over other available techniques for characterising wood and its degradation products. Results from hardwood pyrolysis studies have been found to accord well with those from FTIR data (Faix, *et al.* 1987). Faix and his colleagues reviewed earlier work focussed on wood and produced the first systematic attempt at identifying not only the prominent products but also the numerous degradation products of wood Identification of lignins has received most attention, somewhat to the neglect of polysaccharides. Identification of the latter has been found to be more difficult than that of lignin markers because of the less diagnostic mass spectra from which the molecular ion may be absent, and because of the number of positional and structural isomers that can be generated by carbohydrate dehydration. Compilations of lignin pyrolysis products have been published by Ralph and Hatfield (1991) and Meier and Faix (1992). Names of pyrolysis products from wood have altered a great deal as research in this area has progressed

and understanding of lignin structure has increased. This can make comparison of pyrolysis products from study to study time-consuming and confusing.

Much of the literature has concentrated on the identification of pyrolysis products rather than markers for wood degradation. An early exception to this was Borgin *et al.* (1975b) who used this method of analysis in a general way to study the effects of ageing on wood constituents. Hedges *et al.* (1985) brought out one of the earliest studies of pyrolysis products of archaeological and geological wood remains. Saiz-Jimenez *et al.* (1987) produced the first comparison of Py-GC/MS data with that from ^{13}C-NMR and chemical solubilisation analysis in characterising buried woods in relation to recent wood. Hatcher *et al.* (1988) published a study showing the effects of increasing degradation on pyrolysis products produced from wood. Hedges *et al.* (1988) identified markers (elevated vanillic acid versus vanillin) for aerobic degradation of lignins in wood. Wilson *et al.* (1993) published the first systematic study of marine archaeological wood samples comparing the results of a number of analytical methods, including Py-GC/MS. More recently, Camarero *et al.* (1994) and Nelson *et al.* (1995) have published more data on aerobic degradation products identified in archaeological woods by Py-GC/MS. Van Bergen *et al.* (2000) have published the first paper since Benner *et al.* (1984) that compares systematically the variation in yield of a series of new diagenetic markers with archaeological woods from various different burial environments.

8.4.3 Experimental Method and Materials

Samples from each of the sections taken from the Roman plank and from both inner and outer wood of the range of oak artefacts chosen for this study were analysed using pyrolysis-gas chromatography/mass spectroscopy. Sample preparation consisted of freeze-drying prior to powdering to a homogeneous wood flour with agate ball and sample chamber, in conjunction with a powder milling machine. Samples of recent and historic wood (E1/Inn; E2/Inn; and WH1/Inn) were extracted ultrasonically three times using dichloromethane /methanol (1:1 v/v). Extracts were removed and the residues were dried under a stream of N_2. This extraction was not found to be necessary with the degraded archaeological samples, as can be seen in their pyrograms. Indeed, as can be seen in the results below, pyrograms of archaeological wood show more peak separation and are generally clearer to interpret than those of fresh modern wood of the same species. After processing, samples were stored dry and in cool, dark conditions until analysed, to reduce the possibility of continued degradation.

Filament pyrolysis was performed using a Chemical Data Systems Pyroprobe 1000 connected to a Carlo Erba GC coupled to a Finnigan 4500 mass spectrometer. Samples for the filament pyrolysis were loaded into quartz tubes into the CDS 1000 Pyroprobe. The temperature of the pyrolysis interface temperature and GC injector was set at 250 °C. Pyrolysis time was 10 seconds at 610 °C. The CE GC oven was programmed from 35 °C (5 minutes) to 310 °C (10 minutes) at a rate of 4 °C min^{-1}. Separation was achieved using a fused-silica capillary column (50 m x 0.32 mm) coated with CPSil-5 CB (film thickness 0.4 μm). Helium was used as the carrier gas. The Finnigan mass spectrometer was operated at 70 eV, scanning the range *m/z* 35-550 at a cycle time of 1 second. Compound identifications were

based on mass spectral data and retention time comparisons with reference samples and data reported in the literature (Pouwels *et al.* 1987; van Smeerdijk and Boon 1987; Ralph and Hatfield 1991; Stankiewicz *et al.* 1997).

8.4.4 Results and Discussion

The current discussion considers only the results from a selection of inner sections of the Roman plank and the oak artefacts, though results from the other samples analysed proved valuable in assessing both repeatability of results and sequence in trends and are used to inform certain of the conclusions.

Figure 8.7 (next page) shows the partial ion chromatograms of a sample of fresh oakwood and a sample from the Roman plank as representative pyrograms. Peak numbers refer to the identified compounds listed in Table 8.4 (following).

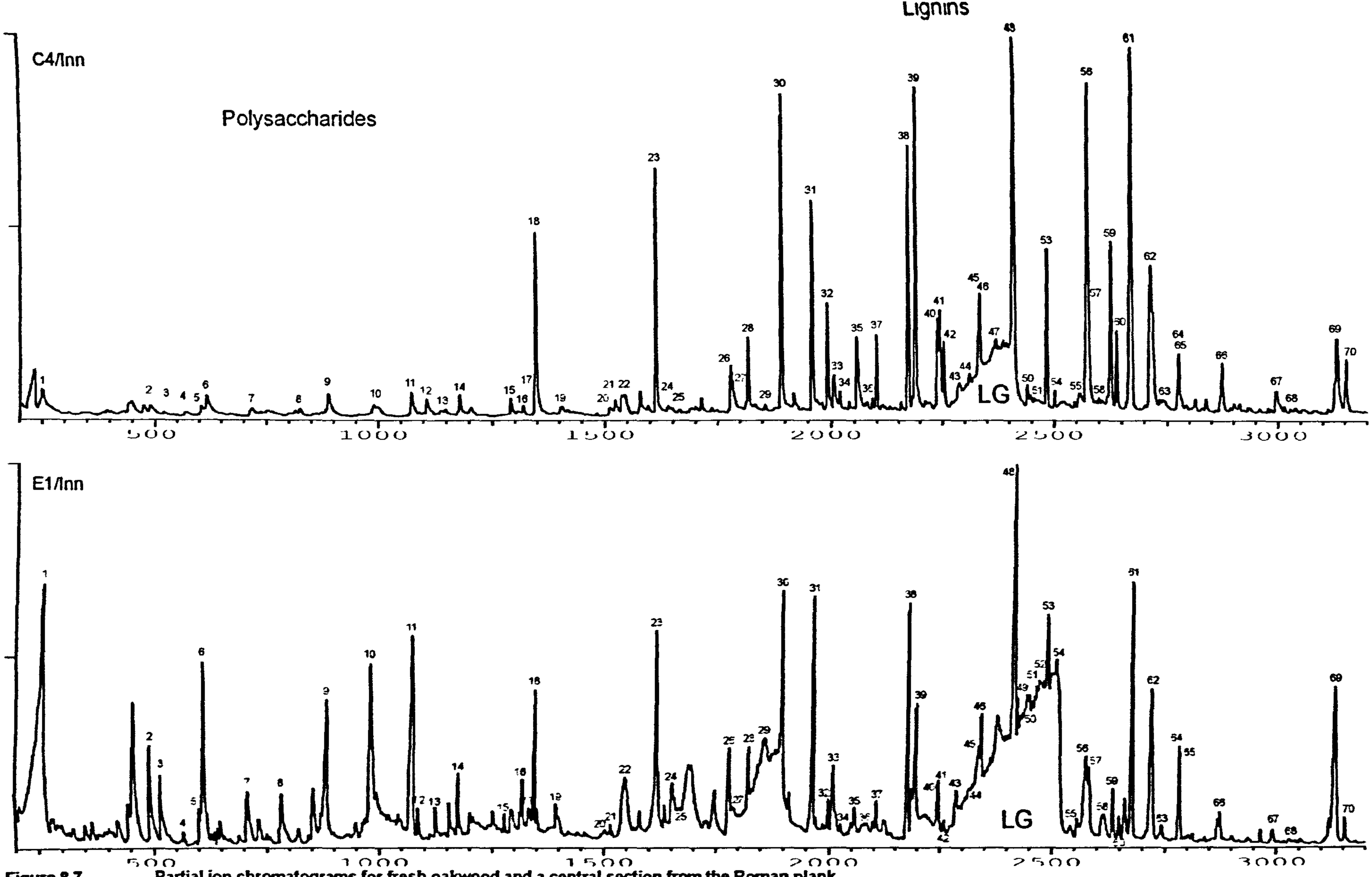


Figure 8.7 Partial ion chromatograms for fresh oakwood and a central section from the Roman plank

Seventy compounds were identified in all wood pyrolysates, in addition to the composite peak Levoglucosan. These, along with associated originating wood constituents, are listed in Table 8.4.

Peak	Compound	m/z values	Origin
1	2-Hydroxypropanaldehyde	43+74	Cellulose (?)
2	Toluene, Thiophene, Hydroxy-ketobutenal	91+92/97+98	Biodegraded lignin (?)
3	Furan-3-one	54+84	Cellulose
4	3-Furaldehyde	95+96	Cellulose (?)
5	Pentan-2,4-dienol	53+82	Polysaccharides (?)
6	2-Furaldehyde	95+96	Cellulose
7	Hydroxymethyl furan	97+98	PS/Cellulose
8	Furan-2-one	55+84	Cellulose
9	5-Me-2-furanone (β-Angelicalactone)	55+98	Cellulose
10	5-Me-2-furaldehyde	109+110	Cellulose
11	4-Hydroxy-5,6-dihydro-2(H) pyran-2-one	58+114	HC (Xylose Marker)
12	Phenol	66+94	Biodegraded Lignin
13	3-Hydroxy-2-methyl-2-cyclopentene-1-one	55+112	Cellulose
14	2-Hydroxy-3-methyl-2-cyclopentene-1-one	55+112	Cellulose
15	2-Methylphenol	107+108	Biodegraded Lignin
16	Rhamnose Marker	43+128	Polysaccharides
17	3- and 4-Methylphenol	107+108	Biodegraded Lignin/? Protein?
18	Guaiacol	109+124	Lignin
19	2-Methyl-3-hydroxy (4H) pyran-4-one	71+126	HC (Xylose Marker)
20	Rhamnose Marker	43+128	Polysaccharides
21	2,4-Dimethylphenol	107+122	Biodegraded Lignin?
22	5-hydroxymethyl-2-tetrahydrofuraldehyde -3-one	57+69+43	Polysaccharides
23	Methyl Guaiacol	123+138	Lignin
24	1,2-Benzenediol	64+110	Lignin
25	5-Hydroxymethyl -2-furaldehyde	97+126	Cellulose
26	Methoxybenzenediol	140+125	Lignin
27	3-Methoxy-1,2-benzenediol	78+124	Lignin
28	Ethyl Guaiacol	137+152	Lignin
29	4-Methoxy-1,2-benzenediol	78+124	Lignin
30	4-Vinylguaiacol	135+150	Lignin
31	Syringol	154+139	Lignin
32	4-(prop-1-enyl)-guaiacol (eugenol)	149+164	Lignin
33	5-Methyl-3-methoxy-1,2-benzenediol	139+154	Lignin
34	4-propanyl-guaiacol	137+166	Lignin
35	4-formyl-guaiacol (vanillin)	151+152	Lignin
36	C2-1,2-Benzenediol	123+138	Lignin (?)
37	4-(prop-2-enyl) guaiacol (*cis*-isoeugenol)	149+164	Lignin
38	4-methyl-syringol	153+168	Lignin
39	4-(prop-2-enyl) guaiacol (*trans*-isoeugenol)	149+164	Lignin
40/41	4-acetyl-guaiacol + Guaicylpropan-2-one	151+166/162+166	Lignin
42	G — C = C = C	162+147	Lignin

Table 8.4 **List of pyrolysis products and their origins**

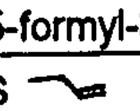
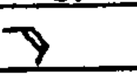
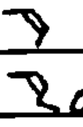
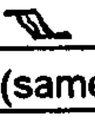
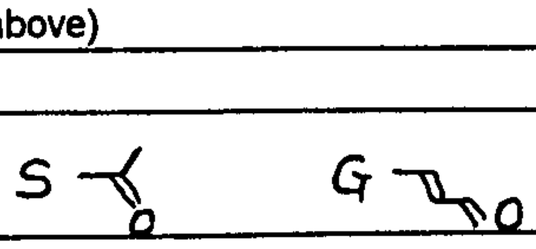
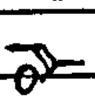
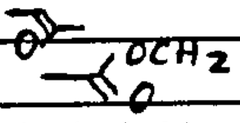
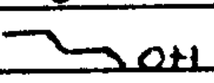
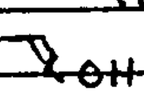
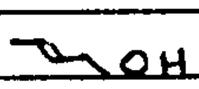
Peak	Compound	m/z values	Origin
43	5-ethenyl-3-methoxy 1,2-benzenediol	151+166	Lignin
44	"Vanillic acid" methyl ester	151+182	Biodegraded Lignin
45	Guaiacylpropan-2-one	137+180	Lignin
46	4-ethyl syringol	167+182	Lignin
47	5-(1-propanyl)-3-methoxy 1,2-benzenediol	91+180	Lignin
48	Di-methyl-vinyl syringol	180+165	Lignin
49	"Vanillic acid"	168+153	Lignin
50	G 	180+151	Lignin
51	5-(2-Z-propenyl)-3-methoxy 1,2-benzenediol cis	91+180	Lignin
52	5-formyl-3-methoxy 1,2-benzenediol	167+168?	Lignin
53	S	119+194	Lignin
54	S	167+196	Lignin
55	5-(2-E-propenyl) m.c. trans	91+180	Lignin
56	Syringyl Aldehyde	181+182	Lignin
57	S 	94+119	Lignin
58	G 	137+180	Lignin
59	S 	192+177	Lignin
60	S (same as above)	192+177	Lignin
61	S 	119+91?	Lignin
62	S & G 	196+181+153/178+ 135+147	Lignin
63	G 	137+180+124	Lignin
64	S 	167+210+168	Lignin
65	S 	181+212+197	Lignin
66	Syringic Acid	181+210+153	Biodegraded Lignin
67	S 	168+212+167	Lignin
68	S 	154+167+210	Lignin
69	S	208+137+165	Lignin
70	C16F.A. & S 	154+167+210	Extractives/Lignin
71	Levoglucosan (2316-2434)	60+73	PS/Lignin

Table 8.4 **List of pyrolysis products and their origins (con't)**

Figures 8.8, 8.9, 8.10, and 8.11 show the results for the inner, less-deteriorated layer of wood from the range of artefacts under study here.

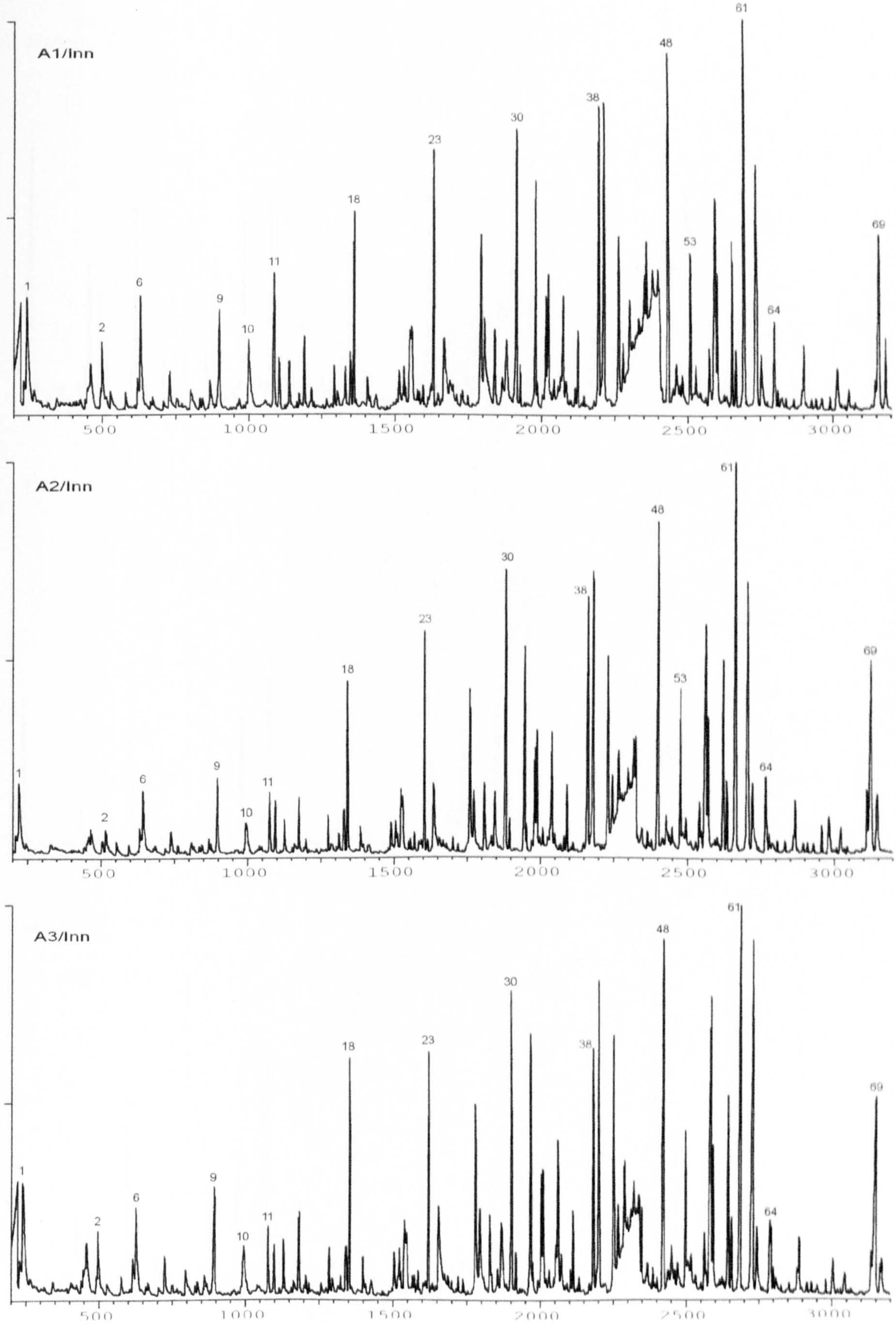


Figure 8.8 **Partial ion chromatograms for sections from ends and centre of Roman plank**

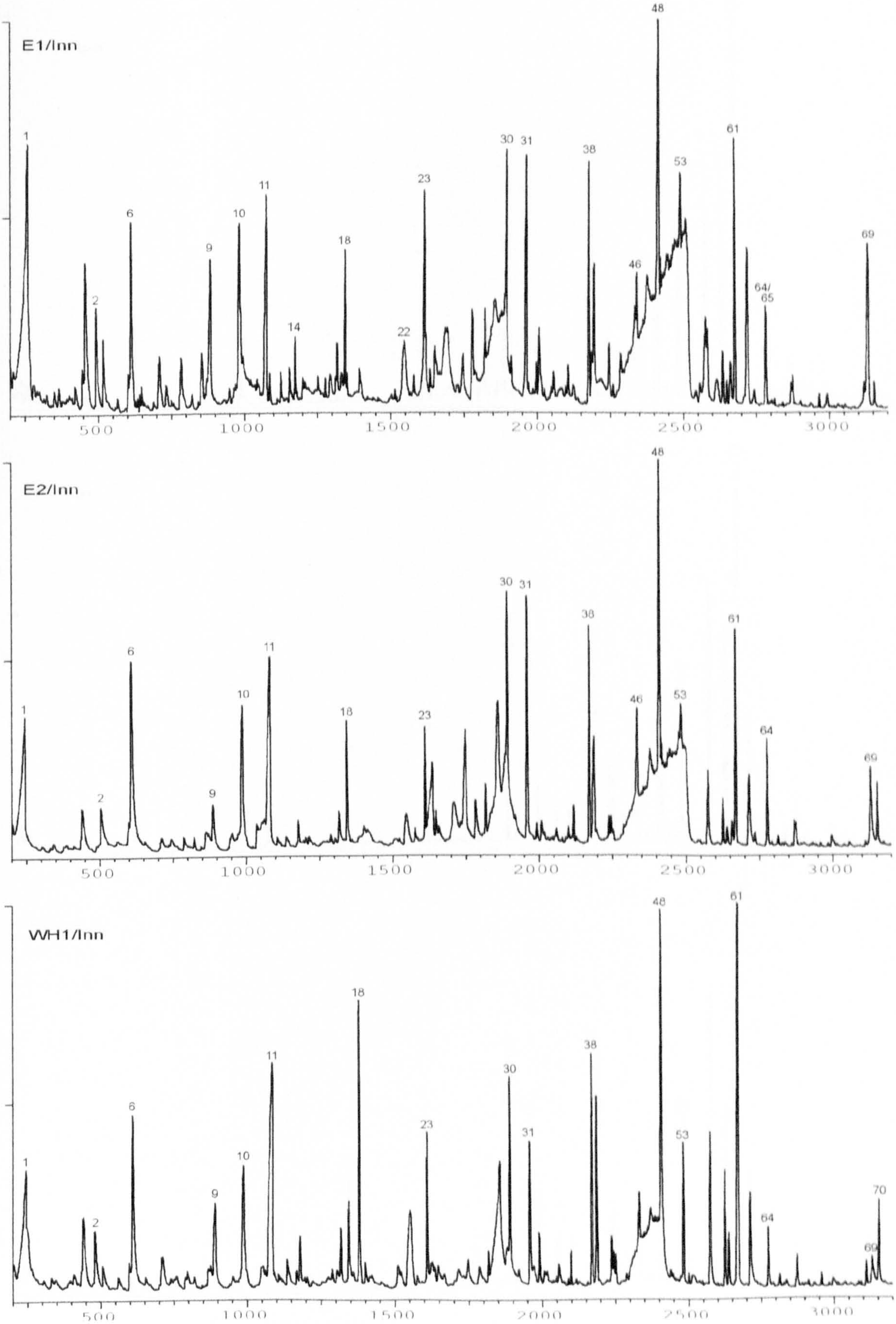


Figure 8.9 **Partial ion chromatograms for fresh oak, dry archaeological wood, and WH1**

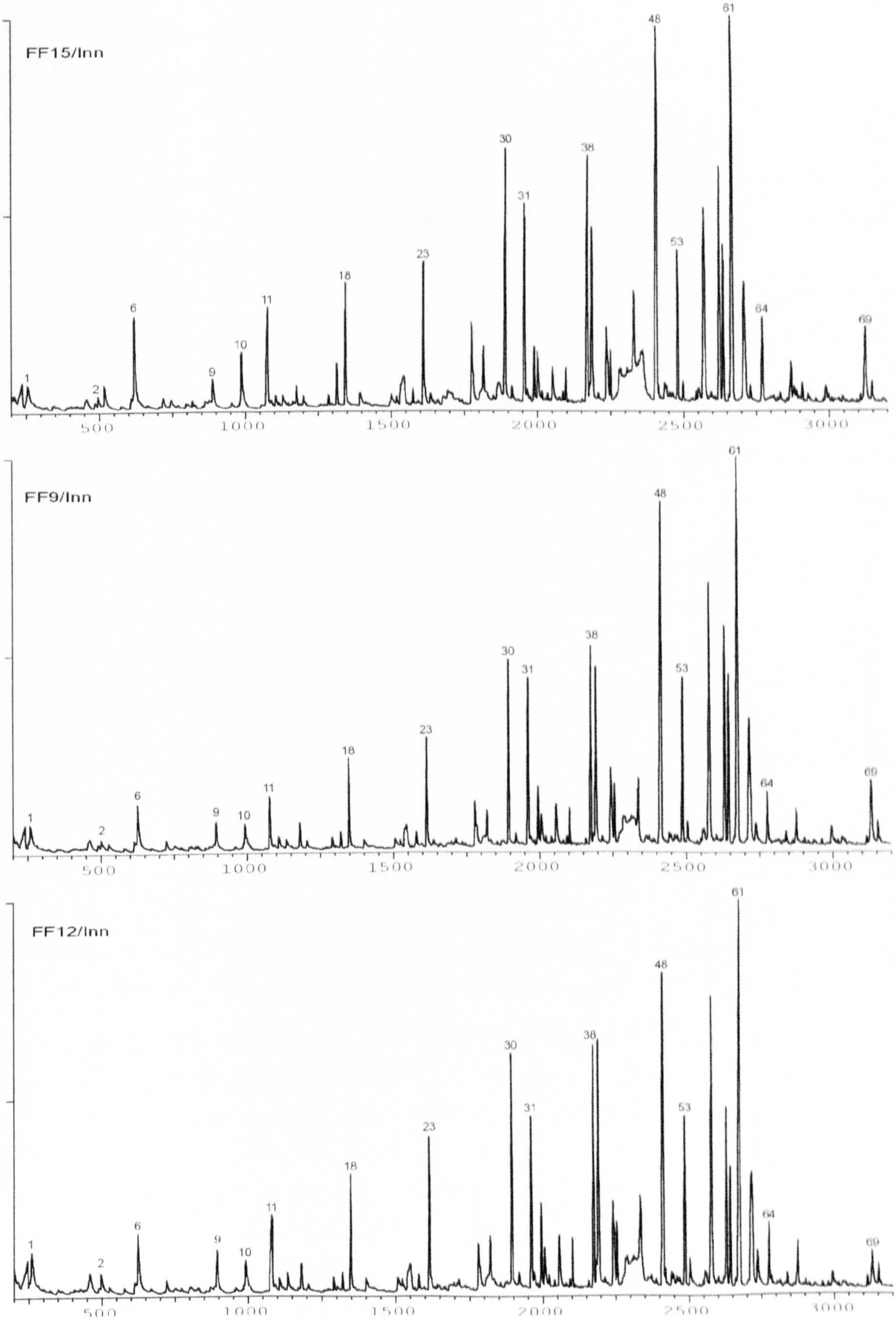


Figure 8.10 **Partial ion chromatograms for less-deteriorated artefacts**

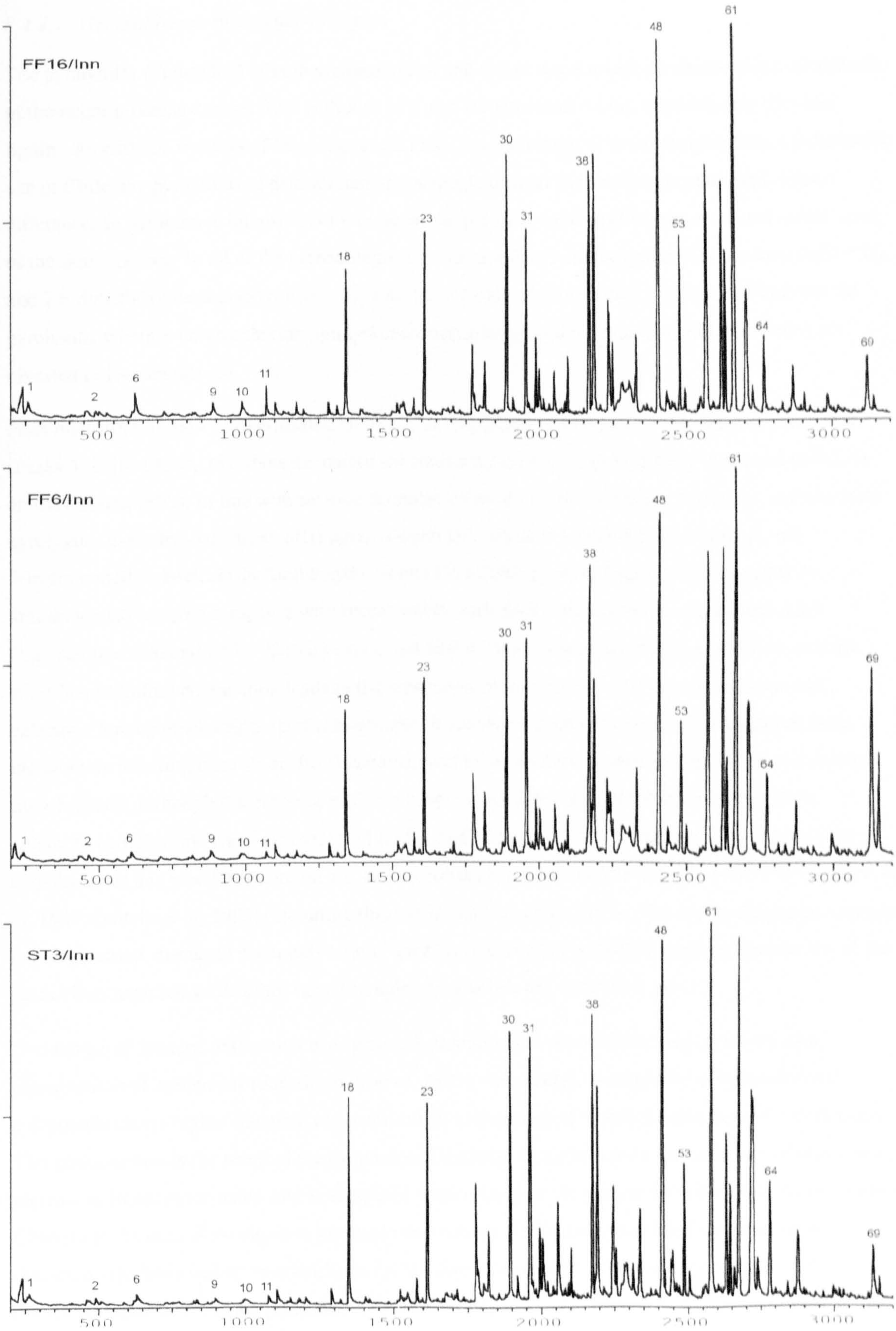


Figure 8.11 **Partial ion chromatograms for more-deteriorated artefacts**

8.4.4.1 General trends in degraded samples

The pyrolysates (Figure 8.7) of both archaeological and recent wood reveal the characteristic distribution of the major products derived from cellulose (C); also levoglucosan = LG), hemicellulose (He) and lignin. As with the findings of Diaz-Vaz *et al.* (1991) in their study of wood samples from a palaeolithic site in Chile, the pyrograms of deteriorated archaeological wood show very systematic and distinct differences in the relative intensities of various of the pyrolysis products between fresh and recent wood of the same species. In all of the archaeological wood samples, 2-Methoxyphenols (Guaiacyl units = G) and 2,6-dimethoxyphenols (Syringyl = S), with their vinyl, ethyl or methyl substituents dominate the pyrolysate, whereas polysaccharide pyrolysis products (furaldehydes, furanones and pyranones) are revealed in less abundance.

Peak intensities of most carbohydrates, in particular the pentoses (Peaks 4, 7, 11) relative to hexoses (Peaks 3, 8-10, 19, 22, 25), show decreased intensities ranging from only slightly decreased (WH1) to entirely absent (FF3), in line with relative degradation levels for the artefacts. Curiously, carbohydrate pyrolysates 2-Methyl-3-hydroxy (4H) pyran-4-one (19), which is a hemicellulose marker, and 5-hydroxymethyl-2-tetrahydrofuraldehyde-3-one (22) exhibit equal or higher intensity yields in archaeological samples compared with recent wood, until degradation levels are quite advanced (e.g., samples FF6 and ST3). We can expect the first of these (which is a xylose marker) to increase, since hemicellulose degradation leads to the separation of the polymer into xylose mannose and galactose, among other stripping of side-groups. It seems reasonable to explain the second of these increases as resulting from an artificial enhancement by breakdown products from the more complex carbohydrates, although the presence of decay fungi in wood has been observed to contribute to enhanced carbohydrate fractions measured (Zabel and Morrell, 1992). Certain of these trends with carbohydrates and wood degradation are well established in the literature (Hedges *et al.* 1985; Wilson *et al.* 1993; Galletti *et al.* 1995), including this last (Diaz-Vaz *et al.* 1991). The highly diagnostic changes to levoglucosan, discussed separately below, have been somewhat neglected, perhaps because few of the researchers analysed sufficiently varied samples to establish any consistent trend.

Dominance of syringyl derivatives over guaiacyl products is in concordance with pyrolysis data characteristic of hardwoods (Saiz-Jiminez *et al.* 1987). In general, the majority of lignin-derived compounds shows higher intensities in deteriorated archaeological woods than in fresh or recent wood. This phenomenon is the result of the proportional decrease to carbohydrate fractions, rather than any net increase to lignin pyrolysates, and is examined more closely in the section discussing C:L ratios (below). Changes to the ratio of syringyls to guaiacyls that occur with the more degraded samples is also discussed separately below, as is evidence for the degradation level provided by the presence of catecholic lignin degradation products.

8.4.4.2 Levoglucosan

The pyrograms of all wood samples are dominated by a wide peak running approximately from scans 2300-2430 (Peak 71, Table 8.4), with a base peak at *m/z* 60 + 73 (Reid *et al.* 1993). This has been assigned to Levoglucosan, sometimes called anhydroglucopyranose (Galletti *et al.* 1995) and is composed of pyrolysis fragments originating from polysaccharides as well as a number of lignin pyrolysates (Figure 8.7, [71]). Changes to the total area of levoglucosan appear to be particularly diagnostic for degradation level in wood. Levoglucosan yield can be seen to decrease dramatically with degradation, and follows the regular trend shown in other data gleaned from the artefactual wood, such as residual cellulose content. Diaz-Vaz and Kelly, *et al.* (1991) link these results to the suppressive effect of high ash content on the formation of levoglucosan.

Since levoglucosan varies in the range of scans over which it extends and is particularly irregular in shape, accurate measurement of peak area could be thought to be problematic. This variation in extent of range might be taken, in itself, to predict degradation level in archaeological wood, since it can be seen that the relative number of lignin peaks that levoglucosan spans seems also to reduce in a regular fashion with increasing degradation. In the pyrograms displayed above, levoglucosan can be seen to span peaks 43-54 in fresh modern oak wood; peaks 43-53 in dry historic oak; peaks 43-48 in archaeological waterlogged woods in relatively good preservation; peaks 43-45/46 in wood of medium degradation; and only peak 43 in seriously-degraded woods. This sort of easily-observed trend brings interpretation of pyrolysis data well within the reach of the practising conservator and has the potential to be correlated with such characteristics as measured residual cellulose contents and fibre saturation point, to inform treatment choices of archaeological wooden artefacts.

8.4.4.3 Polysaccharide/lignin ratios

Data for the table below (Table 8.5) was calculated by the summing of total areas measured for the following peaks:

Polysaccharides: 1, 3-11, 13-14, 16, 19-20, 22, 25

Total Lignins: 15, 18, 21, 23-24, 26-70

Ratios based on peak heights are also reported.

Sample	*PS:L Ratio (Peak Area)*	*PS:L Ratio (Peak Height)*
A1/Inn	0.30	0.21
A2/Inn	0.17	0.13
A3/Inn	0.21	0.16
E1/Inn	0.64	0.43
E2/Inn	0.80	0.34
WH1/Inn	0.76	0.35
FF15/Inn	0.19	0.13
FF9/Inn	0.13	0.08
FF12/Inn	0.19	0.11
C4/Inn	0.08	0.04
FF16/Inn	0.07	0.04
FF6/Inn	0.04	0.02
ST3/Inn	0.04	0.02

Table 8.5 Polysaccharide/lignin ratios for samples from Roman plank and artefacts

It can be seen from these results that C/L values decrease dramatically with degradation. Similar findings were made by Diaz-Vaz *et al.* (1991); Borgin *et al.*(1975b) Saiz-Jimincz *et al.* (1989); and Obst *et al.* (1989), and accord with our knowledge about the higher susceptibility of carbohydrates to chemical and biological degradation.

8.4.4.4 Guaiacyl/syringyl ratios

Benner *et al.* (1984) point out that anaerobic biodegradation of the polysaccharide component seems tightly coupled with lignin biodegradation. Though lignin degradation and loss may appear much less dramatic in comparison to carbohydrate losses in archaeological waterlogged woods, Py-GC/MS results show significant changes to both lignin structure and relative abundance ratios.

Hardwood lignins consist of both 2-methoxyphenols characteristic of guaiacyls and 2,6-dimethoxyphenols characteristic of syringyls. Simple phenol units, *p*-hydroxyphenyls tend to show up only in legumes and monocotyledons. Studies of wood by Py-GC/MS have categorised woods and described wood degradation according to the ratios of these three main groups of pyrolysates, commonly abbreviated to H, G, and S (Faix *et al.* 1987). Problems arise in constructing these ratios systematically since ideas are changing as to which of the groups to assign certain of the pyrolysis decomposition

products, in particular the catechols (see also Section 8.3.4.5), degradation products resulting from demethylation of lignins (Hatcher *et al.* 1989). Originally all were assigned to guaiacols (Faix, *et al.*), but more recent studies suggest the need to assign certain of them to syringyls (van Bergen *et al.* 2000).

One of the most commonly observed phenomena in degraded hardwoods is the selective loss of syringyl moieties relative to guaiacyl moieties (Hedges *et al.* 1985; Diaz-Vaz *et al.* 1991). Two possible mechanisms have been suggested to explain this. Selective removal of syringyl-rich cell-wall material by microbial action as a result of its lesser degree of cross-linking has been suggested by Hedges *et al* (1985). The second mechanism under discussion (Hatcher *et al.* 1989; van Bergen *et al.* 2000) involves demethoxylation (see also section 8.3.4.5 below). This process could lead to the formation of monomethoxyphenols (i.e., guaiacyl units), thus effectively enhancing guaiacyl/syringyl ratios.

Table 8.6 shows the comparative G:S total peak areas for the artefacts tested. Data for the table below was calculated by the summing of total areas measured for the following peaks:

Guaiacyls: 15, 18, 23-24, 28-30, 32, 34-37, 39-42, 44-45, 49-50, 58, 63

Syringyls: 21, 26-27, 31, 33, 38, 43, 46-48, 51-57, 59-61, 64-70

Sample	G:S Ratio (Peak Area).	G:S Ratio (Peak Height).
A1/Inn	0.58	0.63
A2/Inn	0.58	0.64
A3/Inn	0.65	0.69
E1/Inn	0.37	0.47
E2/Inn	0.52	0.52
WH1/Inn	0.69	0.68
FF15/Inn	0.34	0.41
FF9/Inn	0.32	0.37
FF12/Inn	0.42	0.47
C4/Inn	0.59	0.63
FF16/Inn	0.42	0.51
FF6/Inn	0.32	0.38
ST3/Inn	0.45	0.50

Table 8.6 Guaiacyl/syringyl ratios for samples from Roman plank and artefacts

The results shown above are not as straightforward to interpret as those reported in the literature. As mentioned previously, choice of peaks to assign to each category is problematic, but if kept consistent between samples should produce comparative results. Calculation of peak areas can not be considered either particularly accurate or reproducible where the establishment of a consistent baseline is so difficult. Van Bergen *et al.* (1993) chose to use peak height over peak area to construct guaiacyl/syringyl

ratios, claiming that they gave accurate enough data for general comparisons and trends to be produced. Selective and enhanced loss of syringyls with degradation is certainly clear from examination of the pyrograms included in this report. This perhaps could be seen as another example of the level of expert knowledge required by the practising conservator to interpret the results from Py-GC/MS analysis.

8.4.4.5 Catechols (benzenediols).

Additional evidence for degradation in wood is provided by the presence of benzenediols. These catecholic substances largely result from the demethylation of guaiacyl units. According to Hatcher *et al.* (1989), this is one of the first modifications to lignin structure to take place after the selective removal of carbohydrates. Demethylation of the methoxyl group of the 2-methoxyphenols (guaiacyls) is accepted to result in the formation of 1,2-benzenediol (Van Bergen *et al.* 1994). Small amounts of this compound are occasionally detected in modern undeteriorated wood (Ralph and Hatfield, 1991). Data from the present study have highlighted the presence of a number of different highly distinct 3-methoxy-1,2-benzenediol derivatives, in particular those with the C_3 side chain preserved. These provide important evidence for a similar demethylation process with the 2,6-dimethylphenols (syringyls), with the implication that they, too, leave degradation products rather than merely experience selective removal. Partially-preserved side-chains indicate that this demethylation too must take place very early on, during the initial stages of degradation. The presence of 3-methoxy-1,2-benzenediol in pyrolysates of recent wood samples, albeit in very low relative amounts, would seem to suggest this.

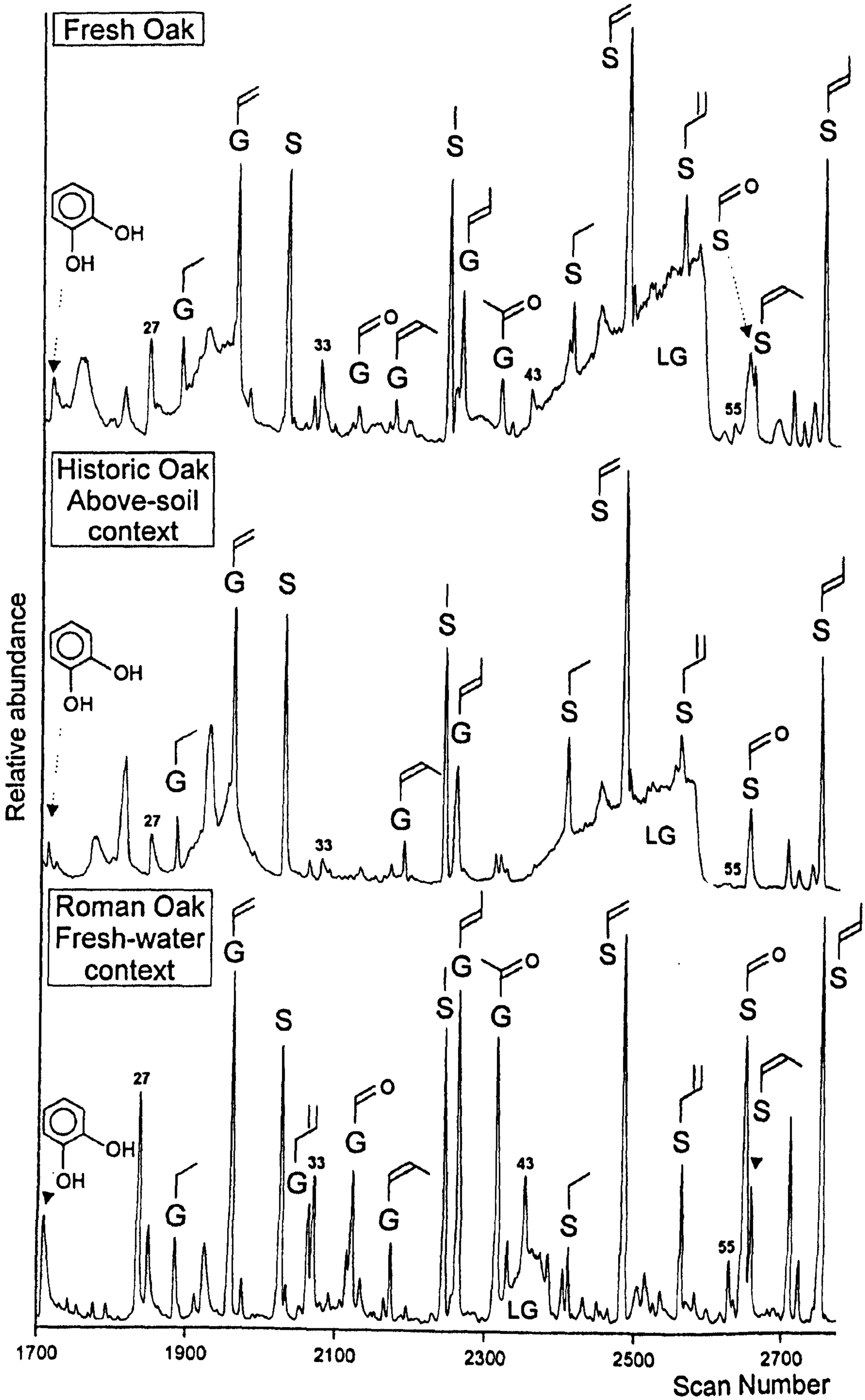


Figure 8.12 **Partial total ion chromatogram of benzenediols oak samples** **(van Bergen *et al*, 2000)**

Benzenediol derivatives of both guaiacyl and syringyl degradation can be observed in peak numbers 15, 24, 29, 36 (1,2-benzenediols). and peak numbers 21, 26, 27, 33, 43, 47, 51, 52, 55 (3-methoxy-benzendiols) in the pyrograms shown above. Equivalent guaiacyl- and syringyl-derivatives (Table 8.4: methyl, ethyl, 1-propenyl, propyl, 2-propenyl (*cis*)., 2-propenyl (*trans*)., etc.), exhibit the same elution orders. Regular trends can be observed with these pyrolysis products in degraded archaeological woods. More-degraded samples show enhanced levels of these products, while recent and historic woods tend to show them absent or in very minor amounts. The most degraded samples, FF6 and ST3 appear to show slightly reduced peak intensities, particularly for the benzendiols, 3-methoxy-benzenediols. This is consistent with the enhanced reactivity of these products as a result of the extra free hydroxyl groups present. Dehydroxylation is predicted to complete the removal of these products as far as their chemical evidence in pyrolysis studies is concerned (van Bergen *et al.* 2000).

8.4.4.6 Significance to sorption properties of archaeological wood

The presence of these extra hydroxyl groups on lignin degradation products is of significance in explaining greatly-increased hygroscopicity and elevated fibre saturation points measured in degraded archaeological wood. Loss of polysaccharides could be expected to greatly reduce hygroscopicity of this material. And though the presence of augmented amounts of shorter-chain carbohydrate fractions could be expected to contribute to this observed phenomenon, the quantities of these fractions actually measured as remaining in degraded material would not alone appear able to account for this increase to water binding sites. However, hydroxyl sites opened up as a result of lignin degradation could account for the increased hygroscopicity observed in archaeological waterlogged woods.

It is clear from the discussion above that results from Py-GC/MS yield a large range of diagenetic indicators of degradation level for archaeological woods. Loss to carbohydrates, changes to levoglucosan, changes to the relative intensity of guaiacyl over syringyl, and the appearance of 3-methoxy-1,2-benzenediols are all easily identifiable and follow predicted trends. The natural affinity of this type of analysis to the design of conservation treatments seems clear.

8.5 Summary

This chapter has established the usefulness of a number of instrumental analysis techniques in the determination of degradation levels in waterlogged archaeological wood. The advantage of these techniques has been seen to lie in the fact that a list of clear diagnostic markers exists which can be searched for in the results from these analyses. Identification of these markers does not necessarily presume a specialist understanding. Furthermore, very small samples only are required to carry them out and average sample throughput time is very short in comparison to standard laboratory tests applied to wood analysis.

This means that logistically, such techniques are much less expensive than the array of indirect measures discussed above. They are also most satisfactory from a scientific point of view. They are even more satisfactory as diagnostic tools, since they measure changes to holocellulose content or other

variables of interest directly, rather than attempting to measure them by an indirect diagnostic that also measures a number of other chemical processes. Furthermore, they are more accurate, in the sense that they do not contain so much possibility of measurement error. For these reasons, although these tools are superficially more high-tech than those customarily used by conservators, they actually require much lower levels of technical knowledge, time, and materials than do our existing diagnostic tools, and yield much more accurate and direct information on the variable of interest to the conservator choosing treatments for deteriorated archaeological wood. Moreover, these analytical techniques allow rapid screening of large numbers of samples and provide insight into the extent of wood degradation.

It seems likely that the future of archaeological wood studies aimed at answering conservation questions is likely to lie with such techniques.

Conclusion

Waterlogged wood conservation is ultimately directed towards effective drying of the artefact, since through this procedure is the best hope for its stabilisation. Successful treatment must achieve the removal of almost all water from the artefact without collapse, shrinkage, dimensional change of any sort, or stress-related damage, either in the course of treatment or during its subsequent life in store or on display. This is a tall order, especially when added to the cost-saving factors which must now also be factored into conservation treatments of this material. Nevertheless, we already have a number of adequately successful methods for the conservation of archaeological wood. What we don't have is all the information we might want for the modification of these techniques to provide fully predictable results for the widely variable material which comes in for treatment, or for the economical treatment of large structures and bulk assemblages.

Chapters 1 through 4 of this thesis comprise a synthesis of a wide range of disparate disciplines whose literature have not yet been brought together for their possible cooperative contribution to the conservation science of waterlogged wood. It is for this reason that considerable emphasis was given to this section of the thesis. It is hoped that in the process it was made clear just what proportion of these other disciplines' research is truly applicable to archaeological material, and where large gaps in our knowledge of the materials science of waterlogged wood lie. Many of conservation's past mistakes in treating this material have stemmed from assuming that it shares the properties of fresh wood, and certain of these assumptions may be continuing to limit our development of improved treatment techniques for waterlogged wood.

Chapter 1 clarified just which of the sources of variability in wood were likely to significantly affect its physical, chemical and water holding characteristics. Species differences were found to be important mostly in the context of softwood vs. hardwood distinctions, largely because of the differences to durability produced by differing amounts of extractives and different levels and type of lignins present. Large variations in native bulk density were also seen to have an important effect on moisture carrying capacity. The importance of taking into account past environment and construction techniques when considering some artefacts was also considered.

Chapter 2 attempted to bring together a complete picture of the degradation vectors affecting the condition of the waterlogged wood which comes in for conservation. Statements were also made about the comparative contribution of each of these to the final condition of the wood.

There is currently a lot of research being directed towards defining waterlogged burial environments, and the discussion in Chapter 2 makes it clear that a single definition of the chemical and physical effects of waterlogging in soil can not be relied on. It was also made apparent that a clear picture of the chemical and physical nature of the lignocellulose matrix of wood is still in the process of being refined by wood scientists. Most of the conservation literature fails to define it accurately, and it is hoped that the description given in this thesis may sort out some of the misconceptions about it. It was revealed in this chapter that recent work on lignin degradation paths has exposed the fact that lignin degradation leads to

an increase in numbers of hydroxyl sites on the breakdown products. Furthermore the susceptibility of lignins to degradation was clearly established, leading to the questioning of the standardly held belief in conservation research that degradation of waterlogged wood involves solely carbohydrate loss. The correction of this assumption has the potential to affect conservation treatment programs where up to now they have been fairly exclusively aimed at treating the carbohydrate remains in the wood.

It was stressed in this chapter that elements of preburial decay must be taken into account in our conception of the condition of this material. In particular, the role of aerobic fungi in the degradation of archaeological waterlogged wood must be acknowledged. It has generally been discounted by conservators of this material up to now. It was shown in this chapter that the fact that physical evidence of these organisms is lacking in this material is most probably due to subsequent continued decay once in the burial environment. Other evidence for their role in wood degradation remains. For example, it appears probable that it is basidiomycetes fungi who are responsible for the degradation of lignins characteristic of waterlogged wood, and the net increase to low molecular weight intermediates of both, lignin and carbohydrates, responsible for the increased hygroscopicity of this material – levels which can not be explained either by soft-rot and bacterial decay or by chemical decay processes alone.

The intention behind the synthesis of Chapters 1 and 2 was to make it clearer that the complexity of the interrelationships between the chemical and physical characteristics of waterlogged archaeological wood, their interdependency and almost infinite number of possible permutations, make it probable that we may have to become more realistic in our expectations of the conclusions we are able to draw from the analysis of archaeological wood.

Chapter 4 made the point that our aims and expectations of conservation treatments of this material could also do with re-examination. It is probably that we ask too much in pressing for a single treatment for all waterlogged wooden artefacts. Misconceptions and lack of information about the movements and chemical interactions of treatment chemicals within the wood matrix led to much of problems with past treatments and continue to dog our attempts to develop new ones and tailor those we have to the needs of the individual artefact. This chapter attempted to define more clearly the distinctions between each of the main categories of treatment approach in current use—what their aim is and what they actually achieve.

It was made clear that further research into the chemical nature and sorption patterns of our archaeological material would allow us to build the more over-reaching models of the behaviour of waterlogged wood and treatment chemical and processes which could inform the treatment process for the conservator.

The aim of this doctoral research was partly to do just that, and partly to identify some quick, reliable and accessible techniques which the conservator might use himself to assess the condition of waterlogged objects undergoing treatment. Since his primary concern in treatment is with issues such as permeability, diffusion rates, internal surface calculation, and drying behaviour, the primary focus of this research was towards techniques establishing the sorption characteristics of archaeological wood. Chapter 3 established the general lack of research into this area of archaeological wood studies up till now, and

Chapter 5 investigated the practicality of designing an easy and inexpensive method for obtaining this type of information for conservation purposes.

The discussion in Chapter 3 resulted in the clarifying of a number of points which make it clear why we are having such a difficult time predicting the effects of bulking treatments and drying of our waterlogged wood. Estimations of void volumes in all wood are complicated by the irregularity of the surfaces provided by the lignocellulose matrix of the cell walls, which mean that pure surface or capillary conditions do not prevail. The gel-like nature of wood substance means that very complicated methods will have to be used to side step swelling effects when attempting to assess pore volume ratios. Modelling of water movements within our archaeological wood are made difficult because the coefficients and constants required by the equations in use by wood scientists have not yet been measured for our material. This is obviously an area which would profit from further research.

None the less, as the discussion in Chapter 3 showed, certain areas of modelling (e.g., Darcy's Law of bulk flow) are going to require a great deal of work before they produce useful results for archaeological waterlogged wood conservation, since many of the assumptions upon which they are based do not hold for archaeological material under conservation treatment conditions.

Chapter 5 found that basic differences between wooden artefacts of differing preservation could be identified from data obtained from standard gravimetric sorption analysis of archaeological wood samples. It was clear that significantly better data was obtained when measurements were initiated from the waterlogged state, rather than in the standard method, from the oven dry state. While the numerical data produced from this study (e.g. FSP) did not seem to produce usable systematic trends, the descriptive data provided by the shape and slope of the isotherm plots was found to be illuminating.

Results from the study of the shape of the isotherms made it clear that multilayer and bulk water interactions make a higher contribution than unilayer interactions as degradation level increased. The implication of this is that mass loss rather than change to chemical constituent ratios is the controlling factor in the water relations of archaeological waterlogged wood — that is, that increased total volume within the wood, produced through degradation, is a more important factor than the specific number of bonding sites remaining within the degraded wood matrix. RD ratios were revealed to differ systematically between more degraded and less degraded woods and mirrored the trends discussed above. Some evidence for reversible hysteresis was given in these results, suggesting that changes in constituent ratios had the potential to show up on sorption isotherms. What was also revealed is that difference between resorption and secondary desorption values is much reduced in more degraded samples, suggesting that the more degraded the wood is, the more permanent the changes taking place within the cell-wall. What is clear from the results in this study is that we may need to abandon our search for a way to obtain the single measure of FSP in favour of more descriptive data about the interactions of water across the whole range of humidities. And this may mean that we need to concentrate in the future on developing a different approach to calculating level of loss to cell wall constituents and internal pore volumes. Application of a larger volume of data to test Jensen's (1997) DIFCON program could be very valuable towards this end.

Sorption measurements are very lengthy in their production and prone to error. Future investigations would profit by the further refining of methods such as DSC, NMR-i and porous plate membrane measurements so that they are appropriate for archaeological wood.

As it became apparent that there is no easy direct route to sorption-related information, a number of alternative diagnostic tools were given critical appraisal for their ability to give accurate and detailed indirect information about wood sorption characteristics (Chapters 6-8). Most of these tools were adopted from wood science for which there is a large literature which discusses their merits and drawbacks, though comparatively little investigation has gone into their applicability to archaeological wood. Chapters 1 and 2 established the very significant differences which exist between the chemical, physical, and mechanical properties of modern undegraded timber and degraded archaeological waterlogged wood. It was not unexpected, therefore, to find that, many of these techniques were less meaningful in practice when applied to degraded waterlogged material, more particularly when used in isolation to draw conclusions about the condition of archaeological artefacts.

Chapters 6 and 7 established the difficulty in drawing systematic trends between physical and chemical test data and sorption characteristics. While certain of the more general expected trends did show up between physical and chemical data, the high error associated with such measurements legislated against their adoption as accurate single diagnostic indicators for characterising the preservation level or water relations of archaeological woods. Bulk constituent analysis in particular failed to provide the improved insight into the chemical preservation of the artefact claimed for it by Hoffmann (1982) and Grattan and Mathias (1987). Results did however conclusively establish the significance of lignin degradation as part of the total degradation of the object, indicating the need for reappraisal of a number of our calculations that rely on this assumption.

Density is one of these, and the tests carried out in the course of this thesis established the need for reappraisal of this measure. Of all single indicators, this is the one most likely to provide information about the state of the internal surfaces of our wood. Results from measurements of cell wall density established conclusively that degraded archaeological woods show significant losses to cell wall density which match up well to measured holocellulose losses and changes to the sorption isotherm. This finding contradicts the accepted understanding about on cell-wall density in archaeological woods, and puts into question the mathematical underpinnings of the PEGCON program which are based on the average figure of 1.5 cm^3, as well as the calculations on which cell wall density from Umax and mass normalised yields are standardly based. There is a real need now for the development of a new set of standardised procedures for physical assessment which are applicable and useable by the waterlogged wood conservator. The picnometric method for measuring bulk and cell wall density was one of these discussed in this thesis.

This thesis investigated two other techniques for obtaining useful information about the condition of waterlogged artefacts– Sibert Drill resistance testing and polarised microscopy. Both of these were found to be valuable in providing detailed and meaningful information about the wood samples, and can be recommended for their simplicity. Future work directed towards applying digital imaging analysis to

micrographs of archaeological woods could be very helpful in obtaining data on changes to internal pore volumes.

As argued in the conclusion to Chapter 7, caution should be exercised towards our current preference for the low-tech approach in the assessment of preservation level of waterlogged wood. Our dependence on many of these measures is seriously flawed. Levels of measurement error inherent to these tests, added to the high complexity of variables controlling the degradation chemistry of waterlogged wood, mean that however large a data set studied, it is highly unlikely that such numerical data will produce dependable conclusions. The fact that this appears to be even further diminished the higher the level of degradation, adds to this concern.

In the end, this thesis argued that the balance of favour must go to a selection of instrumental techniques of analysis, which though again little investigated as yet in terms of archaeological material, showed very real and promising potential when tested with archaeological material in the course of this doctoral research (Chapter 8). It was established that these techniques could provide relatively detailed information about the chemical condition of archaeological artefacts which might be indirectly linked to conclusions about its water relations. And it furthermore argued that this information could be obtained at much lower cost in terms of sample size and preparation, analysis time, and expertise in interpreting results that has previously been assumed.

Chapter 8 established the high potential of three techniques of instrumental analysis as accurate and reliable diagnostic tools for degradation studies. Analyses using FTIR, Py-GC/MS, and elemental analysis revealed a number of useful and easily-recognisable markers for degradation. The systematic trends displayed by the data produced from these analyses make clear their potential to be summarised into systems which could be used to categorise wooden artefacts prior to conservation. Though only indirect connections may be drawn from these trends and sorption characteristics, FTIR at least, may be able to provide direct information about the differing relative proportions of types of water present in archaeological wood samples, but more research in this area is urgently needed.

Results from all three of the techniques applied provided informative data about relative loss of constituents. Though for the most part numerical analysis of the results was not carried out, for example comparing the data obtained with other measures such as wood density or sorption slopes, it seems probable that further study along these lines could be valuable. Pattern recognition of peak traces of both FTIR and Py-GC/MS results, yielded predictable trends, and though not without its risks, seems well within the reach of the practical conservator of this material. Relative losses to carbohydrates over lignins was very easy to assess. A number of valuable degradation markers for waterlogged archaeological wood were collated from the literature, and identified systematically in the results. In addition a series of previously unidentified markers for syringyl degradation (3-methoxy-1,2-benzenediols) were identified during the course of this study. The demethoxylation of lignins is what contributes to the production of extra hydroxyl groups which helps explain the increased hygroscopicity observed in waterlogged archaeological wood.

In this final chapter I argue that the tools of instrumental analysis may be ultimately much less expensive than the array of tests discussed in previous chapters, since they require much lower levels of lab technical knowledge, time and materials, and that their results are ultimately much more accessible to conservation use because of the more precise and accurate information they yield. Where only very small samples are available for testing, instrumental analysis may be the only real viable option. FTIR instruments can cost as little as the X-ray cabinet standard to most conservation laboratories, and a change in approach might allow for the sharing of analytical facilities between a number of conservation laboratories.

It seems likely that the future of archaeological wood studies aimed at answering conservation questions is likely to lie with such techniques.

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