Changes in the chemical composition of archaeological wood caused by exposure to different environments and its relation with the other properties.

A Thesis by:
Mahmoud Youssif Abdelwahab Mohammed

Submitted in total fulfilment of the requirements of the degree of
DOCTOR OF PHILOSOPHY

Grimwade Centre for Cultural Materials Conservation
School of Historical and Philosophical Studies
The University of Melbourne

May- 2018
Abstract

This thesis aims to characterise the deterioration mechanisms of dry cultural heritage wood by applying a multi-analytical technique that is comparable to that used for waterlogged archaeological wood. The deterioration and degradation resulting from the aging of wood, especially waterlogged wood, have been studied extensively compared to wood in dry environments. A similar scenario is repeated with the less information available about the chemical modifications of dry wood during aging, in particular on the molecular level. Previous studies (Crestini, El Hadidi, & Palleschi, 2009; Nilsson & Daniel, 1990) have noted this lack of research on dry wood and its chemical transformations, but this field still requires research into the relation between wood’s chemical composition and how it impacts wood’s other anatomical, physical and mechanical characteristics. This thesis explores also the effect of some other materials associated with wood in art objects on the chemical composition/characteristics of wood. It also seeks to characterise changes and modifications in the chemical composition of archaeological wood, and explain the degradation mechanisms of archaeological wood.

This thesis is divided into three sections. The first section examines the history of wood in cultural heritage (Chapter 1), the properties and structure of wood (Chapter 2) and wood deterioration (Chapter 3). The second section examines the materials and methods involved in the scientific investigation of the deteriorated wooden cultural heritage (Chapter 4). The third and final section analyses the results, discusses them and provides the conclusions of the research (Chapters 6-7). The thesis also includes a case study of the conservation analysis and treatment of a polychrome ancient Egyptian statuette (Chapter 8). The study employed analytical methods to identify the materials used in the object and their deterioration in order to implement a treatment and conservation plan to restore the object to as close to its original condition as possible and to preserve it for a longer period.

Different analytical techniques and instruments were employed to research these degradation mechanisms. Several samples were collected and examined, principally from various places in Egypt as well as from Italy and Australia. Reference samples for the identified taxa were also examined using the same techniques (Chapter 4). Analysis began with visual observation and microscopic studies using the light microscope (LM), a polarising light microscope (PLM) and
a scanning electron microscope (SEM) to identify the wood species and to assess the anatomical and morphological changes of the wooden samples. The physical properties of the samples such as density were also examined and the moisture content of each sample was measured.

A multi-analytical chemical procedure was followed in order to describe the condition of the samples and to track their chemical changes and transformations. Wet chemical analysis (WCA), including Klason lignin and acid-insoluble lignin and ash content measurement was used to determine the holocellulose to lignin ratio (H/L), water soluble substances and the organic soluble substances and the ash minerals content. This was useful in order to compare this study to the previous studies using this technique for analysing the chemistry of wood with cultural heritage significance and also it was used as a reference for the following chemical analytical techniques.

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) was applied on thin slices of the same samples and also applied on extractive-free powder. These results were useful in the interpretation of the high level of extraneous substances extracted, especially by hot water. Very small samples were cut and examined by pyrolysis gas chromatography with mass spectrometer (Py(HMDS)-GC/MS), which was very helpful in understanding the molecular changes in the chemical composition of samples tested (Chapter 4).

Sample were able to be identified by species or family (Chapter 5). For the ancient Egyptian samples, *Ficus sycomorus* (sycamore fig) was the main wood identified and other species included *Faidherbia albida, Taxus baccata*. Other species identified from the samples included: *Pinus sylvestris, Tamarix sp., Picea abies Karst., Pinus halepensis, Ostrya carpinifolia, Cupressaceae* family and *Quercus* sp. Microscopic assessment showed different preservation states for the samples studied, however the trend was that the most ancient samples were the more deteriorated ones. Fungi and bacteria were evident in some samples, especially those from ancient Egypt, but the identification of the biological agent was complicated. Physical measurement (Chapter 6) confirms the trend of decay revealed by the microscopic study as the ancient Egyptian samples had the least density compared to the other cultural heritage samples and reference samples.
The results showed the significant differences between the degradation of waterlogged archaeological wood and the dry wood, both in the chemical modification and in the other properties that occurred subsequently.
Declaration

I certify that:

- the thesis comprises only my original work towards the PhD except where indicated in the Preface,
- due acknowledgement has been made in the text to all other material used, and
- the thesis is less than 100,000 words in length, exclusive of table, maps, bibliographies, appendices and footnotes.

Mahmoud Youssif Adbelwahab Mohammed

May-2018
Preface

The work done in this thesis including collecting samples, the application of the methodology, analysing the data and the preparation of final document was made possible due to the efforts and the collaborations of numerous individual and agencies inside and outside Australia. A description of this collaboration and the contribution of the others towards the thesis is listed below.

Chapter 1: This chapter gives a broad survey of the use of wood in cultural heritage. It examines the applications of wood in a historical and chronological prospective. The work done in this chapter has not been submitted for publication yet.

Chapter 2: This chapter examines the different properties of wood. It discusses the wood macrostructure, microstructure and ultrastructure. The work done in this chapter has not been submitted for publication yet.

Chapter 3: This chapter examines the deterioration of cultural heritage wood. It reviews the different deterioration phenomena of waterlogged wood and dry wood and their causes. The work done in this chapter has not been submitted for publication yet.

Chapter 4: This chapter examines the materials and methods used in the experimental work of the thesis. The work done in this chapter was a result of collaborations with Trees and Timber Institute, National Research Council of Italy (IVALSA-CNR) in Florence, Italy and the Department of Chemistry and Industrial Chemistry at the University of Pisa (UoP) in Pisa, Italy. The candidate was partially funded by the Faculty of Arts, University of Melbourne (Graduate Research in Arts Travel Scheme (GRATS)) to travel to Italy to apply some of the analytical techniques used in this thesis on the cultural heritage wooden samples collected mainly from Egypt. Numerous individuals were involved in this part. Benedetto Pizzo was the host advisor in at IVALSA-CNR and all the work done with his guidance. Wet chemical analysis (WCA), part of the Fourier-transform infrared spectroscopy (FTIR) work and part of the physical measurements were done by the candidate in IVALSA-CNR. The cultivation of the moulds with the help of Elisabetta Feci and part of the microscopic and morphological investigations with the help of Chiara Capretti and Simona Lazzeri were done in the same
institute. Analytical pyrolysis gas chromatography mass spectrometry with in situ silylation (Py(HMDS)-GC/MS) was carried out at the Department of Chemistry and Industrial Chemistry, UoP by the help of Diego Tamburini, Jeannette Jacqueline Łucejko and Maria Perla Colombini.

The other part of the microscopic studies was done using electronic scanning microscope (SEM) facilities in the School of Earth Sciences at the University of Melbourne (UoM) by the candidate and Graham Hutchinson, a laboratory manager in the School of Earth Sciences, UoM. The other part of the FTIR examinations was done in the Grimwade Centre for Cultural Materials Conservation (GCCMC) at the UoM by the candidate. Some of the work is published.

Chapter 5: This chapter examines and discusses the results of the microscopic and morphological studies. Some of the work in this chapter was published.

Chapter 6: This chapter examines and discussed the results of the physical measurements. This work has not published yet.

Chapter 7: This chapter examines and discussed the results of the chemical analysis part. Some of the work in this chapter was published.

Chapter 8: This chapter a case study which was presented in an international conference in Warsaw, Poland. Conference title is Heritage Wood: Research and Conservation in the 21st Century organised by ICOM-CC. The work was a collaboration with Mostafa Abdelfatah, senior conservator, Saqqara region, the Ministry of Antiquities in Egypt.

Two peer reviewed publications to date were part of the work and collaboration done toward the thesis:

- Mahmoud Youssif Mohammed, Mostafa Abdelfatah and Robyn Sloggett, Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture: A Case Study, which will be published in the Heritage Wood: Research and Conservation in the 21st Century volume on the ICOM-CC website. (Accepted for publication June 2015)

- Diego Tamburini, Jeannette Jacqueline Łucejko, Benedetto Pizzo, Mahmoud Youssif Mohammed, Robyn Sloggett and Maria Perla Colombini, 2017. A critical evaluation of the degradation state of dry archaeological wood from Egypt by SEM, ATR-
FTIR, wet chemical analysis and Py(HMDS)-GC/MS, *Polymer Degradation And Stability*. 146, 140-154, ISSN: 01413910.
Acknowledgments

The work done in this thesis was possible only by the support and understanding of my beloved wife, Noura, my children Maryam, Youssif and Adam to whom and to my mother, brothers, sisters and to the soul of my father I dedicate this work. There are many people and organisations that have their inputs in this thesis and I am pleased to thank them all here with no particular order.

Foremost, I would like to express my deep gratitude and appreciation to my principle supervisor Professor Robyn Sloggett who made this study possible by her support, patience and friendship, who kept a sense of humour when I had lost mine, whose selfless time and care were sometimes all that kept me going. My sincere thanks goes to my co-supervisors Dr. Petronella Nel and Associate Professor Uta Wille for their knowledge, continuous support and constructive criticisms. Dr. Nel’s words “Just write, just do it” were always pushing me positively toward finishing the thesis.

Although he is not in my supervision committee, Dr. Benedetto Pizzo has been always available with his support and guidance before, during and after my visit to IVALSA-CNR in Florence, Italy. This work cannot be done without his immense support and hospitality. I cannot find words to describe my ultimate gratitude to him and to all IVALSA-CNR staff members: Dr. Chiara Capretti, Dr. Ilaria Santoni, Ms. Simona Lazzeri, Dr. Elisa Pecoraro, Dr. Elizabetta Peci, Dr. Sabrina Palanti and Mr. Luigi Fiorentino.

I am no less indebted to Dr. Diego Tamburini, Dr. Jeannette Jacqueline Łucejko and Professor Maria Perla Colombini from the Department of Chemistry and Industrial Chemistry at the University of Pisa for their collaboration especially in the Py(HMDS)-GC/MS.

Special thanks also goes to all individuals and supported collaborated in the case study part: Mr. Mostafa Abdelfatah from the Ministry of Antiquities (Egypt) for his collaboration and support throughout the project, Dr. Abeer Fouad Hagrassy from Restoration and Conservation Department at Fayoum University (Egypt) who identified the fungi included in this case study and to Mr. Ashraf Fahmi for his assist in the conservation part.
My sincere acknowledgement goes to all my best friends and colleagues in the Grimwade Centre for Cultural Materials Conservation (GCCMC) at The University of Melbourne in Australia or in The Restoration and Conservation Department, Fayoum University in Egypt for their friendship, valuable advices, moral support and for sharing knowledge, experience and fun. From the GCCMC: Dr. Marcelle Scott who helped me with my settlement and accommodation when I first came to Australia, Dr. Nicole Tse, Ms. Sophie Lewincamp and Mr. Tim Ould. From Fayoum University: Professor Atef Mansour Ramadan, Professor Naglaa Mahmoud Ali Hassan, Dr. Mohamed Mohamed Abdou Abd El-Bar and Mr. Mohamed Anwar Khalil Mohammad.

I am particularly indebted to the Egyptian Government presented in the Cultural affairs and Missions Sector, Ministry of Higher Education for providing me with the scholarship and financial support during the course of my study. Special thanks in the same context goes to the Faculty of Arts at the University of Melbourne for partially supporting my visit to IVLSA-CNR in Italy.

Thanks to all people around me in Egypt and Australia who made this journey easy and possible, thank you all.

Finally, all praises to Allah for the strengths and his blessing in completing this thesis.
INTRODUCTION

CHAPTER 1: WOOD IN CULTURAL HERITAGE (WOOD HISTORY) ........................................ 5
  1.1 THE HISTORICAL DEVELOPMENT OF WOOD BUILDING (STRUCTURES) .................. 5
    1.1.1 Ancient wooden buildings development ....................................................... 6
    1.1.2 A review of significant wooden structures: .................................................. 8
      1.1.2.1 Horyu-Ji (Japan) .......................................................................................... 9
      1.1.2.2 Kizhi Pogost (Russia) ................................................................................. 9
      1.1.2.3 The Fairbanks House (USA) ....................................................................... 10
      1.1.2.4 The Finger Wharf (Australia) ..................................................................... 10
  1.2 WOOD IN FURNITURE ......................................................................................... 11
    1.2.1 Egyptian Civilization ....................................................................................... 11
    1.2.2 Babylonian and Assyrian Civilization ............................................................ 13
    1.2.3 Graeco-Roman Civilization ............................................................................. 13
    1.2.4 Byzantine and Early Medieval ....................................................................... 14
    1.2.5 Islamic Periods Furniture .............................................................................. 15
    1.2.6 Medieval Times (Gothic) Furniture ................................................................. 15
    1.2.7 Renaissance and Industrial Revolution to Present Furniture ....................... 16
    1.2.8 Asiatic Furniture ............................................................................................. 18
  1.3 WOOD IN ARTEFACTS ......................................................................................... 19
    1.3.1 Wood in Carvings and Sculptures ................................................................. 19
      1.3.1.1 Ancient Egypt ............................................................................................... 20
      1.3.1.2 Assyrian, Greek, Roman and Byzantine ...................................................... 21
      1.3.1.3 Medieval ...................................................................................................... 21
      1.3.1.4 The Renaissance .......................................................................................... 23
      1.3.1.5 Grinling Gibbon ........................................................................................... 23
      1.3.1.6 Islamic ......................................................................................................... 24
      1.3.1.7 Asiatic .......................................................................................................... 24
      1.3.1.8 Modern ........................................................................................................ 25
    1.3.2 Wood as Frames .............................................................................................. 25
    1.3.3 Wood in Musical Instruments and Tools ......................................................... 29
      1.3.3.1 Wind Instruments ....................................................................................... 30
      1.3.3.2 String Instruments ...................................................................................... 30
      1.3.3.3 Percussion Instruments ............................................................................... 31

CHAPTER 2: WOOD STRUCTURE AND PROPERTIES ...................................................... 34
  2.1 WOOD STRUCTURAL PROPERTIES (STRUCTURE AND CHEMISTRY OF WOOD) ........ 34
  2.2 INTRODUCTION .................................................................................................. 34
  2.3 WOOD MACRO STRUCTURE ............................................................................. 34
    2.3.1 Tree growth and wood formation ..................................................................... 35
    2.3.2 Annual/Growth rings ...................................................................................... 37
    2.3.3 Sapwood and Heartwood ................................................................................ 38
    2.3.4 Rays ............................................................................................................... 39
    2.3.5 Bark ............................................................................................................... 40
    2.3.6 Cutting direction of wood ............................................................................... 40
  2.4 WOOD MICROSTRUCTURE (CELL LEVEL) ............................................................ 41
2.4.1 Softwood and hardwood (Wood classification).................................................42
2.4.2 Softwood (Gymnosperms or Conifers)..........................................................43
  2.4.2.1 Tracheids.............................................................43
  2.4.2.2 Paranchyma cells..................................................44
  2.4.2.3 Transverse cells...................................................45
  2.4.2.4 Important anatomical features of softwood...........................................45
    2.4.2.4.1 Pits..........................................................45
    2.4.2.4.2 Rays..........................................................46
    2.4.2.4.3 Resin canals..............................................47
2.4.3 Hardwood (Angiosperms or Dicots)..............................................................48
  2.4.3.1 Vessels..............................................................48
  2.4.3.2 Fibres..............................................................49
  2.4.3.3 Parenchyma cells................................................49
  2.4.3.4 Important anatomical features of hardwood........................................50
    2.4.3.4.1 Rays..........................................................50
    2.4.3.4.2 Pits..........................................................50
    2.4.3.4.3 Perforation plates........................................51
    2.4.3.4.4 Tyloses ....................................................51
    2.4.3.4.5 Thickening................................................51
    2.4.3.4.6 Gum canals...............................................51
2.4.4 Palm wood (monocotyledons).......................................................................52
2.5 WOOD ULTRASTRUCTURE AND CELL WALL CHEMISTRY (MOLECULAR STRUCTURE)........52
  2.5.1 Cell wall structure..................................................................................52
  2.5.2 Wood chemistry.......................................................................................54
    2.5.2.1 Arrangement of cellulosic polymers in the cell wall...............................55
    2.5.2.2 Cell wall main compounds.................................................................58
      2.5.2.2.1 Cellulose....................................................................................58
      2.5.2.2.2 Hemicellulose (polyose): .................................................................62
      2.5.2.2.3 Lignin.......................................................................................66
    2.5.2.3 Secondary Components .......................................................................69
      2.5.2.3.1 Extractives................................................................................69
      2.5.2.3.2 Inorganic minerals (Ash).................................................................70
      2.5.2.3.3 Minor polysaccharides (pectin and starch)........................................71
2.6 WOOD PHYSICAL PROPERTIES......................................................................71
  2.6.1 Wood and Water.......................................................................................71
  2.6.2 Swelling and shrinkage............................................................................72
  2.6.3 Appearance...............................................................................................73
    2.6.3.1 Colour.........................................................................................73
    2.6.3.2 Texture.........................................................................................74
    2.6.3.3 Figure..........................................................................................74
  2.6.4 Density......................................................................................................74
2.7 WOOD THERMAL PROPERTIES.................................................................76
2.8 WOOD ELECTRICAL PROPERTIES.............................................................77
2.9 WOOD ACOUSTIC PROPERTIES....................................................................78
2.10 WOOD MECHANICAL PROPERTIES...........................................................78
  2.10.1 Wood Strength.......................................................................................79
    2.10.1.1 Modulus of rupture (MOR):.................................................................80
  2.10.2 Wood Elasticity.......................................................................................81
    2.10.2.1 Modulus of elasticity (E).....................................................................82
2.11 WOOD NATURAL DEFECTS.........................................................................82
  2.11.1 Knots......................................................................................................82
  2.11.2 Reaction Wood......................................................................................83
    2.11.2.1 Compression Wood.........................................................................84
    2.11.2.2 Tension Wood................................................................................84
3 CHAPTER 3: WOOD DETERIORATION AND DEGRADATION.................................86
  3.1 WET AND WATERLOGGED ENVIRONMENT...............................................86
    3.1.1 Chemical changes (Chemical degradation).............................................86
    3.1.2 Physical and mechanical changes resulting from deterioration.............91
    3.1.3 Anatomical and morphological changes..............................................93
    3.1.4 Bio-deterioration:..................................................................................95
### 3.1.4.1 Fungal decay ................................................................. 95
- Wood degradative fungi (decay fungi). ........................................ 96
- Wood staining fungi and moulds ........................................... 100

### 3.1.4.2 Bacterial decay: ......................................................... 101
- Pit membrane and Scavenger bacteria .................................. 102
- Erosion bacteria ................................................................... 102
- Tunnelling bacteria ............................................................. 103
- Cavitation bacteria .............................................................. 103

### 3.1.4.3 Insects, marine borers and crustaceans .................... 104
- Wet (damp) damaged wood insects ....................................... 104
- Dry wood destroying insects .............................................. 104
- Non-destroying insects ...................................................... 105
- Marine borers and crustaceans ......................................... 105

#### 3.2 DRY WOOD ................................................................. 106

##### 3.2.1 Chemical changes .................................................. 106
##### 3.2.2 Physical and mechanical changes ................................. 110
##### 3.2.3 Anatomical changes ................................................ 110
##### 3.2.4 Biodeterioration of dry wood: .................................... 111
- Dry wood insects .................................................................. 111
- Dry wood destroying insects .............................................. 112
- Dry wood non-destroying insects ....................................... 115

### 3.3 FOSSILISED WOOD ....................................................... 115

##### 3.3.1 Silicification .............................................................. 115
##### 3.3.2 Coalification ............................................................. 116

### 4 CHAPTER 4: METHODOLOGY (MATERIALS AND METHODS) ..... 120

#### 4.1 SAMPLES AND SAMPLING: ........................................... 120
- Egyptian Samples: .............................................................. 120
- Italian Samples: ................................................................. 124
- Australian Samples ............................................................ 124
- Reference Samples: .......................................................... 124

#### 4.2 MACROSCOPIC AND VISUAL INVESTIGATIONS: ........... 125

#### 4.3 PHYSICAL AND MECHANICAL MEASUREMENTS ........... 127
- Moisture content ............................................................... 127
- Basic Density ................................................................. 127

#### 4.4 CHEMICAL ANALYSIS ................................................... 128
- Wet Chemical analysis (WCA) .............................................. 128
- Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) ........................................ 130
- Energy-dispersive X-ray Spectroscopy (EDS): ...................... 132
- Analytical pyrolysis gas chromatography mass spectrometry with in situ silylation (Py(HMDS)-GC/MS) ........ 132

### 5 CHAPTER 5: MICROSCOPIC AND MORPHOLOGICAL INVESTIGATIONS ...... 137

#### 5.1 INTRODUCTION: ............................................................ 137

#### 5.2 IDENTIFICATION: .......................................................... 139

#### 5.3 ANCIENT EGYPTIAN SAMPLES .................................... 142

#### 5.4 GRAECO-ROMAN SAMPLES ........................................ 144

#### 5.5 ISLAMIC SAMPLES ....................................................... 145

#### 5.6 MICROSCOPIC RESULT FOR THE FUNGI CULTIVATION ...... 147

#### 5.7 CONCLUSION: ............................................................. 148

### 6 CHAPTER 6: PHYSICAL AND MECHANICAL MEASUREMENTS .......... 150

#### 6.1 MOISTURE CONTENT AND DENSITY ............................... 150
- Egyptian Samples: .............................................................. 153

#### 6.1.1 Ancient Egyptian and Graeco-Roman samples .......... 153
- Islamic Cairo and Modern Era samples ................................ 154
- Italian samples: ................................................................. 154
- Australian samples: .......................................................... 154

#### 6.1.2 Ficus sycomorus samples ........................................ 155

#### 6.2 CONCLUSION: ............................................................. 156
7 CHAPTER 7: CHEMICAL ANALYSIS ........................................................................158
 7.1 Wet CHEMICAL ANALYSIS (WCA) ..............................................................158
 7.2 FTIR ANALYSIS ..........................................................................................163
 7.3 ENERGY-DISPERSIVE X-RAY SPECTROSCOPY (EDS) .....................................170
 7.4 Py(HMDS)-GC/MS ......................................................................................170
 7.5 DISCUSSION: .............................................................................................186
    7.5.1 Faidherbia albida - samples EG-SAQ-1 and EG-SAQ-7 from the Khendjer pyramid site (ca. 1760 BC).................................................................186
    7.5.2 Ficus sycomorus - samples EG-SAQ-3, EG-SAQ-4, EG-SAQ-5 and EG-SAQ-6 from the Khendjer pyramid site (ca. 1760 BC) and sample EG-DAK-1 from Dakhla oasis (332 BC – 395 AD).............187
    7.5.3 Taxus baccata - sample EG-SAQ-8 from the Khendjer pyramid site (ca. 1760 BC).................................................................188
    7.5.4 Tamarix sp. - sample EG-SOH-1 and Pinus sylvestris – samples EG-SOH-2 and EG-SOH-3 – from the city of Jerja (ca. 1787 AD)..............................188
 7.6 CAUSES OF DEGRADATION .........................................................................188
 7.7 CONCLUSIONS ............................................................................................189

8 CHAPTER 8: TREATMENT AND CONSERVATION OF A POLYCHROME EGYPTIAN WOODEN SCULPTURE: A CASE STUDY ....................................193
 8.1 ABSTRACT .................................................................................................193
 8.2 INTRODUCTION ..........................................................................................193
 8.3 MATERIALS IDENTIFICATION AND ANALYTICAL METHODOLOGY .............194
 8.4 RESULTS AND DISCUSSION ......................................................................196
    8.4.1 Pigments.............................................................................................196
    8.4.2 Ground layer ......................................................................................199
    8.4.3 Binder .................................................................................................199
    8.4.4 Old restoration material ......................................................................199
    8.4.5 Black colour on skirt..........................................................................200
    8.4.6 Wood ..................................................................................................201
    8.4.7 Moulds ................................................................................................202
 8.5 CONSERVATION TREATMENT ...................................................................202
    8.5.1 Documentation ..................................................................................202
    8.5.2 Cleaning .............................................................................................203
    8.5.3 Consolidation .....................................................................................204
    8.5.4 Structural repair ................................................................................204
 8.6 CONCLUSION .............................................................................................206
 8.7 REFERENCES .............................................................................................207

SUMMARY, CONCLUSION AND FURTHER WORK: ............................................211

REFERENCES: .....................................................................................................216

APPENDICES .......................................................................................................235
  APPENDIX A .....................................................................................................235
    List of ancient Egyptian samples codes used in the thesis and in the publications ..................................................235
  APPENDIX B .....................................................................................................237
    Chapter 8 in press work ................................................................................237
    This appendix shows the version before the final corrections of the paper ..................................................237
  APPENDIX C .....................................................................................................255
    Photograph documentary of the case study examined in Chapter 8 before and after conservation ........................................255
List of figures:

Figure 1: Early stages of the plant development and primary tissues (Tsoumis, 2019). ....... 35
Figure 2: The development of the primary tissues and the secondary tissues. In addition to transformation of the fascicular and interfascicular cambium into a cambium (Miyashima, Sebastian, Lee, & Helariutta, 2013) ................................................. 36
Figure 3: The difference between the Periclinal division and the Anticlinal division of the cambium cells (Haygreen & Bowyer, 1989)................................................................. 37
Figure 4: All the components of the macrostructure of the tree trunk (Tsoumis, 2019) ....... 38
Figure 5: The different macroscopic anatomical feature as they appear in the different cutting direction of wood (Tsoumis, 2019).............................................................................. 41
Figure 6: The difference between softwood and hardwood (tree and cell level). After Arno (1993). ............................................................................................................................... 42
Figure 7: Comparison between earlywood and latetwood in softwood tracheids (Howard & Manwiller, 1969). ................................................................. 43
Figure 8: The different types of cells of the microstructure of hardwood (Hoadley, 2000) ... 48
Figure 9: The different types of pores and their distribution way in hardwood. Left diffuse porous, middle ring-porous and right semi-ring porous (Bahador, Namdari, & Matinfar, 2017)........................................................................................................... 49
Figure 10: The microstructure of wood cell wall (ML: middle lamella, P: primary wall, S1: secondary wall 1st layer (outer), S2: secondary wall 2nd layer (middle), S3: secondary wall 3rd layer (inner), W: warty layer (Côté, 1967). ............................................................... 53
Figure 11: The cell wall ultrastructure including border bits (Eaton & Hale, 1993) ............ 54
Figure 12: Wood chemical components (Unger et al 2001, p:16)........................................ 55
Figure 13: Hierarchical modelling of softwood hygro-elastic illustrates the macro, micro and ultrastructure of wood (Harrington, 2002 after University of Canterbury, 1996, design by Mark Harrington)........................................................................................................ 56
Figure 14: The formation of the cellulose microfibrils and how they are surrounded by hemicellulose network (Adler & Buehler 2013)............................................................... 56
Figure 15: The microfibrils angle and distribution of main compounds in the cell wall of Scots pine (Rowel et al., 2005)................................................................. 58
Figure 16: Structure of cellulose, (a, b, c) after: Desvaux (2005), (d) Kantharaj (n.d.) ...... 60
Figure 17: The crystalline structure of cellulose Iα and cellulose Iβ (Barsberg, 2017)........ 60
Figure 18: Reducing and Non-Reducing end-group of the cellulose compound (Börjesson & Westman 2015)........................................................................................................ 61
Figure 19: The structure of Arabinoglucuron-oxylan in Softwood (Brandt et al., 2013) ...... 64
Figure 20: The chemical structure of the Glucuronoxylan (Brandt et al., 2013) ............... 65
Figure 21: Chemical structure of lignin: coniferyl, sinapyl and p-coumaryl alcohols (Moore, Robson & Trinci, 2011)................................. 68
Figure 22: Wood decayed by brown rot. A) Cubic deterioration feature. B) Transmission Electron Microscope of wood cell wall after the degradation of the carbohydrates. C) Brown cubical rot by Oligoporus amarus. MP middle lamella/primary walls, S secondary wall, L lumen. After (Schmidt & Czeschlik, 2006) ....................................... 97
Figure 23: SEM. Erosion of the white rot fungi in birch. After (Eaton & Hale, 1993) ....... 98
Figure 24: The impact of the soft rot fungi on the S2 layer of the latetwood of the Corsican Pine (SEM, transverse surface after (Eaton & Hale, 1993)......................................... 100
Figure 25: Suggested illustration of silicification sequence of wood cell (Fengel, 1991, p.167 after Furuno, 1986)................................................................. 116
Figure 26: Aging and fossilisation of wood (Fengel 1991, 154)......................................... 117
Figure 27: The location of the Egyptian samples collected for the study (Google Maps, 2018) ................................................................. 121
Figure 28: The location of samples EG-Is.C-1, 2, 3 and 4 on the map of Islamic Cairo (Hafez, 2012) ............................................................... 122
Figure 29: Micro-furnace Multi-Shot Pyrolyser EGA/Py-3030D (Frontier Lab, 2013) ..... 133
Figure 30: Transverse section (a), radial section (b) and tangential section (c) of sample EG-SAQ-1 ........................................................................ 140
Figure 31: Transverse section (a), radial section (b) and tangential section (c) of sample EG-SAQ-3 ........................................................................ 140
Figure 32: Transverse section (a), radial section (b) and tangential section (c) of sample EG-SAQ-4 ........................................................................ 140
Figure 33: Transverse section (a) and radial section (b) of sample EG-SAQ-1 .................................................................................. 140
Figure 34: Transverse section (a), radial section (b) and tangential section (c) of sample EG-SAQ-6 ............................................................................... 140
Figure 35: The radial section (a) and the tangential section (b) of sample EG-DAK-1 ..... 140
Figure 36: The tangential section (a) and the vessel element structure of sample EG-Is.C-1 ............................................................................... 141
Figure 37: Transverse section (a), radial section (b) and tangential section (c) of the modern Ficus sycamorus (Sycamore Fig) wood (InsideWood, 2004 onwards) ............................................................................................................................ 141
Figure 38: SEM of RLS (top) of samples EG-SAQ-3 shows a strong attack by fungi is visible inside cells, and TS (bottom) shows hyphae inside vessel (c), spores inside cell lumen and cell wall of the parenchyma cells(d) ............................................................................................................................ 143
Figure 39: EG-SAQ-1 (RLS): evident fungi hyphae inside rays (arrows) are visible (SEM) .......................................................................................... 143
Figure 40: Decay of sample EG-SAQ-7; a) TS (LM) shows the detachments (arrowed) of cell walls due to biological decay; b) TS (PLM) the presence of biological decay is confirmed by the loss of birefringence, due to the decay of cellulose. C) and d) RLS (SEM a heavy decay produced by fungi and signs, inside the cell wall of vessel, of a probably bacterial attack are visible (arrows) ........................................................................................................................................ 144
Figure 41: Transverse section of samples EG-SAQ-5 (left) and EG-SAQ-8 (right), shows the severe degree of degradation of the cell wall structure because of the attack of microorganisms in both earlywood and latewood .................................................................................................................................... 144
Figure 42: a) Transverse section of sample EG-DAK-1 from Dakhla showing the good condition of the wood structure. b) Radial section of sample EG-ASW-1 showing fungi hyphae within the vessel element ............................................................................................................................ 145
Figure 43: (Transverse sections 5x): Sample EG-SOH-1 (Tamarix sp.) shows a perfect state of preservation, confirmed by the polarised light (left) (Light Microscope). Polaring Microscope (left), Light microscope (right) Arrows show the damage caused by the preparation method .................................................................................................................................... 146
Figure 44: LM images of thin sections of samples a) EG-SOH-1 (Tamarix sp., TLS, 2.5x), b) EG-SOH-2 (Pinus sylvestris, RLS, 20x), c) EG-SOH-3 (Pinus sylvestris, RLS, 10x) and d) EG-SOH-3 (Pinus sylvestris, TS, 5x). Some of the main anatomical features are indicated .................................................................................................................................... 146
Figure 45: Brown mould grown on sample EG-SAQ-8 and identified as Alternaria spp. ..... 147
Figure 46: Mould identified as Aspergillus spp. for sample EG-SAQ-4 (a) and sample EG-SAQ-8 (b) .................................................................................................................................... 148
Figure 47: The moisture content and the density values for all samples grouped from left to right as: Ancient Egyptian samples, Islamic Cairo and Modern samples, Italian samples and Australia samples .................................................................................................................................... 152
Figure 48: Basic density of the Egyptian samples (ancient Egypt and Graeco-Roman period) ................................................................. 154
Figure 49: The different values of the density and moisture content of the cultural wooden samples identified as Ficus sycomorus and the reference Ficus carica L. sample ...... 156
Figure 50: H/L ratios and ash content percentage of Egyptian wooden samples................. 161
Figure 51: Comparison between the FTIR spectra of sample EG-SAQ-5 and the reference Ficus sycomorus .................................................................................................................. 165
Figure 52: Comparison between the FTIR spectra of sample EG-DAK-1 (blue spectrum) and the reference Ficus Carica L (orange spectrum). ................................................................. 166
Figure 53 (a & b): FTIR spectra of sample EG-SAQ-2 (a) and EG-SAQ-5 (b) before and after extraction .................................................................................................................. 167
Figure 54 (a & b): FTIR spectra of samples: a) EG-SAQ-6 in comparison with reference Ficus sycomorus; b) EG-SAQ-8 in comparison with reference Taxus baccata. .......... 169
Figure 55 (a & b): FTIR spectra of samples: a) EG-SOH-1 in comparison with reference Tamarix sp.; b) EG-SOH-2 and EG-SOH-3 in comparison with reference Pinus sylvestris .................................................................................................................. 169
Figure 56: EDS spectrum of sample EG-SAQ-2. It shows the presence of the calcium Ca in high intensity which suggest that the ash content is affected by the preparation material that was put on the wooden substrates to prepare it for painting......................................... 170
Figure 57: Py(HMDS)-GC/MS profiles for samples a) sound Faidherbia albida and b) EG-SAQ-7. Peak labelling refers to Table 11 In Italic: lignin pyrolysis products .......... 171
Figure 58: Py(HMDS)-GC/MS profiles for sample EG-SOH-3, c) EG-SAQ-5. Peak labelling refers to Table 11. In Italic: lignin pyrolysis products. .................................................................................. 177
Figure 59: Py(HMDS)-GC/MS profiles for sample EG-ASW-1. Peak labelling refers to Table 11. In Italic: lignin pyrolysis products.......................... 178
Figure 60: Py(HMDS)-GC/MS profiles for samples a) sound Pinus sylvestris, b) EG-SOH-2, c) EG-SOH-3. Peak labelling refers to Table 11. In Italic: lignin pyrolysis products. 179
Figure 61: Distribution of categories of lignin pyrolysis products expressed as percentages for all the samples from Egypt and the corresponding sound wood samples. 182
Figure 62: Distribution of categories of holocellulose pyrolysis products expressed as percentages for all the samples from Egypt and the corresponding sound wood samples. .................................................................................. 185
Figure 63: Object 18241 prior to conservation treatment. Shows the separation (squares) of the statuette parts................................................................. 195
Figure 64: SEM-EDS of the black sample. A and B are SEM images. C is the EDS pattern. .................................................................................................................. 197
Figure 65: PXRD spectrum of black pigment with a crystalline phase of calcite, graphite and quartz .................................................................................................................. 197
Figure 66: PXRD spectrum of blue pigment with a crystalline phase of calcite, Egyptian blue and .................................................................................................................. 198
Figure 67: PXRD spectrum of dark yellow pigment with a crystalline phase of calcite, yellow .................................................................................................................. 198
Figure 68: PXRD spectrum of the ground layer with a crystalline phase of calcite and quartz. .................................................................................................................. 199
Figure 69: FTIR spectrum of a binder in black pigment................................................. 200
Figure 70: FTIR spectrum of the previous restoration material compared to the PVA control .................................................................................................................. 200
Figure 71: FTIR spectrum of the black deposits on the skirt, ground layer and black pigment. .................................................................................................................. 201
Figure 72: SEM of the wooden support (Ficus sycomorus). It shows good integrity of the microstructure and the ultrastructure of the cell wall. No signs of biological attack were obvious.

Figure 73: The object 18241 during the documentation and in the first stages of conservation. It documents in more details the condition of the statuette (a) and its size compared to real human body (b).

Figure 74: Structural consolidation for the object 18241 showing the areas where the cotton wool was used (arrows).

Figure 75: The object 18241 after treatment.
List of tables

Table 1: Major hemicellulose components (*Partial solubility) (Sjöström, 1981) .............. 64
Table 2: Semiquantitative analysis of lignin and carbohydrate components obtained by Py-GC/MS of aged lime wood samples (% of pirogram peak area) (Popescu et al., 2007, p. 73) ........................................................................................................................................ 108
Table 3: The different sites of the Egyptian Samples and their approximate date .......... 123
Table 4: Reference samples used, their origin, location and the cultural heritage samples compared with ........................................................................................................................................ 125
Table 5: Samples used in the Py(HMDS)-GC/MS test, their identification and description 134
Table 6: The identification of Egyptian wooden samples and the type of biological decay if presents ........................................................................................................................................ 138
Table 7: Summary of the SEM sections of the cultural heritage Ficus sycomorus tested samples and the section of the same species in the literature ........................................ 140
Table 8: Moisture content and density of all samples ........................................................... 150
Table 9: Wet chemical analysis of ancient and archaeological and reference wood samples ........................................................................................................................................ 159
Table 10: Assignments of IR absorption bands for the analysed cultural heritage wood samples ........................................................................................................................................ 164
Table 11: Wood pyrolysis products identified by Py(HMDS)-GC/MS and divided into categories. The molecular weight (MW) of the derivatised compounds, the main m/z peaks in the mass spectra (base peak in bold), the attribution of the pyrolysis products to the corresponding wood component (H=Holocellulose, L=Lignin, G=Guaiacyl lignin, S=Syringyl lignin) and to the specific categories (dem=demethylated/demethoxylated compounds) are shown ........................................................................................................................................ 171
Table 12: Pyrolytic H/L for the archaeological Egyptian samples and sound wood samples of the same species ........................................................................................................................................ 180
Table 13: Mould species identified from the samples taken from the part above the skirt .. 202
Table 14: List of the samples examined in the publication and their alternatives in the thesis ........................................................................................................................................ 235
Introduction
**Introduction**

Wood is one of the main materials used in the manufacture of Artefacts and ancient objects; its use ranges from small objects to large churches and temples. Saving these wooden heritage items is a great challenge with incontestable significance.

Trying to restore and conserve wooden Artefacts is very time consuming and expensive, so prevention being better than cure (Rivers & Umney, 2003), it is essential to understand what is happening inside wood when exposed to environmental degradation factors, the stages of wood deterioration, the mechanism of wood degradation and patterns of degradation. Armed with this knowledge modern scientists are able to develop preservation techniques that will ensure preservation of wood (Crestini et al., 2009; Rowell, 1990).

To understand wood deterioration, it is necessary to understand the changes in the molecular composition of wood and their impact on the other physical, mechanical and anatomical characteristics of wood (Modugno et al., 2008).

Section one explores the history, properties and deterioration of wood cultural heritage. The first chapter examines the history and the development of wood across the historical periods, the common uses of wood throughout time and gives some examples of famous techniques and artefacts. Chapter 2 examines wood’s different properties including anatomical, chemical, physical and mechanical characteristics. Chapter 3 considers the deterioration process and phenomena of both dry and waterlogged wood.

Apart from stone, wood is the most commonly utilised material in the cultural heritage. Wooden remains and Artefacts have numerous types, forms and techniques, ranging from primitive tools to the remarkable temples of Japan. The significance of conserving this great heritage cannot be ignored.

As Rowell and Barbour (1990, p. xi) identify:

> There is a great need for preserving wood in the many forms that remain from ancient to modern times, not only because it will be interesting to future generations, but to use
it to study the cultures and climate throughout history and to examine the wood-aging process itself.

As prevention is better than cure, so it is necessary to understand what is happening to wood internally during exposure to environmental factors, what are the stages of deterioration in wood and the mechanisms of wood degradation and degradation patterns. Equipped with this information conservators and conservation scientists can follow a sensible course to develop preservation techniques and conservation strategies that will allow the wood to remain for generations (Rowell & Barbour, 1990).

To accomplish this goal, it is essential to understand the changes in the molecular composition of wood and the changes to the other physical, mechanical and anatomical characteristics of wood. According to Modugno et al. (2008) the characterisation of the chemical composition of archaeological wood is of primary significance to understanding the degradation undergone by wooden artefacts and thus to the development of suitable consolidation and conservation methodology.

A number of previous studies have focused on the changes in waterlogged Archaeological wood (Grattan & Mathias, 1986; Jordan, 2001; Jordan, 2003; Yohsei, 2005; Christensen et al., 2006; Colombini et al., 2007; Capretti et al., 2008; Modugno et al., 2008; Pournou, 2008; Bardet et al., 2009; Colombini et al., 2009 and others). Many other studies have concentrated on changes in bio-deteriorated wood (El-Sonbaty, 1997; Blanchette et al., 1990; Genestar, 2007; Gelbrich, Mai & Militz, 2008). While there are a limited number of studies analysing the chemical changes of waterlogged wood, even fewer examine the chemistry modifications in dry archaeological wood. Similarly, the effect of other environmental factors on wood properties have been the subject of less scientific work than the influence of biological factors (Feist, 1990; Anderson, 1991; Blanchette et al., 1994; Hon, 2000; Caba et al., 2007; Genestar & Palou, 2006; Crestini et al., 2009).

These gaps form the subject and the question of this thesis. What changes occur in the chemical composition of archaeological wood as it deteriorates? What changes occurred to the other properties as a result of this chemical modification or degradation? The focus of this thesis is therefore to make a comparison between waterlogged or wet archaeological wood (previous studies) and dry archaeological wood (experimental work), in order to understand more
comprehensively what deterioration mechanisms occur and to more effectively inform conservation decision making.
1 CHAPTER 1: Wood in cultural heritage (wood history)

Timber, which is wood that has been harvested to use, has been used by man since earliest times. It has been used for numerous purposes including burning for warmth and cooking, implements for agriculture, tools, religious carvings, weapons and building. It is certainly one of the oldest construction materials and is still used in large quantities for structural, semi-structural, decorative and other purposes in building (Scott, 1968; Youngs & Hamza, 2016).

Wood has some properties and advantages that makes it preferable material. It has strength to weight ratio that is three times higher than what concrete has and from three to four times higher than that of steel. It is easy to be formed by hand or by machine and available in a wide diversity of colours, textures, grain patterns and densities. Moreover, it has the ability to absorb the impact and move with the changes in loads, temperature and moisture. Wood is also the only renewable natural resource with structural properties (Dolby et al., 1988; Richardson, 1976; Walsh-Korb, & Averous, 2019).

These days, using wood in architecture has additional considerations and attractions than many other construction techniques, as the use of wood is seen to have fewer environmental impacts. Such benefits include low water pollution, low greenhouse gas (GHG) emissions, low air pollution and smaller solid waste requirements compared with concrete and steel (Qu et al., 2012).

1.1 The historical development of wood building (structures)

Wood is still considered to be the most useful building material, even after the comparatively recent innovation of metal forms and concrete for structural work. It remained until the industrial revolution the only material with which man could make complete architectural frameworks, or parts such as beams, rafters, and purlins all capable of withstanding bending and tension (Davey, 1961), and it was the only material that could be worked with the tools then available (Findlay, 1975). For centuries wood was the only material capable of spanning large distances. There is much knowledge to be gained historically and technically in studying the development of the wooden structures through the ages from the ingenious, simple prehistoric buildings to the highly developed handcrafted timber buildings of the Medieval Europe or those of the Tang Dynasty in China and the highly technical wood industry of the present day (Dolby, Hammer, & Jeppsson, 1988).
According to Richardson (1976), despite it might have been anticipated that wood will be outdated and will eventually be excluded as a building material because of the development of more uniform manufactured materials such as concrete, metals or plastics, but according to him those predictions were incorrect. Wood is still considered as one of the most widely used materials, in spite of these rapid technological developments that have taken place in the field of plastics (Diamant, 1970). Because the manufacture of wooden products consumes less energy than that required for manufactured materials such as steel and concrete, timber production is likely to remain more prominent (Campbell, 1997).

Historically wood occupies a significant place in the history of architecture. In Japan, more than 90% of Japanese constructions identified as a cultural national property are built with wood. The most famous and the world’s oldest wooden building still standing is the Horyu-Ji temple from the latter half of the seventh century (Yokoyama et al., 2009).

Knowledge about the construction of wooden buildings varied enormously from culture to culture and reflects cultural differences. In some societies, each family had to know how to erect a wooden house, while other cultures had professional carpentry that goes back millennia (Pryce, 2005).

### 1.1.1 Ancient wooden buildings development

Wood or timber products used in construction vary widely in the degree to which the wood has been transformed from its initial state (Kottas, 2011) and depend on the availability of wood, the means of transport the knowledge of builder, the tools used and the climate (Dolby et al., 1988). The historical developments in wood as a building material reflect the increasing complexity of the human engineering capability (Hansen & Berg, 1971).

In Egypt, traces of buildings consisting of wooden posts between which rush walls were secured, have been found in round dwelling-pits in predynastic Merimde (4800 and 4300 BC). As well as in Ma’adi (in Cairo) these traces reflect settlement patterns as after people settled in one place tents were replaced by permanent houses, consisting of a framework of poles that easily erected and taken down and covered with mats or skins. This structure became a permanent skeleton consisting of posts and beams, and finally, the interstices are filled with wattle and daub, or bricks, to form lasting habitation (Hansen & Berg, 1971).
Early buildings in Europe consisted of a large roof carried by forked upright, driven into the ground in one or two rows and with ridges resting in the forks. This primitive building technique differentiated between supporting and supported parts. The walls did not form part of the load carrying system but only served as a shell and consisted of earth, stone, wattle, and daub or wood battens. This design improved during the Iron Age with the improvement of the building and carpentry tools and that gave people the ability to store forage and crops at home.

According to (Dolby et al., 1988), in the Middle Ages (5th to the 15th century), the construction methods for wooden buildings had reached a high level of sophistication. The walls usually formed a part of the load-bearing system. Usually, there were three techniques which depended on the availability and abundance of wood; corner timber technique, framework with horizontal planking and method of stave buildings. In poorly wooded areas timber saving techniques were developed such as ‘half-timbering.’

In the first techniques, wood logs were constructed horizontally and locked together in the corner by different kind of notching or dovetailing (Kniffen, 1969; Kniffen & Glassie, 1966). The second technique of the framework with horizontal planking separates the loads carrying posts from filling-up walls. The planking fits into the posts by a slit that permits sliding, which allows movement in the timber, and with the passage of time, the gets tighter. While in the stave building the walls consist of vertical timber planking of large dimensions carrying the loads to form , in most primitive form the planks were dug into the ground but in more developed forms the planks were placed on a ground sill and stabilised with a top plate (Dolby et al., 1988)

On the other hand, the half-timbering is a flexible and timber saving method using short pieces of timber, a half-timbered wall consists of a framework of wood with primary and secondary members, and the space between is filled with readily available materials such as wattle and daub, clay sundried or in later years burnt bricks (Dolby et al., 1988).

Timber was the most important material for building bridges around the world, and even today choosing wood bridge constructions is framed by economic and ecologic considerations (Dietrich, 2010) and wood is still widely used for short- and medium-span bridges (Ritter, 1990).

Using timber in bridge constructions predominated until the nineteenth century (1850) when the Bessemer converters produced the mass-production inexpensive steel (Dietrich, 2010;
While simple bridges made of timber logs were used by humans to surpass barriers, the first timber bridge documented is the bridge of Pharaoh Menses crossing the Nile, dates to 3000 B.C. Similar plain beam or cantilever bridges can be found in Asia today (Schwaner, 2010).

Another ancient bridge was recorded 35 feet wide and 600 feet long, and built in 783 B.C. over the Euphrates River in Babylon (Ritter, 1990). With the start of the scientific revolution (from around 1550) through to the 18th century, the design and building of timber bridges had a significant development. That period provides the first illustration of the use of frame truss bridge construction and by the end of the 18th century, the United States and Russia were leading this architectural form. In the 19th century, the sophistication and use of timber bridges increased in response to the growing need for public works and transportation systems associated with the industrial revolution. During this period the truss and arch bridge represented the most popular form of bridge constructions (Schwaner, 2010).

### 1.1.2 A review of significant wooden structures:

Hansen & Berg (1971) claim that circle of stones, uncovered near Ahrensburg in Schleswig-Holstein, Germany and dated from the twelfth millennium B.C. may have served to weight the tent walls and so may be an evidence of man’s first wooden building construction.

A brief survey of significant structures from across the globe indicates something of the broad scope of the subject of the wooden cultural heritage in the built environment. This point to the need to be able to develop robust and relevant treatment methodologies underlining both the need for, and the value of this thesis.

The choosing of these structures examples depends on their cultural significance. In addition, the selection included examples from different geographic places, with different structural aspects, with different structural functions and dated back to various ages.
1.1.2.1 Hōryū-Ji (Japan):

The Hōryū-Ji is a Buddhist temple that was built in Ikaruga, Nara Prefecture after the introduction of Buddhism to Japan in 552 AD. The constructions of the five-story temple’s pagoda (stands at 32.45 metres in height and is approximately 20x20 metres in width), the Golden Hall (Kondo), the inner Gate (Chumon) and most of the surrounding corridor (Kaino) are the oldest still standing wooden buildings in the world (Hansen & Berg, 1971; Popham & Venturi, 1990; Pryce, 2005).

The wood (Japanese cypress) used in the centre pole of the five-story pagoda is estimated through a dendrochronological analysis and X-ray photography done by Nara Institute to have been felled in 594 AD. Relying on this information with the assumption that this wood was used soon after this date, the suggested construction date of the pagoda is about a century earlier than what was previously agreed (Web-Japan, 2001).

The Hōryū-Ji temple significance is not only its value for the history of art as it illustrates how the Chinese Buddhist architecture was adapted in Japan but also its contribution to the history of religion as it represents the introduction of the Buddhism from China to Japan and moreover the artistic value as one of the masterpieces wooden architecture examples in the world ("Buddhist Monuments in the Horyu-ji Area," 1993; Cartwright, 2017; Satoshi, 2006).

1.1.2.2 Kizhi Pogost (Russia)

Located on a single island on Lake Onega in Karelia, the pogost of Kizhi ("Kizhi Pogost," 1990) consists of the Church of the Transfiguration (Preobrazhenskaya Tserkva), the Church of the Intercession of the Holy Virgin (Prokrova Bogoroditsy Sobor) (Miltchik, 2000) and an octagonal clock tower.

The Church of the Transfiguration is the larger of the two, and it was used during the summer. It is very famous for its 22 onion domes and considered as the sole example of the culmination of the development of the multi-domed wooden church (Kelley, 2000; Kozlov & Kisternaya, 2004). According to Kozlov et al. (2000), the church was built in the southern part of Kizhi island in 1714 and a recent chronological study revealed that its timber was logged not later
than 1710-1711 (Kozlov & Kisternaya, 2004). The building is 37 m high, 29 m long from east to west and 26.6 m wide and occupied an area of 349 m² (Kozlov et al., 2000). The structure incorporates three octahedrons set one on the top of another with transitional quatrhedrons. More than 2000 logs with an average diameter of 30.1 cm and 3–5 m in length were used in the structure (Kozlov & Kisternaya, 2004). There is a poetic legend about the craftsman who built this church, that claims that after completing it he threw his axe into Lake Onega, saying “this church was built by Master Nestor; there never was, nor will be another one to match it” (Kelley, 2000; Pryce, 2005).

The Church of the Intercession (Winter Church), is a simpler structure ("Kizhi Pogost," 1990). It is 32 m long, 8.7 m wide and 27 m high. The average diameter of the logs is 30 cm, and the average tree ring width is 1.7 mm. The building history has been widely discussed. It was previously assumed that it was built in 1764, but it was revealed by several studies that it was constructed during different periods beginning at the end of the 17th century and continuing until 1750. The same dendrochronological study was done to the elements belonging to the second building period (1722) and revealed that the timber was logged from 1712 to 1716 (Kozlov & Kisternaya, 2004).

The Kizhi ensemble passed many and significant transformations and restoration projects from the time it was built till the present.

1.1.2.3 The Fairbanks House (USA)

The Fairbanks House located in Dedham, Massachusetts is considered to be the earliest frame house in North America which is still standing and dated back to between 1637 and 1641. It was originally constructed by Jonathan Fairbanks of the Fairbanks family in 1637. This house is long recognised for its early construction date, old features, and unrestored condition retains cedar clapboards on the upper portion of the north wall preserved by the addition of a rear lean-to at an early date. Furnishings and accessories, all belonging to members of the Fairbanks family-although not necessarily those who lived in the house-enable volunteers to interpret all periods of the house's history (Cummings, 2002; Pratt & Pratt, 1956).

1.1.2.4 The Finger Wharf (Australia)
The Finger Wharf is located in the Woolloomooloo Bay in Sydney and was designed by Henry Deans Walsh. It was built between 1910 and 1916. This wharf is the largest timber-piled jetty in the world. It is two and half times longer (410m) and two and quarter times wider (64m) than other significant Finger wharves at Walsh Bay. It sits upon one thousand wooden piles, each pile is 30m long and is driven into the soft mud of the harbor. The wharf was originally used for exporting wool, embark troops and import cars. In 2000 the Wharf had been converted and conserved with the carpenters' workshop at the northern end removed and replaced with a similar-scale residential building. The gate posts and fence on Cowper Wharf Road probably date the original wharf. Now it is altered to accommodate hotel, apartments and retail/restaurant precinct (MacMahon, 2001; Pryce, 2005).

1.2 Wood in Furniture

“From the remotest ages to the present day, of all the materials applicable to the interior construction and adornment of the home, wood has been man’s first favourite and proven friend” (Period furniture, 1940). According to Oxford Dictionary furniture is the movable articles that are used to make a room or building suitable for living or working in, such as tables, chairs, or desks ("Furniture,"). Using wood in construction furniture has many advantages, apart from its aesthetic and decorative properties, it makes it possible to produce furniture which is lightweight compared to metal or plastic (Richardson, 1976).

1.2.1 Egyptian Civilization

The nature of the Egyptian dry climate enables the preservation of an enormous amount of wooden furniture that has been kept intact (Harris, 1965; Lucie-Smith, 1979; Morley, 1999; Blanchette, et al. 1991). Mural paintings, reliefs and sculpture scenes reflect the characteristics of the Egyptian interior and furniture and how it was used (Harris, 1965; Morley, 1999). Examples of Egyptian excellence in furniture industry can be seen as early as from the Old Kingdom (2686–2181 BC) illustrated in the furniture of Queen Hetep-heres (Reisner, 1929). The development of the Egyptian furniture continued to reach the highest degrees of
sophistication from at least the eighteenth dynasty (1567-1320 BC), though the tools to produce it were more cumbersome and in most cases less efficient than those of modern cabinetmakers (Green, 2007).

Ancient Egyptian furniture provides us with clear evidence of the ability and the knowledge of carving, turning, inlaying, veneering, painting and joining wood (Morley, 1999; Period furniture, 1940). Ancient Egyptians the furniture mainly for sleeping, seating and storage. Those pieces vary from beds, chairs, stools, chests to headrests. As mentioned by (Morley, 1999) the decayed companion chair of the chair of Queen Hetep-heres (2500 BC), the oldest extant chair in the world, was originally decorated with coloured composition inlays, set in gold.

Ancient Egyptian furniture had unique design characteristics, such as the way in which ending the legs is done with the piece with lions’ paws or hoofs of the bulls (Period furniture, 1940), the decoration of the object with heliographic writing. Beds construction adopted design principles suitable for the hot climate to allow the air circulation around the body (Lucie-Smith, 1979). The best known two examples of Egyptian furniture are the furniture of Queen Hetepheres, wife of Senefro, and the furniture of the Boy King Tutankhamun (1361-1352 BC).

Wood species that were used in ancient Egypt vary from local and native timbers- acacia, sycamore, fig, tamarisk, date palm, willow and poplar to imported ones like cedar, cypress and juniper from Syria, ebony from Africa and other timbers like ash, beech, oak, yew and elm (Harris, 1965; Killen, 1980, 1994, 2017; Morley, 1999; Rivers & Umney, 2003). The shortage or the defects of the timbers was a factor that led the Egyptians to use techniques like the application of a veneer or the applying of a layer of gesso as a ground layer before painting the object or decorating it with gold sheet, foil and leaf. Plywood was discovered in a coffin from the step pyramid at Saqqara (Killen, 1994) (2700 BC) that was made of six thin layers of wood held together by wooden pegs, with the grain running in the alternating directions.

Many tools were adopted in ancient Egypt like mallets, saws with copper or bronze blades, axes, chisels, bradawl and drills (Killen, 1980; Lucas, 1948; Rivers & Umney, 2003). For levelling timber, adzes were used since the woodworking plane was not invented until later. This is perhaps one reason why the Egyptians ground the wood surface with sand and overlaid
it with gesso, ready for gilding or painting. In some cases, they applied a transparent varnish (Rivers & Umney, 2003). Many types of joints were used in ancient Egypt including plain butt joint, the mitre joint secured by dowels, shoulder-mitres and double shoulder- mitre, plus dovetails and halving joints (Gale et al., 1999; Lucie-Smith, 1979).

1.2.2 Babylonian and Assyrian Civilization

The information about ancient Babylonian and Assyrian furniture mostly relies not on actual specimens, because of the limited remains survived, but on how those examples were illustrated in sculptures and works of art (Curtis, 1996).

The representation of the animal legs, mainly lions, tigers, horses or bulls as the ends of the furniture piece, whether it was a chair, table or couch was introduced in Babylonian and Assyrian furniture, and in this, the Assyrians resembled the Egyptians. The Assyrians also used square legs with a base of inverted pine-cones, and the contraction involved more framework than in Egyptian furniture. Tables and thrones, as drawn from works of art, appears to have been inlaid with ivory. Chairs were sometimes supported by animal and human figures and sometimes prisoners, and when the chair is high, a footstool of wood encased in metal was placed before each.

Generally, furniture of Assyrian and Babylonian was more solid and substantial than the Egyptian one and the joints and corners were less harsh and severe ("Assyrian Decoration," 1891; Lucie-Smith, 1979; Period furniture, 1940; "Studies in Furniture Design. First Parallel. Egyptian-Assyrian," 1883; Curtis, 1993).

1.2.3 Graeco-Roman Civilization

A similar situation as for Assyrian furniture is evident in that of ancient Greece, as the pieces which have survived are not enough to draw a complete illustration about the furniture during this period. So, the knowledge of Greek furniture is derived mainly from vase-paintings and sculptures or reliefs (Liversidge, 1965; Lucie-Smith, 1979; Richter, 1966): Furniture of the Greeks had two functions, ceremonial and practical (Lucie-Smith, 1979) and consisted of
chairs, stools, couches, tables and chests (Richter, 1966). It is clear that it resembled the Egyptian prototype, but also some distinct features indicated an influence on the successive cultures (Rivers & Umney, 2003). The coaches had the double purpose of the modern sofa and bed, the tables were small and easy to carry, and boxes took the place of the existing wardrobes (Richter, 1966).

Roman furniture developed directly from the Greek but with the tendency to luxury with the use of precious wood in the late Republican times (509-27 BC) (Lucie-Smith, 1979). Such wood included citron and maple with the lavish using of veneering, plating and inlay work. The wardrobe, which was probably introduced in the Hellenistic age, was in everyday use (Richter, 1966). The furniture pieces found in the parts of the Roman empire (i.e., England, Belgium, Holland and Germany) are uniform as a result of the spreading of the Roman civilization round the Mediterranean and across Europe (Liversidge, 1965; Richter, 1966; Rivers & Umney, 2003).

During the Greek and Roman times, the primary wood used were maple, beech, willow, citron, yew, oak, juniper, fir alaternus, holly, lime and zygia. The most prized was the citron. Furniture was formed by tools such as the axe, the saw, the plane, the hummer, the chisel, the borer, the knife, the lather, the screw-driver, the file, the compass, the rule, the level and the plummet and joined by shapes-round, rectangular or dove-tailed dowels and tenons (Richter, 1966).

1.2.4 Byzantine and Early Medieval

Evidence of the Byzantine furniture is derived chiefly from manuscript illustrations, ivories and mosaics. Furniture made in this period appears to have been produced as two types, one made by joiners and that was used in houses and the other made by the cabinet-makers (Hunt, 1965). The Byzantines were able to use the lathe and the paneled construction process to prevent ivory cracking after shrinkage. This kind of furniture had the advantage of mobility with easily moved pieces becoming popular especially during the Romanesque period (AD 1000-1300) (Rivers & Umney, 2003)
1.2.5 Islamic Periods Furniture

Furniture in Islamic periods did not initially have distinguishing features, but by the time it had absorbed the art and the technologies of the preceding styles and of contemporary civilizations, Islamic styles of production were unique. Furniture was little used in the Islamic interiors. Low benches or couches were covered by textiles, carpet and rugs (Pile, 2005, p. 74). One of these important features of Islamic furniture is the arabesque which was developed through the eighth and ninth centuries reaching its main characteristics in the twelfth century. It was born of the twinning of flowers and leaves together, as found around the arcades of Ibn-Touloun in Cairo. The art of arabesque has been seen in all countries reached by Islam from India in the east to Spain in the west. The arabesque has the characteristic of the continuous repetition that forms the ‘infinite rapport’ where the design has no beginning or end and covers that whole surface. The other sophisticated developed technique was the inlay which is considered similar to mosaic (Faure & Pach, 1921, pp. 242-243; Litchfield, 2004; Morley, 1999, p. 66). Religious and ceremonial furniture appeared in Islamic countries also such as the minbar (pulpit), maqsura (screen enclose for the ruler), Holy Quran stand and deket el mobalegh (the deck used for by a man who makes the echo of imam).

1.2.6 Medieval Times (Gothic) Furniture

Because of the impacts of the wars and black death during the Middle Ages (500-1500 AD), furniture production was declined and limited to simple domestic necessities (Rivers & Umney, 2003, p. 6). As a result, there are not many actual specimens of furniture before the twelfth century. Information from this time can be taken from the real pieces, art illustrations or descriptions in inventories. Most of this information refers to the furniture of the upper class and was related to the type of architecture of the Gothic period which spread over most of Europe. As an outcome of the nomadic life that resulted from the population migration due to the plague war, furniture was neither solid or heavy so it was either left abandoned in a temporary dwelling or was made to be transported. The most important furniture article was the chest or coffer, that was used for transporting goods, storing, seating if it had a flat top, like a table and sometimes as a bed (Ash, 1965, pp. 26-27; Lucie-Smith, 1979, pp. 33-36). Different species of wood were employed in Gothic furniture such as elm, beech, lime, apple, pear, walnuts, cypress, pine and fir, but oak was the staple wood, because it was so plentiful.
and highly esteemed (Ash, 1965, p. 30; *Period furniture*, 1940, p. 18). Carving was a favourite decoration technique during Gothic period, besides inlay or intarsia, painting and gilding (Rivers & Umney, 2003, pp. 8-9). In late Gothic times, furniture was either painted or left unprotected without the application of oil, wax or polish which exposed the furniture to the fungi attack eventually (*Period furniture*, 1940, p. 18).

1.2.7 Renaissance and Industrial Revolution to Present Furniture

The sixteenth century carried a significant development in the domestic furniture. New houses were built in England after the War of Roses and as a result, they needed furniture to equip them. Foreigners began to reintroduce board construction as opposed to panel-set-in-frame which allowed them to make solid pieces as wide as they wanted; as a consequence, joined furniture declined. In Italy, new pieces of furniture appeared in the fifteenth century and continued through the sixteenth like the cassapanca* and cassone**.

Carving became the favoured mode of ornament, and after the third decade of the century onwards the carved cassone appeared to resemble the Roman sarcophagi. In France, the oak was replaced by walnut from about 1530, which allowed finer and more detailed work. In Spain, the furniture tended to be massive and unrefined in quality, and like the cassapanca, there was the vargueno which is a chest on a stand. During the 1560s, the first wooden bow fretsaw was introduced to enable joiners to cut small pieces for inlaying. By the end of this century, new inventions occurred like the chest-of-drawers in Italy and the revolving chair in France.

Protecting surfaces by oil polishing with linseed and nut oils was the first method to be used, then the use of beeswax and turpentine towards the end of the sixteenth century (Honour, 1965, pp. 36-65; Lucie-Smith, 1979, pp. 53-68; Morley, 1999, pp. 113-116; "*Period furniture*", 1940, pp. 47-55; Rivers & Umney, 2003, pp. 9-12).

The furniture of the seventeenth century was similar to that of the present one. In Holland, the cupboard began to be replaced by flamboyant lacquer cabinets that were being brought from India or cabinets decorated with equally exotic ebony and tortoise-shell (Scheurleer, 1965, pp.

---

* cassapanca is a massive combined seat and chest that was used in the living apartment
** cassone is chest used particularly for decoration
European manufacturers began to adopt popular Indian techniques, like the use of caning for seats and back of chairs beside other techniques like the lacquering, japanning, arabesque and the Baroque (1670-1720). A cabinet on a stand was a typical seventeenth-century feature as the carved buffet was of the sixteenth. Another chief innovation and technique of this century was the large mirror, the sofa, the glazed bookcase, the Tunbridge ware, the plain table and as demand for comfort and luxury the upholstery.

Oak was the main wood for this century, and it remained so until the Charles II period when it was displaced by walnut, beech, cherry, cedar, olive, yew and laburnum beside ash, pine and maple in America (Lucie-Smith, 1979, pp. 69-92; "Period furniture", 1940, pp. 88-124; Rivers & Umney, 2003, pp. 12-20).

So many changes occurred during the eighteenth century in the furniture style and technology including machinery that it is often called the ‘Golden Age of Furniture’. This century began with Baroque to Rococo (1720-1760) to end with Classical revival (1760-1800). The designs became more sophisticated and luxurious, and many new items and designs were invented like the console table, kidney table, gate-leg table, china cases, corner cabinet, commodes, exercising horse, upholstered wing chair, Lit à la Polonaise in France and more. Later in the century, Egyptian motifs were used in French furniture after Napoleon’s campaign in Egypt in 1798 and later this feature was adopted in England.

Mahogany was the main wood utilised during this century because of its strength, hardness, toughness, consistency in structure, dimensions stability, durability and splitting resistance. Also, satinwood was used in the second half of the century for its golden colour and fine figuring (Brunhammer, 1965, p. 110; Lucie-Smith, 1979, pp. 93-116; Rivers & Umney, 2003, pp. 20-26).

The nineteenth century was characterised by the development of machinery (circular saw planers, mortises, borers, dovetail-cutters and veneer cutter) and the revival of old styles like the neo-classical, rococo and the Graeco-Roman revival with the return to some designs like the small bookcases and the long dining table. There were, however, new designs like the bedroom chair, kneeling chair and the beginning of the modern style. Calamander, rosewood and later the African mahogany was used in America. Walnut, yew, cherry and maple were

The twentieth century can be appropriately called the machine age. The new art styles like Expressionism, Futurism, Cubism, etc. inspired the modern furniture, and it is claimed that the genesis of modern furniture coincides almost with the birth of abstract painting and sculpture. The design became simpler, never copied from nature and neither symbolic nor ornamented. Many materials have been used including wood, wood-based products, metals, plastics, glass fibres, Lucite, Perspex, paper and aluminium. Animal glue was replaced by the synthetic glue or adhesive for assembly and laminating processes and French polish replaced by nitrocellulose lacquers (Lucie-Smith, 1979, pp. 169-207; Rivers & Umney, 2003, pp. 35-41; Schaefer, 1965, pp. 290-307).

### 1.2.8 Asiatic Furniture

Information about Chinese furniture can be derived from books and archaeological materials. Earliest excavated pieces were found in tombs of the Chu Kingdom, of the late Warring State period (475-221 BC), they were often decorated with painted or carved lacquer (Wu Bruce, 1995, p. 1). Considerable development of furniture took place during the Han dynasty when the K’ang was used for sleeping and reclining on along with tables and stools. More progress occurred afterward and can be seen in those excellent examples that were produced in the Ming dynasty (1368-1644) and Ch’ing dynasty (1644-1911). Chinese furniture was made from different types wood, the most favoured ones are those called hua-li mu, tzu-t’m and huang-hua-li, which probably rose wood and its varieties, as well as Cassia siamea and Pterocarpus. Chinese furniture is famous of two types, the bamboo furniture which was used during summer and outdoor use and lacquered furniture which was for permanent use because of its insect resisting ability. Chinese furniture has the unique feature of not using nails or dowels but depending on mortise and tenon. The use of veneer was not usual, and linking of different wood in one piece was recorded (Medley, 1965, pp. 276-279). Chinese named wood types according to their appearance, colour and smell regardless of the species of wood tree. Some of these names are, huanghuali, zitan, jichimu, tieli which are all hardwoods (Wu Bruce, 1995, pp. 19-22).
In Japan, the furniture was minimal and living was possible without furniture at all. The furniture was built-in and the portable, when made, was solid with no legs and has storage spaces to suit the mobility of the interior space. The scarcity of the furniture in Japan (and similar in Korea) was due to the tradition of seating as the residual construction was built to function as furniture. The residents were sitting on the floor directly (on a thin mat called *tatami*) and sleep on bedclothes (Kim & Choi, 2003; Lassen, Wormley, & Butler, 2017). As a result, they did not use beds but tables and chairs. One of the features of Japanese furniture is the screens, which were used to divide rooms, for privacy and as shields against draughts (Hillier, 1965, pp. 280-283). The rare Japanese furniture was traditionally highly polished or lacquered and decorated with small scale decorations of plants, animals or landscape (Aronson, 1965, p. 276).

In the Indus Valley, there is no evidence that beds, couches or chests were used, and it was until the first century AD when the representation of the first beds appeared, compromising a wooden frame with turned legs and covered with a mattress (Chritie, 1965, pp. 284-288).

### 1.3 Wood in Artefacts

Wood is relatively easy to work with simple tools and as a result, it was one of the favourite materials of art and for carvers, sculptors and artists

#### 1.3.1 Wood in Carvings and Sculptures

“Since early times the carving of wood has been practiced, from simple peasant work fashioned with a knife to the elaborate work of Baroque churches” (Findlay, 1975, p. 210). The fibrous structure of wood gives it considerable tensile strength so that it may be shaped and carved more freely and more thinly than stone (Rogers, 2016), however, it may give the carver some limitation because of texture and fibre direction (Rogers, 2016). The classification of wood as hardwood or softwood does not limit its use for sculpture. Some types of wood are close-grained, so they can be cut easily while others are open-grained and stringy. Carvers prefer wood that has a close even texture and does not split, also the one that can be seasoned without much distortion and which is relatively stable against humidity (Findlay, 1975, p. 210; Rogers, 2016).
1.3.1.1 Ancient Egypt

Lucas claimed that the art of carving and the craft of joining cannot have been known in Egypt before the late pre-dynastic period when the copper tools were available (Lucas, 1948, p. 508); however, it was mentioned earlier by (Rogers, 1867, p. 33) that the Egyptians were distinguished by their superiority in sculpture work at a very early period. This superiority continued during the dynastic period and illustrated in many masterpieces that still until this time witness the highest degrees of workmanship.

Sheikh Al Balad (Chief of the Village) or Ka-aper Statue, discovered in 1860 and named by workers in Saqqarah and dated back to the Old Kingdom (Bickerstaffe, 2008, pp. 20-21; Tarbell, 1896), is the oldest known life-size statue in ancient Egypt (El-Shahawy, 2005, p. 79). It is considered historically to be the very first piece of wood carved to the very highest degree of excellence (Hasluck, 1977, p. 131). It is carved from a block of sycamore with joined arms and quartz inlaid eyes. It provides a realistic presentation of the human figure (Vandersleyen, 1983, pp. 62-63).

Egyptians were applying wood carving reliefs as ornaments to furniture, boxes, and toilet implements. The elements used included animals, plants such as lotus, papyrus and palm, winged globe, scarabeus (winged beetle), the egg and serpent, the rosette, fishing, besides the human figures and hieroglyphs. Most of those carvings were coloured as part of their finish (Hasluck, 1977, pp. 132-133).

Wooden sculpture throughout Pharaonic history was mainly made of native timbers such as acacia, sycamore, and tamarisk, and sometimes a combination of these. Imported wood species like ebony and cedar were also occasionally used. In the New Kingdom (c. 1570- c.1069 BC), imported wood species were favoured for the production of royal statues in wood, and proportionally more private statuary was made of ebony (Harvey, 2009).

Many wooden objects from the Old Kingdom (2686 BC – 2134 BC) and later were composites, included a ground layer comprising calcium and binder such as gum Arabic. These composite materials create additional challenges in the preservation of Egyptian wooden objects (see case study in Chapter 8).
1.3.1.2 Assyrian, Greek, Roman and Byzantine

As mentioned previously, little wood carving that remains from these ancient. The wood carving in Assyria is evidenced in that examples of furniture ornamented with the heads of bulls, lions and rams and feet of lions and hoofs of bulls.

The situation is not much different in ancient Greece, the earliest example recorded is the chest of Cypselus of Corinth chest dated to 655-625 B.C, which is carved of cedar and decorated with figures and bas-reliefs, some in ivory, gold or ivory part gilt and inlaid on the four sides on top (Gardner, 1896, pp. 16-17; Hasluck, 1977, p. 135). One of the features of the Greek carving is that the legs of the chairs are carved to represent the legs and feet of lions, and the back legs terminate at the top with a carved representation of the anthemion. In addition, some sculptures were covered with gilt or gold. The carvers had to consider the general proportion and pose of the figures and the arrangement of the masses, rather than any elaboration of details in the shape of muscles or bones (Hasluck, 1977, p. 136). Parkes (1931, p. 57) also mentioned that Greek wood-sculpture was largely architectural and frequently polychromic.

Cedar was used for many Greek statues as literature mentioned beside ebony, cypress, oak and olive were used to make gods statues (Gardner, 1896, p. 16) beside yew, fig and others (Murray, 1890, p. 97).

The carving of wooden ornamentation during the Roman period was a continuation of the Greek and Etruscan style illustrated in the carved limbs of animals carved as legs and arms of chairs and couches. Wood species used were cypress, cedar, ebony, beech, box, olive, pear and oak (Hasluck, 1977, pp. 138-140).

The style of wood carving during the Byzantine period involved covering the whole field with the design, leaving the extent of groundwork very small and the ornament was highly symbolic.

1.3.1.3 Medieval

The art of wood carving during the fifteenth century reached a very high point. Illustrated by these rood screens with their roods and figures and their galleys and tracery work at St. John and the Virgin. In England, the pulpits, stall ends, choir stalls, the fine hammer-beam
and other wooden roofs of the eastern countries and other furniture of the churches all showed high levels of the carver’s art.

Linen paneling was much used during this period. The Perpendicular style, the vine, maple and ivy were popular. The Tudor flower and the four-leaved flower were characteristic of this perpendicular style. The works reached a high degree of quality which was seen in the small designs, the details, the minuteness and the mechanical strength. Red, blue, green, white and gilding were used as colours for carved woodwork.

The general scheme was planned by one master craftsman or artist, but the fulfilling of each section was left to the individual craftsman creating a great variety of treatment and endless diversity (L. R. Rogers, 2016). Bosses, decorations usually seen in the ceilings or roofs formed where cross-members of a roof or ceiling intersect, were a feature of Gothic work and were sometimes carved with grotesques, delicate foliage, angels and so forth.

This period can be divided into three principal parts: first, The Early English (1180-1275) characterised by the suits of mouldings, its three-lobed foliage, the conventional arrangement and on a spiral plan, and the dog-tooth ornament. Second, the Decorated Period (1275-1375) which divided into the geometrical where the style of the tracery was constructed on a geometrical plan, and the curvilinear where the tracery is arranged in a much free manner with free-hand carves lines. This period is discernable from its natural depiction of foliage, the elements being the oak-leaf, vine, ivy and similar natural forms. The ball-flower ornament is a feature of this period. Third, the perpendicular (1375-1536) distinguished by its very large windows, the ornament which had a much flatter nature and the mouldings which were flatter and more insignificant. As the style merged into the Tudor, the window head became flatter, and then became what is called four-centered arches. After that the influence of the Renaissance became dominant and the Gothic gradually faded (Hasluck, 1977, pp. 144-156).

During the medieval period, screens and other fitting were produced for the Coptic churches of Egypt by the Christian workmen. Some cedar panels in the British Museum from the door of the church Sitt Miriam (13 century) are carved in shallow relief and the four foliage panels are Oriental in character, intricate and fine both in details and finish (L. R. Rogers, 2016).
1.3.1.4 The Renaissance

The Renaissance began in Italy and rapidly spread to Germany, France, Spain and the smaller adjoining countries then later to England. The Italian and French Renaissance is characterised by lightness, airiness and grace. The elements used to consist of a profusion of fruits and flowers, cupids, ribbons, dolphins, sea-horses’ centaurs, satyrs and griffins. All arranged on a scrollwork base and in as light a manner as possible.

The Spanish Renaissance incorporated the same elements except that the development was more powerful and luxuriant. In Germany and England, the Gothic obtained a firm hold and influenced the new style. The style became stiffer, stronger and showed deeper symbolism. In England, the Tudor style appeared as a mixture between the Renaissance and Gothic style. Later the Elizabethan style grew characterised by appropriate and pleasant strapwork, square-worked newels and baluster and shafts, tapered pilasters, being narrower at the bottom, the use of caryatides and the extended employment of paneling plain and elaborate (Hasluck, 1977, pp. 161-170).

1.3.1.5 Grinling Gibbon *

During the 17th century a new style of wood carving emerged and pioneered by Grinling Gibbon and continued through the 18th century. The new style was based on the Renaissance partaking (Rogers, 1867, p. 36) and characterised by the use of foliage, birds and flowers in freely loosen manner and significant attention to details (Hasluck, 1977, p. 172).

Later in the early Victorian period, the furniture carved ornamental detail was of the kind known as “Baroque.” The ornament appears to have been prompted more by the desire for display and show than for the real necessities of ornament (Hasluck, 1977, p. 173).

---

* Grinling Gibbons was born in Rotterdam on 4 April 1468. He came early to England and established a new carving style based on the Renaissance partaking but with a distinct phase essentially English
1.3.1.6 Islamic

The art of wood carving reached a very high level of skill shown in most of the Islamic countries. The high level of art is apparent in the different wooden elements done by the Muslim craftsman such as wall linings, ceiling, pulpits and the several kinds furniture. Images of animals, humans and creatures were not popular in Islamic art because the illustration of individuals in painting or sculpture is not encouraged from a religious Islamic view. Forming unending visual geometric complexity is a feature in the Islamic carved-wood with object or wall totally covered and no part left without ornament (Grabar, 1987, p. 187).

1.3.1.7 Asiatic

In ancient India, Hindu temples illustrate the professionalism of the Indian sculptor. Artists used teak, sandalwood and rosewood to make doors, ceilings and various fittings in high degree of degree of sophistication and quality (Remadevi & Joshi, 2011).

In Bombay, foliage, fruit and flowers are frequently adapted to a scheme of fret-cut decoration for doors or windows beside the frames of chairs and tables edges.

In Japan, wooden sculpture is more well-known than sculpture in stone. The art of wood-carving was for a long time employed solely for temples decoration and was only gradually used for the ornamentation of the secular buildings. The leading masters of the Japanese wood-carvers were Korean and Chinese, and the history of wood-carving is associated with the history of Buddhism and Buddhist temple decoration and sculpture (Richard Henry, 1901) that was introduced to Japan in the six century (Okochi, 2016). The Buddhism related statues stayed almost the main style made until the Edo period (17th- 19th centuries) (Horton, 2007).

The Japanese carver was also involved painting or gilding his statues. Larger carvings were made of several pieces of wood, securely and deftly fastened together with the smaller ones carved from a single piece of timber. Hidaro Jingro who was active from the late in the early 17th century is credited with leading a new movement to make wood-carving the life and soul of Japanese architecture. Richard Henry (1901) divided the Japanese wood-carving into four
classes. The first consists of low-relief carvings in solid wood with sharp outlines. The second are high-relief carvings in solid wood. The third is the pierced carvings, which are probably the most characteristic type of architectural wood-carvings used in the temples. The last is the relief encrusted carving which was commonly used for panels and allowed the carvers to create pictorial effects.

In China, one of the characteristics of carving is the finial of the newel post, so consistently left almost straight in profile and deeply carved with monsters and scrolls. A deeply improved moulding, bearing a strong resemblance to the gadroon pattern, is commonly used to emphasise edges, and the dragon is arranged in curves that imitate.

1.3.1.8 Modern

In the twentieth century, wood was being used by many sculptors as a medium for construction as well as for carving. New technology including new manufacturing process and a range of new adhesives enabled laminated timbers, chipboards, and timber in block and plank form to be glued, jointed, screwed, or bolted together, and given a variety of finishes (Rogers, 2016).

1.3.2 Wood as Frames

The frame can be described as the border or case of pictures, mirrors, etc. It is also the wood skeleton of an upholstered chair (Aronson, 1947, p. 75). The focus here is mainly on the first meaning, the picture frame. The picture frame has many roles or functions. It has been used to protect the picture or the painting, as a physical attachment to the wall, to improve of the colour and the content, as a boundary of the picture’s border and focusing the spectator’s attention on the subject, as an outline of transition between the real world and the picture, to create harmony with the surrounding interior decoration and to isolate the picture from the distracting background (Mitchell & Roberts, 1996, p. 8).
It is not easy to track the beginning of the idea of framing. Painting and relief carving have had borders from early times. Geometric margins have been used on vase and tomb paintings between 2000 and 1000 BC, dividing narrative scenes and decorations into horizontal bands. Later vertical divisions were added as in the Tomb of Sennefer in Luxur 1453-1419 BC, while architectural frames, not wood, were applied to wall carving (Mitchell & Roberts, 1996, p. 10). The rounded stucco arch frame with ornamental vine presumably of a mummy portrait which was found in Hawara, Egypt and dated back to the second century (Grimm, 1981, p. 51) has been suggested to be the earliest picture frames.

In the classical Greece period, the border of mosaics became the organising structure of the whole, arranging figures and scenes into an abstract design of circles and spandrels squares and lozenges. Each country developed forms such as the Italian Renaissance cassetta frame and the 18th-century French Rococo frame. Frames may also be divided across national boundaries, by style: Renaissance, Mannerist, the polished wooden cabinetmaker's frame, Baroque, Palladian and Rococo, the Roman 'Salvator Rosa', Neoclassical frames, and the academic or artists' frames of the nineteenth- and twentieth-centuries (Mitchell, n. d.).

In the twelfth and thirteenth centuries, carved wooden frames appeared. The first models were in one piece with a painted ground. The panel has its surface lowered by gouging into a shallow box shape, the surrounding wall of which became the frame. The whole panel was then covered in gesso and gold leaf so the image can be painted on a smooth flat surface (Kanter & Bisacca, 2008; Mitchell & Roberts, 1996, p. 11).

According to Day (1998a), free-standing panel painting only appears to have been common in the twelfth century. The need for better framing methods increased with the spread of the portable, independent painted units (mostly altarpieces). Eventually, a more efficient method which used mitered moulding strips was developed to avoid the costly time-consuming panel with a frame made from one piece of wood. This type is known as an engaged frame where the simple wooden moulding strips attached to the outside edge of the wooden panel and finally gilding and painting took place.

The large heavy frames of the fourteenth and fifteenth century gained an additional function; it helped to illuminate the altarpiece as the gold was used on altarpieces to reflect
light onto the painting, thus illuminating and giving the subject a majestic glow (Mitchell & Roberts, 1996, p. 11; Powell, 2010, p. 2).

During the fifteenth and the sixteenth century the increase in secular frames in Italy, the artistic centre of Europe during the Renaissance, resulted in the structural tabernacle frame being replaced by relatively simple rectangular frames with classically-inspired patterns and decoration. Columns, pediments, and bases disappeared leaving only a decorated frieze between narrow mouldings. This type of frame is known as the cassetta (Italian for “small box”) frame, and it was the introduction of the basic modern frame (Day, 1998b), their frames were always wooden, and each country had its version of this cassetta (Mitchell & Roberts, 1996, p. 11; Powell, 2010, p. 2).

The middle of the sixteenth to the late of the seventeenth century witnessed the appearance of the Mannerist frame in the Netherlands, Britain, Italy and Spain where they employed exaggerated organic or Classical architectural forms to create dynamic and sophisticated settings (Mitchell, n.d.).

By the seventeenth century the Dutch frame which had existed since the fifteenth century had fully evolved with more sophistication. The polished black frames were made of ebony or had an ebony finish and were made by combining various flat and round mouldings.

In the seventeenth century, with the Baroque period the genre painting was developing in Northern Europe, the demand for non-religious subjects and portraits increased which led to the production of various types of frames. The painting began to be a decorative item hung on the wall in domestic or civil spaces. The patronage of the arts shifted from church to the kings, and the artistic centre shifted from Italy to France where the golden age of the frame-making started.

By the middle of this century the Louis XIII frame style had emerged which was characterised by a close bonding of ornamentation to the profile and straight rails with decorative borders. Three mouldings make up the patterns: an inner, middle and outer. Leaf, branch and flower elements are tied together in a web-like pattern on the surface. The most common organic motifs are oak or laurel leaves bordered by ribbons, husks or leaf tips. The general style came out of French architectural Baroque ceiling and door frame design. In this period known as
The Baroque (c. 1600-1730) there was a preference for organic rather than geometric patterns. The bunches of overlapping leaves, usually laurel and oak, were boldly carved.

The essential characteristics of the Louis XIV frame style are overall carving with generally lower relief than on Louis XIII and Louis XV frames. This period often incorporated cross-hatching as well. There are two common types of Louis XIV frame patterns, one that has straight sides and the other is the one synonymous with the Baroque and has cartouches in the corners and centers containing shells, leaves or fleur-de-lis on a broadly hatched ground (Day, 1998c; Mitchell & Roberts, 1996, p. 11).

At the beginning of the 18th century, the Regency frame style emerged which has more emphasis in the corner and centres where the organic decorations often overlapped the panel and flowed into the sight edge. The Rococo style flourished in the 1730’s, the designs were elegance, grace, charm and curving naturalistic decoration. The basic characteristics consist of S and C-scrolls, swept rails, asymmetrical contours and cartouches. Baroque and Rococo frames reverted to gilding, except in Spain which used polychromy. Their dynamic came from the 'cartouches' of curling leaves, shells and volutes carved in the corners and often the centres of each rail.

In the 18th century, also there was a renewed interest in the ancient world which expressed in the Neoclassicism style. The Neoclassical frame has two types, one with a flat profile like an architrave or entablature moulding, while the other has a concave profile. The typical Neoclassical frame does not have any focal embellishments but does have splendid decoration all around the perimeter (Day, 1998d) and characterised by its simple ornaments of moulded composition (Mitchell).

With the reign of Napoleon, the luxury market was brought to its end. Mass production was encouraged and there was a limiting of the hand-carved frames, and so the Empire frame spread quickly across Europe, disseminated with the help of patterns books (Day, 1998e).

During the nineteenth century, frames became more eclectic. The industrial revolution forced many carvers and framers to leave the profession, and production workers made most of the frames. The styles of the first forty years are marked by repetitious, standardised models and
were cheaply made. The result was, frames with poor quality decoration and bad joints (Day, 1999; Mitchell & Roberts, 1996).

1.3.3 Wood in Musical Instruments and Tools

Most early musical instruments, apart from metallic trumpets and those made from animal horns, were made of wood. They fall into two main groups; stringed instruments and wind instruments, but there are also wooden percussion instruments (Findlay, 1975, p. 215). Most of the tree parts or even all may be used in the making of musical instruments; in Africa and Mexico, slit-drums are carved from trunks. In Finland, Switzerland and Amazonia bark is wound in a spiral for horns (Dournon & Arom, 1981, p. 16). Gourd rattle is one of the earliest instruments in which wood has been used. A calabash, held by a wooden handle, is filled with pebbles or other small hard objects to make the rattle sound when the player shakes the gourd.

The acoustic properties of wood give it a preference for soundboards on musical instruments. The sound velocity in dry wood parallel to the grain is similar to that in steel. However, since the density of wood is much lower, it has low sound wave resistance and high damping of sound radiation (Moavenzadeh & Cahn, 1990, p. 1). Bucur (2006) made a broad survey of the acoustic properties of wood and put a standard for resonance wood that all species with remarkably regular anatomical structure and high acoustic properties come under the label “resonance wood” (Bucur, 2006, pp. 173-216).

From the Medieval times, the musical instrument has been considered as a piece of art. The instruments were decorated by carving, inlay, marquetry decoration, painting and arabesque. This attitude can also be seen in the Far East, the wooden body of the drum was lacquered and the skins were covered with colourful paintings (Sachs, 1977, p. 241). By the middle of the sixteenth-century the decoration of the Italian keyboard instruments was highly ambitious as evidenced in a spinet made by Annibale Dei Rossie at Milan in 1555, where the front is inlaid with a simple lozenge-pattern, while a delicate carving surrounds the keyboard in the Italian Renaissance idiom. This art form reached its summit in the school of the Cremona violin makers, especially made by Antonio Stradivari. His work is characterised by a careful selection of the wood type and by the elegance of the forms and the subtle finishing off the details (Musical instruments as works of art. Victoria and Albert Museum, 1968). In the
Renaissance, the viol was more than an acoustic machine. It was characterised by the elegance of its curves, by the harmony of its proportions and by the bright transparency of its varnish. The instruments were carefully joined, turned, carved and inlaid; precious materials were used including exotic wood. During this period, the violin and other instruments were given their classic shapes (Sachs, 1977, p. 302).

1.3.3.1 Wind Instruments

Wind instruments are played by blowing down a hollow tube. As the length of the tube down which the air vibrates dictates the pitch, many different notes can be obtained when holes are drilled at intervals along the length (Sentance, 2003, p. 155).

The main requirement of wood species used in these instruments is to give high dimensional stability, high density and fine structure. In addition, the wood must provide ease of turning, boring and drilling (Bucur, 2006, p. 182). The ideal wood for this purpose should resist distortion and be able to be easily finished when oiled. African Blackwood, ebony, granadilla and some fruit wood species like pear and apple are the best in this. Maple wood is traditionally used in making the bassoon, which is then stained and varnished (N. H. Fletcher & Rossing, 1998, p. 725). Sycamore is also mentioned by (Findlay, 1975, p. 217) as used in the construction of the bassoon as the heavy dense hardwoods such as coccus wood are not suitable for its production but these dense wood were used to produce the flutes.

Many wood-wind instruments have been used historically; flutes in ancient Egypt and Mesopotamia, pan-pipes in America (sometimes made from solid pieces of wood with channels hollowed out inside them) (Sachs, 1977). The didjeridu (or yiraki) in Australia, approximately 1.2 to 1.5 metre naturally hollowed wooden tube by termite or fire (Fletcher, 1996, p. 11; Fletcher et al., 2001, p. 87), has been in continuous use in the indigenous communities for at least 1500 years (Subedi, 2014; Troy, 2013).

1.3.3.2 String Instruments

String instruments are those have strings of wire, hair, or sinew stretched across a wooden frame (Sentance, 2003, p. 155). The harp was the most prized instrument in ancient Egypt, and it had different types- arched harp, shoulder harp and angular harp. Harps also were known in the Sumerian culture, and perhaps this was the origin of the Egyptian example. Lyres and
lutes also were known in the ancient world, spinets and harpsichords came later. Viol and violin family are almost entirely of wood (Findlay, 1975, p. 215). In the violin, the bulging back of the body is made of or two maple boards and slightly depressed near the outline, the sidewalls or ribs are also made of maple but are extremely thin so that they need to be reinforced by narrow ribbons of pinewood called linings that follow the outline of the body (Sachs, 1977, p. 353). According to (Findlay, 1975, p. 215) maple and sycamore are used for the back, handle, bridge, neck, scroll and ribs. The belly, bar blocks, linings and sound post are of European spruce. Ebony is used for the tailpiece, fingerboard, nuts, screws, button and pegs, which last may also be made from boxwood or rosewood and the only wood considered to be suitable for the bow is brazilwood. In the piano, the soundboard is commonly made of Canadian Stika spruce or spruce from Carpathians (Romanian pine). The bridges which hold the pins are made of beech or rock maple. Various hardwood species have boon used for the case including rosewood, mahogany, walnut, and ebony.

1.3.3.3 Percussion Instruments
The percussion instrument is the name of the family of instruments (perhaps the most ancient in existence) which are usually played by striking a resonating surface with stick hands (Kennedy & Kennedy, 2007, p. 555). They have been commonly used from early times in various activities like; religious rites, dances and long-distance communication.

Many kinds of instruments go under this category; the Egyptian and Sumerian sistrum, the Egyptian clappers and concussion sticks, the aboriginal Australian clicking sticks, the many kind and type of drums in all cultures, the castanet and the xylophone (Sachs, 1977, p. 353; Sentance, 2003, p. 55). The xylophone originated among primitive men. It is set of wooden bars, each supported at two points and struck with sticks or clubs. The simplest form of xylophone may be called the leg xylophone. The player sits on the ground, lays two or three rough slabs of wood across the legs and strikes them with two clubs. Sometimes a pit is dug between the legs (Sachs, 1977, p. 353).

Many kinds of wood are used for percussion instruments. Drum rims are made of ash or beech, sometimes even plywood. Drumsticks could be of hickory, lancewood, rosewood, or hornbeam. Castanets, which give characteristic colour to flamenco and other Latin dances, are composed of two round pieces of hardwood, either rosewood or ebony. The xylophone is
comprised of a series of wooden bars of different size and species (maple, walnut, spruce, exotic species) (Bucur, 2006, p. 184).

Beside what was discussed, there are many other uses of wood, the list is inexhaustive, but that the aforementioned areas illustrate the focus areas for the thesis research.
2 Chapter 2: Wood structure and properties

In Chapter one I examined the history of the use of wood. This demonstrated the significance of the wooden objects as documents of human ingenuity and development. This chapter examines the different wood properties that characterise it among the different other cultural materials and influence its durability against the deterioration factors and help us to understand the deterioration processes which will be examined in the next chapter. In this chapter, wood will be discussed as a material, its properties, structure and chemistry. A relation between wood chemical composition and different properties will be included in the context also to reflect the main objective of the thesis. These characteristics will be tested and examined practically in the following section of the thesis.

2.1 Wood Structural properties (structure and chemistry of wood)

2.2 Introduction

Wood is defined as “the hard fibrous material that forms the main substance of the trunk or branches of a tree or shrub, used for fuel or timber” ("wood," 2010). It can be described also as an organic material consists mainly of a complex of polysaccharides (cellulose and hemicellulose) and polyphenols (lignin) beside other secondary components of extractives and traces of inorganic matter all this perform sophisticated fibrous structure of different kind of cells which have various functions giving the wood its diversity and beauty. Wood is divided mainly into two main categories; hardwood and softwood plus other types of palmwood and recently the artificial wood can be included in an independent subcategory.

2.3 Wood Macro Structure

Wood is severed from plants such as trees and shrubs characterised by their vascular tissues that are divided to xylem and phloem. Season plants that have their tissues or stems change each year cannot be considered as woody plants. To gain xylem a plant should live for several years with each year more tissue is added to the diameter of the stem to gain eventually the trunk which is suitable for commercial lumber (Cronquist et al., 2018).
2.3.1 Tree growth and wood formation

The growth of the tree stem vertically and horizontally depends on the division and formation of the cells in two zones (Fig. 1); the apical (on the tip) and lateral (on the side) meristems. The height of the tree and the stem increases by the growth in apical meristem at the tip of the tree. The increase in this area occurs by the rapid division and elongation of active cells to form the primary peristems consisting of protoderm, ground meristem and protocambium which later grow to become the primary tissue composed of Epidermis, ground tissue and vascular tissue (bundles) respectively (Eaton, 1993, pp. 4-5). The vascular tissue is responsible for conducting water and food and providing the required mechanical support to the plant, and the ground tissue consists of cells needed for photosynthesis, food storage, regeneration, protection and support while the dermal tissue’s function is to reduce the loss of water and provide protection (Eaton, 1993, p. 5; Thomas, 1977, p. 4).

Vascular bundles are strands of cells sitting in the ground tissue making a circle around the pith that consists of parenchyma cells. Each bundle consists of three zones; primary xylem (inside), primary phloem (outside) with the fascicular cambium developing in between. With the maturation of the tree, interfascicular cambium is formed in a latter stage between the vascular bundles and eventually forms a circle or cylinder of cambial cells around the stem. The initial fascicular cambium and the interfascicular cambium formed is called vascular cambium which is one of the two lateral meristems beside the cork cambium that is responsible for generating the cork cells (Eaton, 1993, p. 5; Fujita & Harada, 2000, p. 26; Preininger, 2013, pp. 40-42). The focus here is on the vascular cambium as it is mainly responsible mainly for
increasing the stem girth and producing the commercial wood by forming the secondary tissues or secondary growth.

Vascular cambium cells can divide in two directions, radial direction (periclinal) and side or tangential direction (anticlinal), as illustrated in Figures 2 and 3. In the periclinal division the cambial cell, the mother cell, is divided into two cells; one is the initial cell, and the other is the daughter cell. The latter one continues its own division to produce secondary xylem inward or secondary phloem outward while the primary mother cell still has the ability to divide again to create another daughter cell (Eaton, 1993, p. 6; Fujita & Harada, 2000, p. 26; Milton, 1995, pp. 3-4; Savidge, 2003, p. 1; Unger & Unger, 2001, p. 1; Vaganov et al. 2006, p. 72). The rate of the inside division to produce secondary xylem is more frequent than the division making secondary phloem and this explains the difference in the thickness between xylem zone and phloem zone which is a lot less (Eaton, 1993, p. 6).

Initial cambial cells are two types, fusiform and ray cambial initials. Fusiform initials are oriented in axial direction and more elongated. Their division yields longitudinal cells in hardwood and softwood (vessels, axial parenchyma, fibresand tracheids) while the ray initials are forming ray parenchyma and ray tracheids (Eaton, 1993, p. 6). This stage of the development of the different type of cells after division called differentiation which enables the different cells to perform their functions (Dinwoodie, 2000, p. 7; Rathgeber et al., 2016; Unger et al., 2001, p. 11). These types of cells will be discussed later in this chapter.
After the division and at the beginning of the formation of the secondary tissue cells are thin with a primary wall however they are capable of enlargement and elongation. Enlargement in earlywood tracheids occurs in the radial direction while the vessels enlarge in all directions. Eventually, after reaching the final size, the secondary wall starts to build itself on the inner side of the primary wall, simultaneously the lignification takes place especially in the outer layers of the cell wall. After the formation of the secondary wall and the lignification, the cell wall will reach the maturation stage and the component will die except in the parenchyma cells which live for a longer period before dying and turning sapwood to heartwood (Eaton, 1993, pp. 6-7; Rathgeber et al., 2016; Thomas, 1977, p. 1).

2.3.2 Annual/Growth rings

The growth or the division of the vascular cambium is active in summer and in the spring periods of the year in temperate wood. This activity adds more xylem layers to the stem and depending on the time; the layers can be different in size and wall thickness of their cells. Layers incrementally added in the spring period have large lumens and thinner cell walls to assist in conducting sap and are called earlywood, while layer added in the summer have narrow lumens and thicker cell wall to provide the required mechanical support and called latewood (Fig 4). These two layers increments form the annual ring (growth ring) which is more obvious in the transverse section. This difference in the appearance between summer and spring layers is highly noticeable in the softwood tracheids and the ring-porous wood vessels of hardwood. Counting the annual rings can help in estimating and understanding tree age when done in the lower part of the truck or large root. More advanced scientific techniques such as

![Figure 3: The difference between the Periclinal division and the Anticlinal division of the cambium cells (Haygreen & Bowyer, 1989).](image-url)
dendrochronology or tree-ring dating are used for dating works of arts and historical buildings made of wood. The situation is different in the case of extra-tropical wood as there is less fluctuation in the rainfall or temperature around the year or the day which results in the almost continuous growing of cell layers so these rings may not be discernible. On the other side, some species such as mangrove species of *Diospyros* or *Simmondsia* can form non-annual rings (Carlquist, 2001, p. 13). For this reason, the increment name will be growth rings as they are not annual or seasonal.

More information about wood dendrochronology and some samples can be found in (Cook & Kairiukstis, 1992; McGinnies, 1963; Querrec et al., 2009; Schweingruber, 1993).

![Figure 4: All the components of the macrostructure of the tree trunk (Tsoumis, 2019)](image)

**2.3.3 Sapwood and Heartwood**

As the name suggests, sapwood is the band of cell layers that do the functions of conducting sap as well as providing mechanical support and food storage at some level (Fig 4). As the growth of the tree continues vascular cells (tracheids and vessels) reach maturation and the contents of the cells die whereas the parenchyma cells remain alive for a longer period. Eventually however they start to die and hence convert the wood in this zone (where the parenchyma has died) from sapwood to heartwood. The reason for the formation of heartwood has not been clearly explained. The heartwood starts from cells around the pith providing support to the tree with no engagement in the vital activities. Once started, the heartwood continues to add more layer each year. There is a difference in the colour of the sapwood and the heartwood areas, and this difference can be abrupt or gradual or hardly seen in some species. Heartwood is usually darker in colour because of the infiltration of some organic
compounds such as tannins, resins, gums and aromatic compounds that occupy the cell lumens and cause incrustation to the cell wall pits. This darkness is due to the oxidation process that occurs to the phenolic products within the dead tissue of the heartwood (Eaton, 1993, pp. 7-10). In archaeological and works of art objects, not any darkness or change of colour can be interpreted as sapwood and heartwood but, it can be just a result of injury or response to wounds (Eaton, 1993, p. 9), attack by bio agents (Unger et al., 2001, p. 11), degradation of the chemical components (Hoffmann & Jones, 1990) or by natural aging or exposure to heat(Matsuo et al., 2011).

The formation of heartwood is accompanied with some anatomical features in both softwood and hardwood. In hardwood trees, this is characterised by the formation of balloon-like outgrowth from the parenchyma cells into the lumen of the adjacent vessel. In softwood, this transition from sapwood to heartwood can cause pit aspiration, which can be seen more in the early wood than the latewood, both tyloses and pit aspiration can affect the wood permeability negatively (Eaton, 1993, p. 8; Sjöström, 1981, p. 11) (this will be described more below).

The difference is not only in colour but it is also in the aroma, weight, density and solutions permeability. Heartwood tends to be more aromatic, heavier, denser and less permeable to water and preservatives especially in hardwood. This is confirmed by the experimental work which is represented in chapter 6 on the relatively recent oak samples (Quercus spp.) as investigations and measurement have been carried out on both sapwood and heartwood.

Generally, given the same moisture content, both heartwood and sapwood have similar strength because of the chemical structure and lignification of the cell wall are built after the division of the vascular cambium with no change after heartwood transition. The heartwood is however more durable than the sapwood because of the presence of the poisonous (toxic) compounds that work as repellents against insects and microorganisms.

2.3.4 Rays

Rays will be examined under the different cells of softwood and hardwood.
2.3.5 Bark

In some cultures, bark, more than wood, is one of the principal sources of art inspiration such as in the Australian Aboriginal communities and their complete bark paintings. Bark cells are growing from the two lateral meristems areas; vascular cambium and cork cambium (phellogen). As the focus, here is on wood bark will be mentioned just briefly.

Bark tissue in trees is divided to two main areas; inner bark and outer bark. As referred to above the inner bark layer is generated and formed by the secondary phloem cells resulting from the division of the vascular cambium. This layer is thin (0.5-15 mm) and has similarities and differences with the wood cell structure. It has longitudinal and ray parenchyma cells, however, the conducting elements whether they are tracheids in softwood or vessels in hardwood are lacking. These have been replaced by similar cells called sieve cells in addition to phloem fibres and highly lignified stone cells in softwood. In hardwood, there is another cell called a companion parenchymatous cell, which is associated with the sieve element.

The outer bark layer is relatively thicker layer (1.3-30 cm) than that produced by the cork cambium. This meristem area is formed just before the peeling of the non-expandable epidermis layer by the pressure created by the expansion of the living second tissue. The cork cambium which also called phellogen is a one-cell-wide circle layer that divides periclinally and developed from the parenchymatous cells of the peristem layer or the cortex parenchyma cell. With its waxy thin-walled cells and thick lignified cells, outer bark can provide a tree with the proper protection against moisture loss and shocks (Sjöström, 1981, pp. 98-102).

2.3.6 Cutting direction of wood

Wood can be identified by its distinct anatomical features that can be studies in different cutting directions or planes. As illustrated in Figure 5, these directions are; Transverse (Cross), Radial and Tangential sections. The features appear in the cross section when the wood is cut in a direction perpendicular to the fibre’s orientation or the longitudinal axis of the stem. All wood structure from pith to bark including growth rings (earlywood and latewood), sapwood and heartwood and rays can be seen in the stem transverse section with the naked eye or with the aid of magnification lens.
Under higher magnification, more ultrastructure features can be seen or identified such as cell types, resin canals, the degree of decay and degradation of the wood tissue and cell wall and so on. When cutting wood in a longitudinal direction following the radius of the growth rings it should, ideally, pass from bark to the pith of the stem. This section should show all the features that appear in the cross section but in a longitudinal way.

The tangential section is another longitudinal section that is cut tangentially to the growth rings, and it is perpendicular to the radial section. The most important feature that is studied in the tangential section is the ray cells that help significantly in the identification of wood.

**2.4 Wood microstructure (cell level):**

The previous section examined the gross structure of the tree stem and the preeminent characteristic layers as well as the main differences between softwood and hardwood. This section will take the wood under the microscope for more detailed ultrastructure anatomical characteristics.

Wood cells can be divided into three broad categories: conducting cells, supporting cells and storage (Sjöström, 1981). In hardwood, vessels are doing the conducting function while fibres are responsible mainly for mechanical support. In softwood, tracheids are doing both jobs. Parenchyma cells do storage in both hardwood and softwood.
2.4.1 Softwood and hardwood (Wood classification)

As mentioned above wood is mainly divided into two main categories; hardwood and softwood which together comprise most of the wooden cultural heritage remains and archaeological finds. In less proportion come palm trees wood, which has been used mainly in the structures and ceilings and in less extend in some carvings (i. e. Tiki palm statues). In the recent years, the man has been capable of modifying wood materials by using different technologies to produce the modified wood products (i. e. plywood, laminated wood, etc.) which is the most common at present, however, the use of these kinds of wood is going back the ancient Egyptian era.

The difference between softwood and hardwood is related to botanical and anatomical descriptions and classifications in the first place and has no association with wood hardness or natural durability(Parham & Gray, 1984, p. 1) (Fig 6). There are softwoods that harder than many hardwoods and vice versa (balsa wood is a good example for that). The classification subcategories each group depending on the principal cell types it has as explained below.

![Diagram of Softwood and Hardwood](image)

*Figure 6: The difference between softwood and hardwood (tree and cell level). After Arno (1993).*
2.4.2 Softwood (Gymnosperms or Conifers)

Softwood is the category of wood that comes from evergreen trees, which belong to the Class of gymnosperms and also known as conifer trees or conifers. According to Raven et al. 1999, they are much older than hardwoods being up to 300 million years old while hardwoods are about 150 million years of age. Leaves have the scale shape or the needle shape while the seeds have no covering on them and form a cone shape. Softwood tree consists of one main trunk or stem with smaller branches surrounding, with the longest of them are the closest to the ground with the shortest are in the top of the trees which gives the tree the triangular shape. Softwood trees provide most of the timber produced in the world with more the 75 percent. They have also preferred in paper industry because of the long straight fibres they have.

Softwoods have a relatively simple structure that consists mostly of one kind of cells, which are called tracheids with about four or five types of cells maximum in most of the species (these cells, however, are tracheid or parenchyma cells). This gives softwood simplicity in the appearance and difficulty in identification.

2.4.2.1 Tracheids:

Tracheids conform about 90 to 95 percent of the softwood volume. With a length of three to five millimeters, which is about 100 times longer than their width. Tracheids can provide the required mechanical support to gymnosperms based on the conducting ability of the cell sidewalls pits. Some softwood species have spiral thickening in the inner-wall side of the longitudinal tracheids (i.e., Douglas fir). The length of tracheids is about 100 times of the diameter which is different in earlywood and latewood in the radial direction, but the tangential diameter is almost the same, so it is usually used for measurements and description (Fig. 7).

Tracheids are longitudinal and strand-like cells that have both conductivity and supporting properties, they conduct water and mineral salts from roots to leaves and branches and also transport nutrients from leaves to the other elements of the tree. They additionally support the trees against wind and dry conditions. Longitudinal tracheids, which are used to refer to tracheids in general, are elongated cells with pointed closed ends, which overlaps the end of
the cells above and below. In the cross section, they appear like squares, rectangles or hexagonal shapes (except in compression wood where they tend to be rounded).

The other tracheids are called strand tracheids. They are shorter than the longitudinal tracheids and are arranged in strand like strings located nearby or surrounding the resin canals.

![Figure 7: Comparison between earlywood and latewood in softwood tracheids (Howard & Manwiller, 1969).](image)

### 2.4.2.2 Paranchyma cells:

Softwoods also have other cells; parenchyma cells (longitudinal (axial), epithelial and ray parenchyma cells). They are short and relatively thin-walled cells with simple pits that are used mainly to store carbohydrates and extraneous materials. Axial or longitudinal parenchyma cells are compromised in strands around the wood fibres. They can be observed in the transverse section of low magnification as small dots. They can be arranged in three different ways; diffuse parenchyma in which the stand or single cell in transverse section is seen to be scattered among the tracheids of the growth ring, zonate or banded parenchyma where numerous cells or strands are grouped in one area in the growth ring, and marginal or terminal parenchyma where the parenchyma cells are located at the border of the growth ring either at the beginning of it or at edge of the latest grown cells.

Epithelial parenchyma cells are related to resin canals (will be discussed below) as the latter are the result of epithelial cell development and they are not cells or elements themselves. Epithelial parenchyma are excreting cells that surround intercellular cavities, which form the resin canals vertically or horizontally. They can be thin-walled with no pits and undignified (as can be observed in pines) or thick-walled, lignified and with pits (as in larch). Ray parenchyma are radial parenchyma cells with simple pits and thin walls, and they play a crucial role in the
identification of conifers with respect to the intersection part when the ray parenchyma meets the longitudinal tracheids.

### 2.4.2.3 Transverse cells

Softwood has horizontal or transverse cells that are arranged perpendicular on the wood tracheids and axial parenchyma cells. These cells can be included in the two categories above as they are divided into ray tracheids, ray parenchyma, and epithelial parenchyma. Ray tracheids have border pits that are smaller than that found in the longitudinal tracheids. They are found in some softwoods especially those belonging to the Pinaceae including pines, larch, Douglas fir and others. In some ray tracheids species are oriented above and below the ray parenchyma in one row or more (as is the case in hard pine), and there are projections similar to teeth as a result of wall thickening which called dentate ray tracheids. This can help in the identification of species.

### 2.4.2.4 Important anatomical features of softwood:

#### 2.4.2.4.1 Pits:

Pits are responsible for transporting the sap in the xylem. This occurs mainly in the longitudinal direction and by the bordered pits in the axial tracheids. Pits are formed by discontinuation in the secondary wall forming two main types; bordered and simple pits and sometimes semi or half bordered pits. The first one is located mainly between the tracheids while the simple pit always found between the parenchyma cells, and the semi-bordered pit is located between parenchyma and tracheid cell.

Pits consist of two main parts; pit cavity or chamber, which is the missing part of the secondary wall and pit membrane, which consists of middle lamella and primary wall. In simple pits the cavity width in almost the same but in the bordered pit it the cavity is narrowed toward the middle lamella and have in the middle hole called pit aperture. Pits are formed in pairs in both walls of the adjacent cells so they are composed of one middle lamella and two primary walls.
Pits have another classification in softwood depending on the cells they connect. Intratracheal pits are pits connecting two longitudinal tracheids, pits connecting axial longitudinal tracheids with ray tracheids and crossfield pits which connecting ray system with the longitudinal tracheids, those later ones have more than one shape. Intratracheal pits are usually bordered and found in significant numbers in the radial longitudinal cell wall than the tangential wall. They are bordered with rounded outlines with the function of sap transfer, and also the pit membrane works as a barrier against gases and pathogens and prevents them from passing between tracheids (Choat et al., 2007). The numbers of bordered pits also reduced in the latewood than earlywood, and the bigger radial diameter of axial tracheids is the more numerous bordered pits. The bordered pits have the same shape but their orientation in the cell wall has different patterns as they can be arranged in one row along the cell wall, two rows of pits and in some three or four rows as seen in *Picea* spp., *Pinus* spp and redwood respectively.

However bordered pits control the sap movement in the longitudinal by the cell lumen, they are plying different role when we talk about archaeological or dried wood. The permeability of dried wood (also in heartwood) is less than it in green wood due to what is called pit aspiration in which the pit aperture is closed by the torus when is pulled and force by the menisci when water is escaping the wood. Pit aspiration occurs when wood is being dried and also in the transition of sapwood to heartwood. This modification is less in the latewood bordered pit because of the rigidity of the pit membrane compared to earlywood. Therefore, permeability in latewood is more than it in earlywood for the archaeological or seasoned wood. As the consolidates and preservatives move in wood in the same way the sap does, the aspiration no doubt is playing a role in wood preservation and influencing the impregnation of archaeological wood by consolidants.

When the axial tracheids cross the ray parenchyma cells, the cross-field or ray crossing pits are seen in the radial section. The pits in this area have different shapes; window-like or Fenestriform, pinoid, cupressoid, piceoid and taxodioid which can be found in *Pinus resinosa* and *Pinus sylvestris*, hard pines (except previous species), *Chamaecyparis*, *Picea* and *Abies* respectively.

2.4.2.4.2 Rays:

Rays are important features in conifers and are an important key in identification when seen from the radial and tangential sections. They are extended in the radial direction in a ribbon-
like manner from bark to pith across the growth rings in order to deliver water and nutrients horizontally across the xylem thickness. When resin canals are not presented (uniseriate rays), softwood rays tend to be narrow in a uniform fashion. Rays compromise mainly of two ray cells, ray tracheids and ray parenchyma which are arranged in transverse or horizontal orientation. If the rays contain both samples type, they are called heterocellular rays but when they are just of one kind they are called homocellular rays. The average volume of rays, including in conifers, is small with a range of five to nine percent.

Rays in softwood or conifers are divided into two categories; uniseriate rays, rays without resin canals, and fusiform rays which are combined by horizontal resin canals. Uniseriate rays when seen in the tangential direction are one cell wide with a mean height of six to nine millimeters comprised of ten to fifteen cells. These rays can be combined with the two rays’ cells (tracheids and parenchyma) or can be compromised solely of them.

Fusiform rays are mainly related to the horizontal resin canals. The nomenclature comes from the spindle-like shape seen in the tangential section. These contain ray tracheids, ray parenchyma as well as epithelial parenchyma cells, which surround one or rarely two transverse resin canal/s in the middle. At the end pointed ends of the fusiform rays, ray tracheids and ray parenchyma are arranged in a similar matter as is seen in the uniseriate rays. Fusiform rays are found in the four genera that contain resin canal with different volume percentage. The volume of the total fusiform rays in softwood does not exceed one percent while the minimum ratio to the uniseriate rays is 1-60 in larches, 1-40 in spruces and 1-25 in Douglas fir.

2.4.2.4.3 Resin canals:

The resin canal is one of the anatomical features of the softwood, but they are not wood elements. They are formed by vertical and horizontal epithelial parenchyma cells surrounding tubular intercellular cavities which secrete resins in the built canal which can be used to protect wood against other organisms or/and to heal a cut or damaged tissue, in this case, the resin canal is called traumatic resin canal. Traumatic resin canals are small only slightly bigger than tracheids and arranged in one row usually in the earlywood section of the growth ring. Unlike regular resin canals that are found in certain softwoods, traumatic resin canal can be seen in all softwood.
2.4.3 Hardwood (Angiosperms or Dicots)

Unlike softwood, hardwood which is referred to as porous wood has more complex tissue consisting of more cells and less uniform structure. Conductivity, supporting, storage and gum secreting which occurs in some species are the functions of these different kinds of cells. There is no big substantial difference in the proportion of them except in the epithelial parenchyma which is (Fibres 40-65%, vessel elements 20-40% and rays with longitudinal parenchyma 5-30% (Unger et al., 2001). While softwood tracheids have both functions of transporting sap and supporting wood, these two roles are divided between vessels and fibres in hardwood.

2.4.3.1 Vessels

Vessel are short (0.2-1.3 mm) with large-diameter (between 0.005-0.5 mm) cells that are connected one to another at the end to create pipe or tube-like called vessel members that can reach 10 cm length and in few cases over two meters. They are responsible for conducting water and sap. The connection areas between each two vessels are called plates and sap is transported via these plates by single or multiple perforations (Fig 8).

![Figure 8: The different types of cells of the microstructure of hardwood (Hoadley, 2000).](image)

The distribution of vessels in the growth ring enables hardwood to be classified to three groups; diffuse, ring-porous and semi-ring-porous wood. The first type is found when vessel elements are distributed equally throughout the growth ring, and in almost uniform size (aspen, maple and birch). The ring-porous wood is hardwood with relatively large vessels in the earlywood and apparently smaller vessels or pores in the latewood (ash and oak) while in semi-ring-porous (or semi-diffuse porous) vessel elements size is reduced gradually from earlywood toward
latewood without a distinguished zone (black walnut). Vessels can be found as solitary or multiple pores and the latter can be seen as clusters, chains, diagonal rows, radial multiples or tangential bands.

![Image: The different types of pores and their distribution way in hardwood. Left diffuse porous, middle ring-porous and right semi-ring porous (Bahador, Namdari, & Matinfar, 2017).]

### 2.4.3.2 Fibres

The other type of cells in hardwood are the fibres cells which are divided into two categories; tracheids fibres and libriform fibres. Both types are responsible for the mechanical support for angiosperms, however, the latter ones contribute more in this matter. Libriform fibres are characterised as long narrow cells with their length exceeding 1.5mm and with tapering ends and thick walls. This thickness in about 20 to 40 µm and they have simple pits. The fibres tracheids are shorter and have less advanced bordered pits, and also their ends are less pointed.

### 2.4.3.3 Parenchyma cells

As in softwoods, hardwoods also have axial and ray parenchyma cells. Axial parenchyma cells are more abundant in hardwood with thin-wall cells used for storage, and when available they have simple pits. They are instrumental in the identification of hardwood because of their different arrangement which can be seen in cross section. Generally, longitudinal parenchyma is classified into two categories depending on their association with vessels. The parenchyma cells are associated with vessels that are called paratracheal, while those which are not adjacent to vessels are called apotracheal and both of them are divided into other subgroups. Paratracheal (which means the parenchyma sit beside the vessels) parenchyma has different
patterns: scanty parenchyma, when it is one cell adjacent to wood pore or vessel. Vasicentric parenchyma, when they have centrally surrounded the vessel; winged when the parenchyma cells wing from one or the two sides of the vessel; lozenge when they surround the pores in diamond or elongated oval shape, confluent when the cells extend to contact the other cells surrounding the neighbouring vessel; unilateral when parenchyma cells are seen around half of the vessel in half circle shape beside other marginal, reticulate and scalariform shapes in some species.

Apotrachael (which is not adjacent to the vessels) parenchyma include diffuse single scattered cells which are too small to be seen by the naked eye and also cells that are arranged in visible tangential strands amongst Fibres. Epithelial parenchyma are thin-wall cells that are found vertically and horizontally around intercellular cavities. They secrete gum into the gum canals.

2.4.3.4 Important anatomical features of hardwood:

2.4.3.4.1 Rays

Rays in hardwood are not just uniseriate as the case of most of the softwood rays but they are variable and considered to be homocellular as they consist only of parenchyma cells. Two types of ray parenchyma can be seen in hardwood. Cells that are found in the top and bottom of the rays are called upright cells and the remaining cells are called procumbent cells. Rays in hardwood have a different arrangement that can be very valuable in the identification process.

2.4.3.4.2 Pits

Pits in hardwood are responsible for side-to-side (lateral) conduction between vessels and tracheids fibress. Vessel bordered pits are dominant for this function and divided into three sections, alternate, opposite and scalariform depending on the pits orientation and arrangement on cell wall. Pits of hardwood however bordered but their membranes are different from those ones in softwood.
2.4.3.4.3 Perforation plates

As stated above hardwood vessels are connected end-to-end together in a pipe-like fashion by perforated plates. This perforation is formed by protoplast enzyme and it has been suggested that they are responsible for dissolving the cell wall at this area as the vessel matures. The perforated plates are two types; simple and multiple. The simple perforation is round and open, and the multiple perforated plates are scalariform, reticulate and ephedroid shapes (Eaton and Hale, 1993)

2.4.3.4.4 Tyloses

An important anatomical feature of hardwood are the tyloses. Tyloses are projections or outgrowth of the cytoplasm of the parenchyma cells (axial or ray) into the lumen of the adjacent vessel through intercellular pitting. The formation usually occurs during the transition of the sapwood to heartwood as the tree ages. Tyloses are also formed as a result of infection by fungi or bacteria or injuries and/or when the wood is subject to drought. The balloon-like projection contains what is usually in the parenchyma cells such as starch, crystals, gum, etc.

2.4.3.4.5 Thickening

The importance of vessels spiral thickening here is that it can confuse and mislead the identification especially archaeological and historical wood which may have decay pattern similar to the normal spiral thickening vessels. This can also be the case with the slit-like aperture of the minute pits between vessels which arrange together in grooves on the secondary wall of the vessels. Spiral thickening is found more in the northern temperate wood and in the vessels tips of the tropical wood if occurs (Illic, 1950).

2.4.3.4.6 Gum canals

Some species have intercellular cavities surrounded by epithelial parenchyma cell that can be vertical or horizontal, but they rarely occur together. They are also can be normal or traumatic; the first one is hardly found in wood of commercial importance.
2.4.4 Palm wood (monocotyledons)

Plamwoods have been used in cultural heritage particularly for architectural structures like ceilings and doors or windows lintels. They belong to sub-division of monocotyledons that goes under angiosperms too. This kind of wood or tree has no growth rings in it making it easy to be identified.

2.5 Wood ultrastructure and cell wall chemistry (molecular structure)

2.5.1 Cell wall structure

As the tree or the plant grows new cells are added to the already existing tissue to eventually the mature trunk that can support the tree crown with its leaves and seed as well as conduct water and minerals absorbed by roots to up to the crown by the xylem tissue and the nutrients down by the phloem, and store carbohydrates till they are needed (Dinwoodie, 2000). These functions are, as previously mentioned, achieved by the different cells. The formation and structure of the various cell types are the same except some non-thickened parenchyma ray cells.

The wood cell wall compromises of three main layers: middle lamella (ML), primary wall (PW) and secondary wall (SW) (Wiedenhoeft, 2012, p. 18) which consists of three sub-layers: S1, S2, and S3 (Fig 10). The formation starts with a very thin wall that has the ability to enlarge and expand, and after reaching the final size the thin wall loses it plastic properties, and new layers are added to the wall in a process called differentiation this ends with the maturation of the cell. In the early stages after division the cell will develop a pectin-rich cell plate will be separated into two cells with two thin PW. The cell then expands to reach the mature size and length. After this stage, the deposition or the thickening of the SW will take place on the inside part of the PW, followed by the lignification process which is completed simultaneously with formation of the SW (Sjöström, 1981). Eventually the fluid will disappear, and the cell will die (except parenchyma cells) with hollow lumen.

The thin layer between cells is called middle lamella (ML) and works as an adherent lignified layer between the adjacent cells. The thickness of the ML is 0.2-1.0 µm. Moving inside toward
the lumen there is the primary wall, which is even thinner than the middle lamella with a thickness of about 0.1-0.2 µm. Sometimes it is hard to recognise the two layers (ML and PW) from each other; in that case, both the ML and PW of the adjacent cells are called the compound middle lamella (CML). The third inner layer, which is the thickest region of the cell wall, is the secondary wall that is developed after the enlargement of the PW stops following the division. The secondary wall starts with a thin layer adjacent to the PW, which is S1 followed by the widest layer of the cell wall S2 and eventually the S3, which is similar in thickness to S1.

According to (Fengel & Wegener, 1989, pp. 15-16), the S3 layer is only seen in the parenchyma cells and followed by a tertiary wall layer (T), while in the conducting cells the S2 layer is followed by a tertiary wall (T). According to them, it is the orientation of the fibrils that differentiates between the S3 layer in the parenchyma cells and in the secondary layers. The fibrils in the T layer have a slight slope that is not strictly in a parallel order. This layer also has more concentration of the non-structural substances. However this explanation is debatable and is no more generally accepted (Unger et al., 2001, p. 14). In most species, there is another warty (W) layer in the most inner side toward the cell lumen that has some warts-like projections (Fig. 10) (Sjöström, 1981, p. 16; Unger et al., 2001, p. 14).

Figure 10: The microstructure of wood cell wall (ML: middle lamella, P: primary wall, S1: secondary wall 1st layer (outer), S2: secondary wall 2nd layer (middle), S3: secondary wall 3rd layer (inner), W: warty layer (Côté, 1967).
Some areas in the cell wall lack a secondary wall, these areas are called pits, and are the main vertical lumen-to-lumen conduction (Fig 11). Pits are formed in pairs that can be bordered, simples or half-bordered. Just before the start of the S1 formation the bordered pits start and with the deposition of the secondary wall the development of the pit occurs by the conical depression of the secondary wall arches over the primary wall to form the pit cavity or the pit chamber (Choat, Cobb, & Jansen, 2008)

![Figure 11: The cell wall ultrastructure including border bits (Eaton & Hale, 1993)](image)

### 2.5.2 Wood chemistry

Wood chemistry can be divided to main compounds which are cellulose, hemicellulose, and lignin plus extraneous constituents (Fig. 12). These form the main compounds of the wood cell wall that are found in all wood species and the minor extractive low molecular compounds that are found in different proportions according to the wood species and also to the condition of preservation of the wood. First, the main chemical structure of the cell wall will be explained followed by minor components.
2.5.2.1 Arrangement of cellulosic polymers in the cell wall

The main three components of the cell wall chemistry are cellulose, hemicellulose and lignin. These compounds are organic polymers that form the complex chemistry of the cell wall plus pectin and other minor compounds. The proportion of each compound is different depending on the wood species with the dominance of cellulose in all cases (40-55%) then hemicellulose (25-40%) and lignin (18-33%) (Eaton, 1993). Whereas cellulose is mostly crystalline in the cell wall, hemicellulose is amorphous and lignin is amorphous and isotropic (Sjöström, 1981). The distribution of these polymers is not only different from hardwood to softwood is also different from sapwood to heartwood, earlywood to latewood and from cell wall layer to another.

Cellulose, as mentioned, is the most abundant polymer and its molecules aggregate in bundles usually refer to as microfibrils. These microfibrils are oriented with respect to the fibres axis in a special angle in each layer of the cell wall, which is called the microfibril angle (MFA) (Rowel, 2005).

*Some scientists employ the term polyoses instead of hemicellulose (Fengel & Wegener, 1989, Fengel (1983, 1984, 2003)).
Figure 13: Hierarchical modelling of softwood hygro-elastic illustrates the macro, micro and ultrastructure of wood (Harrington, 2002 after University of Canterbury, 1996, design by Mark Harrington)

Many studies have been done on the MFA (it generally refers to microfibril angel of cellulose in the S2 layer as illustrated in Figures 13 and 14 (Barnett & Borham, 2004, p. 461)) because it is one of the most used and useful parameters to determine the mechanical properties of wood. Thicknesses of the cell secondary wall along with MFA both are considered to be responsible for most of the wood mechanical properties. The microfibril consists of 36 cellulose molecules parallel to each other and bonded together by hydrogen bonds and surrounded by a matrix of hemicellulose and encrusting lignin with a width of 10-20nm (Sjöström, 1981) (Figs. 14, 15). Microfibrils are then organised together to form lamellae or clustered microfibrils.

Figure 14: The formation of the cellulose microfibrils and how they are surrounded by hemicellulose network (Adler & Buehler 2013)
The middle lamella is considered mainly as a cellulose-free layer that contains pectin and lignin principally, it contains only about 20-25% of the total lignin of the all cell wall.

Cell walls are constructed from these main three polymers in the microfibril form. Microfibrils are oriented in different ways and angles in each layer. The primary wall as mentioned is a thin layer in which the microfibrils are oriented in a random net-like network (Milton, 1995) in the outer portion while in the interior they are near to perpendicular (Sjöström, 1981). CML of typical softwood has around 8.4% lignin, 1.4% hemicellulose and just 0.7% cellulose of the total weight.

In the secondary, wall microfibrils have a precise orientation with lignin and hemicellulose in between, which form coherent lamellae that build each layer (Sjöström, 1981). S1 is a very thin layer of about 0.2-0.3 µm consists of 3-4 lamellae where the microfibrils are nearly perpendicular on the long axis of the fibres (Milton, 1995) with an angle up to 70° (Sjöström, 1981). Some references have reported that microfibril orientation can be either a right-handed or left-handed helix (Sjöström, 198; Dinwoodie, 2004), others mentioned it could be oriented in alternate right-handed and left-handed helix, while different group reported that they have a single helical orientation (Gibson 2012). Taking Scots pine as an example, we can notice that S1 consists of mostly lignin with 51.7% then cellulose with 30% and 18.3% for hemicellulose (Rowel, 2005).

The smaller the microfibril angle is, the stiffer the wood giving the less shrinkage in the longitudinal direction it has. This is well illustrated in the S2 layer of the secondary wall as shown in Figure 15. This layer is the thickest in the entire cell wall (1 µm in earlywood to 5 µm in latewood) and is formed of about 30-40 lamellae that can increase to 150 in the latewood. The microfibrils are deposited in this layer spirally around the cell wall with a more acute angle that varies between 10° in earlywood and 20°-30° in latewood. In Scots pine the proportions of cellulose, hemicellulose and lignin are 54.3%, 30.6% and 15.1% respectively (Rowel, 2005).

In the later stage of the cell wall development, the angle of the microfibril increases again similar to S1 layer to form up to 6 lamellae of the S3 (0.1 µm) layer with MFA of 50°-90°. The distribution of chemicals in this layer in Scots pine is however different from S1 with a very
small amount or no lignin and dominance of hemicellulose (87%) while cellulose is 13% (Rowel, 2005).

2.5.2.2 Cell wall main compounds:

2.5.2.2.1 Cellulose

Cellulose is the principal building compound in the wood cells comprising up to about half of the dry weight (Milton, 1995, p. 9) most of it located in the S2 layer (Sjöström, 1981). Cellulose is a carbohydrate monosaccharide polymer that is made up of a long chain of simple sugar (glucose C\textsubscript{6}H\textsubscript{12}O\textsubscript{6}). Glucose is produced as a result of photosynthesis process in the leaves or needles and flowers then downwards via the phloem tissues to the lateral meristem (cambium) tissues as well as to the tips of the roots, flowers and branches.

Long cellulose molecules are formed afterwards by the end-to-end linkage of β-D-glucose (β-D-glucopyranose) molecules (Milton, 1995, p. 9), which are linked together by glycosidic covalent links at the C1 and C4 position (Meyer & Misch, 1936; Sjoetroem, 1993; Walker, 2006) with a bond angle of 117°, giving the molecule ability to be straight and linear (Fengel, & Wegener, 1989). The linkage between the two glucose molecules takes place by eliminating one water molecule between their hydroxyl groups at carbon 1 and carbon 4 (Fengel & Wegener, 1989, p. 67). The number of glucose units in each cellulose molecule is called the degree of polymerisation (DP), so the more glucose molecules the greater degree of polymerisation of the cellulose, which can stretch to 7000-15000 units (Gibson, 2012).
Each glucose unit in chair conformation is rotated 180° with respect to the unit next to it, and the pair forms cellobiose \( \text{C}_{12}\text{H}_{20}\text{O}_{10} \), which is the principal repeated unit in the cellulose with a length of about 1.03 nm (Fig. 16). The linear cellulose molecules have the tendency to form intra-molecular and inter-molecular hydrogen bonds to make cellulose bundles, which in turn aggregate to form the microfibrils. Microfibrils aggregate to form fibril and then fibril aggregation forms the fibres (Fig. 17). Cellulose microfibril has some areas where cellulose molecules are parallel and this region is called crystalline cellulose and some other amorphous where cellulose is less ordered. The majority wood cellulose is crystalline with about 65% crystallinity areas (Rowel, 2005). X-ray diffraction and polarised light can be used to assess the crystalline structure of cellulose (Chapter 5).

The crystallisation of cellulose can have different forms depending on the origin of the cellulose and the treatment undertaken on it named these forms are cellulose I, cellulose II, cellulose III and cellulose IV. It is important to note that cellulose I, which is the native cellulose, is available in the natural cellulotic materials (Dinwoodie, 2000). This cellulose was assumed to be composed of one type of homogeneous crystals, but recent studies confirmed that it consists of two types of crystal allomorphs at least (Horri, 2001). These two types are referred to as cellulose I\( \alpha \) and cellulose I\( \beta \) (Fig 16); the first one dominates in some bacteria and algae (i.e., valonia ventricosa), while the later one is more dominant in the cellulose of higher plants including wood, cotton and ramie fibres where the S2 layer has most of the components (Atalla & VanderHart, 1984; Nishiyama et al., 2003).

The two allomorphs have different asymmetry in which cellulose I\( \alpha \) crystallises in the triclinic \( \text{P}_1 \) space group while cellulose I\( \beta \) crystallises in the monoclinic \( \text{P}_2_1 \) space group and the former has one cellobiose unit per unit cell while the later has two cellobiose moieties per unit cell (Viëtor et al. 2000, Sugiyama et al. 1991). Both allomorphs can be however found in one cellulose sample and even more in one microfibril (Viëtor et al. 2000, Nishiyama et al. 2003).
Figure 16: Structure of cellulose, (a, b, c) after: Desvaux (2005), (d) Kantharaj (n.d.).

Figure 17: The crystalline structure of cellulose $\alpha$ and cellulose $\beta$ (Barsberg, 2017)
As shown in Figure 18, a cellulose molecule chain has two ends, one is the reducing end, and the other is the non-reducing end depending on the OH group. The end that has the OH group in the C1 position is the reducing end because C1-OH is an aldehyde hydrates or hemiacetal group while, the OH group in the C4 position at the other end is alcoholic and thus has non-reducing properties (Fengel and Wegener 1989).

The degree of polymerisation and molecular weight of cellulose has a relation as the following:

\[
DP = \frac{M}{162}
\]

where 162 is the molecular weight of anhydroglucose unit and M is the molecular weight of cellulose (Sjöström 1981), or by following this general equation:

\[
DP = \frac{\text{Molecular weight of cellulose}}{\text{molecular weight of one glucose unit}}
\]

In order to know the molecular weight cellulose needs solubilisation and isolation, which can vary depending on the origin of the sample from 50,000 to 2.5 million (Fengel and Wegener 1989).

Cellulose can also be referred to as other different names or types based on the procedure of the isolation process. Cross and Bevan Cellulose plus Kürschner cellulose are of these examples. The first is obtained by chlorination of the wood meal followed by washing with aqueous solution of 3% sulfur dioxide (SO₂) and 2% sodium sulfite (NaSO₃). In this case most of the yield matter is cellulose I plus some hemicellulose. The second is obtained by refluxing the wood meal by a mixture of nitric acid and ethyl alcohol (1:4 v/v) three times for one hour then water washing and drying (Rowel, 2005). The availability of cellulose to water and microorganisms is what classifies cellulose as accessible or non-accessible, which has a direct relation to the crystallisation of cellulose. Crystalline surfaces are accessible, but the rest of the
crystalline parts are not. The opposite is the case in the non-crystalline part where most of the cellulose is accessible by water with the exception of some parts covered by hemicellulose and lignin (Rowel, 2005).

Cellulose has a Young modulus of 320 and needs 25 MPa to be amorphous in water. Cellulose is insoluble in most of solvents, and it is strongly resistant to strong alkalis and diluted acids. It can only be swollen by alkalis while it can be dissolved in strong acids such as 45% hydrochloric acid, 50% phosphoric acid and 72% of sulfuric acid H$_2$SO$_4$ as used in the experimental part in this thesis. Because of its high association with hemicellulose and lignin, it is hard to isolate pure cellulose from wood (Rowel 2005). Young's modulus is about 130 GPa, and its tensile strength is close to 1 GPa (Gibson, 2012)

2.5.2.2.2 Hemicellulose (polyose):

Unlike cellulose, hemicellulose is a polysaccharide compromising homo- and heteropolymer consisting of different sugars such as; D-glucopyranose, D-xylopyranose, D-mannopyranose, D-galactopyranose, L -arabinofuranose, plus their uronic acid derivatives such as D-glucopyranosyluronic acid, and D-galactopyranosyluronic acid and more minor sugars. Also, the chain length of hemicellulose is relatively shorter than cellulose with average DP of 100-200, and it is a branched polymer and amorphous instead of being linear and crystalline as the case of cellulose. Moreover, hemicelluloses are soluble in alkali and are easy to be hydrolysed by acid to its monomeric compounds (Sjöström, 1981; Rowel, 2005; Eaton & Hale, 1993). Hemicellulose acts as supporting net in the cell wall with its percentage that ranges between 20 to 30 percent of the dry weight of wood.

There is a difference between softwood hemicellulose and hardwood hemicellulose. The difference is also seen even in the hemicellulose of the same tree between stem, branches and roots (Sjöström, 1981) or in the case of compression wood when the percentage of D-galactose increases considerably. As they usually consist of more than one sugar type, they are sometimes referred to by the sugars of which they consist such as galactoglucomannan hemicellulose, which has galactose, glucose and mannose sugar.
2.5.2.2.2.1 Softwood hemicelluloses:

Softwood hemicellulose consists principally of galactoglucomannan with the approximate percentage of 20% followed by arabinoglucuronoxylan and some minor polysaccharides. Arabinogalactan is available in much more significant amount in the heartwood of larch compared to other species.

Galactoglucomannan is the main hemicellulose in softwood and consists of linear or possibly slightly branched backbone chain linked by (1→4) linkages between β-D-glucopyranose and β-D-mannopyranose with branches of α-D-galactopyranose linked by (1 →6)-bonds (Sjöström, 1981; Rowel, 2005). This hemicellulose has two fractions that have different in the galactose contents. The lower galactose fraction has a ratio of 0.1:1:4 galactose: glucose: mannose and is referred to as glucomannan, while the fraction that has higher galactose content has a ratio of 1:1:3 respectively. The backbone chain of glucose and mannose has acetyl groups substituted at the C2 and C3 positions on average of one group per 3-4 hexose units. These acetyl group can be more easily cleaved by alkali than acids while the galactoglucomannan itself can be simply depolymerised by acids especially the bonds between galactose units and the main backbone chain (Sjöström, 1981).

Arabinoglucuronoxylan (Fig 19), which is next most common constituent of hemicellulose with 5-10 percent, consists of a framework of β -(1→4) xylopyranose units with partial substitution at the C2 position with branches of 4-O-dimethyl-α-D–glucopyranosyluronic acid groups on an average of two to every ten xylose units plus α -(1→3) branches of L -arabinofuranose, on average, every 1.3 xylose units per ten xylose units. This hemicellulose type can stabilises against alkali-catalyst degradation because of the arabinose and uronic acid substituents while the arabinose side chains can be easily hydrolysed by acids (Sjöström, 1981).

Arabinogalactan is a hemicellulose with low viscosity and high water solubility, which is found as a major component in the heartwood of larches (Larix), which is found in small amounts in
the other wood species. It has a backbone of $\beta-(1 \rightarrow 3)$-linked D-galactopyranose units with side-chains of galactose and arabinose sugars and few glucuronic acid residues (Sjöström 1981, Kelly 1999).

Beside these main hemicellulose sugars there are other polysaccharides that consist of L-arabinofuranose, D-galactopyranose, D-glucopyranouronic acid and D-galactopyranuronic acid (Rowel 2005, Sjöström 1981) also in compression wood there is about 10 percent $(1 \rightarrow 4)$-$\beta$-D-galactan and 2-5 percent $(1 \rightarrow 3)$-$\beta$-D-glucan (Sjöström, 1981).

Table 1: Major hemicellulose components (*Partial solubility) (Sjöström, 1981)

<table>
<thead>
<tr>
<th>Hemicellulose type</th>
<th>Occurrence</th>
<th>Amount (% on wood)</th>
<th>Composition</th>
<th>Molar ratios</th>
<th>Linkage</th>
<th>Solubility*</th>
<th>DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>Galacto- glucomannan</td>
<td>Softwood</td>
<td>5-8</td>
<td>$\beta$-D-Manp $\beta$-D-Glc p $\alpha$-D-Galp Acetyl</td>
<td>3 1 1</td>
<td>$1 \rightarrow 4$ $1 \rightarrow 4$ $1 \rightarrow 6$</td>
<td>Alkali, water*</td>
<td>100</td>
</tr>
<tr>
<td>(Galacto)- glucomannan</td>
<td>Softwood</td>
<td>10-15</td>
<td>$\beta$-D-Manp $\beta$-D-Glc p $\alpha$-D-Galp Acetyl</td>
<td>4 1 0.1</td>
<td>$1 \rightarrow 4$ $1 \rightarrow 4$ $1 \rightarrow 6$</td>
<td>Alkaline borate</td>
<td>100</td>
</tr>
<tr>
<td>Arabino-glucuronoxylan</td>
<td></td>
<td>7-10</td>
<td>$\beta$-D-Xylp 4-O-Me-$\alpha$-D-Glc p $\alpha$-L-Araf</td>
<td>10 2 1.3</td>
<td>$1 \rightarrow 4$ $1 \rightarrow 2$ $1 \rightarrow 3$</td>
<td>Alkali, dimethylsulfoxide*, water*</td>
<td>100</td>
</tr>
<tr>
<td>Glucuronoxylan</td>
<td>Hardwood</td>
<td>15-30</td>
<td>$\beta$-D-Xylp 4-O-Me-$\alpha$-D-Glc p $\alpha$-L-Araf</td>
<td>10 1 7</td>
<td>$1 \rightarrow 4$ $1 \rightarrow 2$</td>
<td>Alkali, dimethylsulfoxide</td>
<td>200</td>
</tr>
<tr>
<td>Glucomannan</td>
<td></td>
<td>2-5</td>
<td>$\beta$-D-Manp $\beta$-D-Glc p</td>
<td>1-2 1</td>
<td>$1 \rightarrow 4$ $1 \rightarrow 4$</td>
<td>Alkaline borate</td>
<td>200</td>
</tr>
</tbody>
</table>
2.5.2.2.2 Hardwood hemicelluloses:

Table 1 summarises the main difference between softwood and hardwood hemicelluloses. The later has glucuronoxylan as a principal hemicellulose followed by glucomannan plus some minor polysaccharides.

Glucuronoxylan (Fig 20), which is O-acetyl-4-O-methylglucurono-β-D-xylan, as mentioned is the major hemicellulose in hardwood with the different percentages that vary from one species to another and ranged between 15-30 percent of dry wood. It composed of (1→4)-linked β-D-xylopyranose units as the backbone. For about ten xylose units there are seven acetyl residues connected to them at the position C2 or C3 plus one (1→2)-linked 4-O-methyl-α-D-glucopyranosyluronic acid.

Second hardwood hemicellulose is glucomannan with a percentage of 2-5 percent. It consists of (1→4)-linked β-D-glucopyranose and β-D-mannopyranose with equal ration in some species or 1:2 ratio in other species. This hemicellulose has weak resistant against acids and can be easily depolymerised (Sjöström, 1981). Besides, there are some minor polysaccharides that are similar to that which is available in softwood with more significant to the living tree.

Figure 20: The chemical structure of the Glucuronoxylan (Brandt et al., 2013).
2.5.2.2.3 Lignin

The description of lignin provided by Brunow et al. (1999) and quoted by Ralph et al. (2004) can be quoted again here:

This description is not a chemical definition of protolignins, but summarises the main structural features based on knowledge available today. Protolignins are biopolymers consisting of phenylpropane units with an oxygen atom at the p-position (as OH or O–C) and with none, one or two methoxyl groups in the o-positions to this oxygen atom. These o-positions may alternatively be C-substituted or O-substituted with other substituents than methoxyl. Only a few of the aromatic units are substituted in other ring positions. A few percent of the building blocks in protolignins are not phenylpropane units. The side chain is missing or shortened, or the unit is replaced by a quinoid group. The phenylpropane units are attached to one another by a series of characteristic link-ages (β–O–4, β–5, β–β, etc.) or, alternatively, exist as members of a series of characteristic end groups (e.g. cinnamaldehyde units). Practically all the types of structural elements detected in protolignins have been demonstrated to be formed on oxidation of the p-hydroxycinnamyl alcohols in vitro (Freudenberg & Neish, 1968; Adler, 1977). The structural elements in protolignins are not linked to one another in any particular order. Protolignins are not optically active. The polymer is branched and cross-linking occurs. In addition, the following facts should be noted: (1) there are strong indications of the occurrence of linkages between protolignin and carbohydrates, (2) some types of protolignins are esterified with phenolic acids (grass lignins with p-coumaric acid and certain other lignins, such as aspen lignin, with p-hydroxybenzoic acid), and (3) scattered observations suggest that there are some units, for example, dihydroconiferyl alcohol units, that can- not be thought to have been produced on oxidation of p-hydroxycinnamyl alcohols (Ralph et al., 2004).

For more in-depth review of lignin and lignification biosynthesis see; Ralph et al., 2004, Vanholme et al., 2010; Boerjan et al., 2003; Morreel et al., 2004; Morreel et al., 2004a; Christensen et al., 2000; Jouanin & Lapierre, 2012; Walker, 2006; Sjöström, 1981)

Lignin is the third major component of the wood, after cellulose is the second most abundant natural polymer on earth (Pilate et al., 2012, Boerjan et al., 2003) and the most used raw material for pulp and paper production (Baucher et al., 2003). It is amorphous, very complex, aromatic three-dimensional polymer made up of C–O–C and C–C linkages (Rowel, 2005). It
operates as an encrusting medium in the cell wall and round the microfibrils, providing rigidity and mechanical strength to the wood cell (Vanholme et al., 2010), besides decreasing water permeability, allowing transport of sap and water through the vascular system (Morreel et al., 2004). Additionally, lignin has a vital role in wood durability and protection against biological degradation (Marita et al., 2001; Vanholme et al., 2010; Pilate et al. 2012, Boerjan et al., 2003).

Lignification process is believed to starts after formation of the primary wall ceases. It begins at the cell corner before laying down the secondary wall layers and continues to accumulate with the deposition of S1, S2 and S3 layers.

According to the previous recent studies, the process can be summarised in the following way. Synthesis of the monolignols is initiated by deamination of the phenylalanine (Pilate et al., 2012) and the building blocks for the lignin are produced by a series of hydroxylation and O-methylation mechanisms on the aromatic ring. At the same time, the side-chain carboxyl converts to an alcohol group (Pilate et al., 2012). After their synthesis, the lignin monomers are transported to the cell wall where they are polymerised and linked together in a combinatorial fashion via radical coupling reactions, to generate a variety of structures within the polymer (Morreel et al 2004; Boerjan et al., 2003). That starts with the dehydrogenation of the monolignols by oxidative enzymes, such as peroxidases or laccases, with the formation of radicals and eventually by the influence of the macromolecular environment of the cell wall racemic polymer is composed (Morreel et al., 2004).

As stated by Sjöström (1981), many studies have reported that covalent linkages must exist between lignin and wood polysaccharides. Some separation and analysis of lignin and carbohydrates protocols concluded that xylan and galactoglucomannans in softwood are bounded mainly via xylose, arabinose and galactose moieties (Sjöström, 1981). Lignin is more concentrated in the middle lamellae, and its proportion in the secondary wall is low, but because of the thickness of it, most of the cell wall lignin is located in the secondary wall of softwood (70% in earlywood and 80% of latewood). In hardwood, syringyl units are more concentrated in the secondary wall of fibres cells, and they are dominant in the parenchyma cells while the fibres middle lamellae have more amount of the guaiacyl lignin (Sjöström, 1981; Eaton & Hale, 1993).
Lignin is almost insoluble substance in its native state in the majority of solvent and has much lower hygroscopicity properties compared to cellulose and hemicellulose, and thus it can reduce the changes in dimensions after variations in the moisture content. Also, it cannot be broken down to monomeric units because, even when hydrolysed, it retains high susceptibility to oxidation and readily undergoes condensation reactions (Walker, 2006; Sjöström, 1981). Because of the difficulty of its separation and isolation without degradation, measuring the molecular weight of lignin is usually unreliable. The molecular weight of milled wood lignin (MWL) in softwood is about 20000, however, in hardwood this figure is lower.

Acid soluble and insoluble lignin (Klason lignin) can be obtained by removing the holocellulose from the previously extracted grounded wood by hydrolysis with 72% sulfuric acid $\text{H}_2\text{SO}_4$ (Sjöström, 1981), which is the procedure used in the experimental chapter/s to make the conventional analysis of the chemical compounds.

Basically, there is a main difference between softwood (gymnosperms) and hardwood (angiosperms) lignin. While phenylpropane is the fundamental unit for lignin generally, guaiacyl lignin phenylpropanoid (one methoxyl group added to the phenol ring) is available principally in almost all gymnosperms and is composed mainly of coniferyl alcohol (4-hydroxy-3-methoxycinnamyl) units. Syringyl lignin (two methoxyl groups added to the phenol ring) is available in all hardwoods (Eaton & Hale, 1993), and it contains monomeric units from coniferyl alcohol and sinapyl alcohol (3,5-dimethoxy-4-hydroxy-cinnamyl).

![Chemical structure of lignin: coniferyl, sinapyl and p-coumaryl alcohols](Moore, Robson & Trinci, 2011).
Coniferyl and sinapyl alcohol along with p-coumaryl alcohol are the three p-hydroxycinnamoyl alcohols precursors of lignin or of the monolignols, and they are different according to the availability of a methoxyl (-O-CH$_3$) group on the aromatic ring at the C3 and C5 positions (Walker, 2006) (Fig. 21). Unlike cellulose lignin or lignins are not regular structures. They have variable compositions and structures that make the probability of finding two identical lignin macromolecules very low (Ralph et al., 2004).

### 2.5.2.3 Secondary Components

#### 2.5.2.3.1 Extractives

Extractives are extraneous constituents that present in minor proportion (exception in some trees that have 30% tannins and larches that have 20-30% arabinogalactan) of the wood dry weight of the wood. They may be infiltrated entirely into the cell walls, or they may occur as surface deposits or as plugs in cell lumen. The majority of these substances are organic compounds (sometimes contain inorganic salts/minerals) that can be extracted by cold/hot water and organic solvents such as ethanol, toluene, acetone and dichloromethane. Therefore, they are called or classified by the solvent used to extract them (i.e., water-soluble, ethanol/toluene soluble extractives… etc.) (Rowell et al., 2013). According to Sjöström (1981), they can also be classified into three groups; aliphatic compounds, which include mainly fats and waxes, terpenoids and terpenes compounds and phenolic compounds. Additionally, they can be categorised into two main groups relating to their economic importance; polyphenols and oleoresin. The first group can be found in both angiosperms and gymnosperms and include tannins, flavones, fatty acids, fats, volatile hydrocarbons and waxes. The oleoresin is found in the resin canals of some conifers and includes terpenoids, tall oil, rosin, volatile monoterpenes, wood turpentine and so on.

The extractives are more concentrated in the heartwood, and they have a considerable influence on the wood odour and colour besides the durability that they give against biological factors. They can also decrease the permeability of wood and can affect wood specific gravity, hardness and flammability (Milton, 1995; Rowell, 2005).

Extractives in softwood can be found in the resin canals, parenchyma cells and heartwood (Sjöström, 1981), oleoresin is the resin generated by the epithelial parenchyma cells whether vertically or horizontally and it can be exuded rapidly in the sapwood area in case of injury.
Most of the oleoresin is fatty acids, which is about 50% in spruce and can reach 70-80% in pines. Fatty acid esters (fats and waxes) and sterols are the main components of the resin in the parenchyma cells. The heartwood of softwood has the larger amount of the extractives that are generated after the death of the living cells of the sapwood (Sjöström, 1981).

Hardwood species have less extractive content than softwood (Rowell, 2005), but like softwood, most of this content is in the heartwood region (Rowell, 2005). They are located in the parenchyma cells (Sjöström, 1981) and consist of monoterpenes, fatty acids, alcohols and triterpenoids and diterpenoids on some occasions (Walker, 2006).

The extraction process is undertaken by first grinding wood to a fine powder then by using Soxhlet extraction with solvent and water. The powder is left in paperboard thimble for 4-18 hours. Then the flask containing extractives is evaporated and dried to a constant weight. By knowing the initial oven dry weight of the flask and the weight after extraction, approximate quantitative measurement of the extractive can be obtained (that was the procedure followed for the experimental work). Advanced techniques can be then used for qualification analysis using devices like nuclear magnetic resonance and gas chromatography (Walker, 2006).

For more information about extractives, their chemistry and effect on wood properties see; Walker, 2006; Hon & Shiraishi, 2001; Sjöström, 1981; Fengel & Wegener, 1989; Hillis 1987, Gang et al., 1996.

2.5.2.3.2 Inorganic minerals (Ash)

The inorganic matter includes elements that are components of newly growing tissues such as potassium K, calcium Ca, sodium Na, phosphorus Pb and magnesium Mg as carbonates, oxalates, and sulfates, or bound to carboxyl groups in pectic materials. Beside other elements like Si, B, Mn, Fe, Mo, Cu, Zn, Ag, Al, Ba, Co, Cr, Ni, Rb, Sr, Ti, Au, Ga, In, La, Li, Sn, V, and Zr (Rowell 2006). This inorganic matter plus mineral salts are referred to as the wood ash content. Based on the dry weight of wood this inorganic matter compromises only a very minor proportion of wood weight that is about less than 1% or 5% in temperate or tropical wood respectively (Dinwoodie 2000), however in the case of archaeological and deteriorated wood this number is suggested to increase significantly (Unger et al., 2001; Chapter 7).
2.5.2.3.3 Minor polysaccharides (pectin and starch)

Besides containing the major carbohydrates, cellulose and hemicelluloses, wood, whether it is a softwood or hardwood, has small amounts of minor polysaccharides such as pectins, starch, and proteins. Pectins are polysaccharide polymers that made up of repeating $\alpha$-(1$\rightarrow$ 4) D-galacturonic acid linked units. They are found in the membranes of the bordered pits between wood cells and in the middle lamella. The concentration of pectins is high in the parenchyma cell walls in the inner bark because of their role as a binder. Pectin is also found as the methyl ester. Starch can be found in small amounts in wood but it is the principal reserve polysaccharide in plants. It typically occurs as granules which are composed of $\alpha$-(1$\rightarrow$ 4) D–glucopyranose units (amylose) or $\alpha$-(1$\rightarrow$ 4) with branches about every 25 glucopyranosyl units at $\alpha$-(1$\rightarrow$6) (amylopectin) (Rowell 2005).

2.6 Wood Physical Properties

2.6.1 Wood and Water:

The relation between wood and water or wood-water properties have been studied extensively and many literatures can provide detailed information about this point (Rowell, 2005a; Walker, 2006; Mantanis et al., 1994 1994a, 1995, 1995a; Skaar, 1984; Stamm, 1935; Klein & Bröker 1990, Unger et al., 2001).

The determination of wood moisture content will be explained in the experimental chapter, so this will be discussed briefly here.

Wood is a hygroscopic material that can gain and lose water easily by the changes in the surrounding moisture level. These moisture content has a direct influence on the other physical, thermal, biological and mechanical properties of wood. After felling, trees contain two types of water, termed free water and bound water. Free water is the water that fills the cell lumens freely while the bound water* is trapped or bounded to the cell walls. The percentage of the

* Bound water is held tightly within the cell wall by physiochemical bonds as the water molecules are attracted to the cell wall by hydrogen bonds sites that are available in hydroxyl group of the wood components in the amorphous regions
weight of both types of water by the weight of the dry weight of wood is referred to as wood moisture content MC, which varies from one species to another.

While drying, wood or timber starts to lose the free water. When all the free water is lost and all the bound water remains wood has reached what is termed fibre saturation point (FSP), which ranges from 20-50 percent depending on the species (Rowell, 2005a). At this stage, wood will retain its original dimensions but with loss of bound water below FSP wood will retract. The adsorption of water below FSP will result in an expansion of wood dimensions, as is the case when wood is exposed after oven-drying. Wood will continue to lose and gain water in relation to the surrounding relative humidity (RH) and temperature. It equilibrates with these conditions when they stay constant for a period of time. The moisture content at this stage is termed equilibrium moisture content (EMC).

When wood spaces or pores are completely filled with water, the moisture content, in this case, is at maximum and is termed maximum moisture content (MMC). This value can range from 92% for hornbeam and 111% for oak to 205% for poplar in the central European wood but can reach 800% in deteriorated waterlogged wood (Unger et al., 2000).

### 2.6.2 Swelling and shrinkage

As mentioned, swelling and shrinkage occur as results of adsorption or desorption of water below FSP respectively. The measurement can be done by following these equations:

Problems occurring after the shrinkage and swelling of wood are caused by the anisotropic properties of wood, as the wood swells and shrinks in different directions with varying proportions of each depending on changes in the water content. Changes in the dimensions in the longitudinal direction are negligible that is only about 0.1 to 0.2 percent from green to oven-dry of most wood species (Simpson & TenWolde, 1999), while it is the most in the tangential direction (Fig). The shrinkage in the radial direction is about half of that in the tangential direction. These changes in response to moisture content may lead to serious damage to Artefacts, especially large objects and board or panels and works of art including warping, cupping, twisting, bowing, spring, etc. These damage phenomena can increase in a serious way if the wood was cut from reaction wood (resulting from tension in hardwood and compression
in softwood) or juvenile wood (wood close to the centre of the tree), where longitudinal shrinkage is excessive that may reach two percent of the green size after oven-drying (Simpson & TenWolde, 1999). Also, it has been noticed that shrinkage is usually proportional to wood density. The denser wood is, the more shrinkage can occur.

Direct exposure to water contact for an extended period of time, like the case in waterlogged wood, can lead to irreversible damage to wooden objects. These damages caused following the shrinkage of waterlogged wood are attributed to the weakness of the wood strength due to the decomposition of the cell wall constituents and decline in the crystallisation of the remaining cellulose. These chemical changes increase the hygroscopicity of the wood because of the high reachability of the hydroxyl groups and the breakdown on the remaining ones and thus increasing its swelling and shrinkage across all directions. Shrinkage stress is caused by the surface tension of the water column leaving the wood cells which cannot be resisted by the weak cell wall of the waterlogged drying wood, which leads eventually to the irreversible collapse of the wood (Unger et al., 2001, 30, 31).

2.6.3 Appearance

Appearance in wood is controlled mainly by colour, texture and figure which will be examined below.

2.6.3.1 Colour:

Colour is one of the aesthetic and decorative values increasing the variability and the attractiveness of wood. The colour is typically generated by chemical coloured extractives embedded in the cell wall, so it is more often seen in the heartwood area while the colour of the extractive-free raw wood is pale straw, which is characteristic of the sapwood in most of the timbers (Dinwoodie, 2001). As described previously in this chapter, deposition of extractives is associated with the formation of heartwood thus in some species there is a sharp difference in colour between sapwood and heartwood areas (except some wood species; i.e., ash and spruce where extractives are not produced).

Colours can vary from the soft white colour in pine, spruce and maple to the highly valuable dark-coloured ebony. In addition to some colours are characteristic such as the red mahogany, the wood of the greenheart or the purpleheart.
However, wood can be discoloured especially on the surface by the exposure to different factors as the case in old wood. The light-coloured wood surface can yellow if it is left directly exposed to sunlight (Sinclair & Vincent, 1964). Some others can bleach (Bulian & Graystone 2009). Natural aging causes colour changes by mild thermal oxidation (Matsuo et al., 2011) as well as different factors like seasoning, thermal treatments, fungal attack, metal rust stain, chemicals, which cause discolouration and staining.

2.6.3.2 Texture:
Texture is a feature that can differentiate between different kind of wood species depending on whether they are softwood or hardwood. It depends on the arrangement, and the size of cells and accordingly wood can be classified as fine-textured, coarse-textured (i.e. boxwood and ash wood respectively), even-textured or uneven-textured.

2.6.3.3 Figure:
Growth rings, grains, rays and knots form what is termed as the timber or wood figure’s which is defined as “ornamental markings seen on the cut surface of timber, formed by the structural features of the wood” (BS 565 1972, Bulian & Graystone, 2009; Dinwoodie, 2001). Grain is the alignment pattern of the more or less vertical cells or cells deviation. These patterns include cross-grain, diagonal or wavy grains with spiral, helix, interlocked or fiddleback alignments (Bulian & Graystone, 2009; Dinwoodie, 2001). In oak, the rays add one characteristic figure referred to as silver or light-coloured ribbon-like grain because of its significant depth and width. Growth rings also add an additional pleasant appearance to the timber produced by the variable distribution of the different cell types or the thickness of the cell walls and controlled by the width of the growth rings and the proportions of earlywood and latewood. Such patterns are more recognised in the tangential face than in the radial face, where the successive intersected growth layer produce series of concentric arcs (Dinwoodie, 2001).

2.6.4 Density

Density is defined as the mass per unit volume or the ratio of mass and volume (kg/m3) however in wood we cannot just use this equation directly without considering moisture content and any other material that occupies wood porous. So many types of densities can be
measured for wood depending on the moisture content or the condition when the test is performed. Without writing all the equations, these densities can be mainly classified to: oven-dry density (based on the mass and volume of the oven dried wood), air-dry density (based on the mass and volume of the air-dried wood), green density (based on the mass and volume of the green volume of wood when green) and there are two methods that most used for archaeological object especially the have regular shape which are:

$$\text{Basic density} = \frac{\text{Oven–dry mass of wood}}{\text{Volume of the wood when saturated with water (green)}} \text{ g/cm}^3$$

This method is most used with waterlogged wood regardless of the shape and is sometimes expressed as conventional density (Unger et al., 2001) and,

$$\text{Nominal density at } x\% \text{ moisture content} = \frac{\text{Oven–dry mass of wood}}{\text{Volume of the wood at } x\% \text{ moisture content}} \text{ g/cm}^3 \text{ (Walker, 2006)}$$

This method is also used for dried archaeological wood especially those of regular shape where dimensions can be measured. This latter method was used in (Chapter 4).

Specific gravity is the ratio of wood density to water density at 4°C (1000 kg/m3). Since both wood and water have the same volume, the specific gravity will be the ratio of the mass of wood to the mass of water at same temperature. Specific gravity is used frequently and is sometimes preferable to density measurements because it is based on the oven dry weight (mass) of wood eliminating variations due to moisture content.

Density is a direct indication of wood properties and varies greatly depending on the condition, component and species. The average value is about 176 kg/m3 for balsa to about 1230 kg/m3 for lignum vitae at 12% moisture content (Dinwoodie, 2000), and in general, most of the wood species have densities between 320 and 720 kg/m3 (Simpson & TenWolde 1999). Although, density varies greatly from one species to another and due to moisture content, the actual density of the cell wall is the same for all wood species with approximately 1500 kg/m³. Thus, we can estimate the porosity of wood by following the oven-dry density measurement.
(i.e., the oven-dry density is 300 kg/m³) that means that the wood cell wall substance consists 1/5 of the total volume of the specimen and the rest is porous.

In archaeological wood, density is an excellent indicator of the degree of wood deterioration and preservation. Generally, old historical wood is expected to have less density than a recent one of the same species because of the reduction of wood substances by biological factors including fungi and insects, by weathering and natural aging and by hydrolysis to cell wall components.

2.7 Wood Thermal Properties

The thermal properties of wood include thermal conductivity, specific heat, heat capacity, thermal diffusivity, and the coefficient of thermal expansion. Thermal conductivity is defined as: “the steady-state heat flow rate per unit area per unit of temperature gradient through unit thickness in the direction perpendicular to the isothermal surface. It is expressed in W/m-K (Btu-in-ft²-h°F)” (TenWolde et al., 1988).

Wood is known to be a relatively weak thermal conductive medium because of the porous nature of its elements. Factors like wood density, thermal conductivity direction, extractive content, grain direction, structural irregularities such as checks and knots, fibril angle, temperature and moisture content can influence thermal conductivity of wood (Simpson & TenWolde, 1999). For example, denser wood is more conductive. The thermal conductivity of wood also increases in the fibre direction to about double that perpendicular to the fibre. The thermal conductivity of wood is also proportional to moisture content, temperature, and extractives content.

Specific heat and heat capacity are related properties. Heat capacity is the “ratio of the amount of energy absorbed by the associated temperature rise” and specific heat is the heat capacity per mass unit. Unlike conductivity, the heat capacity of wood does not change by the difference in density or the species however it does vary according to moisture content and temperature. Dry wood has less heat capacity than wood that contains water and consequently less specific heat whereas pine, because of its moisture content has a specific heat similar to brick.

How fast wood reacts to the surrounding heat is called thermal diffusivity, which is defined as “the ratio of conductivity to the product of heat capacity and density” (Simpson & TenWolde,
1999) and expressed as m2/s (TenWolde et al., 1988). This value is low in wood compared to metal, stone or brick (wood: 0.161 x 10^-6 m^2/s, steel: 12.9 x 10^-6 m^2/s) and so wood will not be too hot to touch as the other materials.

One of the confusions is if wood expands by heat and arising temperature or contracts (shrink). What comes to mind immediately that wood shrinks as it is heated or is dried. On the contrary, wood (that contain moisture) is similar other materials expands by raising the temperature as a respond to the increased distance between its molecules and therefore increases the magnitude of their oscillations and retract by cooling however these dimensions changes are very small compared to shrinkage of wood occurs because of loss of bounded water (Dinwoodie, 2000; Simpson & TenWolde, 1999).

The coefficient of thermal expansion is a measure of the change of wood dimensions in response to changes in temperature. In dry wood, expansion can occur in all directions however it is more pronounced in the radial and tangential direction than the longitudinal direction by a percentage of 5:1-10:1 (or more). The coefficient of thermal expansion is not related to specific gravity in the longitudinal direction (Weatherwax & Stamm, 1946) however it is proportional to specific gravity in the radial and tangential directions perpendicular to grains (Dinwoodie 2000; Simpson & TenWolde, 1999).

Other heat-related properties are combustion factors, which include the ignition of wood and its fuel value. The ignition value is when wood starts to decompose exothermically, and it is about 275 °C.

According to (Rowell et al., 2005), wood is not actually burning when it is exposed to an ignition source. Rather, what is seen when wood heated up is a thermal degradation of wood lead to evaporation of inflammable and volatile gases that burn in contact with an ignition source.

### 2.8 Wood Electrical Properties:

Wood has a weak electrical conductivity because the metallic ions, by which the electrical conductivity occurs, are only present in wood as impurities. Since conductivity is increased
with higher moisture content, air-dried wood is an excellent insulator and used in the electrical tools handles. The electric conductivity of wood is greater in the fibre direction than the cross direction (up to four times in softwood and can reach eight times in hardwood). Archaeological wood, especially sea waterlogged wood or wood with added preservatives can have relatively higher electrical conductivity (Simpson & TenWolde, 1999).

Other electrical properties relate to wood are dielectric constant and dielectric power factor. The former is the “potential energy per unit volume stored in the material in the form of electric polarisation when the material is in a given electric field” (Simpson & TenWolde, 1999). This value is proportional to the temperature and moisture content, and it is higher in the longitudinal direction than the cross direction.

The dielectric power factor a measure of the energy converted to heat after removing the magnitude field that the wood was placed in. This power factor which is significant in wood, is proportional to density and moisture content and is usually but not always higher parallel to the grains than across the grains (Simpson & TenWolde, 1999).

2.9 Wood Acoustic Properties:

Wood is good sound insulator. The velocity of sound parallel to fibres is about double or three times more than it across the fibres. Dense wood reflect sound; hence it is popularly used in making musical instruments and conference and concert hall interiors (Wegst, 2006).

2.10 Wood Mechanical Properties:

The mechanical properties of wood are the properties that measure the medium’s behaviour under the applied forces. Such features are particularly important in construction, buildings, and furniture more than the portable objects. Wood is anisotropic and orthotropic material that behaves differently in each of the three perpendicular directions or axes (longitudinal, radial and tangential) when force is applied. For instance, the tensile strength of timber is about twenty times more in the longitudinal direction parallel to grains than in the cross-grain
direction. Similarly, the compression strength is about ten times higher parallel to the grains (Winandy & Rowell, 2005; Walker, 2006).

*Stress* ‘σ’ in the perspective of this chapter is a measure of the internal distribution of force within a material in response to application of external force, while *strain* ‘ε’ is a measure of the material response to this applied force and its ability to deform. Accordingly, stress can be calculated as the change in the dimension per unit of the dimension (Rivers & Umney 2001).

Tensile, compression and shear are the three main stresses. The first relates to the material expansion by pulling or elongating it. The second relates to pushing the material and shear stress causes segments of the material to slide in different directions (Winandy & Rowell, 2005). Compression, tensile and shear strengths are present in the bending test or bending stress (Unger et al., 2001).

2.10.1 Wood Strength

Strength can be defined as “the measure of force or stress needed to break an object” (Rivers & Umney, 2003). Typically, strength correlates with wood density such that the low density is an early indication of how weak the wood is. However, the strength of wood can be affected by many factors some of which are related to the material itself and other related to exterior factors. For example, wood shows much higher resistance to applied forces parallel to the grains than perpendicular to them, whether it is tensile or compression strength. The quality of wood and the absence of natural defects increase its strength dramatically. According to Rivers and Umney (2003), knots in wood reduce the strength because of the abnormal tissue and grain direction and by creating cross-grain distorted xylem tissue. Cross-grained or short-grained wood occurs generally when grain direction is not parallel to the long axis of the wooden element. This feature can be a result of the spiral grain in the tree itself (mentioned previously in this chapter) or the method by which the wood was sawn and results in loss of strength. This can be especially significant in linear furniture elements such as legs and spindles. Natural defects that affect strength include also splits, pitches, checks, bark pockets and reaction wood (compression or tension).

Compression wood has more compression strength and lower tensile strength than normal wood. It also has a lower modulus of rupture and modulus of elasticity. Tension wood, on the
other hand, has obviously less compression strength in the fibre direction and its greater tensile strength may be attributed to its low lignin content and the high cellulose percentage. Accordingly, the opposite can occur if the content of lignin is high and the cellulose is low resulting in material with low tensile strength and high compression strength (Rivers & Umney, 2003, Unger et al., 2001).

Exterior factors affecting strength include insects and microorganisms plus the environmental conditions and chemicals. Wood destroying fungi and insects can affect all the mechanical properties of wood as they destroy and eat the wood substance or cause damage. There is a proportional relation between reducing wood moisture content below FSP and wood strength, which can reach triple in the oven-dry sample of the same fresh wood. Wood strength is also inversely proportioned with temperature. (Winandy 1,2,3,4, has extensive work related to wood strength and its relation with different factors). The wood strength of all measured species ranges between 1-40 MPa (Walker, 2006; Unger et al., 2001).

There is a strong relationship between the chemical composition of wood and its strength such that many physical and mechanical properties derive from the chemical properties in the first place (Winandy & Rowell, 2005; Winandy & Rowell, 1984). For example, Because of its high degree of polymerisation and linear structure, cellulose is considered to be the most responsible attribute for wood strength. Hemicellulose on the other side is acting like a matrix to increase the baking density of the cell wall. According to Winandy and Rowell (2005), hemicellulose is working as a coupling agent that has the ability to associate with the noncrystalline areas cellulose and the more amorphous hydrophobic lignin. Lignin mechanically is acting as stiffening agent that binds the carbohydrates molecules together within the fibre cell wall plus holding fibres together.

### 2.10.1.1 Modulus of rupture (MOR):

*Modulus of rupture* is the measure used to determine wood strength before rupture and it is expressed in force per area or Pascals (Pa, MPa or GPa) (Green et al., 1999).

For a rectangular or square beam that is under central loading the modulus of rupture is calculated by following the formula:
MOR = 1.5*P*L^2/ b*h^2

Where;
L= Length of the beam or the specimen
P=Width of the beam or the specimen
H=Height of the beam or the specimen

2.10.2 Wood Elasticity

Elasticity is the ability of the material to retain its original shape after removing the applied force. The stress range for elasticity is defined as a proportional stress. Since the shape-retention cannot be 100% immediately for any material, there is no material that is perfectly elastic (Record, 1914), and wood is no exception (Winandy & Rowell, 2005).

Plasticity, on the other hand, is the ability of the material to undergo permanent change in shape or dimension without returning to the original state. Wood plasticity can be increased by wetting and heating processes such as steaming or boiling (Record, 1914).

In the bending test (a method for evaluating wood’s elasticity), the specimen is supported at the two ends, and applied force perpendicular to the specified axis is placed in the middle of the sample span. The side of the material that is facing the force is compressed while the lower surface is elongated in tension. After applying the force on a wood specimen perpendicular to the grains, the sample will react according to the amount of stress and strain generated by the load applied. At moderate levels, the deformation of the specimen is recovered after removing the load and a linear relation can be drawn between stress and strain where the strain is proportional to the stress. The wood is therefore described as elastic where an increase of stress will produce a proportional increase in strain. When the stress exceeds the proportional or the elastic limit of the wood, permanent plastic changes and/or failure will occur. Beyond this limit, any increment of stress will produce strain that is no longer proportional (Rivers & Umney, 2001).

Owing to this property of bending strength, maximum load is reached after passing the proportional limit load by 150-200 percent (Rivers & Umney 2001).
2.10.2.1 Modulus of elasticity (E)

The focus in the mechanical tests carried in this thesis was to measure the modulus of elasticity (‘E’ or MOE), which is called Young Modulus in the case of tensile and compression stresses although the value is sometimes confused with wood stiffness ‘K’.

Modulus of elasticity is significant in case of wood generally and in archaeological wood particularly. It is used as a parameter in the bending test to judge material stiffness and rigidity (Rivers and Umney 2003). It is simply the ratio of stress to strain up to the proportional limit. E is intrinsic to the material regardless of the dimension or geometry while K, is dependent on the material and its size. In other words, different sizes of the same material can have the same E but different K values (Winandy & Rowell, 2005).

The values of the E and K are defined by the following formula:

\[ E = \frac{\text{stress}}{\text{strain}} \text{ or } E = \frac{\sigma}{\varepsilon} \]

\[ K = \frac{AE}{L} \]

A=Cross-sectional area
L=length

2.11 Wood Natural Defects

In many cases woodworkers, carvers or artists find undesirable defects in the piece of wood they have, which prevents in some limit the final artistic product. These defects are mostly related to natural growth irregularities.

2.11.1 Knots

Knots are simply bases of side branches embedded in the stem of the tree or a bigger branch. They affect the technical properties of wood, but on the other hand, they add some aesthetic feature to the wood figure. The longitudinal axis of the knot branch is up to 90 degrees on the main branch or the stem.

With the tree growth, side branches are added to the top of the tree and the end of the main branches and the lower side branches or limbs will die and eventually drop. At the same time more, increments are added around the side branch base at the cambial zone of the stem with
no change in the case of the side branch, and therefore a distortion of the fibres around the knot is created.

The part of the side branch base that is growing simultaneously with the stem while the branch is living forms tight intergrown knots constituted by the annual rings of growth that are partially or entirely intergrown with the surrounding growth rings of the stem. After the side limb or branch falls, a small part of it will remain as a projection of the stem. This part will be embedded inside the stem with the growth of the tree and will become encased inside the new wood increments that are added around it. This part will form an encased and usually loose knot. The first kind of knot is a red knot and has a conical shape while the latter is referred to as black knot and sometimes contains pitch or bark pockets that are cylindrical in shape.

Further to this classification, wood knots can be classified according to their size, firmness and soundness. The part inner to the bark usually has fewer knots and is therefore the best grade. The part interior to that has encased knots and is the lowest grade while the most inner part has mostly the intergrown knots and hence classified as intermediate grade.

As mentioned previously knots affect the mechanical properties of wood, and therefore they are considered as defects besides the irregular fibre structure around them. This property is shown in the bending stress when the load is perpendicular to the grains and especially where knots are close to the centre of the beam and applied force. Moreover, knots have different physical properties than the surrounding tissue. They tend to be more solid, dense, dark-coloured and have more resins or extractives. This makes the response to the surrounding factors different in both knots and surrounding tissue.

2.11.2 Reaction Wood

Reaction wood is a response of the tree stem or branch toward an abnormal factor or load such as wind, poor root development, soil creep (Walker, 2006) and/or the weight of the tip of the branch or limb. the response is created to return the tree as much as possible to its normal state (Green et al., 1999). Formed wood is termed differently in softwood or hardwood. In the first, it is termed as compression wood while in the latter it is tension wood. Reaction wood has many different or abnormal properties than normal wood in respect to chemical, physical, anatomical or mechanical factors including high density and specific gravity.
2.11.2.1 Compression Wood

Compression wood is commonly formed in gymnosperms where it is found on the lower side of the leaning branch or stem. This wood usually has higher density and compression strength than the regular wood, but on the other hand, it has lower tensile strength. Under the bending test, this wood has a lower modulus of elasticity and modulus of rupture (Reivers & Umney, 2001). Its specific gravity is about 30-40 percent higher than normal wood (Green et al., 1999). Anatomically this wood has considerably wide growth rings on the lower side of the leaning limb or stem, and narrower growth rings on the upper side.

Tracheids are shorter and are about 30 percent less than the normal wood with folded and bent tips. There is also an absence of the S3 layer in the secondary wall, and the cellulose microfibrils have an angle of about 45 degrees which significantly affect the longitudinal shrinkage that can reach 1-2%. This compares to 0.1-0.2% of the longitudinal shrinkage common to the normal wood. Compression wood has up to 10 percent less cellulose than normal wood and higher lignin and hemicellulose (Schweingruber, 2007).

2.11.2.2 Tension Wood

Tension wood is the reaction wood occurring within the angiosperms. It contradicts compression wood in some properties: the tension strength and cellulose proportion of this wood are higher while the compression strength is lower than normal wood (Dinwoodie, 2001). Similarly, it has specific gravity ranges from 5-10 percent higher than the normal wood, which can be tripled in some cases (Green et al., 1999; Schweingruber, 2007)
3 Chapter 3: Wood deterioration and degradation

Wood starts ageing immediately after cutting the tree and this process continues with the passage of time. The ageing process is influenced by the combined effect of many variables including surrounding factors (weathering or microorganisms), wood species and the nature of the environment. Deterioration occurs through several basic modalities include: chemical change, biological decay, and mechanical or physical damage. Artefacts for example can be buried in a terrestrial or a marine environment which can also be aerobic or anaerobic. Some specimens last for thousands of years in a dry desert under ambient conditions that discourage the growth of microorganisms (Fengel, 1991, pp. 153-154; Unger et al., 2001, p. 11). In this chapter, information about wood degradation and different deterioration phenomenon will be provided with the description of wood behaviour and the relation between chemical composition and other characteristics.

3.1 Wet and waterlogged environment

Microbial decay in aquatic environments is slow, resulting in timescales extending over centuries for the progressive degradation of waterlogged archaeological wood. Typically the breakdown of polysaccharide components of the wood cell walls in large timber structures (Landy et al., 2008) causes a loss of cellulose and hemicellulose leading to the formation of water-filled cavities (Colombini et al., 2009).

3.1.1 Chemical changes (Chemical degradation)

Chemical degradation in waterlogged archaeological wood can be summarised as hydrolysis process which follows the swelling of the secondary walls loosening the microfibrils and initiating access to the cell wall component (Fengel, 1991, p. 161). The process of hydrolysis prefers carbohydrates and polysaccharides components causing micromorphological changes that impact on the anatomical and physical characteristics of the cell wall leaving a material with lower levels of carbohydrates, higher lignin levels and ash content than typical fresh wood (Passialis, 1997, p. 111).
For example, wooden artefacts may contain only lignin with no presence of holocellulose (Christensen et al., 2006). Whereas with fresh wood, holocellulose content (the total amount of cellulose and hemicelluloses) is about 70%, and the lignin content is about 30%. Where wood has been buried under the ground, the holocellulose is considerably decomposed and tends to disappear (Yohsei, 2005).

Acid waterlogged wood deteriorates due to sulfuric acid produced from either chemical damage through the acid hydrolysis of cellulose, or physical damage of the wood’s pore structure because of the crystallisation of the sulphate minerals (Giorgi, Chelazzi, & Baglioni, 2005).

The degradation sequence of waterlogged archaeological wood starts from the lumen-side toward the middle lamella (Fengel, 1991, p, 161), and the loss of the secondary cell wall because of the hydrolysis of carbohydrates ending with the collapse of the residual lignin skeleton (Hoffmann & Jones, 1990). According to Hoffmann and Jones (1990), differences in the texture and colour of oak samples attributed to the chemical degradation of the softer parts in the outer area. The loss of carbohydrates in these areas caused the S2 and S3 layers to shrink and detach from the S1 layer. The study reported that the degradation process in angiosperms starts by changes to the lignocellulose complex ultrastructure followed by attacking the cellulose in the S2. Following this the lignin debris from S1 becomes loose and shrinks leading to the degradation of the S1 layer and eventually the whole system collapses with only the middle lamellae left. The degradation process occurs in one cell completely then moves to the adjacent cell.

In considering these processes, hemicellulose is usually the first compound that starts to degrade (Kohdzuma, Minato, & Katayama, 1996, pp. 681-678) as it is the weakest constituent against acid hydrolysis whereas crystalline cellulose can endure longer periods (Blanchette et al., 1991). These characteristics relate to the chemical structures of both compounds as hemicellulose is composed of several glycosyls or sugars with many short-branched chains while cellulose is formed only from one type of glycosyl and the crystalline one has no short-branched chains (Gao et al. 2014, p, 499).
The resistance of cell wall chemical components may be expressed in ascending order as; p-Hydroxyl and vanillyl lignin structural units; syringyl lignin units; pectin; cellulose and hemicelluloses. The degradation process starts from the cell lumina toward the secondary wall which suggests the hydrolysis of the wood compounds giving that biological deterioration degrades hemicellulose and cellulose (and sometimes lignin) simultaneously.

The lignin may also have insufficient methoxyl groups that have degraded side chains and tend to be more condensed (which is described as a start of the coalification process) leading to the weakening of the middle lamellae and causing alterations and swelling of the cell or in some cases collapsing it. The previous study (Gao et al., 2014) also confirmed the relationship between the chemical composition of the cell wall and its anatomical structure where the deformation of the secondary wall is proportional with degradation of the cellulose.

A study of waterlogged *Paulownia spp.* by Fourier transform infrared spectroscopy (FTIR) showed that the chemical composition of the wood is substantially altered which can be seen in the depolymerisation and loss of crystallisation of the cellulose. The effect on hemicellulose was greater whereas lignin showed minimal change (Deng & Zhang, 2008).

The nature of the water and sediments where the wood is buried has a great impact on the degradation process as does the wood species, length of submersion and the condition of the original artefact. For example, wood can be preserved in good condition in an anoxic environment in the deep-sea water even after hundreds of years (Sandstrom et al., 2002; Wilson et al., 1993; Sandek et al., 2014; Passialis, 1997; Capritti et al., 2008). Moreover, the temperature of the burial site plays a catalyst role in the degradation process as warm water can encourage biological deterioration to occur (Wilson et al., 1993, p. 600). The degradation begins from the outer part into the core of the wood (Wilson et al., 1993; McConnachie et al., 2008) and degraded parts may appear weak, spongy or bulky with water while the inner part tends to be relatively fibrous, compact and resistant (Capritti et al., 2008). Some elements in water (iron, sulphur and acids) can also play a catalyst role and accelerate degradation. Acidic sites with the presence of iron and low sulphur can lead to the reduction in the molecular weight of hemicellulose and then decrease in the polymerisation of cellulose as a result of the oxidative process (Almkvist & Persson 2008; Sandström et al., 2002, Emery & Schroder, 1974).
Acceleration in the degradation process is seen when metal elements such as screws, nails or bolts remain attached to wood in wet environments. What happens is a cycle of degradation that starts with the degradation of metal from the acidity of the wood, and the consequential corrosion products of the metal reduce the wood strength. The degradation of both the wood and metal element eventually causes the weakening of the joints and will impact on the whole structure of the object.

Different metals can cause deterioration of wood in various ways as the wood degrades around the metal fastener. Accumulation of acid in the crevice between the fastener and wood is the cause of degradation in some metals. Acid accumulation increases when the chloride ions migrate to the crevice as a result of corrosion which increases in the seawater, and in the presence of iron the process is accelerated even more. The mechanism is slightly different in copper and copper alloys, as the corrosion product in the crevice will have an alkaline nature that degrades the wood eventually around the metal (Baker, 1974, 1980).

Loss of the wood polysaccharides is the main distinguished phenomenon of the waterlogged wood degradation that have been examined within several studies (Hoffman 1981; Hedges 1989; Tamburini et. al., 2014; Deng, 2008; Christensen et. al., 2006; Pizzo 2010; Bradet et. al., 2002; Wilson et al., 1993; Wilson et al., 1983; Bates et al., 1991; Blanchette et al., 1991; Lucejko et al., 2012; Passialis, 1997; Capretti et al., 2008; Ucar & Yilgor, 1995; Fengel, 1991; Giachi et al., 2003 and more).

Ucar and Yilgor (1995) showed that the softwood xylan side chain named as arabino-4-0-methylglucuronoxylan was preferentially cleaved and was more susceptible than the other soft polyoses mannan. The reduction in carbohydrates is directly proportional to the level of degradation, however, the most significant impact derives from loss of cellulose. As mentioned in Fengel (1991, 163), the study of 2,500 years old oakwood by Wazny (1976) identified two degraded zones: the highly degraded one had 2.5% cellulose and a lower lignin content than fresh wood, while the other had 7% cellulose and higher lignin content. The amount of polyoses, on the other hand, was similar in the two zones.

The extended preservation of wood artefacts in a wet environment will cause these polymers to leach and hydrate (Bardet, Foray, & Trân, 2002, p. 4389). On the other hand, in lignin, the main intermonomeric bonds can still exist which indicates the lower modification of the
waterlogged wood lignin (Colompini et al., 2007) which is sometimes identical to the fresh wood (Bardet et al., 2002). In addition, the molecular weight of the lignin could increase due to the decreasing of the phenolic groups and the possibility of forming interlignin bonds during the oxidation process (Colompini et al., 2007, 171-172). Hence the degradation of the wood carbohydrates does not necessarily indicate changes in the arrangement of the polymers chemical network (Berdet 2002, 4389).

Van Bergen and others (2000) study of archaeological oak in different environments provided evidence of the demethylation of the lignin syringyl units. This explained part of the degradation mechanism of the angiosperms lignin where the formation of 3-methoxyl-1,2-benzenediols is a degradation product of the 2-methoxyphenols units. The 3-methoxyl-1,2-benzenediols was found in fresh wood in small amounts that increased noticeably in the old waterlogged marine wood suggesting that demethylation starts in the very early stages of wood degradation. Loss of 2,6-dimethoxyphenol moieties is one of the most observed phenomena in the degradation of hardwood lignin. Selective removal of the syringyl-rich cell wall material is one of the mechanisms of this loss. The other is the formation of monomethoxyphenols (i.e. guaiacyl units) by demethoxylation which could be occur in a rapid one-step process or alternatively a long slow two-step process which starts with demethylation followed by dihydroxylation over millions of years to occur.

Cellulose degradation is the leading factor that impacts on wood alteration. Inorganic elements may substitute the organic matter of the wood depending on the nature of the water, or the soil within which the wood was buried. For example, wood can be capsulated by phosphate, silicates, calcium or iron (Cavallaro 2011, p: 454). These elements can impact the state of preservation of the excavated wood after isolating it from the original or the preserving environment which can lead to iron-crystallised oxidation reactions or acid hydrolysis of cellulose.

Furthermore, waterlogged wood may have a greater carboxyl content, especially the acid and salt carboxylic groups (where the first is mainly associated with the hardwood species). While holocellulose is the only factor that is responsible for cation exchange capacity ‘c. e. c’ which is used to measure and determine the environmental effect on the carboxyl content of wood. Its elevated levels in ancient wood accompanies the decrease in the amount of holocellulose
to about 16.1% may be attributed to the oxidative attack to the residual lignin (Giachi et al., 2003, pp: 80, 82).

Waterlogged wood tends to have less soluble extractives as some are dissolved in water. Over a period of 12 months hydrolysis of glycerides can be noticed with no changes to resin content (Fengel 1991, p. 160; Assarsson & Akerlund, 1967). Prolonged submersion in water not only extracts the water-soluble extractives but can also reduce the amount of organic soluble matter (Ucar & Yilgor 1995, p. 130). The mineral content in the wood increases over time during the aging process (Giachi et al., 2003, p. 78). The type of minerals and their quantities which may reach up to 19% depends on the environment and its composition. Iron, copper, silicon or calcium compounds, for example, can precipitate and crystallise in different places in the wood cells including the lumen or the cell wall itself (Fengel, 1991, pp. 165-166).

3.1.2 Physical and mechanical changes resulting from deterioration

As suggested by Rowell (1990, p. 421) the aging process affect the chemical and physical characteristics of archaeological wood. Changes in the chemical composition such as degradation of the cell wall matrix and the depolymerisation of the polysaccharides (cellulose and hemicellulose) and polyphenols (lignin) impact wood strength, integrity and aesthetics. Such characteristics can be seen when waterlogged wood is dried including shrinkage, checking or cracking. Degraded waterlogged wood has no tensile strength and can be easily squeezed to extract water from it (Hoffmann & Jones, 1990, p. 38).

As it is typically used in the conservation laboratories, the physical properties of the waterlogged wood are considerably evaluating the preservation state (Babinski et al., 2014, p. 372). The greater the decrease in wood mass and volume, the more deteriorated and porous it is and consequently the less basic density it has (Babinski et al., 2014, p. 373). Wood basic density (WBD) is directly related to wood moisture content (WMC). At the same time, wood strength can be decreased by the degradation of any of the main wood components (Bardet 2002, p. 4387).
Deteriorated waterlogged wood can be physically identified by the change in the colour that turns it from light to dark, and also it becomes softer, less dense with high moisture content (MC). The MC has been used as an indication of the degree of deterioration: the more moisture content the wood has, the more deteriorated it is. However, this percentage is not an absolute number reflecting the state of deterioration. Some samples can have up to 1000% moisture content in a good state while some other can show the degradation phenomena at 150 percent (Kohdzuma, 2014; Hoffmann & Jones, 1990; McConnachie, 2008). This increase in moisture content is a result of the reduction in the chemical composition and the loss of the chemical constitutes which forms voids or gaps that are consequently filled by water (Kohdzuma, 2014).

Furthermore, this increase in the moisture content, along with the resulting deformation that has occurred to the wood cell ultrastructure can leave irreversible changes in the appearance and dimensions of the artefacts such as cupping, wrapping, high shrinkage percentage, diamonding, splitting, disintegrating and may lead to physical collapse if not treated in the proper way (Passialis, 1997, p: 111).

The anisotropic properties of wood are worsened under the effect of draining water by drying if not correctly excuted. The shrinkage percentage differs according to the cutting direction: shrinkage is five times in the radial direction more than in the longitudinal and half that of the tangential direction. The loss of wood constituents will leave a very weak skeleton that cannot resist the loss of water and shrinkage can exceed 60% in some cases. Deformation in the case of waterlogged wood starts if the moisture content is over 30% of the standard fibre saturation point (FSP) when the wood starts to lose not only cell wall water but also the physical free water in the lumen, macro-spaces and the newly formed voids after deterioration.

The collapse of waterlogged wood after drying can be attributed initially to the deformation of the chemical composition of the cell-wall constitutes that are left it in a fragile state. As water tries to evaporate from the small pit between two cells, its high surface tension creates a pressure of attraction inside the cell which encourages influx of outside air to enter the cell. This air is itself blocked by the water surface tension in that pit which leads to buckling and deforming the cell with the loss of water (Kohdzuma, 2014). However, as a result of degradation of the cellulose that is characteristically in the secondary wall micro-fibrils the
anisotropic characteristics of the degraded wood are reduced (Macchioni 2003; Capritti et al., 2008, p: 876).

As the degradation of the three principal polymers continues, the damage to the wood cell wall extends and consequently the porosity will increase while the cellulose degree of crystallisation will decrease, which all eventually contribute to the collapse of the compression strength of ancient wood (Unger et al., 2001; Gao et al, 2014, p. 498).

3.1.3 Anatomical and morphological changes

Microscopic investigation plays a significant role in evaluating the deterioration and the preservation state of archaeological and old wood (Capritti et al., 2008, p. 869). For example, waterlogged wood is distinguished by the difference in hardness and colour in different places to form two or three distinctive zones. The harder zone has a woolly appearance while the softer one has a clear-cut appearance because of the degree of degradation that may have occurred to whole fibres (Hoffmann & Jones 1990, pp. 37-38). The degradation of the cell wall’s chemical composition also has its direct impact on the anatomical features of the waterlogged wood. Distortion of the secondary wall, middle lamellae or even the pits membrane are all morphological changes that can be identified under microscopic examination (Gao et al., 2014, p. 500)

Waterlogged oak shows evidence of losing the secondary wall of wood ultrastructure as this area absorbed the Astra blue dye which has large molecules (molecular weight (MW) 1000) and the whole tissue turned to brown to blue whereas fresh oak only absorbed the red chrysoidine-acridine (MW of chrysoidine, 249 and acridine red, 465). The loss of the secondary wall may be attributed to the swelling of the cell wall with the help of the hydrolysis of hemicellulose. In the more degraded soft part the S2 and S3 layers had shrunken and detached from the S1 layer with no evidence of fluorescence or birefringence as a result of losing almost all carbohydrates. By consisting of degenerated lignin skeletons of S2, the S1 in this stage still have some crystalline cellulose indicated by the birefringence. In the most degraded and softest parts of the sample, the S1 layer was disappeared with a brittle, weak middle lamellae and a residue of S2 in the lumina of fibre cells, while the S3 was still intact. Although wood may lose most of its constituents when submerged for long period, the shape can still be maintained by
the water filling the gaps created and supporting the fragile middle lamellae that left with the (Hoffmann & Jones 1990, pp. 39-45).

The microscopic study of waterlogged oak and ash wood by Hoffmann and Jones (1990, pp. 46-63) showed an abrupt, sharp transition between the soft degraded part and the hard-swollen sound parallel to the wood surface and this distinction has no relation to the anatomical features of the wood. Heavily degraded cells were adjacent to intact cells. That swollen fibre cell wall starts to break down from one cell layer to another, and the carbohydrates of one cell have to be dissolved entirely before beginning degradation in the next cell which can be caused by the differences in the lignification, the packing density of the lignocellulose complex and extractives contents that coating the cell wall. In the Dutch elm, there was a transition zone between the heavily degraded part and the slightly degraded one constituted by fibre cells. In poplar wood, latewood vessels and fibres showed more resistance than the earlywood elements. On the other hand, the softwoods (spruce) are more resistant, even after hundreds of years of waterlogged conditioning; showing weakening of the S1 but no major swelling to the secondary walls, and no noticeably degraded different zones. In this case, the degradation starts in particular cells and the transition area that increases over time till the whole tissue degrades eventually. Even though the resin canal parenchymatous cells and the ray cells stay intact.

The degradation progress in hardwood starts by loss of the lignocellulose ultrastructure after swelling of the secondary wall by water. This is followed by hydrolysis of the hemicellulose and attacks on the cellulose in S2 and S3 either from the lumen side or the border between S1 and S2. The process decreases its crystallinity and the degree of polymerisation. While the lignin skeleton turns granular and may detach from S1 (which in sequence collapses) only the middle lamellae stays to keep the wood shape with water (Hoffmann & Jones 1990, p. 63).

According to Hoffmann & Jones (1990), different studies show that cell corners, middle lamellae and pits membrane are the most durable components against ultra violet (UV) light as they have encrustations that insulate the relatively low carbohydrates content and protect it against the hydrolysis.
3.1.4 Bio-deterioration:

When the tree dies or is cut, the ageing process starts as a part of a natural cycle to return to its original compounds. Microorganisms are involved in this process under the right conditions as a part of our ecosystem (Fengel, 1991, p. 154).

Biological factors mainly concern the ability of microorganisms to attach wood which in turn depend on the environment conditions: whether the object was in wet soil or submerged underwater, whether aerobic or anaerobic conditions apply in addition to the temperature and pH factors (Gilbertson, 1980; Blachette et al., 1990). It is known that brown rot fungi are the most dangerous organism that attacks wood and that it can destroy it faster than soft rot or white rot varieties. However, in some anaerobic cases, bacteria play a leading role in the deterioration process (Kim & Singh 2000, pp. 135-136). Tolerating the absence of oxygen is different from one microorganism to the other in the following order: erosion bacteria, tunnelling bacteria, soft rot fungi and the brown rot fungi (Kim & Singh 2000, p. 136). This degradation of wood is mainly due to the enzymatic processes of biotic agents (fungi and bacteria) (Capretti et al., 2008).

Biodegradation can be further classified into two main categories: fungal decay and bacterial decay. The following provides a summary of the main organisms that attack wet and waterlogged wood.

3.1.4.1 Fungal decay

Fungi are considered to be the most dangerous destroying enemy against wet wood. They can leave the wood cracked, spongy, stained and rotted. The colour of wood after attack is used to differentiate between the main types of wood destroying fungi. It can be left in a brown colour as with brown rot, or a whitish colour as with white rot. Also, the wood can be stained by different colours depending on the attacking fungi which may occur under conditions of suitable moisture content. Dry environments or excessive moisture can significantly restrict the activities of the most common fungi (brown rot and white rot) which destroy wood structure rapidly. These conditions, on the other hand, cannot prevent the colonisation by other slower fungi (soft rot) which can survive in more extreme conditions (Blanchette et al., 1991, p. 4). Morphological changes in the ultrastructure of wood have been used to identify and
differentiate between various kinds of biodeterioration, evidence of particular fungal decays and distinguish biodeterioration from non-biological processes (Blanchette et al., 1990; Blanchette et al., 1991; Blanchette, 2000; Macchioni et al., 2013; Capretti et al., 2008; Erikson et al., 1990; Nilsson et al., 1990; Singh & Butcher 1990; Obst et al., 1990; Kim & Singh, 2000; Schwarze, 2007; Schmitt et al., 2005; Powell et al., 2001; Macchioni et al., 2012; Blanchette et al., 1990). Degradation usually occurs by enzymes secreted by the fungi hyphae which can catalyse the chemical reactions that may lead to the modification of the different wood components.

### 3.1.4.1.1 Wood degradative fungi (decay fungi).

Wood degradative fungi or decay fungi may be classified into three subcategories: brown rot, white rot and soft rot. This classification has been used in relation to the colour and texture of the infested wood and has yet to be generally accepted (Schmidt, 1994; Uger et al., 2001; Schmidt, 2006).

#### 3.1.4.1.1.1 Brown rot

Brown rot decay is caused by types of fungi belonging to the basidiomycetes (such as *Antrodia vaillantii, Oligoporus amarus* and *Gloeophyllum trabeum*). They mainly attack and depolymerise the carbohydrates leaving the lignin unaltered, providing the wood is brown colour after the oxidation of the lignin skeleton is left exposed (Unger et al., 2001; Illman, 1991; Schmidt & Czeschkli, 2006). Some studies suggest the that metabolism of lignin or the demethylation of lignin phenolic and nonphenolic units occurs in conjunction with the depolymerisation of polysaccharides (Blanchette et al., 1990). Wood that is attacked by this kind of fungi is cracked, fragile and after drying it will have many cracks along and across the fibres resulting in a cubic deterioration feature (Fig. 22). Wood tends to lose a considerable percentage of its strength birefringence as a result of the degradation of cellulose with the increase in the shrinkage ratio even after a short period of attack by these fungi however the wood may be in the same physical outside appearance. Eventually wood becomes very weak and brittle that consists mainly of lignin which can be crumbled by the slightest touch.
The hyphae of the fungi colonise softwood tracheids primarily from the cell lumen attacking the S2 layer. It then proceeds to the S1 and S2 layers. In the progress, the deterioration of the cell wall becomes porous, and the middle lamellae and secondary wall layer become hardly distinguishable.

3.1.4.1.1.2 White rot

As with brown rot, the name of white rot came from the appearance of wood after the attack by these fungi which typically leave the wood in a light colour due to fungi associated with the basidiomycetes family mainly and rarely with ascomycetes family. These fungi attack angiosperms more often than gymnosperms where they attack the syringyl lignin. This substance degrades more easily than the guaiacyl lignin which is only presents in gymnosperms (Kim & Singh 2000; Blanchette et al., 1990). They can attack all wood compounds (i.e.
Trametes versicolor) simultaneously at the same time, or they can be selective (i.e. Phellinus pini) by choosing just lignin to attack leaving white coloured pockets that have either detached cells or cells without middle lamellae. However, in general they are all attacking the lignin (Blanchette et al., 1990, pp. 144-146). This type also produces what is known as consecutive attack (Unger et al., 2001) in which the fungi attack lignin, then the cellulose and hemicellulose. The resistance of wood elements to white rot is different in the cell itself and between the different cell types. White rot erodes the cell wall and reduces its thickness (Fig. 23). The cell corners show high resistance compared to other parts of the cell because of the high lignin content. The fibre cells of the angiosperms are more susceptible than the tracheids of the gymnosperms and then the vessels of the angiosperms which show more durability than the fibre cells and ray cells because of their high lignin content. Orientation in the cell is also a factor as well as the monomer composition of the lignin.

Brown rot and white rot require oxygen to grow however they can tolerate very low oxygen concentration. They also need sufficient moisture content that should be above fibre saturation point (over 28%) and below the total saturation of the wood (Blanchette et al., 1990). The optimum temperature for white and brown rot basidiomycetes fungi is between 25 and 30 °C and optimum pH of 3.5-5.5.
3.1.4.1.1.3 Soft rot

The name soft rot derives from the soft state of wood when it is damp or humid. It caused by fungi that belong to Ascomycota and Deuteromycota (Goodell, Qian, & Jellison, 2008; Lee, 2000) such as Chaetomium and Ceratocystis species (i.e. Chaetomium globosum). Soft rot fungi can survive in extreme conditions compared to the brown rot and white rot fungi. They also attack all wood components (mainly cellulose and hemicellulose) and modify the lignin (Blanchette, 2000). This type of rot is often associated with wood degrading bacteria (Kim & Singh, 2000). Soft rot fungi can tolerate higher and lower pH value than the white or brown rot fungi. It occurs mainly by the attack of about 300 different species of a total of 1600 species of ascomycetes and deuteromycetes.

The degradation pattern of the soft rot can be divided into two types (Daniel & Nilsson, 1998; Blanchette, 1990; Nilsson et al., 1989; Blanchette, 2000; Goodell et al., 2008). The first type is characterised by very thin fungi hyphae that penetrates the secondary wall from the lumen and arrive in the S2 wall. They then start making L shape by penetrating in a parallel direction to the wood fibres and the cellulose microfibrils, or by making a T shape by producing hyphae branches alongside the S2 layer. This creates chains of cavities that have conical ends by enzymatic reaction around the hyphae. The second type mainly occurs in hardwood and has an erosion feature that is distinguished by the erosion of the secondary wall which is similar to the eroding effect of some types of bacteria and the white rot fungi (Kim & Singh 1990; Goodell et al., 2008). It leaves eventually the middle lamellae and part of S1 layer with similar mechanism to that produced by white rot with the different of degrading the middle lamellae and S1 in case of white rot. Crystalline cellulose typically shows more resistance to soft rot than the amorphous region which was spotted as demonstrating a greater degree of polymerisation.

Soft rot decreases the strength of wood significantly in the advanced stage of deterioration as a result of degrading the cellulose and forming cavities in the secondary wall. Timbers infected with soft rot appear normal in the first stage as the decay features cannot be spotted by the naked eye. However, the decay can proceed inside the wood itself and cause sudden failure of the object or structure (Fig. 24).
3.1.4.1.2 Wood staining fungi and moulds

These fungi are not classified as destructive as they do not penetrate the wood ultrastructure or impact on the mechanical strength of wood. Instead, they stain and dye the wood different colours according to the fungus type or the substrate itself. These fungi feed on the free sugars and nutrients that are already available in the parenchyma cells and they require very high moisture content with optimum 95% and 20-40 °C temperature. When the moisture content lowers to 65% the activities of these fungi decrease (Blanchette, 1995).

3.1.4.1.2.1 Stain fungi

Stain fungi also belong to the Ascomycota and Deutromycota subdivisions of the Plant kingdom. They grow on the surface of the wood and their hyphae can usually penetrate in the sapwood feeding on sugars, starch, proteins and other ready nutrients in the parenchyma cells or resin canals. Irreversible discolouration is caused by the fungi hyphae, spores pigments or extracellular pigments. Blue stain is the most common type as it is produced by hundred different species of fungi and colonises both softwood and hardwood. The hyphae are large in diameter compared to the brown rot or the white rot hyphae and have a blue to grey-black colour. Although these fungi do not have an enzymatic destroying impact on the cell wall and do not affect the wood strength, they may cause a high aesthetic impact on the appearance of the works of arts. A blue stain caused by *Aureobasidium pullulans* can cause severe damage to
the painted wooden surface including paint flaking and discolouration (Unger et al., 2001, pp. 107,123; Blanchette, 1995). On the other hand, the green stain created by Chlorociboria was popular with artists in the fifteenth and sixteenth centuries to develop a very durable and resistant green for natural scenery of trees and leaves in different artworks (Blanchette, 1995).

3.1.4.1.2.2 Wood Moulds

Wood moulds only grow on the surface of the wood, and they belong to the Ascomycota and Deuteromycota fungi. They do not impact the wooden strength as they do not penetrate into the wood. They have no colour usually and discolouration is caused by the accumulation of the spores on the wood surface. They can be a reliable indication of further possible decay as they may be followed by more dangerous stain and destroying fungi. Moulds can colonise not only wood surfaces but also paint surfaces and varnishes. Moulds (i.e. Aspergillus fumigatus and Aspergillus niger) have to be dealt with precaution due to health impacts, and they usually have a characteristic odour (Unger et al., 2001, pp. 107-108, 131).

3.1.4.2 Bacterial decay:

Bacteria has been given less emphasis in the context of wood biological deterioration. It is typically considered to play a secondary role in the decay process however in some cases where the wood is preserved under anaerobic conditions bacteria can be the main factor in wood degradation (Kim & Singh, 2000, p. 136; Landy et al., 2008; Singh & Wakeling, 1997). Degradation of bacteria is slow compared to fungal decay (Blanchette et al., 1990). Bacteria attacking wood can be divided into two main categories: pit membrane degrading bacteria and cell wall degradating bacteria (Unger et al., 2001; Blanchette et al., 1990) plus scavenger bacteria that attack already decayed wood (Blanchette et al., 1990; Blanchette, 1995; Blanchette, 2000; Blanchette, 2003). It has also been shown that some species of anaerobic bacteria can slowly degrade waterlogged wood even under near anoxic conditions, eroding mainly the cellulosic components as the source of nutrients (Modugno et al., 2008).
3.1.4.2.1 Pit membrane and Scavenger bacteria

Pit membrane bacteria usually attack softwood more than hardwood and sapwood more than heartwood. After a short period of infection, they increase the porosity of wood by degrading the pit membrane of tracheids and ray parenchyma (Blanchette, 1995; Blanchette et al., 1990; Unger et al., 2001). These bacteria select regions which are rich in pectin and cellulose and have no lignin in the pit membrane to degrade including the margo and torus (Jurgens & Blanchette, 2005). Scavenger bacteria can survive in anaerobic conditions, and they usually follow the tunnelling and erosion bacteria in the attack which increases the porosity of the cell wall and makes it difficult to identify the initial cause of deterioration (Blanchette et al., 1995; Jurgens & Blanchette, 2005).

3.1.4.2.2 Erosion bacteria

Erosion bacteria which can be divided into two divisions according to the shape of the troughs they make when eroding the cell wall: striped (strained) bacteria and conical erosion bacteria (Kim & Singh, 2000). They attack the cell wall of both softwood and hardwood (Unger et al., 2001), which can differentiate them from the eroding soft rot fungi that attack only hardwood (Blanchette et al., 1990). They are considered one of the dominant deterioration factors in marine environments (Singh & Kim, 1997) as they can tolerate less oxygen concentration than the tunnelling bacteria (Björdal, 2000). They are identified by the grooves and troughs they make which start from the lumen toward the compound middle lamellae where they attach by the formation of glycocalyx (Landy et al., 2008) eroding and thinning the cell wall a groove-like manner, although they usually do not cause significant damage to the middle lamellae or S3 layer.

In the waterlogged and anaerobic condition, the cause uneven degradation for the S2 layer consisting of an amorphous residual in the cell wall and bacteria (Blanchette, 1995; Unger, 2001; Blanchette et al., 1990). This type of decay can be identified by its nonhomogenous distributed degradation pattern where untouched fibre can be found adjacent to extremely degraded ones. Upon drying, they cause irreversible collapse to the S2 layer that supports the remaining middle lamellae (Blanchette et al., 1995).
3.1.4.2.3 Tunnelling bacteria

These bacteria adhere to the lumen side by extracellular glycocalyx (Landy et al., 2008) and to the secondary wall through bordered pit membrane champers when the lumen is blocked by extractives (Jurgens & Blanchette, 2005). In advanced stages, the attacked moist wood looks very soft and dark with a butter or granular texture. In earlier stages the wood could take light yellow or light brown colour (Blanchette et al., 1990).

The bacteria attack the carbohydrate-rich S2 layer and degrade all the secondary cell wall layers without following the orientation of the cellulose microfibrils (Jurgens & Blanchette, 2005). To a lesser extent, they also attack lignin areas like the middle lamellae and sometimes the bordered pit membranes (Blanchette 2000, p. 194). The degradation is characterised by minute tunnels in the secondary wall with a single bacterium in the top of each tunnel. With the division of the single-cell bacteria, more branches of tunnels generate and in the advanced stage of deterioration, degradation accumulates in central area with many irregular branches of fine narrow tunnels (Blanchette, 2000; Unger et al., 2001; Blanchette et al., 1990; Landy et al., 2008, p. 107). Tunnels created by these bacteria have bands or crescent-shaped walls making them very distinguishable (Kim & Singh, 2000).

3.1.4.2.4 Cavitation bacteria

Cavitation bacteria attack the carbohydrates in the S2 layer of the secondary wall gaining entrance by making a small hole in the S3 layer without degrading it, or via direct penetration through pit border membrane chamber forming cavities with angular diamond or irregular shapes. These shapes increase in size with increasing numbers of bacteria. These cavities can be perpendicular or parallel to the cell wall axle. After degrading the polysaccharides in the S2 layer which provides the support to the S3 layer, the latter layer collapses consequently. The cavities of this kind of bacteria can further extend to the S1 layer (Blanchette, 2000; Blanchette et al., 1990; Jurgens & Blanchette, 2005; Unger et al., 2001; Landy et al., 2008; Singh & Butcher, 1991; Kim & Singh, 2000).
3.1.4.3 Insects, marine borers and crustaceans

3.1.4.3.1 Wet (damp)/ damaged wood insects:

Insects attacking damp, decayed or wet wood are not as proliferate as those infesting dry wood. This section will focus on insects that need some source of dampness, high moisture content of wood or prior decay in order to attack wood. These insects belong to Coleoptera (beetles) and Isoptera (termites) as the foremost two groups that destroy wood plus the wood wasps.

3.1.4.3.2 Destroying insects

Coelostethus pertinax or known as the common house borer is one of the beetles that attacks and destroys damp wood. It belongs to Anobiidae family and prefers softwood that has been decayed already by fungi mainly in the earlywood parts. Another more prominent and familiar Anobiidae insect is the death watch beetle (Xestobium refouillosum). The common name derives from the sound that the beetle makes when trying to attract the other sex during the mating season. Unlike most of the wood destroying insects, the wander larvae of the death watch beetle bore deep into the wood causing serious damage especially in optimum conditions of 22-25 °C and 80% relative humidity. Earlywood of the hardwoods, commonly oak, is the main area that is attacked, while the latewood is more resistant. Attacks have often occurred in damp, wet seasoned structural timbers, although it is not common in the wooden sculptures or furniture. The presence of the decay fungus Donkioporia expansa, which is the often found with this pest, enhances the development of the beetle however it is not necessary for its evolution or growth (Umney & Rivers, 2003, pp. 299-300).

Subterranean termites belong to different families and a widespread around the world. They require a source of moisture which can come from the earth where they nest which can be 100 meters away from the attacked wood (Unger et al., 2003, p. 77). Some species such as Termitidae termites require previous damage by fungi, or they can make a fungal garden in the nests, as they do not have symbiont flagellates and need cellulose that is more digestible. On the other hand, others have the symbiont flagellates in their intestines such as the Rhinotermitidae termites, and they prefer moist wood. Middle lamellae of latewood which is surrounded with earth particles is one of the characteristics of the subterranean termites where
they prefer earlywood with no faecal pellets in the feeding space. Contrary to what occurs in the case of dry-wood termite attack.

3.1.4.3.3 Non-destroying insects

There are other species that use wood for different purposes. *Dermestes Lardarius* L or larder beetle is one of these insects that attack materials of animal origin and can also be found in textiles, books and other art objects where they also use wood for pupation. This beetle attacks only already decayed wood. *Niptus hololeucus* (Fald.) is another no-destroying insect that attacks the few millimetres of wood that already deteriorated by fungi or other pests to feed on animal products or grains. Similarly, the larvae of *Nacerdes melanura* (L.) penetrates about 10 millimetres in the surface of decayed softwood or hardwood that are in contact with a source of water periodically (Unger et al., 2001, pp. 80-82).

3.1.4.3.4 Marine borers and crustaceans

When conditions are favourable, marine borers and crustaceans can cause severe damage in short periods of time by insects that belong to the Bivalvia and the Crustacea classes. The degree of water salinity, water temperature and oxygen level are all factors that control their activities.

Teredinidae family or shipworms which belong to the Bivalvia are more active in warm water than cold water and can be hazardous even in salty water (Unger et al., p. 134; Blanchette et al., 1990). The most important genera belong to the Teredinidae are the Yeredo and Bankia; while in the Crustacea the deterioration rate is slower and does not penetrate deeply into the wood surface tunnelling that is parallel to the surface caused by the gribbles of the Limnoridae family (Unger et al., p. 134, Lopez-Anido, 2004).
3.2 Dry wood

Wood is a biodegradable material that decay by the effect of the different environmental factors including temperature, humidity, pollutants, light or solar irradiation, ozone content, microbiological factors and/or types and species of wood. The combination of these factors leads to different degradation processes chemically, physically or microbial (Popescu et al., 2007). By comparison to waterlogged wood, dry wood can stay in a better-preserved condition over time due to the relative absence of the favourable factors such as moisture and biological agents (Schmitt et al., 2015). Nonetheless, in some cases the wood in a dry area like in Egypt can be found so fragile and brittle and it is very difficult to take a sample from (Crestini et al., 2009). This example is apparent in some samples of this work (as in the case of EG-SAQ-5 and EG-SAQ-8 samples examined in this thesis).

3.2.1 Chemical changes

Archaeological wood in dry environments has less intention in comparison with waterlogged wood that may be due to the slow rate of deterioration. The impact of ageing on wood when exposed to environmental factors in dry conditions is minimal (Unger et al., 2001, p. 11). Wood is capable of absorbing sunlight which creates free radicals as a result of degradative chain reactions and leads to changes in wood colour. The presence of lignin in wood is responsible for light absorption and the formation of the free radicals (Fengel, 1991; Caba et al., 2007; Feist, 1990; Williams, 1986; Anderson, 1991; Williams, 2005; Hon, 2000).

Chemical alterations can also result from the reduction of moisture content, access to oxygen and enzymes of microorganisms. These chemical modifications include reduction of the fats, resins and waxes in the first three to four months followed by a reduction in the fatty acids, higher alcohols, hydrocarbons and resin acids (Fengel, 1991, p. 155).

The depolymerisation of lignin and other cell wall constituents, followed by the subsequent break down of the wood microstructure is associated with weight loss of wood. Temperature can play the role of a catalyst in photochemical reactions (Feist, 1990). Air pollutants such as
sulphur oxides, nitrogen oxides can break the double bond in the cellulose chain to produce shorter chains with a low molecular weight which can lead the fibre to be brittle and yellow (Thomson, 1986).

Fengel and Strckhlhuber (1985) in their study on 15-year-old seasoned pine wood showed an increase in the oxidation degree of lignin of sapwood and heartwood, however, no noticeable changes found in the percentage of wood components in 365-year old wood samples (Fengel, 1991, p. 156).

During the natural ageing process, the acetic acid formed by splitting of the hemicelluloses O-acetyl groups initiates a slow hydrolysis process that can decrease the polyose content of wood. The partly oxidised extractives also removed by evaporation, diffusion in the direction to the surface or by water movement.

In the dry conditions, and after few hundred years, the cellulose may retain its crystalline structure with no obvious difference to the cellulose of a fresh wood while the amount of the acid-soluble lignin decreases. On the other hand, there is could be an increase in the lignin degree of condensation and the poly-conjugated systems numbers as a sequence of the oxidation process (Ganne-Chédeville et al., 2012; Popescu et al., 2009, p. 1359; Popescu et al., 2007).

According to Nakao et al. (1989) the crystallinity of cellulose treated with heat, as an artificial ageing, increases during the first stages between (150-200 °C) but this modification changes rapidly at higher temperatures. Fengal (1991, p. 163) according to the previous study also mentioned that softwood cellulose crystallinity increases in the first 500 years and then remains constant for about 2,000 years approximately. That cannot be taken as a general rule as the cellulose crystallinity of hardwood decreases continuously from the early stages of the ageing process. Guaiacyl lignin according to Fengal (1991) is more resistant to ageing than syringyl lignin which can give the softwood fibres and the hardwood vessels the ability to stay longer compared to the hardwood fibres.

On his study on 5000 years old Egyptian *Acacia nilotica* and *Tamarix spec* blanks, Fengel (1991, p. 157) found no big change in the cellulose amount with of 55.2% and similar for lignin with 39.6%, but the amount of the hemicellulose was dropped significantly to 5.2% only.
A study by X-ray photoelectron spectroscopy (XPS) on limewood (*Tilia cordata*) from painted supports revealed that the ration of the carbon to oxygen O/C increases by time with the increase in the oxygen atoms and the decrease in the carbon atom.

Table 2: Semiquantitative analysis of lignin and carbohydrate components obtained by Py-GCMS of aged lime wood samples (% of pirogram peak area) (Popescu et al., 2007, p. 73)

<table>
<thead>
<tr>
<th>Compound</th>
<th>Reference</th>
<th>150</th>
<th>180</th>
<th>180 (insects)</th>
<th>270</th>
</tr>
</thead>
<tbody>
<tr>
<td>Carbon dioxide</td>
<td>7.14</td>
<td>8.87</td>
<td>10.2</td>
<td>6.99</td>
<td>10.00</td>
</tr>
<tr>
<td>Lignin peaks</td>
<td>18.3</td>
<td>22.1</td>
<td>25.8</td>
<td>26.25</td>
<td>26.27</td>
</tr>
<tr>
<td>Guaiacyl(G)type phenols</td>
<td>7.14</td>
<td>8.25</td>
<td>10.1</td>
<td>10.11</td>
<td>9.5</td>
</tr>
<tr>
<td>Guaiacol</td>
<td>0.95</td>
<td>1.40</td>
<td>2.26</td>
<td>2.39</td>
<td>1.05</td>
</tr>
<tr>
<td>Guaiacol, 4-methyl-</td>
<td>1.20</td>
<td>1.20</td>
<td>1.01</td>
<td>1.24</td>
<td>0.88</td>
</tr>
<tr>
<td>Guaiacol, 4-ethyl-</td>
<td>1.24</td>
<td>0.97</td>
<td>0.90</td>
<td>0.68</td>
<td>1.26</td>
</tr>
<tr>
<td>Guaiacol, 4-vinyl-</td>
<td>1.18</td>
<td>1.66</td>
<td>1.90</td>
<td>1.96</td>
<td>1.51</td>
</tr>
<tr>
<td>Eugenol</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.44</td>
</tr>
<tr>
<td>Isoeugenol (<em>trans</em>)</td>
<td>1.57</td>
<td>1.91</td>
<td>2.08</td>
<td>2.06</td>
<td>1.98</td>
</tr>
<tr>
<td>Vanillin</td>
<td>0.53</td>
<td>0.54</td>
<td>0.73</td>
<td>0.65</td>
<td>0.59</td>
</tr>
<tr>
<td>Homovanillin</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>0.50</td>
</tr>
<tr>
<td>Guaiacyl acetone</td>
<td>0.47</td>
<td>0.57</td>
<td>0.64</td>
<td>0.54</td>
<td>0.70</td>
</tr>
<tr>
<td>Coniferylaldehyde</td>
<td>–</td>
<td>–</td>
<td>0.64</td>
<td>0.59</td>
<td>0.59</td>
</tr>
<tr>
<td>Syringyl (S) type phenols</td>
<td>11.16</td>
<td>13.8</td>
<td>15.7</td>
<td>16.14</td>
<td>16.77</td>
</tr>
<tr>
<td>Syringol</td>
<td>2.52</td>
<td>3.58</td>
<td>4.77</td>
<td>5.03</td>
<td>3.75</td>
</tr>
<tr>
<td>Syringol, 4-methyl-</td>
<td>1.58</td>
<td>1.77</td>
<td>1.84</td>
<td>1.78</td>
<td>2.46</td>
</tr>
<tr>
<td>Syringol, 4-vinyl-</td>
<td>2.37</td>
<td>3.18</td>
<td>3.63</td>
<td>3.82</td>
<td>4.00</td>
</tr>
<tr>
<td>Syringol, 4-allyl-</td>
<td>0.88</td>
<td>1.02</td>
<td>1.00</td>
<td>0.97</td>
<td>1.36</td>
</tr>
<tr>
<td>Syringol, 4-propenyl-(cis)</td>
<td>3.05</td>
<td>3.44</td>
<td>3.44</td>
<td>3.46</td>
<td>3.84</td>
</tr>
<tr>
<td>Syringaldehyde</td>
<td>0.76</td>
<td>0.88</td>
<td>1.02</td>
<td>1.08</td>
<td>1.36</td>
</tr>
</tbody>
</table>

The main carbohydrates peaks

<p>| Propanal-2-one                  | 1.82      | 1.77| 1.86| 1.83          | 1.89 |
| 2,3-Butanedione                 | 6.10      | 6.18| 6.88| 6.84          | 6.56 |
| Hydroxyacetaldehyde            | 2.48      | 1.46| 1.03| 0.94          | 0.87 |</p>
<table>
<thead>
<tr>
<th>Compound</th>
<th>Value 1</th>
<th>Value 2</th>
<th>Value 3</th>
<th>Value 4</th>
<th>Value 5</th>
</tr>
</thead>
<tbody>
<tr>
<td>Acetic acid</td>
<td>22.26</td>
<td>15.8</td>
<td>14.2</td>
<td>13.80</td>
<td>14.02</td>
</tr>
<tr>
<td>Hydroxypropanone</td>
<td>2.65</td>
<td>3.04</td>
<td>2.95</td>
<td>2.68</td>
<td>2.19</td>
</tr>
<tr>
<td>3-Hydroxypropanal</td>
<td>2.98</td>
<td>2.10</td>
<td>1.91</td>
<td>1.82</td>
<td>1.64</td>
</tr>
<tr>
<td>Butanedial</td>
<td>4.38</td>
<td>4.65</td>
<td>3.98</td>
<td>3.76</td>
<td>3.45</td>
</tr>
<tr>
<td>2-Furaldehyde</td>
<td>2.49</td>
<td>2.66</td>
<td>2.73</td>
<td>2.69</td>
<td>2.50</td>
</tr>
<tr>
<td>Dihydro-methyl-furanone</td>
<td>1.55</td>
<td>1.35</td>
<td>1.15</td>
<td>1.04</td>
<td>1.10</td>
</tr>
<tr>
<td>(5H)-Furan-2-one</td>
<td>1.25</td>
<td>1.15</td>
<td>1.03</td>
<td>1.01</td>
<td>0.92</td>
</tr>
<tr>
<td>1,5-Anhydro-4-deoxy-pent-1-en-3-ulosene</td>
<td>1.40</td>
<td>1.74</td>
<td>1.48</td>
<td>1.78</td>
<td>2.26</td>
</tr>
<tr>
<td>2-Hydroxy-1-methyl-1-cyclopentene-3-one</td>
<td>1.51</td>
<td>1.59</td>
<td>1.60</td>
<td>1.57</td>
<td>1.63</td>
</tr>
<tr>
<td>Levoglucosan</td>
<td>3.18</td>
<td>3.44</td>
<td>1.83</td>
<td>1.75</td>
<td>3.48</td>
</tr>
<tr>
<td>Total carbohydrates peaks</td>
<td>62.08</td>
<td>52.9</td>
<td>50.1</td>
<td>49.20</td>
<td>50.67</td>
</tr>
</tbody>
</table>

That may be a result of the degradation of the hemicellulose and amorphous cellulose where crystalline cellulose and lignin shows more resistant respectively. It was noticed that the most significant figures were in the 150 years old samples and the authors attributed that to the degradation and the loss of the low molecular weight compounds such as extractives, hemicellulose and amorphous cellulose in the first period of aging as a result of oxidation and hydrolysis surface reactions then the wood starts to change slowly (Popescu et al., 2009).

In a similar study (Inari et al., 2006), heartwood part of beech wood was examined. The resulted ratio of O/C was decreased in the first stage of the treatment. Extractives in dry wood can be increased by a significant amount due to the degradation of biopolymers. (Crestini, 2009, p. 152)

Degradation of wood in the displays or exhibitions can be subjected to again as well. The conditions are different than the condition for the wood exposed to the outdoor weathering conditions. The degradation rate in this case is controlled by the fluctuation and the time of exposure to factors like relative humidity, temperature, oxygen penetration, mechanical loading, microorganisms.
3.2.2 Physical and mechanical changes

The change in the colour of naturally aged wood compares to artificially aged can be made according to research by Matsuo et al. (2011). Since aging changes the colour of wood changed, colour is a tool to evaluate wood quality. By the time the wood colour turns from light to a darker colour; its hue is softly changed to red. The change in wood colour starts after harvesting of the tree and is primarily caused by mild thermal oxidation by exposure to air.

Wood exposed to dry aerobic conditions will darken and may have some deformation such as split and checks. As the wood colour is darkened, the light reflectance is decreased if dried under high temperature. This dark colour may be attributed to the migration of extractives to the surface or the formation of compounds that have greater light absorption. Increasing the temperature decreases the equilibrium moisture content because of the reduction of hemicellulose in relation to other chemical products with less hygroscopicity or by the closure of the micro pores in the wood cell wall. Increasing the loss of weight and decreasing wettability are different results of ageing wood by heating as reported by Christiansen (1994) on a study on the yellow-poplar veneer.

Microscopic analysis confirms that dry wood has fine cracks. Such deformations may be alleviated in case of ancient objects as a result of the weak ultrastructure of wood in the area of the middle lamellae and the secondary wall (Unger et al., 2001, p. 14)

3.2.3 Anatomical changes

The study of five-thousand-year-old well-preserved samples of Acacia nilotica and Tamarix sp from ancient Egypt revealed holes in the intercellular walls loosening the middle lamellae and S1 layer. However, no significant chemical changes apart from hemicellulose were identified. Also, a change in the colour of the cell wall substance was evident as it became dark indicating the conversion of the lumin-side toward the middle lamellae was in progress. By contrast, samples of Juniperus drupacea from Chattuscha, the capital of the Hittite Kingdom in Asia Minor (1900-1200 BC) kept in dry conditions, and non-buried showed equally well-preserved structure but on the other hand, the cell wall had been reduced, and it was difficult
to distinguish the different layers. The degradation of these two samples is mostly chemical owing to the carbohydrates low percentage of (5.1% where less than 0.5% was constituted was polyoses. (Fengel, 1991, pp. 156-157).

Further studies by Popescu and other (Popescu et al., 2007; Popescu et al., 2006) indicate that ageing of wood can affect the anatomical and morphological properties of lime wood by showed decreasing the fibril diameter and cellulose crystallite size.

3.2.4 Biodeterioration of dry wood:

In dry conditions where wood has a moisture content below the fibre saturation point attack by microorganisms cannot occur. However, such conditions do not prevent insect attack which can destroy all the wood structure (Nilsson & Daniel, 1990). Furthermore, wood has been found infested by white, brown and soft rot in dry environments (Crestini et al., 2009; Blanchette, 2003; Nilsson & Daniel, 1990; Blanchette, 2000). This suggests that wood cannot stay completely dry in nature as a result of many natural and remains vulnerable to microbial attack. That leaves structural and ultrastructural damage making confusing in the interpretation of the main cause of decay whether it was aging or microbial (Nilsson & Daniel, 1990). This confusion was present in some of the samples EG-SAQ-2 and EG-SAQ-5 examined in this thesis as it will be discussed in the chapter 5.

3.2.4.1 Dry wood insects

Wood is a nutrient-rich material in carbohydrates constituting as a central component of the cell wall structure. This acts as a host for microorganisms which consequently attract bigger creatures in the animal kingdom, the insects. Carbohydrates beside other nutrients including protein and natural adhesive materials in the processed wood also attract some insects directly without previous fungal infestation (as the case with wood-destroying insects). Insects use wood as a source of food, shelter and breeding (Unger et al., 2001). Whereas some insects attack only softwood or hardwood some insects attack both. Other insects exhibit preferences for decayed wood. sound and dry wood and some attack already decayed wood. Temperature, moisture content and nutrients control also condition the life process of the insects in wood. Among the four life stages of the insect (egg, larva, pupa and adult) the larval stage of the
woodworm is the most dangerous especially in the wood-destroying insects where the larva stage is protected and can extend to several months feeding on the wood substance.

The identification of the colonising insects is achieved by analysing data about the tunnel size and orientation inside wood, the frass characteristics and the type of wood itself (Blanchette, 1995). The common pests attacking wood belong to orders of Coleoptera (beetles) and Isoptera (termites) (Unger et al., 2001, p. 51). Other insects cause less damage, as they do not destroy or feed on wood but are using it as a shelter (ants) or for breeding (ambrosia beetles). Whereas insects can be classified according to the impact they cause when colonising wood, they can also be classified, also, according to the type of wood they attack (softwood or hardwood, xylem or bark) or according to the condition of the wood they attack (dry, damp and decayed or living trees) which is the one chosen here with excluding living trees insects. The information here will not discuss in details the characteristics of attack and the identification of the insects, for this information, see (Unger & Unger, 1986; Unger et al., 2001; Schmidt, 2006; Eaton & Hale, 1993; Unger, 1990; Cymorek, 1984).

### 3.2.4.1.1 Dry wood destroying insects

Wood destroying insects use wood as a source of food. Beetles and termites are the most dangerous threat against dry wood heritage including was buildings or artistic objects.

#### 3.2.4.1.1.1 Beetles (Coleoptera)

Beetles larvae or what is commonly termed woodworms are the active stages of a beetle's life which have role in destroying the wood structure. The most common beetles are furniture beetles (Anobiidae), powder post beetles (Lyctidae) and longhorn beetles (Cerambycidae).

##### 3.2.4.1.1.1.1 Furniture beetles (Anodiibae)

*Anobium punctatum* (common furniture beetle), *Ptilinus pectinicornis* and *Ernobius mollis* (bark borer) are the most common Anobiidae beetles that attack dry wood. *Anobium punctatum* is prominent in this list as it attacks wood and plywood that made from natural glue in furniture or different art objects and buildings. It is also prevalent in many areas worldwide including...
Europe, North America, Australia, New Zealand and most of the temperate countries. The larvae, which live up to two years in oak and from four to eight years in softwood, can digest wood cellulose and hemicellulose by the yeast cells in their digestive system, allowing it to feed on old wood. Also, the presence of protein can enhance the larval growth, but it is not required for survival (Unger et al., 2001, pp. 57, 62). It attacks both softwoods and hardwoods with the preference of sapwood of the softwood (Umney & Rivers, 2003, p. 296) and can negatively impact wood strength in optimum temperatures of 21-24 °C and moisture content of 28-30%.

*Ptilinus pectinicornis* is a common beetle throughout most of Europe, Mexico, Asia Minor and South Africa. It can completely destroy the interior including heartwood of dry hardwoods with small pores like beech, maple, poplar and willow (Unger et al., 2001, pp. 67-68). *Ernobius mollis* attacks softwood bark which has been left on timber in North America, Australia, New Zealand, South Africa and Europe. The larvae live between the layers of bark and the outermost of the sapwood and depend on the starch content for its development. The attack will cease once the bark is removed.

**3.2.4.1.1.1.2 Powder post beetles (Lyctidae)**

The larvae of powder post beetles live inside wood with very low moisture content, feeding only on sapwood. It gains the name from its ability to transform the sapwood of hardwoods to a fine powder (Umney & Rivers, 2003). *Lyticus brunneus* (brown powder post beetle) attacks wood in tropical areas and more recently Europe, North America, Australia and Japan. Within the four-month life of the larvae, it leaves only a thin layer on the surface while entirely disintegrating sapwood. It needs hardwood with large vessels in order to allow to lay the eggs. The arvae live on sugar and require minimum of 1.5% content of starch. The beetle requires arid conditions to live with optimum moisture content of 14-16% and temperature of 26-27 °C.

**3.2.4.1.1.1.3 Longhorn beetles (Cerambycidae)**

House longhorn beetle (*Hylotrupes bajulus*) which belong to the Cerambycidae family attacks dry wood in temperate Europe, Asia Minor, Africa and the Americas (Unger et al., 2000, p. 72). The larvae feeds on softwood sapwood and prefers of earlywood. It can also utilise...
cellulose and hemicellulose. The larval period can vary between three and ten years depending on optimal conditions (temperature of 24-30 °C) and the availability of protein and vitamin B. The larvae can also survive in extreme conditions, fasting for months causing damage to wood structure.

3.2.4.1.1.2 Termites (Isoptera)

Termites which are considered to be the most destructive in tropical and warm areas (Umney & Rivers 2003, p. 196) impact not only on the integrity of timber buildings but also proceed to attack portable objects including panel paintings (Blanchette, 1995, p. 64). They attack both softwood and hardwood with a preference for low-density earlywood. Individual species of wood exhibits different resistance against termites, whereas termites differ in their way of attacking according their species. There are more than two thousand different species of termites of are causing extreme damage to wood and therefore gained their economic significance (Unger et al., 2001, pp. 73-74). While avoiding the systematic classification, termites can be divided into four main groups according to the type of host wood they attack: Dry-wood termites, tree-dwelling termites, damp-wood termites and subterranean termites (Unger et al., 2001). The latter two were discussed in the wet and waterlogged wood section, this section focuses on dry-wood termites.

3.2.4.1.1.2.1 Dry wood termites

Dry wood termites are capable of attacking wood with low moisture content. They make clean channels in different directions which are characterised by smooth walls. As with powder post beetles, dry termites leave an only thin layer on the surface over the destroyed structure, hence they are also commonly referred to as “powder post termites”.

*Kalotermes flavicollis* (fabricius) and *Cryptotermes* brevis (walker) both belong to the termite family Kalotermitidae. The first attacks wood in the Mediterranean region, coastal Asia Minor and New Zealand and can live on dry wood or previously decayed damp wood. The second considered a more destructive termite that attacks dry wood (Unger et al., 2001, p. 77). It can
tolerate quite dry conditions and been found all over the world in warm climates including Queensland and Sydney in Australia.

### 3.2.4.1.2 Dry wood non-destroying insects:

The deterioration phenomena for wood decay is not limited to the destruction of the inside structure of wood but includes damage caused by different kind of non-destructive insects that use wood for breeding or as a shelter and/or sometimes as a source of food for a temporary period. These insects usually colonise previously damaged wood where the larvae lifespan relatively short and can be found together with the adult. *Formicidae* (Ants), *Dermestidae* (Hide beetles), and Oedemeridae beetles are examples of these insects. Ants can attack dry wood as well as trees and damp wood (i.e. *Lasius fuliginosus*). They cause mechanical problems to the infected wood by hollowing galleries and chewing out earlywood areas.

### 3.3 Fossilised wood

According to Fengel (1999), fossilisation can be sub-classified to two categories. The first group is silicification where the substance of the cell wall is replaced by minerals and the second is coalification in which the cell wall substance is converted to a highly condensed material.

#### 3.3.1 Silicification

The different kinds of wood fossils include grouped under the category of silicification, phosphatisation, carbonisation and sulphides and iron oxides and hydroxides accumulations. The process of silicification begins with the deposition of silica in the lumina of the wood cells, mainly in terrestrial environments and in some cases in marine environment. Whereas carbonisation occurs under both conditions. Phosphatisation is exclusively a marine process. In exceptional circumstances, it can occur in terrestrial while the accumulation of iron compounds occurs terrestrial conditions where sulphides accumulation providing favourable pH conditions (Fengel, 1991, p. 166 after Buurman, 1974).
Figure 25 below shows the four phases of wood silicification. In phase one the silica fills the wood cell lumina then in phase two, the silica continues to accumulate in the lumina, and the cell wall starts to degrade. Thirdly, partial replacement of the cell wall by silica occurs and eventually in the fourth stage, the cell wall is mostly replaced by silica with disappearance of the intercellular substance in some cases. In some cases, the wood genus and species can still be identified from the anatomical characteristics that are preserved.

The destruction of the cell wall structure may be a result of the recrystallisation of the silica from one form to another during the silicification process. Allowing different types of crystals to be identified including opal, cristobalite, chalcedony and tridymite. While the cell wall structure is in good condition in wood-opals, it vanishes with the quartz increasing, and in wood-tridymite, the cellulose is replaced (Fengel, 1991, pp. 166-167 after Furuno, 1986).

3.3.2 Coalification

Coalification is a slow fossilisation process when wood is submerged in water or the ground under anaerobic conditions in which the wood cell wall substance converted to highly condensed compound (Fengel, 1991, 153). This transformation is very slow reducing any observable difference between a sample aged hundreds of thousands of years and another of
several million, however it starts to change rapidly after 10 million years. The conversion is
evident by the deposition of dark material in the lumina, when simultaneously the cell wall is
reduced in thickness. The latewood cell wall also shows more resistance than the cell walls of
the earlywood which is remarkably degraded. It has been reported that the amount of
polysaccharides is significantly reduced compared to the recent wood which can reach about
12 percent in one-hundred-year-old wood and can drop to less than 0.1 percent after 140 million
years combined with the increase in the dark condense material in the cell lumina (Fig. 26).

The lignin amount is in coal also reduced indicating that the conversion involves oxidation,
demethylation and loss of hydroxyl groups. This transformation is explained as evident by

   (1) the loss of methoxyl carbons from the guaiacyl units with replacement by
       hydroxyls and increased condensation, (2) the loss of hydroxyls or aryl ethers with
       replacement by hydrogen, and (3) the loss of alkyl groups with continued replacement
       by hydrogen.

The lignin in brown coal can be altered subsequently by the loss of methoxyl groups, hydrolysis
of aryl ethers and by substitution reactions which cross-link aromatic rings and add hydroxyl
groups and incorporate methyl groups. Following that, dehydroxylation and dealkylation occur
by replacement with hydrogen (Hatcher, 1988; Larsen et al., 1984; Wilson et al., 1984) until
the anthracite stage when extensive aryl ring fusion occurs (Wilson et al., 1993,p. 599).
Methodology
4 Chapter 4: Methodology (Materials and Methods)

4.1 Samples and Sampling:

Archaeological and old wood samples were collected from different sites and different countries. The aim was to collect samples with varying stages of degradation and from different environments. Therefore, samples from Egypt were collected to test the impact of the dry environment. On the other side, waterlogged wooden samples from Italy were also tested to compare them with the first group and finally samples of more recent wood (around 100 years old) from Australia were examined beside the reference samples of the old specimens.

The samples comprised five groups from sites in Egypt and one set of Italian samples.

4.1.1 Egyptian Samples:

Egyptian Samples were collected from storage and terrestrial sites as parts of both known and unidentified objects (Fig. 27). Group 1: Samples from Saqqara from Khendjer Pyramid site, which is located 800 metres in the south-east of the step pyramid of Saqqara. The location is 56 metres higher above sea level and 33 metres above the planted cultivated valley. The excavated pieces were buried 2 metres underground and had mostly been reburied after previous excavations. The local weather is dry, and rainfall is rare. Summer temperatures average 36 degrees Celcius maximum with an average minimum of 18 degrees Celcius. The winter average is 22 degrees Celsius maximum and 10 degrees Celsius minimum. If the samples are contemporary with Khendjer pyramid, they are dated to the thirteenth dynasty 1760 BC. Samples are EG-SAQ-1/2/3/4/5/6/7 and 8.

Sample number EG-DAK-1 was found buried in an ancient excavation site from Dakhla oasis. The site of the sample collected from Dakhla oasis dated back to the Graeco-Roman Period and location weather characterised by its arid condition and being sunny mostly throughout the year. The climate is very hot in summer and very cold on winter nights.
Sample EG-ASW-1 was found buried in Edfu temple site, Aswan governorate. Climate in this site is similar to the previous location. Its dry and sunny throughout the year with rare showers.
Hot weather during summer which can reach over 40 °C in six months of the year ("Climate Edfu," 2018).

Samples EG-Is.C-1/ 2/ 3 and 4 were collected from different sites in old Islamic Cairo, which has dry, hot summer and is occasionally rainy in winter. Samples are as the following; EG-Is.C-1 is from a piece of wood from Baibars al-Jashnakir (Baibars II) mosque. EG-Is.C-2 is from Beit El-Harawy (El-Harawy House). EG-Is.C-3 is from El-Moez St., Sultan Qalawun (1222-1290). EG-Is.C-4 is Found buried in Said Al-Soadaa (the happiest) Khankah, the first khankah in Egypt, (Fig. 28).

Figure 28: The location of samples EG-Is.C-1, 2, 3 and 4 on the map of Islamic Cairo (Hafez, 2012)
Samples EG-SOH-1, EG-SOH-2 and EG-SOH-3 were taken from the crown, the body and the base, respectively, of a painted column found in the El-Seiny mosque in the city of Jerja (south Egypt, Sohag governorate). This is one of the warmest places in Egypt with an annual mean temperature of 23.5 °C. The mosque was built in 1787 AD. The site is close to the Nile bank, thus there might be water under the surface.

All the samples were taken from different fragments with no aesthetic, functional, economic or social cultural values it was the possible to collect them for destructive analysis. However, the informative and the experimental/scientific values still persist and this gives this research its significance. Samples were collected by sterile gloves and the tools were treated with ethyl alcohol where possible. The collection process done as a join research work between the author and the Ministry of Antiquities emp in the relevant region (please refer to the last chapter).

<table>
<thead>
<tr>
<th>Sample</th>
<th>Origin</th>
<th>Era and estimated age</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-SAQ-1</td>
<td>Khendjer Pyramid site - Saqqara</td>
<td>Ancient Egypt (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-2</td>
<td>Khendjer Pyramid site - Saqqara</td>
<td>Ancient Egypt (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-3</td>
<td>Khendjer Pyramid site - Saqqara</td>
<td>Ancient Egypt (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-4</td>
<td>Khendjer Pyramid site - Saqqara</td>
<td>Ancient Egypt (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-5</td>
<td>Khendjer Pyramid site - Saqqara</td>
<td>Ancient Egypt (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-6</td>
<td>Khendjer Pyramid site - Saqqara</td>
<td>Ancient Egypt (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-7</td>
<td>Khendjer Pyramid site - Saqqara</td>
<td>Ancient Egypt (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-8</td>
<td>Khendjer Pyramid site - Saqqara</td>
<td>Ancient Egypt (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-DAK-1</td>
<td>Dakhla oasis, New Valley Governorate</td>
<td>Graeco-Roman period (332 BC – 395 AD)</td>
</tr>
<tr>
<td>EG-Asw-1</td>
<td>Edfu temple site, Aswan governorate</td>
<td>Ptolemaic period (Graeco-Roman) (237 BC - 57 BC)</td>
</tr>
<tr>
<td>EG-Is.C-1</td>
<td>Baibars al-Jashnakir (Baibars II) mosque, Islamic Cairo (1309–1310 AD)</td>
<td></td>
</tr>
<tr>
<td>EG-Is.C-2</td>
<td>Beit El-Harawy (El-Harawy House), Islamic Cairo</td>
<td>Islamic Cairo/ Modern Era (1731 AD)</td>
</tr>
</tbody>
</table>
### 4.1.2 Italian Samples:

Italian samples were available in IVaLSA-CNR Florence and were brought from two main locations. Samples It-S8, It-S12, It-S16, It-S19, It-S20 are spruce samples came from an old beam which was originally located in Padua. Samples IT-VA, IT-VPA-2, IT-VPA-29, IT-VPA-33 and IT-VPA-38 came from the old site of Herculaneum, near Villa dei Papiri in Italy. They were waterlogged initially and when taken they were placed in a store without any cataloguing and left to dry under uncontrolled conditions. In addition, some of them were partially burnt and/or attacked by insects.

### 4.1.3 Australian Samples

The Australian samples were generously donated by Professor Robyn Sloggett (Grimwade Centre for Cultural Materials Conservation, The University of Melbourne). They were among private collections of other samples (not tested) with an approximate age of 100 years.

### 4.1.4 Reference Samples:

Reference samples of the tested and identified old species were collected and tested to compare their results with the ones of the archaeological and older wooden samples (Table 4). These samples are: Taxus baccata L., Pinus sylvestris, Picea abies, Ficus carica L., Ostrya carpinifolia Scop., Cupressus sempervirens L. and Tamarix spp. which were provided by
Dieter Becker from the International Wood Collectors Society (IWCS). Faidherbia albida was provided by Centro Studi Erbario Tropicale (CSET), University of Florence, Italy (catalogue number FT-8461, collected on the 10 April 1909 by A. Pappi in Eritrea-Bogos and identified by E. Chiovenda. Ficus sycomorus was available at the CNR-IVaLSA (Florence, Italy).

<table>
<thead>
<tr>
<th>Reference samples</th>
<th>Origin</th>
<th>Provided by</th>
<th>To be compared with:</th>
</tr>
</thead>
<tbody>
<tr>
<td>Taxus baccata L.</td>
<td>Germany</td>
<td>IWCS</td>
<td>EG-Saq-8</td>
</tr>
<tr>
<td>Pinus sylvestris</td>
<td>Germany</td>
<td>IWCS</td>
<td>EG-SOH-2 and EG-SOH-3</td>
</tr>
<tr>
<td>Picea abies</td>
<td>Germany</td>
<td>IWCS</td>
<td>EG-Is-C-4</td>
</tr>
<tr>
<td>Curpressus sempervirens L.</td>
<td>Italy</td>
<td>IWCS</td>
<td>EG-Unknown</td>
</tr>
<tr>
<td>Ostrya carpinifolia Scop.</td>
<td>Italy</td>
<td>IWCS</td>
<td>EG-F9b</td>
</tr>
<tr>
<td>Ficus carica L.</td>
<td>Italy</td>
<td>IWCS</td>
<td>Was used instead of Ficus Sycamorus</td>
</tr>
<tr>
<td>Tamarix spp.</td>
<td>Germany</td>
<td>IWCS</td>
<td>EG-SOH-1</td>
</tr>
<tr>
<td>Faidherbia albida</td>
<td>Italy</td>
<td>CSET</td>
<td>EG-SAQ-2 and EG-SAQ-7</td>
</tr>
<tr>
<td>Ficus sycomorus</td>
<td>Italy</td>
<td>CNR-IVaLSA</td>
<td>EG-SAQ-3, EG-SAQ-4, EG-SAQ-5, EG-SAQ-6, EG-DAK-1 and EG-Is.C-1</td>
</tr>
</tbody>
</table>

### 4.2 Macroscopic and visual investigations:

The aim was to identify the wood and the type of biological decay if this was present in the sample. The microscopic study also aimed to assess the ultrastructure of the archaeological wood and draw a relation between any changes or modifications of the chemistry and the other properties.

A number of techniques were utilised depending on the preservation state of the wood samples. In case of the well-preserved samples, thin sections (10-20 µm) were taken carefully by a manual cut using a razor blade. Section were oriented parallels to the three anatomical
diagnostic directions; transverse (TS), longitudinal-radial (RLS) and longitudinal-tangential (TLS). Occasionally, sections were stained by 0.1% w/v aniline blue in 50% lactic acid solution in order to highlight the presence or the occurrence of any fungal or bacterial activities. The characterisation of decay of these samples has been carried out by Leica DM LB 2 light microscope at different magnifications. Assessment was carried out using bright-field and polarised light microscopy. The polarised light is used as a useful tool to highlight the remaining crystalline cellulose structure (Bjordal, Nilsson, & Daniel, 1999b).

Furthermore, scanning electron microscope (SEM) was used to confirm the analysis results achieved by the LM as well as to examine the samples that were in worse condition than the first group investigated by the LM and it was not possible to achieve a clean-cut section for them by razor blade or microtome. Very small cube-like segments (approximately 5 x 5 x 5 mm) of each sample were manually cut by a razor blade and then prepared as described by (Bjordal, Nilsson, & Daniel, 1999a, p. 64) and dried using (Balzers CPD 030) critical point dryer, then coated with a thin gold film (15 nm) and examined by using a (Philips XL 20) SEM. The electron source was a tungsten filament and the accelerating voltage of the beam was 15 kV. Images were acquired with a backscattered electron (BSE) detector, and water vapour around 0.5 Torr was used in the sample chamber to dissipate the effects of electron charging which enables uncoated samples to be observed. Most of the samples were examined under different magnifications. A Philips (FEI) XL30 ESEM TMP with energy dispersive spectrometry EDS was used in a later stage for confirmation and to increase the reliability of the results. The EDS uses a liquid-nitrogen cooled Si-Li detector with an area of 10 sq. mm and an ATW2 thin detector window which allows collection of x-rays between B and U. The system operates under Windows 2000. Identification of the samples was done by comparing the resulted images of the microscopic test with the identification keys (Greguss, 1955; InsideWood, 2004-onwards; Jacquiot, Guinier, & Centre technique du bois et de, 1955; Jacquiot et al., 1973; Wheeler, 2011)

After noticing fungi hyphae in some samples during the microscopic examination, the idea came to identify the fungi by re-cultivating them again. In order to do so, a small piece of each sample was placed in a Petri dish with agar media to grow the fungi. After two weeks’ period dishes were observed under Leica WILD M420 stereomicroscope with optical zoom WILD 4000076 5.8-35 X. Identification of the resulted mycelium was done after comparing it with (Hoog & Guarro, 2000).
4.3 Physical and Mechanical measurements

Physical measurements

4.3.1.1 Moisture content

Each sample was weighed and measured accurately before each test. The weighing was repeated after the test to measure the moisture content of the sample during the test. Another fraction/s of the sample left from the cutting was weighed before and after drying to confirm the moisture content.

Moisture content of the samples was measured during the procedure testing the samples by the dynamic mechanical analysis (DMA). The samples were prepared in regular shapes and measured by digital caliber and weighted before oven drying in 103± 2 until reaching constant weight and then the moisture content was determined according to the equation:

\[
MC = \frac{100 \cdot (W_I - W_{OD})}{W_{OD}}
\]

Where,

- MC = Moisture Content
- \( W_I \) = Initial Weight before oven drying
- \( W_{OD} \) = Weight after oven drying

4.3.1.2 Basic Density

Using the information of dimensions of the regular samples, the weight of samples and the moisture content it is possible to determine the basic density of the samples on the specific moisture content of each. Density was measured according to the equation:

\[
\rho (D) = \frac{W_{OD}}{V_I} \text{ g/cm}^3
\]

in specific moisture content for each sample

Where;

- \( \rho (D) \) = Density
- \( W_{OD} \) = Weight after oven drying
- \( V_I \) = Initial volume before oven drying
4.4 Chemical analysis

A wider range of samples has been examined by the conventional wet chemical analysis (WCA) and attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR) than the samples were examined by Py(HMDS)-GC/MS. Because of the availability, wet chemical analysis (Klason lignin and ash content) was performed along with (ATR-FTIR) on some ancient and old Egyptian samples, old Italian samples and relatively recent Australian samples. Tests also were performed on some samples of the same taxa of the Egyptian samples (reference samples). The results of these different techniques were compared and combined to contribute to the conclusion of the chemical degradation of the ancient wood and determine whether the deterioration occurred in the holocellulose/lignin (H/L) scale or in the molecular scale of the wood components themselves.

4.4.1 Wet Chemical analysis (WCA)

The wet chemical analysis was performed following the TAPPI standards T204-cm07, T222-om02 and T211-om02 to measure extractives, lignin content and ash content respectively. The samples were ground by Retsch® ZM200 grinding machine in the case of the fragile small samples and Wiley mill in case of the relatively hard and bigger samples using a mesh size 40-120. After sieving, ground wood was collected from 40-120 mesh, and Soxhlet apparatus extraction was used to extract solubilised materials from the wood in two steps. The first is the organic extraction using solvents of toluene and ethanol with a mixture of 2:1 (v/v) for about six hours with an average five cycles per hour followed by aqueous extraction for eight hours, with two cycles per hour after drying under the hood in room temperature. Afterwards, samples were oven dried to quantitatively measure the compounds solubilised in the organic solvents and the water-soluble compounds. Some of the ground powder was oven dried to measure the moisture content of the tested samples.

The extractive-free powder was used for measuring the lignin content using concentrated sulfuric acid 72% at room temperature with occasional stirring for two hours. The contents were then diluted to 3% H$_2$SO$_4$ for four hours in a boiling temperature. The
residue was then washed, filtered and eventually, oven dried according to the TAPPI procedure T222-om02 for measuring Klaason lignin.

The procedure mentioned above was adapted to measure the acid-insoluble lignin (AIL) with the acid-soluble lignin was determined by UV spectroscopy with absorbance at 205 nm using an extinction coefficient of 110 (AU L)/(g cm) (Aldaeus, 2014), (Dence, 1992), (Yeh et al., 2005). The insoluble lignin was determined gravimetrically after filtration according to the previous procedure. The acid soluble filtrate solution was then diluted until the absorption was between 0.2–0.7 AU. Then the Acid-soluble lignin (ASL) was determined according the next equation (Aldaeus, 2014):

\[
\text{ASL} = \frac{A.D.V}{a.b.M}.1000 \text{ mg/g}
\]

Where;

- \(A\) = Absorption at 205 nm
- \(D\) = Dilution factor
- \(V\) = Volume of the filtrate
- \(a\) = Extinction coefficient of lignin, in g/l cm which is 110 g/l cm, according to TAPPI UM 250
- \(b\) = cuvette path length, in cm
- \(M\) = Weight of sample (as 100% dry matter) before acid hydrolysis/suspension, in g

Total lignin content = AIL + ASL

The holocellulose amount which includes both cellulose and hemicelluloses was later calculated as a complement to 100 of the sum of the results obtained from the other analyses. Depending on its availability, the weight used of the dry samples were between 250mg to 1g.
The ash content measurements were done separately by calculation using oven dried powder and/or by using non-dried powder with measuring the moisture content by following the standard in the TAPPI T 211. The Specimens were placed in crucibles then carbonised over Bunsen burner then moved into a furnace with temperature of 525±25 °C for two hours. The crucibles were then cooled down in a desiccator/s and then weighed. This process was repeated twice at least for each sample.

The ash content was then calculated as follows:

\[
\text{Ash, } \% = \frac{A \times 100}{B}
\]

where

A = weight of ash

B = weight of test specimen, moisture-free (TAPPI 211)

All samples were weighed on an analytical balance with accuracy of 0.01mg. The calculations of wood compounds were based on moisture-free and ash-free of the initial weight as the ash content of the archaeological wood which is very relatively high can affect the quantitative calculation of the components (Pecoraro et al., 2015; Pizzo et al., 2015).

### 4.4.2 Attenuated total reflectance Fourier transform infrared spectroscopy (ATR-FTIR)

Attenuated total reflectance Fourier transform infrared (ATR-FTIR) is a useful technique in characterising wood because of its capability to determine the interaction between the IR radiation and the wooden sample. It can undertake characterisation on dry or wet samples by measuring the radiation absorbance and its intensity using the different functional groups of the wood constituents. Intensities of the FTIR frequencies can give information about the quantities of the functional group and consequently the wood components (Simonescu, 2012) and by calibration we can determine the quantities of these components (Rodrigues, Faix, & Pereira, 1998; Rodrigues et al., 2001; Pizzo et al., 2015). The ATR-FTIR requires a minimal amount of the material that can be prepared in a very short time or used directly without preparation to limit the interference with the original sample. This makes it non-destructive technique, especially when dealing with the cultural and archaeological materials (Lucejko et al., 2015; Mohebby, 2005).
This qualitative ability of this technique can also provide useful information about the wood initial identification and if it is a hardwood or a softwood (i.e. the hardwood lignin consists of syringyl and guaiacyl units while the softwood lignin consists mostly of guaiacyl-type lignin only (Faix, 1991; Hall, 1984; Musha & Goring, 1975; Obst, 1982; Wagner et al., 2015).

ATR-FTIR analysis was achieved as an attempt to evaluate the chemical changes of the decayed wood with respect to the wet chemical analysis and Py(HMDS)-GC/MS.

The test adopted the method reported by Pizzo et al. (2013), Pizzo, Pecoraro, & Macchioni, (2013), Pizzo et al. (2015) and Pecoraro et al., (2015). It was applied on raw wood samples before extraction by organic solvents and water as described in section 4-1-4 (slices and powder), and also on extractives free wood samples and sometimes in earlywood and latewood when applicable. Test was also applied on saw dust powder of the samples and on then slices taken by a normal razor blade. A Bruker FT-IR spectrometer (Alpha) has been used to record the spectra with the settings as: 40 scans per sample, spectral resolution of 4 cm⁻¹ and wavenumber range of 4000–400 cm⁻¹. The spectrometer is equipped with a single diamond reflection attenuated total reflectance (ATR) accessory using zero filling of 2. Each test was repeated between 3 to 5 time at least to insure the consistency of the results.

Minimum level between 1920 and 1880 cm⁻¹ of the atmospheric compensation and offset-correction was applied ATR-FTIR spectra by OPUS 6.5 from Bruker. Powdered samples were pressed against the ATR diamond crystal with a built-in pressure applicator. The pressure applied to the samples was confirmed as correct when a red control spot was aligned on a specific position.

Data of the spectra collected was normalised in the spectral range of 700–1800 cm⁻¹, using two different procedures, namely Min-Max (MMN) and Vector Normalisation (VN). The normalisation of Min–Max procedure sets the absorbance to zero at the selected minimum (1800 cm⁻¹), while the highest value is set to 2 at the selected maximum (between 1015 and 1035 cm⁻¹).

The VN calculates the average y-value of the spectrum which is subtracted from the spectrum decreasing the mid-spectrum to y=0. Calculation of the sum of the squares of all y-values has
been done and the spectrum has been divided by the square root of this sum. The vector norm of the resulting spectrum is 1.

4.4.3 Energy-dispersive X-ray Spectroscopy (EDS):

This test was applied using Oxford INCA device which uses a liquid-nitrogen cooled Si-Li detector with an area of 10 sq. mm and an ATW2 thin detector window which allows collection of X-rays between B and U. The system operates under Windows 2000 via a graphical user interface.

4.4.4 Analytical pyrolysis gas chromatography mass spectrometry with in situ silylation (Py(HMDS)-GC/MS)

The main components of wood consist of polymers with high molecular weight and less than most polymers thus they cannot be analysis by the traditional gas chromatography (GC) (Kusch, 2012). The integration between the pyrolysis and gas chromatography with mass spectroscopy was first reported by (Davison, Slaney, & Wragg, 1954), however some studies suggest that there was earlier attempts to use this technique in analysing polymers (Jones, 2000). Pyrolysis gas chromatography with mass spectrometry is a technique which uses the heat (500-1400 °C) by the pyrolyser to defragment the polymers to components or substances in an inert environment. The defragments are then separated by the chromatography and identified consequently by the mass spectrometry using mass spectra libraries.

Analytical pyrolysis gas chromatography mass spectrometry with in situ silylation (Py(HMDS)-GC/MS) was applied on thirteen samples Egyptian samples collected from different terrestrial sites and storages, as mentioned in the samples section above. Samples are EG-SAQ-2, EG-SAQ-3, EG-SAQ-4, EG-SAQ-5, EG-SAQ-6, EG-DAK-1, EG-SAQ-7, EG-SAQ-8, EG-ASW-1, EG-SOH-1, EG-SOH-2 and EG-SOH-3 and EG-UNKNOWN (Table 5). Before being analysed, all the samples were oven-dried for 24 h at 40-50 °C to remove the residual free water and ground using a ball mill. These samples are identified and investigated as shown in the Table 5:
1,1,1,3,3,3-hexamethyldisilazane (HMDS, chemical purity 99.9%, Sigma Aldrich Inc., USA) was used as a silylation agent for the *in situ* thermally-assisted derivatisation of pyrolysis products. Coniferyl alcohol, sinapyl alcohol, vanillin, syringaldehyde, vanillic acid, syringic acid, acetovanillone, coniferylaldehyde, dihydrocaffeic acid and ferulic acid were synthesised and provided by Prof. Marco Orlandi at the University of Milano Bicocca (Milan, Italy).

The equipment was a micro-furnace Multi-Shot Pyrolyser EGA/Py-3030D (Frontier Lab, Fig. 29) coupled to a gas chromatograph 6890 Agilent Technologies (USA) equipped with an HP-5MS fused silica capillary column (stationary phase 5% diphenyl-95% dimethyl-polysiloxane, 30 m x 0.25 mm i.d., Hewlett Packard, USA) and with a deactivated silica pre-column (2 m x 0.32 mm i.d., Agilent J&W, USA). The GC was coupled with an Agilent 5973 Mass Selective Detector operating in electron impact mode (EI) at 70 eV. The MS transfer line temperature was 300°C. The MS ion source temperature was kept at 230°C and the MS quadrupole temperature at 150°C.

The pyrolysis temperature was 550 °C and the interface temperature was 250 °C. The samples were admixed with 5 µL of HMDS, put into a stainless-steel cup, and placed in the micro-
furnace. Chromatographic conditions were as follows: initial temperature 50 °C, 1 min isothermal, 10 °C min⁻¹ to 100 °C, 2 min isothermal, 4 °C min⁻¹ to 190 °C, 1 min isothermal, 30 °C min⁻¹ to 280 °C, 30 min isothermal. The carrier gas was helium (purity 99.995%) used with constant flow 1.0 mL min⁻¹.

Identification of the compounds was performed after instrumental analysis by comparing their mass spectra with spectra reported in the Wiley and NIST libraries and in the literature (Mattonai et al., 2016; Tamburini et al., 2016; Tamburini et al., 2017), also some compounds were identified on the basis of calculations and similarities between mass spectra.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Identification</th>
<th>Origin</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-SAQ-2</td>
<td>Faidherbia albida</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-3</td>
<td>Ficus sycamore</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-4</td>
<td>Ficus sycamore</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-5</td>
<td>Ficus sycamore</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-6</td>
<td>Ficus sycamore</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-DAK-1</td>
<td>Ficus sycamore</td>
<td>El Dakhla Oasis (Mut)- (332 BC- 395 AD)</td>
</tr>
<tr>
<td>EG-SAQ-7</td>
<td>Faidherbia albida</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-8</td>
<td>Taxus baccata</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-ASW-1</td>
<td>Unidentified</td>
<td>Edfu, Aswan-Edfu temple site (237 BC- 57 BC)</td>
</tr>
<tr>
<td>EG-SOH-1</td>
<td>Tamarix sp.</td>
<td>Jerja, Sohag- El Seiny Mosque (1787 AD)</td>
</tr>
<tr>
<td>EG-SOH-2</td>
<td>Pinus sylvestris</td>
<td>Jerja, Sohag- El Seiny Mosque (1787 AD)</td>
</tr>
<tr>
<td>EG-SOH-3</td>
<td>Pinus sylvestris</td>
<td>Jerja, Sohag- El Seiny Mosque (1787 AD)</td>
</tr>
</tbody>
</table>

AMDIS software was used to integrate the peaks derived from lignin and holocellulose products. Semi-quantitative calculations were performed using chromatographic areas: peak areas were normalised with respect to the sum of the peak areas of all the pyrolysis products identified, and the data were averaged and expressed as percentages. The percentage areas were used to calculate the relative abundances of wood pyrolysis products divided into categories. In this case, the calculations referred to 100% of the wood component corresponding to the considered categories.
Samples were analysed in triplicate and the relative standard deviations associated with the calculated values were always below 10%.
Results, Discussion and Conclusion

Statement of Co-authorship:
This section includes published data of the article “A critical evaluation of the degradation state of dry archaeological wood from Egypt by SEM, ATR-FTIR, wet chemical analysis and Py(HMDS)-GC/MS”

<table>
<thead>
<tr>
<th>Author</th>
<th>Affiliation</th>
<th>Role</th>
</tr>
</thead>
<tbody>
<tr>
<td>Robyn Sloggett</td>
<td>Grimwade Centre for Cultural Materials Conservation (GCCMC), The University of Melbourne, Australia</td>
<td>Supervision</td>
</tr>
</tbody>
</table>
| Maria Perla Colombini  | -Department of Chemistry and Industrial Chemistry, University of Pisa, Italy  
- Institute for the Conservation and Valorisation of Cultural Heritage (ICVBC), National Research Council of Italy, Florence, Italy | Supervision                                                          |
| Benedetto Pizzo         | Trees and Timber Institute (CNR-IVALSA), National Research Council of Italy, Florence, Italy | General guidance and supervision. Participation in the data analysis of WCA and FTIR |
| Jeannette Jacqueline Lucejko | -Department of Chemistry and Industrial Chemistry, University of Pisa, Italy  
- Institute for the Conservation and Valorisation of Cultural Heritage (ICVBC), National Research Council of Italy, Florence, Italy | Revision of the data analysis of FTIR and Py(HMDS)-GC/MS |
| Diego Tamburini         | Department of Chemistry and Industrial Chemistry, University of Pisa, Italy | Application of Py(HMDS)-GC/MS on the Egyptian samples. Major participation in the data analysis of the Py(HMDS)-GC/MS. Participation in writing the article |
| Mahmoud Youssif Mohamed | -Grimwade Centre for Cultural Materials Conservation (GCCMC), The University of Melbourne, Australia  
-Conservation Dept, Faculty of Archaeology, Fayoum University, Egypt | Planning of the project  
Collecting samples  
Application of the scientific techniques except the Py(HMDS)-GC/MS  
Data collection  
Data analysis  
Writing the article |

There are other individuals who helped in this project and they are mentioned in the preface and acknowledgment section.
5 Chapter 5: Microscopic and Morphological Investigations

5.1 Introduction:

The aim of the microscopic analysis of the wooden artefacts and structures is on one hand to identify the materials used in the construction of the artefact to provide secure documentation and in order to understand the technique (Capano et al., 2015) and/or for treatment purposes to ensure the material used in the conservation is compatible with the original material used in the treated subject. On the other hand, microscopic investigations provide a valuable assessment of the preservation state of the old wood and provide substantial help in understanding the cause and mechanism of deterioration.

This study investigated the morphological characteristics of number of dried cultural heritage wooden samples from Egypt. The examination of the microstructure of 8 sample was achieved by means of light microscopy (LM), most of which are dating back to the Islamic era in Egypt. With the exception of sample EG-SAQ-7, all the ancient Egyptian samples were only examined morphologically under the scanning electron microscope (SEM) because of the fragile condition of them which prevent getting clear cut sections for the LM analysis.

Species of all samples except samples EG-Unknown (Cupressaceae family) were identified after comparing the anatomical features of resulted images with the literature mentioned in the methodology section. SEM was also employed to assess the ultrastructure of the samples and to identify the type of the biological decay and its source if present. Samples examined by LM and SEM are shown in Table 6.

Reasonably, ancient wooden sample were in much worse condition than samples from Islamic Cairo or El Seiny Mosque in Sohag, which all of them are dated back between the 12th and the 18th century AD and so the state of preservation was inverse proportional with the approximate age of the wooden samples. Table 6 summarises the results relating to microbial attack and the preservation of wood structure obtained by microscopic observations.
Table 6: The identification of Egyptian wooden samples and the type of biological decay if presents.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Era of the sample</th>
<th>Type of microscopy</th>
<th>Identification</th>
<th>Plant subdivision</th>
<th>Biological decay and its type</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>LM</td>
<td>SEM</td>
<td>PLM</td>
<td></td>
</tr>
<tr>
<td>EG-SAQ-1</td>
<td>Ancient Egypt</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td>compare: <em>Ficus sycomorus</em></td>
</tr>
<tr>
<td>EG-SAQ-2</td>
<td>Ancient Egypt</td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td><em>Faidherbia albida</em></td>
</tr>
<tr>
<td>EG-SAQ-3</td>
<td>Ancient Egypt</td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td><em>Ficus sycomorus</em></td>
</tr>
<tr>
<td>EG-SAQ-4</td>
<td>Ancient Egypt</td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td><em>Ficus sycomorus</em></td>
</tr>
<tr>
<td>EG-SAQ-5</td>
<td>Ancient Egypt</td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td><em>Ficus sycomorus</em></td>
</tr>
<tr>
<td>EG-SAQ-6</td>
<td>Ancient Egypt</td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td><em>Ficus sycomorus</em></td>
</tr>
<tr>
<td>EG-SAQ-7</td>
<td>Ancient Egypt</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td><em>Faidherbia albida</em></td>
</tr>
<tr>
<td>EG-SAQ-8</td>
<td>Ancient Egypt</td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td><em>Taxus baccata</em></td>
</tr>
<tr>
<td>EG-DAK-1</td>
<td>Graeco-Roman</td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td><em>Ficus sycomorus</em></td>
</tr>
<tr>
<td>F9b</td>
<td>Islamic era</td>
<td>✓</td>
<td>x</td>
<td>x</td>
<td>compare: <em>Ostrya carpinifolia</em></td>
</tr>
<tr>
<td>EG-SOH-1</td>
<td>Modern era</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td><em>Tamarix sp.</em></td>
</tr>
<tr>
<td>EG-SOH-2</td>
<td>Modern era</td>
<td>✓</td>
<td>✓</td>
<td>x</td>
<td><em>Pinus sylvestris</em></td>
</tr>
<tr>
<td>EG-SOH-3</td>
<td>Modern era</td>
<td>✓</td>
<td>✓</td>
<td>✓</td>
<td><em>Pinus sylvestris</em></td>
</tr>
<tr>
<td>EG-UNKNOWN</td>
<td>Unknown</td>
<td>x</td>
<td>✓</td>
<td>x</td>
<td><em>Cupressaceae</em> family</td>
</tr>
</tbody>
</table>
Identification:

Transmitted light microscopy was used whenever possible for the identification process. When samples were very delicate to be examined by LM, SEM with lower magnification was used to identify the wood. Identification revealed that all the examined ancient Egyptian samples and the sample dated back to the Graeco-Roman period except sample EG-SAQ-8 were angiosperms (hardwoods), while only the third of the Islamic era samples was angiosperms and the remaining were gymnosperms. The dominant species among the ancient Egyptian samples was the *Ficus Sycamore* (sycamore fig) as it was identified for 6 samples out of 9 all were examined under the SEM. The other three species were *Faidherbia albida* (white acacia) for samples EG-SAQ-2 and EG-SAQ-7 and *Taxus baccata* (common yew) for sample EG-SAQ-8. There was no dominant species among the Islamic samples. Two samples (EG-SOH-2 and EG-SOH-3) were identified as *Pinus sylvestris L* (Scots pine), and both of them belong to the same monument, one sample (EG-Is.C-1) as identified as *Ficus sycomorus L.*, one (EG-Is.C-2) was compared to *Pinus halepensis* L. (Aleppo pine), one (EG-Is.C-3) was *Picea abies* Karst. (Norway spruce) and the last one (EG-Is.C-4) was identified as *Picea abies/Larch.*
<table>
<thead>
<tr>
<th>Sample</th>
<th>Species</th>
<th>Era</th>
<th>Microscopic section/s</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-SAQ-1</td>
<td>Compare <em>Ficus sycomorus</em> L.</td>
<td>Ancient Egypt</td>
<td><img src="image" alt="a" /> <img src="image" alt="b" /> <img src="image" alt="c" /></td>
<td>Figure 30: Transverse section (a), radial section (b) and tangential section (c) of sample EG-SAQ-1</td>
</tr>
<tr>
<td>EG-SAQ-3</td>
<td><em>Ficus sycomorus</em> L.</td>
<td>Ancient Egypt</td>
<td><img src="image" alt="a" /> <img src="image" alt="b" /></td>
<td>Figure 31: Transverse section (a), radial section (b) and tangential section (c) of sample EG-SAQ-3</td>
</tr>
<tr>
<td>EG-SAQ-4</td>
<td><em>Ficus sycomorus</em> L.</td>
<td>Ancient Egypt</td>
<td><img src="image" alt="a" /> <img src="image" alt="b" /> <img src="image" alt="c" /></td>
<td>Figure 32: Transverse section (a), radial section (b) and tangential section (c) of sample EG-SAQ-4</td>
</tr>
<tr>
<td>EG-SAQ-5</td>
<td><em>Ficus sycomorus</em> L.</td>
<td>Ancient Egypt</td>
<td><img src="image" alt="a" /> <img src="image" alt="b" /> <img src="image" alt="c" /></td>
<td>Figure 33: Transverse section (a) and radial section (b) of sample EG-SAQ-1</td>
</tr>
<tr>
<td>EG-SAQ-6</td>
<td><em>Ficus sycomorus</em> L.</td>
<td>Ancient Egypt</td>
<td><img src="image" alt="a" /> <img src="image" alt="b" /> <img src="image" alt="c" /></td>
<td>Figure 34: Transverse section (a), radial section (b) and tangential section (c) of sample EG-SAQ-6</td>
</tr>
<tr>
<td>EG-DAK-1</td>
<td><em>Ficus sycomorus</em> L.</td>
<td>Graeco-Roman</td>
<td><img src="image" alt="a" /> <img src="image" alt="b" /> <img src="image" alt="c" /></td>
<td>Figure 35: The radial section (a) and the tangential section (b) of sample EG-DAK-1</td>
</tr>
<tr>
<td>Standard Reference Sample</td>
<td>Ficus sycomorus L.</td>
<td>Recent</td>
<td>Ficus sycomorus L.</td>
<td></td>
</tr>
<tr>
<td>---------------------------</td>
<td>-------------------</td>
<td>--------</td>
<td>-------------------</td>
<td></td>
</tr>
<tr>
<td>EG-Is.C-1</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Features of the studies wood species used to identify them:**

*Ficus sycomorus* L.: vessels large to very large, axial parenchyma banded, bands very broad and paratracheal; rays 1-16 wide, heterocellular with one marginal row of square/upright cells.

*Faidherbia albida A. Chev.*: vessels medium to very large, solitary and in short radial rows; fibres medium thick-walled; axial parenchyma banded; rays uniseriate, rarely 2-3 seriate, homocellular.

*Tamarix* sp.: vessels large, mostly solitary less often in small clusters; axial parenchyma paratracheal; rays 5-20 cells wide, heterocellular.

*Taxus baccata* L.: resin canals absent; conspicuous spiral thickenings in longitudinal tracheids.

*Pinus sylvestris* L.: large resin canals with thin-walled epithelial cells; rays tracheids with dentated walls. Cross-fields from parenchyma cells to tracheids with one (rarely two) large fenestriform pits.

**Mediterranean pine:** large resin canals with thin-walled epithelial cells; rays tracheids with sometimes dentated walls (it depends from the species); Cross-fields from parenchyma cells to tracheids with 1-6 pinoid pits.
**Ostrya carpinifolia Scop.**:: diffuse-porous, pores infrequently in radial multiples of 2 to 10 pores; simple perforation plates, dense, fine spiral thickenings, rays rarely homogeneous, generally heterogeneous, with 1 to 3 rows of square to slightly upright marginal cells, rays uni to triseriate.

**Picea abies Karst.**:: gradual transition between earlywood and latewood, resin canals bordered by thick-walled epithelial cells; rays heterocellular, generally piceoid pits in the cross fields, generally uniseriate bordered pits in the radial section of tracheids.

**Quercus sp.**:: ring porous, homogeneous rays, uni- and multiseriate.

The investigation revealed advanced deterioration stages of some samples. Some of which have decay patterns of soft rots and possible previous infection by fungi and bacteria. Hyphae of some fungi have been observed under SEM. The main question in these samples was whether the decay in them was due to biological factors or the result of the aging process of the wood. In order to assess the cause of deterioration, a primitive trial was done to cultivate the fungi to identify them. Under an aspetic environment under the hood a small chip was taken from each sample and left in the laboratory for just over two weeks in the agar culture. This resulted in only moulds growing mainly in two samples indicating that the hyphae are either from presetting fungi infection that was in-active or they are hyphae of mould fungi that does not have any impact on the microstructure or the ultrastructure of the cell wall.

### 5.3 Ancient Egyptian samples

These observations revealed that wood decay fungi attacked the wood samples. The presence of fungi was clear in samples EG-SAQ-1, EG-SAQ-2, EG-SAQ-3, EG-SAQ-5, EG-SAQ-7 and EG-SAQ-8 (Figs. 38-39). In addition, for sample EG-SAQ-7 (Fig. 40) the horizontal “scratches” suggested the action of bacteria (Blanchette, 2000). Examining sample EG-SAQ-7 by LM showed detachment of the cell wall because of biological decay. The result was confirmed by PLM as there was a loss of the birefringence due to the decay of cellulose. High magnification images of transverse sections enabled additional degradation features to be observed in some samples.
A certain degree of distortion of the cell walls was observed in most samples and it was particularly emphasised for sample EG-SAQ-5 (Fig. 41). This kind of distortion is usually caused by the drying of the wood. The detachment of cell wall layers (Fig. 41) was also observed because of the fungal/bacterial attack of the cell walls. Samples EG-SAQ-4 and EG-SAQ-6 showed a relatively good preservation state of the wood structure, as the rays were almost intact. Some thinning of cell walls was observed in some areas, which might indicate fungal activities. Nevertheless, fungi were not clearly observed in these samples.
The results highlighted a complicated framework in which multiple degradation factors were simultaneously present in most samples.

5.4 Graeco-Roman samples

Similar to samples EG-SAQ-4 and EG-SAQ-6, the examination of sample EG-DAK-1 which dated back to the Graeco-Roman period showed a better structural condition compared to the older samples from ancient Egypt. The SEM images revealed some thinning in the cell wall...
that can suggest a biological decay. The other sample collected from Edfu temple in Aswan was not identified because of the size, SEM photos showed some signs of biological attack but the identification of this damage could not be attributed to a specific type of fungi (Fig. 42).

![Image](image_url)

*Figure 42: a) Transverse section of sample EG-DAK-1 from Dakhla showing the good condition of the wood structure. b) Radial section of sample EG-ASW-1 showing fungi hyphae within the vessel element*

### 5.5 Islamic samples

All the three samples collected from Sohag (EG-SOH-1, EG-SOH-2 and EG-SOH-3) showed almost intact macrostructure and microstructure which was also reflected on the physical and mechanical condition of the samples and thus thin sections suitable for LM observations were obtained by normal razor blade. They showed a better structural integrity compared to all the other samples with all the anatomical features clearly spotted. The only damage appeared in the sample was most probably caused by the preparation method (Fig. 43).

For sample EG-SOH-1 (Fig. 43), a well-preserved structure of *Tamarix* sp. wood was visible. Most of the defects present in these sections were more likely attributable to the preparation of the section itself rather than an effect of degradation. The radial longitudinal sections (RLS) of samples EG-SOH-2 and EG-SOH-3 clearly revealed, in addition to the tracheid pits common to all softwoods, the large window-like (pinoid) pits visible in the ray structure. This anatomical feature is typical of *Pinus sylvestris* and the easiness of detection indicated a well-preserved structure. Transverse sections (Figs. 43, 44) generally showed a very regular structure of the tracheids, with a few defects mainly caused by the making of the sections and only a slight
distortion of the cell walls in some areas. These observations generally indicate a good preservation state of wood structure in these samples.

Similarly, samples EG-I s.C-1, 2, 3 and 4 which were obtained from different Islamic monuments in Islamic Cairo showed few signs of degradation under the microscopes. The samples were in relatively good condition that allowed the use of a razor blade to make the suitable sections for investigations under the light microscope. Microorganisms including bacteria and fungi were evident in two samples (EG-I s.C-2 and EG-I s.C-4) but without significant modification to the structure of the cell wall.

Figure 43: (Transverse sections 5x): Sample EG-SOH-1 (Tamarix sp.) shows a perfect state of preservation, confirmed by the polarised light (left) (Light Microscope). Polarising Microscope (left), Light microscope (right) Arrows show the damage caused by the preparation method.

Figure 44: LM images of thin sections of samples a) EG-SOH-1 (Tamarix sp., TLS, 2.5x), b) EG-SOH-2 (Pinus sylvestris, RLS, 20x), c) EG-SOH-3 (Pinus sylvestris, RLS, 10x) and d) EG-SOH-3 (Pinus sylvestris, TS, 5x). Some of the main anatomical features are indicated.
5.6 Microscopic result for the fungi cultivation

As a crude experimental trial, a small chip of the wooden samples that showed biological decay was placed in an agar media for two weeks as described in the materials and methods part. The trial was to regrow and cultivate the fungi that previously attacked the wooden object with the objectives of identifying them and also understanding the cause of the decay that led to them. After two weeks, only two samples (EG-SAQ-4 and EG-SAQ-8) showed fungal activities. As the fully saturated wood or the wood with moisture content less than 20% will not be much susceptible to the fungal attack (Unger et al., 2001). That may explain why the EG-SAQ-8 sample had two fungi genus which are the *Alternaria* spp. (brown mould) (Fig. 45) and *Aspergillus* spp. (green/yellow mould) as at the time of the test the sample had the highest moisture content among all the sample and almost 20% (19.72%).

Sample EG-SAQ-4 had green/yellow coloured mould of *Aspergillus* spp. (Fig. 46). As the moulds identified do not cause the decay and the damage that destroy the cell wall structure such as seen for sample EG-SAQ-8 (Figs. 45 & 46b), these fungi could be just a contamination from the burial or the storage sites. These results increased the difficulty of attributing the cause of damaged as discussed in (section 7.6).
5.7 Conclusion

The microscopic studies were successful in identifying the different species of the several wooden samples. Main wood identified was *Ficus sycomorus* (Sycamore fig). Two samples were identified as *Faidherbia albida* (White acacia) both belong to samples collected from Saqqara and dated to the Second Intermediate Period as the site suggests. Hardwood species were the mostly used for the ancient Egyptian samples as Egypt is a poor in wood production so ancient Egyptian artist had to use the local wood which mostly coming from trees belong to the angiosperms sub-division. The only softwood identified was *Taxus baccata* (common yew) which is an imported wood. On the other hand, softwoods were dominant in the samples dated to the Islamic or Modern era. The condition of the samples is subjective to the age. The older samples had the worst state of preservation, while some of the Islamic samples are almost as intact as the recent wood. Investigation revealed that most of the ancient Egyptian samples had signs of biological agent decay including fungi and bacteria. Signs of fungal attack including spores or hyphae were evident in the SEM section of these samples. Decay characteristics of brown rot and white rot were observed in some samples however it was not easy to relate the features noticed to specific type of these fungal attack because of the presence of different signs that can be attributed to both of the fungi in one sample. Bacterial attack was spotted by different alterations and scratches of the cell wall.

Figure 46: Mould identified as *Aspergillus spp.* for sample EG-SAQ-4 (a) and sample EG-SAQ-8 (b)
6 Chapter 6: Physical and Mechanical Measurements

6.1 Moisture Content and Density

This part discusses the result of the physical properties measurements carried out on a wider range of the samples and shown in Table 8 and Figure 47. The tests were done by measuring the moisture content (MC) of the samples as described in the materials and methods in Chapter 4, followed by measuring the volume of the samples to determine their basic density if the specific MC measured for each one.

Table 8: Moisture content and density of all samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Sample Weight before drying/g</th>
<th>Weight After/ g</th>
<th>Moisture Content %</th>
<th>Density G/CM³</th>
<th>Era and location</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Picea abies</em> (L.) Karst.</td>
<td>79.6</td>
<td>72.0</td>
<td>10.5</td>
<td>0.45</td>
<td>Reference</td>
</tr>
<tr>
<td><em>Tamarix</em> spp</td>
<td>110.6</td>
<td>100.5</td>
<td>10.0</td>
<td>0.63</td>
<td>Reference</td>
</tr>
<tr>
<td><em>Ostrya carpinifolia Scop</em></td>
<td>125.7</td>
<td>114.1</td>
<td>10.2</td>
<td>0.77</td>
<td>Reference</td>
</tr>
<tr>
<td><em>Cupressus sempervirens L.</em></td>
<td>74.8</td>
<td>70.7</td>
<td>6.0</td>
<td>0.49</td>
<td>Reference</td>
</tr>
<tr>
<td><em>Taxus baccata</em> L.</td>
<td>114.6</td>
<td>105.3</td>
<td>8.9</td>
<td>0.61</td>
<td>Reference</td>
</tr>
<tr>
<td><em>Pinus sylvestris</em> L.</td>
<td>71.3</td>
<td>64.8</td>
<td>10.1</td>
<td>0.38</td>
<td>Reference</td>
</tr>
<tr>
<td><em>Ficus carica</em> L. (alternative to Ficus sycomorus)</td>
<td>76.0</td>
<td>69.1</td>
<td>10.0</td>
<td>0.43</td>
<td>Reference</td>
</tr>
<tr>
<td>EG-SAQ-1</td>
<td>0.0118</td>
<td>0.0108</td>
<td>9.3 ±</td>
<td>0.27</td>
<td>Ancient Egypt/Egypt</td>
</tr>
<tr>
<td>EG-SAQ-2</td>
<td>0.0132</td>
<td>0.0116</td>
<td>13.8</td>
<td>0.20</td>
<td>Ancient Egypt/Egypt</td>
</tr>
<tr>
<td>Region</td>
<td>Code</td>
<td>Date</td>
<td>Age</td>
<td>Value</td>
<td>Region</td>
</tr>
<tr>
<td>------------</td>
<td>-------</td>
<td>--------</td>
<td>------</td>
<td>-------</td>
<td>----------------------------------</td>
</tr>
<tr>
<td>Ancient</td>
<td>Egypt</td>
<td>Egypt</td>
<td>Egypt</td>
<td>0.0133</td>
<td>14.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0374</td>
<td>7.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0094</td>
<td>13.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0783</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0116</td>
<td>13.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0417</td>
<td>12.4</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0170</td>
<td>19.7</td>
</tr>
<tr>
<td>Graeco-Roman</td>
<td>Egypt</td>
<td></td>
<td></td>
<td>0.0237</td>
<td>7.2</td>
</tr>
<tr>
<td>Islamic</td>
<td>Cairo</td>
<td>Egypt</td>
<td>Egypt</td>
<td>0.0364</td>
<td>6.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0272</td>
<td>5.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0504</td>
<td>9.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0113</td>
<td>9.7</td>
</tr>
<tr>
<td>Modern</td>
<td>Era</td>
<td>Egypt</td>
<td>Egypt</td>
<td>0.0688</td>
<td>6.3</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.3046</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0652</td>
<td>8.0</td>
</tr>
<tr>
<td>Unkown/</td>
<td>Egypt</td>
<td></td>
<td></td>
<td>0.0047</td>
<td>6.8</td>
</tr>
<tr>
<td>Italy</td>
<td></td>
<td></td>
<td></td>
<td>0.1410</td>
<td>8.6</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.0111</td>
<td>11.0</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>0.1505</td>
<td>7.6</td>
</tr>
<tr>
<td>Sample</td>
<td>MC (%)</td>
<td>Density G/CM³</td>
<td>Country</td>
<td></td>
<td></td>
</tr>
<tr>
<td>------------</td>
<td>---------</td>
<td>---------------</td>
<td>-----------</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT-VPA-33</td>
<td>0.0637</td>
<td>0.0593</td>
<td>Italy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT-VPA-38</td>
<td>0.0244</td>
<td>0.0226</td>
<td>Italy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT-S8</td>
<td>0.0506</td>
<td>0.0471</td>
<td>Italy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT-S12</td>
<td>0.0534</td>
<td>0.0492</td>
<td>Italy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT-S16</td>
<td>0.0127</td>
<td>0.0119</td>
<td>Italy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT-S19</td>
<td>0.0536</td>
<td>0.0492</td>
<td>Italy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>IT-S20</td>
<td>0.0303</td>
<td>0.0284</td>
<td>Italy</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aus 1(H.W)</td>
<td>0.0573</td>
<td>0.0527</td>
<td>Australia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aus 2</td>
<td>0.2347</td>
<td>0.2142</td>
<td>Australia</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Aus 3</td>
<td>0.1948</td>
<td>0.1801</td>
<td>Australia</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Figure 47:** The moisture content and the density values for all samples grouped from left to right as: Ancient Egyptian samples, Islamic Cairo and Modern samples, Italian samples and Australia samples.

The measurements were done on all the samples; Egypt, Italy and some relatively recent Australian samples. Results of the samples vary from one sample to another. Moisture content...
(MC) of the sample ranged from about 5 to 19.72 %. The lowest MC was measured for sample G from Islamic Cairo and the highest was for samples EG-SAQ-8 from Saqaara (Ancient Egypt). Sample EG-SAQ-2 showed the lowest density amongst all samples while the section taken from the heartwood of Aus3 sample revealed the highest density with density of 0.20 and 0.99 g/cm$^3$ respectively.

Basic density was measured as an informative parameter to evaluate the state of preservation of cultural heritage wood (Babiński et al., 2014). The low density is indicating the loss of the wood substance and therefore the reduction of its mass which will consequently impact the wood mechanical strength. From the table and the graph above it can be seen that the oldest samples which were dated back to ancient Egypt and the Graeco-Roman period EG-SAQ-1/ 2/ 3/ 4/ 5/ 7/ 8 and EG-DAK-1 have the lowest density among the other samples. Whereas the Australia samples were measured with the highest density.

6.1.1 Egyptian Samples:

6.1.1.1 Ancient Egyptian and Graeco-Roman samples

The analysis of the density results of the Egyptian samples, as illustrated in Figure 48, shows the correlation between the low density levels and the results obtained by the microscopic investigations in general. The chart below shows the density of the ancient Egyptian samples. Sample EG-SAQ-2 had the lowest density among all samples with 0.2 g/cm$^3$, however this sample did not show any visible microbiological attack signs but, on the other hand, the chemical analysis of this samples showed high degree of degradation of the holocellulose, which will be discussed later in the chemical analysis part. The three samples with higher density EG-SAQ-4, EG-SAQ-8-R and EG-SAQ-6 (0.4, 0.51 and 0.59 g/cm$^3$ respectively) showed different results regarding the microbiological attack. Where it was reasonably understood that the sample EG-SAQ-6 has the highest density as the microscopic investigation showed no evidence of fungi or bacteria, the other two sample has signs of biodeterioration. The high ash content which was mostly because of the burial environment or the material used in these Artefacts may contribute to this higher density level of these two samples by increasing the total mass of the samples.
6.1.1.2 Islamic Cairo and Modern Era samples

Unlike the ancient Egyptian samples, the samples dated back to the Islamic or modern era showed higher density and similar moisture content values. That is reasonably understood because of the better state of preservation these samples have which allowed them to be sectioned by a razor blade and examined under the light microscope.

6.1.1.3 Italian samples:

The Italian samples examined showed average density that is higher than the ancient Egyptian samples and lower than the Islamic Cairo samples. The moisture content values of these samples were close to each other with the exception of sample IT-VPA-2 which could be a result of the storage environment as all these sample were stored in IVALSA-CNR before testing.

6.1.1.4 Australian samples:

The Australian samples, which are about 100 years old only showed very high-density values specially the sample taken from the heartwood part Aus1 (H-W) which was measured with
density of 0.99 g/cm\(^3\). The samples were in almost intact condition and the result are similar to results shown in the literature (Stambaugh & Guyette, 2003; Vicelina, José Luís, & Helena, 2018).

6.1.2 **Ficus sycomorus samples**

As the *Ficus sycomorus* is the most common wood species identified in the thesis so a comparison can be made between the results obtained here for the cultural heritage *Ficus sycomorus* samples and the reference *Ficus carica* L. which has the same density in the literature (0.46) (Crivellaro & Schweingruber, 2013). The density and moisture content of reference *Ficus carica* L. was measured in the same way the cultural heritage wood samples were measured and as described in the materials and methods in Chapter 4. The resulted value was 0.43 g/cm\(^3\). All cultural heritage samples have lower density than the reference sample except sample EG-SAQ-6 with a value of 0.59 g/cm\(^3\). Sample EG-SAQ-4 showed the closest density to the reference sample with value of 0.40-0.59 g/cm\(^3\). The other samples showed much lower density values than the reference sample. The apparent higher density of the EG-SAQ-6 sample could be attributed to two main reasons: the first is the sample shown no signs of microbiological decay, the second is that the sample contained high amount of ash minerals because of being buried in a soil and/or because of the technique used in making the artefact by adding the gesso layer on the wood surface to prepare it for painting.

The other two sample that had better density values than most of the other *Ficus* samples found attached one from El-Dakhla oasis (EG-DAK-1/ 0.35 g/cm\(^3\)) which showed non-major modifications to the micro-structure of the cell wall, however there was some signs of brown rot fungi spotted in some areas of the sample and the other from Islamic Cairo (EG-Is.C-1/ 0.23 g/cm\(^3\)) which did not show signs of fungal or bacterial attack (Fig 49).
Figure 49: The different values of the density and moisture content of the cultural wooden samples identified as Ficus sycomorus and the reference Ficus carica L. sample

6.2 Conclusion:

Measuring the density of different cultural heritage wooden samples belonging to different eras showed variation of the data obtained. Samples from ancient Egypt, Graeco-Roman period, Islamic era, Modern era were measured and compared with samples from Italy, Australia and reference samples of the same taxa. The results revealed the decline in the density of the ancient Egyptian samples more than the rest as a result of the aging process and the impact of the microbiological attack specially seen in the samples collected from Saqqara, Egypt. Values of these attacked samples were as low as near the half of the cited and the measured density (samples EG-SAQ-1, 3 and 5).
7 Chapter 7: Chemical Analysis

This chapter shows and discusses the results of the different techniques used to assess the chemical composition of some cultural heritage wood samples from different places in Egypt and belong to different eras. Techniques used in this part were wet chemical analysis (WCA), attenuated total reflectance Fourier transform infrared spectroscopy (FTIR), Energy-dispersive X-ray Spectroscopy (EDS) and analytical pyrolysis gas chromatography mass spectrometry with in situ silylation (Py(HMDS)-GC/MS). The results are discussed in correlation with the other results of the microscopic investigation study and physical measurements.

7.1 Wet Chemical Analysis (WCA)

The WCA was used to quantitatively assess the cultural heritage wooden main components following standard procedure described in the materials and methods part (Chapter 4). The main idea was to separate the different wood compounds. The process included the extraction of the soluble substances, the isolation of insoluble lignin (Klason lignin), measuring soluble lignin, measurement of ash content and measure the holocellulose percentage after getting the data of these mentioned processes. The WCA also aim to measure the H/L value with is a very useful parameter of the preservation state of wood in general and cultural heritage in particular.

As shown in Table 9, the wet chemical analysis reveals not only a big difference between the chemistry of the old samples and the fresh ones but also demonstrates an interesting variability in the compositions of the archaeological samples themselves. In all Egyptian samples except EG-SOH-1 (Tamarix), the ash content is significantly elevated to a much higher percentage than measured for fresh sound samples which reached average of 27.29% as the case of sample EG-SAQ-7 (Faidherbia albida) sample. This high percentage of ash was most probably the result of burying the sample under soil with the deep penetration of the inorganic matter and/or because of the technique that was used for making the artefact by using material like calcium carbonate or the calcite (CaCO₃) or gypsum CaSO₄.2H₂O to make a preparation layer to be painted afterwards.
Table 9: Wet chemical analysis of ancient and archaeological and reference wood samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Species</th>
<th>Organic extractable fraction (W), %</th>
<th>Aqueous extractable fraction (W), %</th>
<th>Lignin (W), %</th>
<th>Holocellulose (W), %</th>
<th>H/L</th>
<th>Ash, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Reference wood samples</td>
<td><em>Taxus baccata</em></td>
<td>11.0</td>
<td>2.3</td>
<td>27.2</td>
<td>59.2</td>
<td>2.2</td>
<td>0.3</td>
</tr>
<tr>
<td></td>
<td><em>Tamarix sp.p.</em></td>
<td>4.1</td>
<td>8.1</td>
<td>20.2</td>
<td>62.3</td>
<td>3.1</td>
<td>5.4</td>
</tr>
<tr>
<td></td>
<td><em>Pinus sylvestris</em></td>
<td>4.1</td>
<td>2.1</td>
<td>25.8</td>
<td>67.8</td>
<td>2.6</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td><em>Ficus sycomorus</em></td>
<td>1.1</td>
<td>4.4</td>
<td>31.1</td>
<td>61.1</td>
<td>2.0</td>
<td>2.3</td>
</tr>
<tr>
<td></td>
<td>picea abies</td>
<td>1.5</td>
<td>0.9</td>
<td>26.3</td>
<td>71.1</td>
<td>2.7</td>
<td>0.2</td>
</tr>
<tr>
<td></td>
<td>cupressus sempervirens</td>
<td>2.3</td>
<td>0.9</td>
<td>34.2</td>
<td>62.3</td>
<td>19.5</td>
<td>0.3</td>
</tr>
<tr>
<td>EG-SAQ-1</td>
<td><em>Ficus sycomorus</em></td>
<td>3.7</td>
<td>25.9</td>
<td>16.9</td>
<td>35.6</td>
<td>2.1</td>
<td>17.8</td>
</tr>
<tr>
<td>EG-SAQ-2</td>
<td><em>Faidherbia albida</em></td>
<td>2.7</td>
<td>45.4</td>
<td>30.3</td>
<td>21.6</td>
<td>0.7</td>
<td>19.7</td>
</tr>
<tr>
<td>EG-SAQ-3</td>
<td><em>Ficus sycomorus</em></td>
<td>8.1</td>
<td>9.7</td>
<td>19.0</td>
<td>63.1</td>
<td>3.3</td>
<td>18.0</td>
</tr>
<tr>
<td>EG-SAQ-4</td>
<td><em>Ficus sycomorus</em></td>
<td>5.9</td>
<td>20.2</td>
<td>30.8</td>
<td>43.0</td>
<td>1.4</td>
<td>11.7</td>
</tr>
<tr>
<td>EG-SAQ-5</td>
<td><em>Ficus sycomorus</em></td>
<td>8.3</td>
<td>29.0</td>
<td>49.6</td>
<td>13.2</td>
<td>0.3</td>
<td>16.8</td>
</tr>
<tr>
<td>EG-SAQ-6</td>
<td><em>Ficus sycomorus</em></td>
<td>6.1</td>
<td>28.8</td>
<td>14.2</td>
<td>50.9</td>
<td>3.6</td>
<td>11.0</td>
</tr>
<tr>
<td>EG-SAQ-7</td>
<td><em>Faidherbia albida</em></td>
<td>7.4</td>
<td>27.2</td>
<td>28.5</td>
<td>36.9</td>
<td>1.3</td>
<td>20.0</td>
</tr>
<tr>
<td>EG-SAQ-8</td>
<td><em>Taxus baccata</em></td>
<td>3.5</td>
<td>11.3</td>
<td>20.4</td>
<td>64.8</td>
<td>3.2</td>
<td>11.1</td>
</tr>
<tr>
<td>EG-DAK-1</td>
<td><em>Ficus sycomorus</em></td>
<td>6.4</td>
<td>39.0</td>
<td>16.8</td>
<td>37.8</td>
<td>2.3</td>
<td>14.5</td>
</tr>
<tr>
<td>EG-SOH-1</td>
<td><em>Tamarix sp.</em></td>
<td>5.4</td>
<td>15.2</td>
<td>18.6</td>
<td>60.9</td>
<td>3.3</td>
<td>5.7</td>
</tr>
<tr>
<td>EG-SOH-2</td>
<td><em>Pinus sylvestris</em></td>
<td>3.5</td>
<td>4.5</td>
<td>22.3</td>
<td>69.7</td>
<td>3.1</td>
<td>0.1</td>
</tr>
<tr>
<td>EG-SOH-3</td>
<td><em>Pinus sylvestris</em></td>
<td>2.8</td>
<td>3.8</td>
<td>25.3</td>
<td>68.1</td>
<td>2.7</td>
<td>1.4</td>
</tr>
<tr>
<td>EG-IS.C-1</td>
<td><em>Ficus sycomorus</em></td>
<td>5.5</td>
<td>19</td>
<td>15.2</td>
<td>50.7</td>
<td>3.3</td>
<td>9.5</td>
</tr>
<tr>
<td>EG-IS.C-2</td>
<td><em>Picea abies</em> Karst.</td>
<td>0.7</td>
<td>24.9</td>
<td>19.3</td>
<td>39.1</td>
<td>2.0</td>
<td>16</td>
</tr>
<tr>
<td>EG-IS.C-3</td>
<td>Mediterranean pine, Possibly: <em>Pinus halepensis</em></td>
<td>0.8</td>
<td>9.1</td>
<td>17.6</td>
<td>62.1</td>
<td>3.5</td>
<td>10.5</td>
</tr>
<tr>
<td>EG-IS.C-4</td>
<td><em>Picea abies</em>/Larch</td>
<td>0.7</td>
<td>16.3</td>
<td>17.7</td>
<td>57.2</td>
<td>3.2</td>
<td>8.2</td>
</tr>
</tbody>
</table>
This suggestion was also confirmed by the EDS analysis which showed high peaks of calcium, sulphur potassium, iron and chlorine in some sample which indicate the use of gypsum as a ground layer on the wooden support. Moreover, this inorganic matter can be attributed to the formation of salts in the porous section of the wood. This large amount of ash and the considerably higher percentage of it in the ancient cultural heritage wooden samples tested as compared to the fresh wood consolidate the decision to exclude the ash content from the total sum of the sample to prevent any interference because this high amount will impact the percentage of the actual constituents of the wood (Pecoraro et al., 2015; Pizzo et al., 2015).

The variation within the results between samples includes both holocellulose and consequently the H/L ratio which is used as a direct parameter to judge the state of preservation of archaeological wood because it gives indication of the material lost as a result of the deterioration process (Łucejko et al., 2015; Łucejko et al., 2012).

The lignin ranges from 14.2% to 49.6% while the Holocellulose amount ranges from 13.2% to 64.8% in the ancient Egyptian samples, the amount that increases to 39.1%- 62.1% in the samples obtained from Islamic Cairo (EG-Is.C-1, 2, 3 and 4) and highest amount was obvious in the samples from Sohag governorate in upper Egypt (EG-SOH-1, 2 and 3) (Tamarix sp. and Pinus sylvestris) with 60.9%, 69.7% an 68.1% respectively.

The ficus sycamore archaeological samples (EG-Is.C-1, EG-SAQ-1, EG-SAQ-3, EG-SAQ-49, EG-SAQ-5, EG-SAQ-6 and EG-DAK-1) had different lignin amounts with respect to the amount in the reference sample (31.1%). Sample EG-SAQ-5 had the highest percentage of lignin (49.6%) while samples EG-SAQ-2 and EG-SAQ-4 are similar to the reference with 30.3 and 30.8% respectively and the other samples showed lower lignin content as seen in Table 9 contradicting the published results for waterlogged wood.

The H/L (holocellulose/lignin) ratios (Fig. 50) varied between 0.3 for sample EG-SAQ-5 and to 3.6 for sample EG-SAQ-6, both belonging to the Ficus sycomorus and found in the same archaeological site. In fact, it is easy to estimate the preferential loss of holocellulose or lignin in an archaeological wood sample by comparing the value with that obtained for a sound wood of the same species. A decrease in the H/L ratio, indicating a loss of carbohydrates, is the
common situation for waterlogged wood, as the polysaccharide components of wood are less stable than lignin underwater. On the contrary, the value here obtained for sample EG-SAQ-6 (3.6) was much higher compared to the fresh wood of the same species (*Ficus sycomorus*, 2.0). In fact, a limited decrease in holocellulose (compared to fresh wood) was accompanied by a conspicuous decrease in lignin (14.2% for sample EG-SAQ-6; 31.1% for fresh *Ficus sycomorus*), thus explaining the increase in the H/L ratio and indicating that lignin was preferentially altered during ageing (and therefore removed during wet analyses). Similarly, to sample EG-SAQ-6, for samples EG-SAQ-3, EG-DAK-1 and EG-SAQ-8 the measured lignin values were lower than those of the corresponding reference fresh wood samples, and the H/L ratios were therefore higher.

![Figure 50: H/L ratios and ash content percentage of Egyptian wooden samples](image)

The case was different with sample EG-SAQ-5 as a relatively interesting high proportion of lignin (49.6%) was associated with a much low proportion of holocellulose (13.2 %) compared to the 61.1 % for fresh *F. sycomorus*, indicating that carbohydrates were preferentially depleted from sample EG-SAQ-5 during ageing. Although it was not possible to analyse the *F. albida* reference wood by wet chemical analysis (WCA), due to the low amount of sample available, a low content of holocellulose was detected in both samples EG-SAQ-2 and EG-SAQ-7 (21.6...
% and 36.9 %, respectively). As the value for holocellulose in most wood species is ca. 60-70 %. These values can be interpreted as a preferential loss of holocellulose in these samples. For sample EG-DAK-1 the relative content of holocellulose was also lower than the corresponding sound wood, highlighting that both lignin and holocellulose were degraded at a similar extent in this sample. The resulting H/L ratio was 2.3, which was comparable to the one obtained for fresh F. sycomorus (2.0). This highlighted that conclusions based on the H/L ratios often need to be integrated with additional information, otherwise the risk of misinterpretation is high.

The samples from the Islamic era in Egypt showed less dramatic figures when compared to the reference samples apart from samples EG-Is.C-3 (picea abies) which has 39.1% holocellulose compared to the 71.1% in the reference sample. In addition, the lignin showed some degradation but to a less degree. The other samples however were degraded at near extend in both holocellulose and lignin.

The extractives amount in most of the samples is very high compared to the reference samples and literatures. That has been previously recorded for ancient Egyptian samples. This elevation in the extractives and especially the aqueous extractives suggests the degradation of the wood residue of the polymers of these specimens had produced low molecular constituents that could be washed during the extraction process (Crestini et al., 2009). An increase in extractable material has been already observed in 240- to 1300-years-old dry Japanese wood (Kohara & Okamoto, 1955), although to a lesser extent compared to our results. Samples EG-SAQ-1, EG-SAQ-2, EG-SAQ-4, EG-SAQ-5, EG-SAQ-6, EG-DAK-1 and EG-SAQ-7 showed that the amount of extractable material was above 20% and, among them, samples EG-SAQ-2 and EG-DAK-1 revealed an amount of extractable material approximately 40%. The values obtained for the aqueous extractives in the fresh wood samples were < 4% (except for Tamarix sp., 8%). This suggested that the wood components (holocellulose and/or lignin) underwent some particular degradation pathways leading to a partial depolymerisation. The so-formed oligomers and/or compounds were then suitable for water extraction, accounting as extractable material in the WCA analysis.

Another reason for this high amount is the precipitated inorganic matter in the samples saw dust that was extracted and so the high percentage of aqueous extractives and ash content is
related to each other (Bettazzi et al., 2003). Therefore, a additional study of the extractives residue is to be completed in a later stage in the future

7.2 FTIR Analysis

Cultural heritage wooden samples were analysed by FTIR using the fingerprint region at 800–1800 cm\(^{-1}\). The interpretation of the data depends on the changes in the absorption bands (Table 10) and therefore a hypothesis of the chemical modification of wooden compounds can be drawn. Table 10 shows assignment of the main infrared bands characteristic of wood which are relevant to the results obtained in this thesis.

Mid-range infrared spectroscopy using attenuated total reflectance technique was adopted and allowed the use of the samples directly on the diamond lens without any preparation. The use of ATR-FTIR is mentioned in literatures (Zhou, Taylor, & Polle, 2011) as a preferred method over the KBr pellet method because of direct application of the sample and the factors that influence the KBr method like the pellet moisture content and inhomogeneity, relative humidity and difference in the pellet thickness.

The infrared spectra results recorded here support the wet chemical analysis results and also reflects the physical and mechanical state of preservation for the samples. The lower the H/L ration the higher is the FTIR peak in the lignin region and also the weaker and the darker the sample is. This example is clearly obvious in sample EG-SAQ-5 (*Ficus Sycomorus*). Figure 51 compares the FTIR spectra of sample EG-SAQ-5 before and after extraction with the reference samples of *Ficus sycomorus* L. The test was done on *Ficus Carica* L reference sample as well and both reference samples had almost identical FTIR spectra.

However, calibration has not been done yet but this technique still gives a quite reliable assessment for the chemistry of the wooden artefact. The regions of hollocellulose, lignin and ash for each sample and the intensity of the peaks indicate the changes in the functional group of the wood constituents.
Table 10: Assignments of IR absorption bands for the analysed cultural heritage wood samples.

<table>
<thead>
<tr>
<th>Band, cm⁻¹</th>
<th>Assignment</th>
</tr>
</thead>
<tbody>
<tr>
<td>3330</td>
<td>OH stretching vibration</td>
</tr>
<tr>
<td>1736</td>
<td>ester groups in hemicelluloses</td>
</tr>
<tr>
<td>1587</td>
<td>C-O vibration in carboxylates (coupled with ca. 1400)</td>
</tr>
<tr>
<td>1578</td>
<td>C-O vibration in metal chelates or salts of conjugated diketones</td>
</tr>
<tr>
<td>1595</td>
<td>C=C in the aromatic skeleton</td>
</tr>
<tr>
<td>1505</td>
<td>C=C in the aromatic skeleton</td>
</tr>
<tr>
<td>1455</td>
<td>asymmetric C-H deformation and aromatic vibration in lignin</td>
</tr>
<tr>
<td>1400/1415</td>
<td>C-O vibration in carboxylates coupled (with ca. 1587)</td>
</tr>
<tr>
<td>1370</td>
<td>C-H symmetric deformation in carbohydrates</td>
</tr>
<tr>
<td>1330</td>
<td>C-O in syringyl ring</td>
</tr>
<tr>
<td>1317</td>
<td>CH2 wagging in cellulose</td>
</tr>
<tr>
<td>1268</td>
<td>guaiacyl ring breathing</td>
</tr>
<tr>
<td>1230</td>
<td>C-O stretching in hemicelluloses</td>
</tr>
<tr>
<td>1217</td>
<td>C-O bond of the guaiacyl ring</td>
</tr>
<tr>
<td>1120</td>
<td>aromatic skeletal vibration and C-O stretching (in lignin)</td>
</tr>
<tr>
<td>1030</td>
<td>C-O-C deformations in polysaccharides</td>
</tr>
<tr>
<td>896</td>
<td>C-H deformation in cellulose</td>
</tr>
</tbody>
</table>

Absorption bands with maxima at 1736 cm⁻¹, 1030 cm⁻¹ and 895 cm⁻¹, which are attributable to polysaccharides (Table 10), showed a high intensity in the sound wood and were drastically reduced (or absent) in sample EG-SAQ-5. In contrast, bands with maxima at 1505 cm⁻¹, 1330 cm⁻¹ and 1217 cm⁻¹, attributable to aromatic skeletal vibrations in lignin, were more evident in sample EG-SAQ-5 compared to reference wood. The band at ca. 3330 cm⁻¹, related to the
OH stretching, also decreased in sample EG-SAQ-5 due to the depletion of polysaccharides. The FTIR spectrum obtained for sample EG-SAQ-5 represents the typical spectrum of an archaeological wood highly depleted in polysaccharides, which is the most common situation in waterlogged environments (Lucejko et al., 2015; Pizzo et al., 2015).

![FTIR spectrum comparison](image)

**Figure 51:** Comparison between the FTIR spectra of sample EG-SAQ-5 and the reference Ficus sycomorus.

A comparison between the FTIR spectra obtained for the other archaeological and sound wood samples mainly confirmed the observations obtained by WCA analysis in terms of preferential loss/preservation of wood components. However, the FTIR spectrum of sample EG-DAK-1 (Fig. 52) was similar to the reference sample, except for a strong decrease in the hemicelluloses bands at 1735 cm\(^{-1}\) and 1230 cm\(^{-1}\). This was actually the result of a comparable degradation of holocellulose and lignin.

In almost all the ancient Egyptian samples there is an obvious decrease in the intensities of the all wood components bands with the absence of the carbohydrates band at the 1738 cm\(^{-1}\). As expected from the wet chemical analysis, the spectrum of sample EG-SAQ-5 shows absence and/or reduction of bands at 1158, 1051 and 898 cm\(^{-1}\) which reflect the deterioration of the
carbohydrates of this sample. Similar results were achieved for the sample EG-Saq-8-S and demonstrated by the SEM examination to show the highly degraded secondary wall and the presence of the middle lamellae that contains most of the lignin as seen in bands 1593, 1510, 1461, 1422, 1320, 1265 and 1226 cm$^{-1}$ in both samples.

![Figure 52: Comparison between the FTIR spectra of sample EG-DAK-1 (blue spectrum) and the reference Ficus Carica L (orange spectrum).](image)

Extraction procedure with both organic solvents and water provided additional information and shed light on the nature of these soluble substances observed in the WCA analysis after comparing the results or the FTIR spectra before and after the extraction process. The spectra showed that in several cases the extraction procedure affected the composition of the samples, resulting in substantial differences in FTIR bands. This was mostly apparent in the case of sample EG-SAQ-2 (Fig. 53a) from Khendjer pyramid’s site in Saqqara. After extraction, a strong relative decrease in the intensity of the absorption bands centred at ca. 1400 cm$^{-1}$ and 1600 cm$^{-1}$ was observed. The simultaneous occurrence of both these bands is associated with the vibration of carboxylates (Colthup, Daly, & Wiberley, 1990). Sound wood does not usually show signals associated with these groups. The decrease in intensity suggests that these carboxylates were water-soluble (at least partially). It has been reported that cellulose degraded by brown rot fungi contains carboxylate groups (Kirk et al., 1991). This, therefore, suggests that these compounds containing carboxylate groups are constituted by modified
oligo-sugars and therefore attributable to a partial alteration of cellulose. However, the band at 1370 cm\(^{-1}\) still showed a relatively high intensity in the spectrum obtained after extraction, the intensity of all signals in the region around 1030 cm\(^{-1}\) was relatively higher, and a band at 896 cm\(^{-1}\) appeared. All these signals are associated with polysaccharides (Table 10). This highlighted that, although partial modifications had occurred, the residual cellulose backbone was still preserved. Similar results were obtained for sample EG-SAQ-7.

The spectra obtained for sample EG-SAQ-5 also presented changes after the extraction procedure. The spectrum before extraction was typical of a wood highly depleted in polysaccharides. In sample EG-SAQ-5, in addition to the high depletion of polysaccharides already discussed, the spectra obtained before and after the extraction procedure provided additional information. After the extraction, the intensity of the absorption band at ca. 1030 cm\(^{-1}\) slightly increased, but the intensity of the band at 1120 cm\(^{-1}\) was almost unchanged (Fig. 53b). This latter band is usually covered by the intensity of the C-O stretching vibration of carbohydrates. This thus highlighted a further decrease in the signals attributable to carbohydrates, which were partially extracted. In addition, the two coupled signals at 1587 cm\(^{-1}\) and 1415 cm\(^{-1}\), due to carboxylates and already observed for EG-SAQ-2, were also detected in sample EG-SAQ-5, although only a slight change was observed after extraction. This was also the case with the two bands at 2930 cm\(^{-1}\) and 2855 cm\(^{-1}\), whereas the band at 1600 cm\(^{-1}\) decreased in intensity. Considering that bands at 2930 cm\(^{-1}\) and 2855 cm\(^{-1}\) are usually associated to CH antisymmetric and CH2 symmetric stretches, respectively, in methyl and methylene groups, and that these signals are not so evident in wood, it can be suggested that sample EG-SAQ-5 was subject, in the past, to a treatment with extraneous organic substances,

Figure 53 (a & b): FTIR spectra of sample EG-SAQ-2 (a) and EG-SAQ-5 (b) before and after extraction.
such as hydrocarbons, rich in aliphatic groups. On the other side, the aromatic structure of lignin was well preserved after the extraction, as the bands at 1600 cm$^{-1}$, 1505 cm$^{-1}$ (both related to the aromatic skeletal vibration), 1420 cm$^{-1}$, 1330 cm$^{-1}$ (attributed to the syringyl ring) and 1120 cm$^{-1}$ were evident in the spectrum.

In the other samples, the extraction did not result in substantial changes in the FTIR spectra. However, in some cases, interesting observations were obtained from a comparison between the spectra obtained after extraction and the reference wood samples. For sample EG-SAQ-6, the extraction did not appreciably change the FTIR spectrum, it did however show some differences compared to the one obtained for the reference samples *Ficus sycomorus* and *Ficus carica* L. In this sample (EG-SAQ-6, Fig. 54a), the two absorption bands at 1730 cm$^{-1}$ and 1230 cm$^{-1}$, both attributable to hemicelluloses, a degradation of this wood component. In addition, the absorption bands at 1505 cm$^{-1}$, 1455 cm$^{-1}$ and 1268 cm$^{-1}$ significantly decreased in comparison to the non-degraded wood, highlighting an alteration in the lignin structure.

In sample EG-SAQ-8, significant differences were present in the region 1300-1800 cm$^{-1}$ (Fig. 54b). A broad band centred at 1578 cm$^{-1}$ completely covered the other bands. This band is characteristic of metal chelates or salts of conjugated diketones (Colthup et al., 1990). Other associated vibrations should be present at 1500-1530, *ca.* 1450 and *ca.* 1250 cm$^{-1}$ (Colthup et al., 1990), however in our case they all overlapped with other wood signals. It has been previously shown that degradation by ligninase (a ligninolytic peroxidase secreted by white rot fungi) of the arylglycerol β-O-4 substructure of lignin produces decomposition in guaiacol and a diketone (Kirk et al., 1986). However, the relatively high intensity of the other bands in the spectrum suggested that the extent of the lignin modification was relatively limited.

The FTIR spectra of sample EG-SAQ-4 showed the decrease in the hemicelluloses bands while for samples EG-SOH-1, EG-SOH-2 and EG-SOH-3 even the bands of hemicelluloses were still evident, highlighting the optimal preservation conditions of these samples (Fig. 55a and b).
Figure 54 (a & b): FTIR spectra of samples: a) EG-SAQ-6 in comparison with reference Ficus sycomorus; b) EG-SAQ-8 in comparison with reference Taxus baccata.

Figure 55 (a & b): FTIR spectra of samples: a) EG-SOH-1 in comparison with reference Tamarix sp.; b) EG-SOH-2 and EG-SOH-3 in comparison with reference Pinus sylvestris
7.3 Energy-dispersive X-ray Spectroscopy (EDS):

For a better understanding of the decay in the ultrastructure level additional investigations were carried out by SEM-EDS. SEM analysis has been already mentioned in the anatomical and microscopic discussion. The EDS analysis confirms the high percentage of the ash content in some samples and the presence of calcium, sulphur potassium, iron and chlorine in some sample which suggest the use of gypsum as a ground layer on the wooden support (Fig. 56).

![EDS spectrum of sample EG-SAQ-2](image)

Figure 56: EDS spectrum of sample EG-SAQ-2. It shows the presence of the calcium Ca in high intensity which suggest that the ash content is affected by the preparation material that was put on the wooden substrates to prepare it for painting.

7.4 Py(HMDS)-GC/MS

Py(HMDS)-GC/MS was applied, adopting the conditions described above. Samples EG-SAQ-2 and EG-SAQ-7 were found in the same archaeological site and the wood was identified as *Faidherbia albida* sp. Figure 57 shows the pyrograms obtained for the sound wood and for sample EG-SAQ-7.
Figure 57: Py(HMDS)-GC/MS profiles for samples a) sound Faidherbia albida and b) EG-SAQ-7. Peak labelling refers to Table 11 In Italic: lignin pyrolysis products.

Table 11: Wood pyrolysis products identified by Py(HMDS)-GC/MS and divided into categories. The molecular weight (MW) of the derivatised compounds, the main m/z peaks in the mass spectra (base peak in bold), the attribution of the pyrolysis products to the corresponding wood component (H=Holocellulose, L=Lignin, G=Guaiacyl lignin, S=Syringyl lignin) and to the specific categories (dem=demethylated/demethoxylated compounds) are shown.

<table>
<thead>
<tr>
<th>No</th>
<th>Compound</th>
<th>MW</th>
<th>m/z</th>
<th>Origin</th>
<th>Category</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1,2-dihydroxyethane (2TMS)</td>
<td>206</td>
<td>73,103,147,191</td>
<td>H/L</td>
<td>Small molecules</td>
</tr>
<tr>
<td>2</td>
<td>2-hydroxymethylfuran (TMS)</td>
<td>170</td>
<td>53, 73, 81, 111, 125, 142, 155, 170</td>
<td>H</td>
<td>Furans</td>
</tr>
<tr>
<td>3</td>
<td>phenol (TMS)</td>
<td>166</td>
<td>75, 151, 166</td>
<td>L</td>
<td>Others</td>
</tr>
<tr>
<td>4</td>
<td>2-hydroxypropanoic acid (2TMS)</td>
<td>234</td>
<td>73, 117, 147, 190</td>
<td>H/L</td>
<td>Small molecules</td>
</tr>
<tr>
<td>5</td>
<td>2-hydroxyacetic acid (2TMS)</td>
<td>220</td>
<td>73, 147, 177, 205</td>
<td>H/L</td>
<td>Small molecules</td>
</tr>
<tr>
<td>6</td>
<td>1-hydroxy-1-cyclopenten-3-one (TMS)</td>
<td>170</td>
<td>53, 73, 81, 101, 111, 127, 155</td>
<td>H</td>
<td>Cyclopentenones</td>
</tr>
<tr>
<td>7</td>
<td>3-hydroxymethylfuran (TMS)</td>
<td>170</td>
<td>53, 75, 81, 111, 125, 142, 155, 170</td>
<td>H</td>
<td>Furans</td>
</tr>
<tr>
<td>8</td>
<td>o-cresol (TMS)</td>
<td>180</td>
<td>73, 91, 135, 149, 165, 180</td>
<td>L</td>
<td>Others</td>
</tr>
<tr>
<td>No.</td>
<td>Compound Description</td>
<td>Retention Time</td>
<td>Peak Numbers</td>
<td>Isolated Molecular Weight</td>
<td>Class</td>
</tr>
<tr>
<td>-----</td>
<td>----------------------------------------------------------</td>
<td>----------------</td>
<td>--------------</td>
<td>----------------------------</td>
<td>-----------------</td>
</tr>
<tr>
<td>9</td>
<td>2-furancarboxylic acid (TMS)</td>
<td>184</td>
<td>73, 95, 125, 169, 184</td>
<td>H Furans</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>unknown holocellulose I</td>
<td>73, 152, 167</td>
<td>H Others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>m-cresol (TMS)</td>
<td>180</td>
<td>73, 91, 165, 180</td>
<td>L Others</td>
<td></td>
</tr>
<tr>
<td>12</td>
<td>2-hydroxy-1-cyclopenten-3-one (TMS)</td>
<td>170</td>
<td>53, 73, 81, 101, 111, 127, 155, 170</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>13</td>
<td>p-cresol (TMS)</td>
<td>180</td>
<td>73, 91, 165, 180</td>
<td>L Others</td>
<td></td>
</tr>
<tr>
<td>14</td>
<td>3-hydroxy-(2H)-pyran-2-one (TMS)</td>
<td>184</td>
<td>75, 95, 125, 151, 169, 184</td>
<td>H Pyranones</td>
<td></td>
</tr>
<tr>
<td>15</td>
<td>unknown holocellulose II</td>
<td>59, 73, 85, 101, 115, 131, 159</td>
<td>H Others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>16</td>
<td>unknown holocellulose III</td>
<td>75, 85, 103, 115, 129, 145, 173, 188</td>
<td>H Others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>Z-2,3-dihydroxycyclopent-2-enone (TMS)</td>
<td>186</td>
<td>59, 73, 115, 143, 171, 186</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>18</td>
<td>E-2,3-dihydroxycyclopent-2-enone (TMS)</td>
<td>186</td>
<td>75, 101, 143, 171, 186</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>19</td>
<td>1,2-dihydroxybenzene (TMS)</td>
<td>182</td>
<td>75, 91, 136, 151, 167, 182</td>
<td>H Hydroxybenzenes</td>
<td></td>
</tr>
<tr>
<td>20</td>
<td>3-hydroxy-(4H)-pyran-4-one (TMS)</td>
<td>184</td>
<td>75, 95, 139, 151, 169, 184</td>
<td>H Pyranones</td>
<td></td>
</tr>
<tr>
<td>21</td>
<td>5-hydroxy-(2H)-pyran-4(3H)-one (TMS)</td>
<td>186</td>
<td>59, 75, 101, 129, 143, 171, 186</td>
<td>H Pyranones</td>
<td></td>
</tr>
<tr>
<td>22</td>
<td>2-hydroxymethyl-3-methy-2-cyclopentenone (TMS)</td>
<td>198</td>
<td>73, 103, 129, 173, 13, 198</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>23</td>
<td>1-hydroxy-2-methyl-1-cyclopenten-3-one (TMS)</td>
<td>184</td>
<td>73, 97, 125, 139, 169, 184</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>24</td>
<td>1-methy-2-hydroxy-1-cyclopenten-3-one (TMS)</td>
<td>184</td>
<td>73, 97, 125, 139, 169, 184</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>25</td>
<td>1,3-dihydroxyacetone (2TMS)</td>
<td>234</td>
<td>73, 103, 147, 189, 219</td>
<td>H Small molecules</td>
<td></td>
</tr>
<tr>
<td>26</td>
<td>guaiacol (TMS)</td>
<td>196</td>
<td>73, 151, 166, 181, 196</td>
<td>G Short chain</td>
<td></td>
</tr>
<tr>
<td>27</td>
<td>unknown holocellulose IV</td>
<td>73, 217, 232</td>
<td>H Others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>28</td>
<td>3-hydroxy-6-methyl-(2H)-pyran-2-one (TMS)</td>
<td>198</td>
<td>73, 109, 139, 168, 183, 198</td>
<td>H Pyranones</td>
<td></td>
</tr>
<tr>
<td>29</td>
<td>unknown holocellulose V</td>
<td>73, 101, 116, 131, 173</td>
<td>H Others</td>
<td></td>
<td></td>
</tr>
<tr>
<td>30</td>
<td>2-methyl-3-hydroxy-(4H)-pyran-4-one (TMS)</td>
<td>198</td>
<td>73, 101, 153, 183, 198</td>
<td>H Pyranones</td>
<td></td>
</tr>
<tr>
<td>31</td>
<td>2-methyl-3-hydroxymethyl-2-cyclopentenone (TMS)</td>
<td>198</td>
<td>73, 103, 129, 173, 13, 198</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>32</td>
<td>2,3-dihydrofuran-2,3-diol (2TMS)</td>
<td>246</td>
<td>73, 147, 231, 246</td>
<td>H Furans</td>
<td></td>
</tr>
<tr>
<td>33</td>
<td>2-furylhydroxymethylketone (TMS)</td>
<td>198</td>
<td>73, 81, 103, 125, 183, 198</td>
<td>H Furans</td>
<td></td>
</tr>
<tr>
<td>34</td>
<td>5-hydroxymethyl-2-furaldehyde (TMS)</td>
<td>198</td>
<td>73, 81, 109, 111, 139, 169, 183, 198</td>
<td>H Furans</td>
<td></td>
</tr>
<tr>
<td>#</td>
<td>Molecule</td>
<td>MW</td>
<td>References</td>
<td>Classification</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>--------------------------------------------------------------------------</td>
<td>----</td>
<td>--------------------------------------------------------------------------</td>
<td>----------------</td>
<td></td>
</tr>
<tr>
<td>35</td>
<td>4-methylguaiacol (TMS)</td>
<td>210</td>
<td>73, 149, 180, 195, 210</td>
<td>G Short chain</td>
<td></td>
</tr>
<tr>
<td>36</td>
<td>1,2-dihydroxybenzene (2TMS)</td>
<td>254</td>
<td>73, 151, 239, 254</td>
<td>H Hydroxybenzenes</td>
<td></td>
</tr>
<tr>
<td>37</td>
<td>2-hydroxymethyl-2,3-dihydroxybenzene (TMS)</td>
<td>200</td>
<td>73, 142, 170, 185, 200</td>
<td>H Pyranones</td>
<td></td>
</tr>
<tr>
<td>38</td>
<td>1,4:3:6-dianhydro-α-D-glucopyranose (TMS)</td>
<td>186</td>
<td>73, 103, 129, 155, 170, 171, 186</td>
<td>H Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>39</td>
<td>Z-2,3-dihydroxycyclopent-2-enone (2TMS)</td>
<td>258</td>
<td>73, 147, 230, 243, 258</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>40</td>
<td>4-methylcatechol (TMS)</td>
<td>268</td>
<td>73, 180, 253, 268</td>
<td>G Dem</td>
<td></td>
</tr>
<tr>
<td>41</td>
<td>4-ethylguaiacol (TMS)</td>
<td>224</td>
<td>73, 149, 179, 194, 209, 224</td>
<td>G Short chain</td>
<td></td>
</tr>
<tr>
<td>42</td>
<td>syringol (TMS)</td>
<td>226</td>
<td>73, 153, 181, 196, 211, 226</td>
<td>S Short chain</td>
<td></td>
</tr>
<tr>
<td>43</td>
<td>1,4-dihydroxybenzene (2TMS)</td>
<td>254</td>
<td>73, 112, 239, 254</td>
<td>H Hydroxybenzenes</td>
<td></td>
</tr>
<tr>
<td>44</td>
<td>arabinofuranose (4TMS)</td>
<td>438</td>
<td>73, 147, 217, 230</td>
<td>H Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>45</td>
<td>4-vinylguaiacol (TMS)</td>
<td>222</td>
<td>73, 162, 177, 192, 207, 222</td>
<td>G Short chain</td>
<td></td>
</tr>
<tr>
<td>46</td>
<td>3-hydroxy-2-hydroxymethyl-2-cyclopentenone (2TMS)</td>
<td>272</td>
<td>73, 147, 257, 272</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>47</td>
<td>E-2,3-dihydroxycyclopent-2-enone (2TMS)</td>
<td>258</td>
<td>73, 147, 243, 258</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>48</td>
<td>4-ethylcatechol (2TMS)</td>
<td>282</td>
<td>73, 147, 179, 231, 267, 282</td>
<td>G Dem</td>
<td></td>
</tr>
<tr>
<td>49</td>
<td>3-hydroxy-2-(hydroxymethyl)cyclohexa-2,4-diene (2TMS)</td>
<td>270</td>
<td>73, 147, 255, 270</td>
<td>H Cyclopentones</td>
<td></td>
</tr>
<tr>
<td>50</td>
<td>eugenol (TMS)</td>
<td>236</td>
<td>73, 147, 179, 206, 221, 236</td>
<td>G Long chain</td>
<td></td>
</tr>
<tr>
<td>51</td>
<td>4-methyloxyringol (TMS)</td>
<td>240</td>
<td>73, 167, 210, 225, 240</td>
<td>S Short chain</td>
<td></td>
</tr>
<tr>
<td>52</td>
<td>3-methoxy-1,2-benzenediol (2TMS)</td>
<td>284</td>
<td>73, 153, 254, 269, 284</td>
<td>S Dem</td>
<td></td>
</tr>
<tr>
<td>53</td>
<td>3,5-dihydrox-2-methoxy-4-hydroxybenzene (2TMS)</td>
<td>286</td>
<td>73, 128, 147, 183, 271, 286</td>
<td>H Pyranones</td>
<td></td>
</tr>
<tr>
<td>54</td>
<td>1,6-anhydro-β-D-glucopyranose (TMS at position 4)</td>
<td>234</td>
<td>73, 103, 117, 129, 145, 155, 171</td>
<td>H Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>55</td>
<td>1,6-anhydro-β-D-glucopyranose (TMS at position 2)</td>
<td>234</td>
<td>73, 101, 116, 129, 132, 145, 155, 171</td>
<td>H Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>56</td>
<td>Z-4-isoegenol (TMS)</td>
<td>236</td>
<td>73, 179, 206, 221, 236</td>
<td>G Long chain</td>
<td></td>
</tr>
<tr>
<td>57</td>
<td>vanillin (TMS)</td>
<td>224</td>
<td>73, 194, 209, 224</td>
<td>G Carbonyl</td>
<td></td>
</tr>
<tr>
<td>58</td>
<td>1,2,3-trihydroxybenzene (3TMS)</td>
<td>342</td>
<td>73, 133, 147, 239, 327, 342</td>
<td>H Hydroxybenzenes</td>
<td></td>
</tr>
<tr>
<td>59</td>
<td>5-methyl-3-methoxy-1,2-benzenediol (2TMS)</td>
<td>298</td>
<td>73, 151, 210, 253, 268, 283, 298</td>
<td>S Dem</td>
<td></td>
</tr>
<tr>
<td>No.</td>
<td>Compound Description</td>
<td>Retention Time (min)</td>
<td>Peaks</td>
<td>Chain Length</td>
<td>Category</td>
</tr>
<tr>
<td>-----</td>
<td>---------------------</td>
<td>---------------------</td>
<td>-------</td>
<td>-------------</td>
<td>----------</td>
</tr>
<tr>
<td>60</td>
<td>4-ethylsyringol (TMS)</td>
<td>254</td>
<td>73, 191, 209, <strong>224</strong>, 239, 254</td>
<td>S</td>
<td>Short chain</td>
</tr>
<tr>
<td>61</td>
<td>E-4-isoeugenol (TMS)</td>
<td>236</td>
<td>73, 179, <strong>206</strong>, 221, 236</td>
<td>G</td>
<td>Long chain</td>
</tr>
<tr>
<td>62</td>
<td>1,4-anhydro-D-galactopyranose (2TMS)</td>
<td>306</td>
<td><strong>73</strong>, 101, 116, 129, 145, 155, 171, 217</td>
<td>H</td>
<td>Anhydrosugars</td>
</tr>
<tr>
<td>63</td>
<td>1,6-anhydro-D-galactopyranose (2TMS)</td>
<td>306</td>
<td><strong>73</strong>, 101, 116, 129, 145, 169, 204, 217</td>
<td>H</td>
<td>Anhydrosugars</td>
</tr>
<tr>
<td>64</td>
<td>2-hydroxymethyl-5-hydroxy-2,3-dihydro-(4H)-pyran-4-one (2TMS)</td>
<td>288</td>
<td><strong>73</strong>, 129, 147, 155, 183, 273, 288</td>
<td>H</td>
<td>Pyranones</td>
</tr>
<tr>
<td>65</td>
<td>4-vinylsyringol (TMS)</td>
<td>252</td>
<td>73, 179, <strong>222</strong>, 237, 252</td>
<td>S</td>
<td>Short chain</td>
</tr>
<tr>
<td>66</td>
<td>1,4-anhydro-D-glucopyranose (2TMS at position 2 and 4)</td>
<td>306</td>
<td><strong>73</strong>, 101, 116, 129, 155, 191, 204, 217</td>
<td>H</td>
<td>Anhydrosugars</td>
</tr>
<tr>
<td>67</td>
<td>1,2,4-trihydroxybenzene (3TMS)</td>
<td>342</td>
<td><strong>73</strong>, 133, 147, 239, 327, 342</td>
<td>H</td>
<td>Hydroxybenzenes</td>
</tr>
<tr>
<td>68</td>
<td>Acetovanillone (TMS)</td>
<td>238</td>
<td>73, <strong>193</strong>, 208, 223, 238</td>
<td>G</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>69</td>
<td>4-hydroxybenzoic acid (2TMS)</td>
<td>282</td>
<td><strong>73</strong>, 147, 193, 223, <strong>267</strong>, 282</td>
<td>L</td>
<td>Acids</td>
</tr>
<tr>
<td>70</td>
<td>4-propenylsyringol (TMS)</td>
<td>266</td>
<td>73, 205, <strong>236</strong>, 251, 266</td>
<td>S</td>
<td>Long chain</td>
</tr>
<tr>
<td>71</td>
<td>1,6-anhydro-β-D-glucopyranose (2TMS at position 2 and 4)</td>
<td>306</td>
<td><strong>73</strong>, 101, 116, 129, 155, 191, 204, 217</td>
<td>H</td>
<td>Anhydrosugars</td>
</tr>
<tr>
<td>72</td>
<td>Vanillic acid methyl ester (TMS)</td>
<td>254</td>
<td>73, 193, <strong>224</strong>, 239, 254</td>
<td>G</td>
<td>Esters</td>
</tr>
<tr>
<td>73</td>
<td>5-vinyl-3-methoxy-1,2-benzenediol (2TMS)</td>
<td>310</td>
<td><strong>73</strong>, 147, 179, 222, 280, 295, 310</td>
<td>S</td>
<td>Dem</td>
</tr>
<tr>
<td>74</td>
<td>Z-4-isopropenylsyringol</td>
<td>266</td>
<td>73, 205, <strong>236</strong>, 251, 266</td>
<td>S</td>
<td>Long chain</td>
</tr>
<tr>
<td>75</td>
<td>1,4-anhydro-D-galactopyranose (3TMS)</td>
<td>378</td>
<td><strong>73</strong>, 129, 147, 191, 204, 217, 243, 332</td>
<td>H</td>
<td>Anhydrosugars</td>
</tr>
<tr>
<td>76</td>
<td>Unknown lignin I</td>
<td></td>
<td><strong>73</strong>, 147, 193, 239, 313, 401, 416</td>
<td>L</td>
<td>Others</td>
</tr>
<tr>
<td>77</td>
<td>Syringaldehyde (TMS)</td>
<td>254</td>
<td>73, <strong>224</strong>, 239, 254</td>
<td>S</td>
<td>Carbonyl</td>
</tr>
<tr>
<td>78</td>
<td>2,3,5-trihydroxy-4H-pyran-4-one (3TMS)</td>
<td>360</td>
<td><strong>73</strong>, 147, 239, 255, 270, 330, 345, 360</td>
<td>H</td>
<td>Pyranones</td>
</tr>
<tr>
<td>79</td>
<td>1,6-anhydro-β-D-glucopyranose (3TMS)</td>
<td>378</td>
<td><strong>73</strong>, 129, 147, 191, 204, 217, 243, 332</td>
<td>H</td>
<td>Anhydrosugars</td>
</tr>
<tr>
<td>80</td>
<td>1,4-anhydro-D-glucopyranose (3TMS)</td>
<td>378</td>
<td><strong>73</strong>, 129, 147, 191, 204, 217, 243, 332</td>
<td>H</td>
<td>Anhydrosugars</td>
</tr>
<tr>
<td>81</td>
<td>E-4-isopropenylsyringol (TMS)</td>
<td>266</td>
<td>73, 205, <strong>236</strong>, 251, 266</td>
<td>S</td>
<td>Long chain</td>
</tr>
<tr>
<td>82</td>
<td>1,6-anhydro-β-D-glucofuranose (3TMS)</td>
<td>378</td>
<td><strong>73</strong>, 129, 147, 191, 204, 217, 243, 319</td>
<td>H</td>
<td>Anhydrosugars</td>
</tr>
<tr>
<td>83</td>
<td>Unknown lignin II</td>
<td></td>
<td>73, 179, 217,342, 358, 415, <strong>430</strong></td>
<td>L</td>
<td>Others</td>
</tr>
<tr>
<td>84</td>
<td>Unknown lignin III</td>
<td></td>
<td>73, 147, 193, 239, 313, 401, 416</td>
<td>L</td>
<td>Others</td>
</tr>
<tr>
<td>85</td>
<td>Vanillic acid (2TMS)</td>
<td>312</td>
<td>73, 223, 253, 267, 282, <strong>297</strong>, 312</td>
<td>G</td>
<td>Acids</td>
</tr>
<tr>
<td>No.</td>
<td>Compound</td>
<td>Formula</td>
<td>Mass</td>
<td>Retention Time</td>
<td>Type</td>
</tr>
<tr>
<td>-----</td>
<td>-----------------------------------------------</td>
<td>---------</td>
<td>------</td>
<td>----------------</td>
<td>--------</td>
</tr>
<tr>
<td>86</td>
<td>Acetosyringone (TMS)</td>
<td></td>
<td>268</td>
<td>73, 223, 238, 253, 268</td>
<td>S, Carbonyl</td>
</tr>
<tr>
<td>87</td>
<td>5-propyl-3-methoxy-1,2-benzenediol (2TMS)</td>
<td></td>
<td>326</td>
<td>73, 147, 179, 209, 296, 311, 326</td>
<td>S, Dem</td>
</tr>
<tr>
<td>88</td>
<td>Coumaryl alcohol (2 TMS)</td>
<td></td>
<td>294</td>
<td>73, 189, 205, 267, 279, 294</td>
<td>G, Dem</td>
</tr>
<tr>
<td>89</td>
<td>Syringic acid methyl ester (TMS)</td>
<td></td>
<td>284</td>
<td>73, 223, 254, 269, 284</td>
<td>S, Esters</td>
</tr>
<tr>
<td>90</td>
<td>Vanillylpropanol (2TMS)</td>
<td></td>
<td>326</td>
<td>73, 179, 206, 221, 236, 311, 326</td>
<td>G, Long chain</td>
</tr>
<tr>
<td>91</td>
<td>Z-coniferyl alcohol (2 TMS)</td>
<td></td>
<td>324</td>
<td>73, 204, 252, 293, 309, 324</td>
<td>G, Monomers</td>
</tr>
<tr>
<td>92</td>
<td>4-hydroxy-3,5-dimethoxycinnamic acid methyl ester (TMS)</td>
<td></td>
<td>310</td>
<td>73, 147, 179, 222, 280, 295, 310</td>
<td>S, Esters</td>
</tr>
<tr>
<td>93</td>
<td>Coniferylaldehyde (TMS)</td>
<td></td>
<td>250</td>
<td>73, 192, 220, 235, 250</td>
<td>G, Carbonyl</td>
</tr>
<tr>
<td>94</td>
<td>Trihydroxycinnamyl alcohol (3TMS)</td>
<td></td>
<td>398</td>
<td>73, 147, 210, 254, 368, 383, 398</td>
<td>S, Dem</td>
</tr>
<tr>
<td>95</td>
<td>Syringic acid (2TMS)</td>
<td></td>
<td>342</td>
<td>73, 253, 297, 312, 327, 342</td>
<td>S, Acids</td>
</tr>
<tr>
<td>96</td>
<td>Unknown lignin IV</td>
<td></td>
<td></td>
<td>73, 179, 209, 237, 280, 310, 325, 340</td>
<td>L, Others</td>
</tr>
<tr>
<td>97</td>
<td>E-coniferyl alcohol (2 TMS)</td>
<td></td>
<td>324</td>
<td>73, 204, 235, 293, 309, 324</td>
<td>G, Monomers</td>
</tr>
<tr>
<td>98</td>
<td>3,4-dihydroxy-5-methoxybenzoic acid (3TMS)</td>
<td></td>
<td>400</td>
<td>73, 137, 147, 223, 253, 297, 385, 400</td>
<td>S, Acids</td>
</tr>
<tr>
<td>99</td>
<td>Syringylpropanol (2TMS)</td>
<td></td>
<td>356</td>
<td>73, 210, 240, 341, 356</td>
<td>S, Long chain</td>
</tr>
<tr>
<td>100</td>
<td>Z-sinapyl alcohol (2TMS)</td>
<td></td>
<td>354</td>
<td>73, 234, 323, 339, 354</td>
<td>S, Monomers</td>
</tr>
<tr>
<td>101</td>
<td>Unknown lignin V</td>
<td></td>
<td></td>
<td>73, 179, 209, 237, 280, 310, 325, 340</td>
<td>L, Others</td>
</tr>
<tr>
<td>102</td>
<td>3,4-dihydroxycinnamyl alcohol (3TMS)</td>
<td></td>
<td>382</td>
<td>73, 205, 293, 355, 382</td>
<td>G, Dem</td>
</tr>
<tr>
<td>103</td>
<td>Trihydroxycinnamyl alcohol I (3TMS)</td>
<td></td>
<td>398</td>
<td>73, 147, 210, 254, 368, 383, 398</td>
<td>S, Dem</td>
</tr>
<tr>
<td>104</td>
<td>Sinapylaldehyde (TMS)</td>
<td></td>
<td>280</td>
<td>73, 222, 250, 265, 280</td>
<td>S, Carbonyl</td>
</tr>
<tr>
<td>105</td>
<td>Trihydroxycinnamyl alcohol II (3TMS)</td>
<td></td>
<td>398</td>
<td>73, 147, 210, 254, 368, 383, 398</td>
<td>S, Dem</td>
</tr>
<tr>
<td>106</td>
<td>Z-2-methoxy-3,4-dihydroxycinnamyl alcohol (3TMS)</td>
<td></td>
<td>412</td>
<td>73, 235, 323, 385, 412</td>
<td>S, Dem</td>
</tr>
<tr>
<td>107</td>
<td>Sinapyl alcohol (TMS)</td>
<td></td>
<td>282</td>
<td>73, 234, 251, 267, 282</td>
<td>S, Monomers</td>
</tr>
<tr>
<td>108</td>
<td>E-sinapyl alcohol (2TMS)</td>
<td></td>
<td>354</td>
<td>73, 234, 323, 339, 354</td>
<td>S, Monomers</td>
</tr>
<tr>
<td>109</td>
<td>E-2-methoxy-3,4-dihydroxycinnamyl alcohol (3TMS)</td>
<td></td>
<td>412</td>
<td>73, 235, 323, 385, 412</td>
<td>S, Dem</td>
</tr>
<tr>
<td></td>
<td>unknown lignin VI</td>
<td>73, 147, 196, 253, 355, 370</td>
<td>L</td>
<td>Others</td>
<td></td>
</tr>
<tr>
<td>----</td>
<td>------------------</td>
<td>-----------------------------</td>
<td>---</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>unknown anhydrosugar I (dimer)</td>
<td>73, 103, 117, 147, 177, 189, 303, 347</td>
<td>H</td>
<td>Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>unknown anhydrosugar II (dimer)</td>
<td>73, 103, 117, 129, 147, 204, 217, 361</td>
<td>H</td>
<td>Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>unknown anhydrosugar III (dimer)</td>
<td>73, 117, 129, 147, 204, 217, 223, 361</td>
<td>H</td>
<td>Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>unknown anhydrosugar IV (dimer)</td>
<td>73, 117, 129, 147, 204, 217, 243, 273</td>
<td>H</td>
<td>Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>unknown anhydrosugar V (dimer)</td>
<td>73, 117, 129, 147, 190, 204, 347, 352</td>
<td>H</td>
<td>Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>unknown anhydrosugar VI (dimer)</td>
<td>73, 117, 129, 147, 204, 217, 289, 361</td>
<td>H</td>
<td>Anhydrosugars</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>unknown anhydrosugar VII (dimer)</td>
<td>73, 117, 129, 147, 204, 217, 289, 361</td>
<td>H</td>
<td>Anhydrosugars</td>
<td></td>
</tr>
</tbody>
</table>

The sample of sound *Faidherbia albida* showed a typical profile for a sound hardwood, with both holocellulose and lignin pyrolysis products with comparable abundances. The most abundant holocellulose pyrolysis products were 2-hydroxy-1-cyclopenten-3-one (#12) and *E*-2,3-dihydroxy-cyclopent-2-enone (#47), whereas anhydrosugars were not detected with high abundances. Lignin monomers *E*-coniferyl and *E*-sinapyl alcohols (#97, 108) were the most abundant lignin pyrolysis products.

Sample EG-SAQ-7 showed a different profile, where holocellulose pyrolysis products were the most abundant. In particular, 5-hydroxymethyl-2-furaldehyde (#34) and 1,6-anhydro-β-D-glucopyranose with different degrees of silylation (#54, 55, 71, 79) showed the highest abundances. Among lignin pyrolysis, only guaiacol (#26) and syringol (#42) were detected with significant abundances. Sample EG-SAQ-2 showed a pyrolytic profile similar to sample EG-SAQ-7.

Samples EG-SAQ-3, EG-SAQ-4, EG-SAQ-5, EG-SAQ-6 and EG-DAK-1 were identified as *Ficus sycomorus* sp. Figure 58 shows the pyrograms obtained for the sound wood and for samples EG-SAQ-3 and EG-SAQ-5.
Ficus sycomorus showed a very similar profile to Faidherbia albida. Samples EG-SAQ-3 and EG-SAQ-5 showed different profiles: sample EG-SAQ-3 revealed a high abundance of holocellulose pyrolysis products, similarly to sample EG-SAQ-7, whereas sample EG-SAQ-5 showed mainly lignin pyrolysis products with a very particular profile. Guaiacol (#26) and syringol (#42) were the most abundant, followed by 3-methoxy-1,2-benzenediol (#52), which is one of the main products of demethylation/demethoxylation reactions (Martínez et al., 2011). Significant abundances for syringaldehyde (#77) and acetosyringone (#86) were detected, whereas lignin monomers (#97, 108) showed very low abundances with respect to the sound Ficus sycomorus. The pyrolytic profile for sample EG-SAQ-4 was similar to the sound Ficus sycomorus. Samples EG-SAQ-6 and EG-DAK-1 showed comparable results to sample EG-SAQ-3.

Figure 58: Py(HMDS)-GC/MS profiles for samples a) sound Ficus sycomorus, b) EG-SAQ-3, c) EG-SAQ-5. Peak labelling refers to Table 11. In Italic: lignin pyrolysis products.
Sample EG-SAQ-8 was identified as *Taxus baccata* sp. The pyrogram obtained showed high abundances of holocellulose pyrolysis products and the profile for lignin pyrolysis products was similar to samples EG-SAQ-7 (Fig. 57) and EG-SAQ-3 (Fig. 58).

The wood species for sample EG-ASW-1 was not identified, thus it was impossible to compare the results obtained with those from the appropriate sound wood sample. Nevertheless, the pyrolytic profile for this sample was so altered with respect to any sound wood, that conclusions about degradation could be drawn out even without a direct comparison. In fact, a few holocellulose pyrolysis product were detected with low abundance, with 1,2-dihydroxybenzene (#36) being the most abundant one. Phenol (#3) and guaiacol (#26) were the most abundant lignin pyrolysis products, as shown in Figure 59. In addition, glycerol was detected in this sample, likely from a previous restoration treatment.

![Figure 59: Py(HMDS)-GC/MS profiles for sample EG-ASW-1. Peak labelling refers to Table 11. In italic: lignin pyrolysis products.](image)

Samples EG-SOH-1, EG-SOH-2 and EG-SOH-3 were taken from different parts of the same object (a wooden column). Sample EG-SOH-1 was identified as *Tamarix* sp. and samples EG-SOH-2 and EG-SOH-3 were identified as *Pinus sylvestris* sp. The pyrolytic profiles for these samples showed the presence of both holocellulose and lignin pyrolysis products with some differences with respect to the corresponding sound wood samples, mainly regarding a slight relative decrease of holocellulose pyrolysis products. For these samples glycerol was detected with different abundances. In particular, glycerol was very abundant for sample EG-SOH-2, for which both the disilylated and the trisilylated forms were detected. These samples were taken from a painted wooden column, which was wrapped with an adhesive tape for storing.
The presence of glycerol could be due to contamination from the tape or from some previous treatments. Figure 60 reports the pyrograms for the sound *Pinus sylvestris* and samples EG-SOH-2 and EG-SOH-3.

![Py(HMDS)-GC/MS profiles for samples](image)

Figure 60: Py(HMDS)-GC/MS profiles for samples a) sound *Pinus sylvestris*, b) EG-SOH-2, c) EG-SOH-3. Peak labelling refers to Table 11. In Italic: lignin pyrolysis products.

Sample EG-UNKNOWN was identified as *Cupressus sempervirens* and the pyrogram showed some slight differences with respect to sound wood. Glycerol was detected in sample EG-UNKNOWN.

The H/L and S/G ratios were calculated for all the archaeological and sound samples and the results are reported in Table 12. The S/G ratios, calculated only for the hardwood species, showed a decrease for all the archaeological samples with respect to the corresponding sound wood samples, with the exception of sample EG-SAQ-4, EG-SAQ-5 and EG-SOH-1. For samples EG-SAQ-4 and EG-SOH-1 the S/G ratio was comparable to that of reference wood.
(Ficus sycomorus), whereas for sample EG-SAQ-5 it was higher. The decrease of the S/G ratio generally indicates a preferential degradation of the syringyl lignin with respect to the guaiacyl lignin.

Table 12: Pyrolytic H/L for the archaeological Egyptian samples and sound wood samples of the same species.

<table>
<thead>
<tr>
<th></th>
<th>F. albida</th>
<th>EG-SAQ-2</th>
<th>EG-SAQ-7</th>
<th>F. sycomorus</th>
<th>EG-SAQ-3</th>
<th>EG-SAQ-4</th>
<th>EG-SAQ-5</th>
<th>EG-SAQ-6</th>
<th>EG-DAK-1</th>
</tr>
</thead>
<tbody>
<tr>
<td>sum H</td>
<td>52.5</td>
<td>84.2</td>
<td>77.0</td>
<td>49.9</td>
<td>79.6</td>
<td>58.5</td>
<td>27.4</td>
<td>75.7</td>
<td>74.3</td>
</tr>
<tr>
<td>sum L</td>
<td>47.5</td>
<td>15.8</td>
<td>23.0</td>
<td>50.1</td>
<td>20.4</td>
<td>41.5</td>
<td>72.6</td>
<td>24.3</td>
<td>25.7</td>
</tr>
<tr>
<td>H/L</td>
<td>1.1</td>
<td>5.3</td>
<td>3.3</td>
<td>1.0</td>
<td>3.9</td>
<td>1.4</td>
<td>0.4</td>
<td>3.1</td>
<td>2.9</td>
</tr>
<tr>
<td>S/G</td>
<td>0.4</td>
<td>0.3</td>
<td>0.2</td>
<td>0.3</td>
<td>0.2</td>
<td>0.5</td>
<td>2.2</td>
<td>0.4</td>
<td>0.2</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>T. baccata</th>
<th>EG-SAQ-8</th>
<th>EG-ASW-1*</th>
<th>Tamarix</th>
<th>EG-SOH-1</th>
<th>P. sylvestris</th>
<th>EG-SOH-2</th>
<th>EG-SOH-3</th>
<th>C. sempervirens</th>
<th>EG-UNKNOWN</th>
</tr>
</thead>
<tbody>
<tr>
<td>sum H</td>
<td>59.1</td>
<td>87.3</td>
<td>34.3</td>
<td>77.7</td>
<td>69.4</td>
<td>72.9</td>
<td>65.6</td>
<td>72.8</td>
<td>62.4</td>
<td>69.0</td>
</tr>
<tr>
<td>sum L</td>
<td>40.9</td>
<td>12.7</td>
<td>65.7</td>
<td>22.3</td>
<td>30.6</td>
<td>27.1</td>
<td>34.4</td>
<td>27.2</td>
<td>37.6</td>
<td>31.0</td>
</tr>
<tr>
<td>H/L</td>
<td>1.4</td>
<td>6.9</td>
<td>0.5</td>
<td>3.5</td>
<td>2.3</td>
<td>2.7</td>
<td>1.9</td>
<td>2.7</td>
<td>1.7</td>
<td>2.2</td>
</tr>
<tr>
<td>S/G</td>
<td>0.1</td>
<td>2.3</td>
<td>2.3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*unidentified species

The sound wood samples showed a wide range of H/L ratios, from 1.0 (Ficus sycomorus) to 3.5 (Tamarix), depending on the wood species. It is important to recall that the pyrolytic H/L ratio does not estimate quantitatively the concentration of wood components, but it is just based on the integration of chromatographic peak areas of selected pyrolysis products. In fact, the natural variability of wood composition from species to species is not as wide as suggested by these results: lignin accounts 20-30% of wood composition, whereas holocellulose accounts 60-70% (Hedges, 1990). The underestimation of the holocellulose content obtained in some cases by pyrolysis (see Ficus sycomorus) is principally due to the fact that low molecular weight pyrolysis products from carbohydrates, such as formaldehyde, methanol, etc., are not detected in the adopted conditions. This underlines the importance of identifying the wood species of an archaeological sample, in order to evaluate its degradation state, because the reliability of these values is always related to the comparison between an archaeological and a
sound wood of the same species. Samples EG-SAQ-2 and EG-SAQ-7 showed H/L ratios higher than the corresponding sound wood, indicating a predominant degradation of the lignin component. A similar result was obtained for samples EG-SAQ-3, EG-SAQ-6, EG-DAK-1 and EG-SAQ-8. Samples EG-SAQ-5, EG-SOH-1 and EG-SOH-2 showed H/L ratios lower than the corresponding sound wood samples, indicating a preferential loss of holocellulose. For samples EG-SAQ-4, EG-SOH-3 and EG-UNKNOWN H/L ratios comparable to the corresponding sound wood samples were obtained, generally indicating a good preservation state of these samples. Sample EG-ASW-1 showed a low H/L ratio, which suggested a high degradation, even if its species was not identified. Actually, this sample represented a very good example that demonstrated the limitations of the H/L ratio. In fact, the H/L ratio for this sample (0.5) could be considered typical of a wood which had undergone loss of holocellulose.

On the contrary, considering the pyrolytic profile (Fig. 58) and the distribution of pyrolysis products, it was evident that lignin had also undergone a high degree of degradation. Consequently, the H/L is a good indicator of the preservation state of archaeological wood mostly if a component is preferentially degraded with respect to the other. When both components are involved in degradation at comparable level, the evaluation of the H/L ratio can lead to partial or wrong conclusions.

Py(HMDS)-GC/MS can overcome these limitations, because of the molecular detail achieved. In fact, the evaluation of the distribution of pyrolysis products divided into categories can integrate the information obtained by the calculation of the H/L ratio and better highlight differences among the samples. Although other techniques can provide an estimation of the H/L ratio (FTIR, NMR; classical wet methods), Py(HMDS)-GC/MS is the only one that can provide additional information at a molecular level, and this is fundamental for a correct interpretation of the results. Figure 61 shows the distribution of lignin pyrolysis products divided into categories for the samples analysed.

For the sound wood samples, just slight differences were detected among the relative abundances of lignin categories of pyrolysis products. Generally, the monomers had the highest relative abundance (40-50%), as usually detected for sound wood, since they are produced by primary pyrolysis reactions, that have high yields when lignin structure has not undergone alterations (Kotake, Kawamoto, & Saka, 2014, 2015; Ramirez-Corredores, 2013). The results for samples EG-SOH-1, EG-SOH-2 and EG-SOH-3 showed slight changes with respect to the corresponding sound wood, indicating that lignin was not significantly affected by degradation.
Samples EG-SAQ-4 and EG-UNKNOWN presented a reduction of the relative abundance of monomers. Sample EG-SAQ-4 mainly showed a relative increase in short chain pyrolysis products, whereas sample EG-UNKNOWN showed a relative increase in acid and demethylated/demethoxylated pyrolysis products. Thus, for these samples lignin had undergone slight degradation at different levels: for sample EG-SAQ-4 an alteration of the structure affecting the side chain of the phenylpropane units, and for sample EG-UNKNOWN a moderate oxidation.

Figure 61: Distribution of categories of lignin pyrolysis products expressed as percentages for all the samples from Egypt and the corresponding sound wood samples.
All the other archaeological samples showed similar results. The monomers were almost completely absent and the lignin pyrolysis products were mainly constituted by short chain compounds and demethylated/demethoxylated compounds. This indicated a drastic alteration of the lignin structure for these samples. It is known that some species of decay fungi can degrade or even metabolise lignin (Blanchette, 2000). In particular, white rot fungi are able to metabolise large amounts of lignin via an oxidative process involving particular enzymes (laccases and ligninolytic peroxidases), causing depolymerisation by C₄-ether breakdown, aromatic ring cleavage, Cα-Cβ breakdown of the aliphatic side-chain and demethoxylation (Martínez et al., 2005). Brown rot fungi mainly attack carbohydrates, but it has also been shown that the action of some species of brown-rot fungi can also demethylate/demethoxylate lignin (Filley et al., 2002; Hatakka, 2005; Martínez et al., 2011; Yelle et al., 2008). Some Py-GC/MS study have demonstrated that the attack of white rot fungi can result in an increase of pyrolysis products with shortened side chain with respect to the original phenylpronane units (del Río et al., 2001; Terron et al., 1995), as well as a small increase in dihydroxybenzenes because of demethylation reactions of the methoxy groups on the aromatic rings (Vane, 2003).

Consequently, the lignin degradation observed for samples EG-SAQ-2, EG-SAQ-3, EG-SAQ-6, EG-DAK-1, EG-SAQ-7, EG-SAQ-8 suggested an attack by white rot fungi. In addition, most of the H/L ratios calculated for these samples were higher with respect to the corresponding sound wood samples, indicating loss of lignin. As already been reported in the literature (del Rio et al., 2001; Vinciguerra et al., 2007), the decrease of the S/G ratio for most of these samples (hardwood species) was also considered a confirmation of the attack by white rot fungi.

Samples EG-SAQ-5 and EG-ASW-1 showed a degradation mostly ascribable to the action of brown rot fungi, as indicated by the H/L ratios 0.4 and 0.5, respectively, which were lower than sound wood samples. Despite the preferential loss of holocellulose in these samples, lignin showed high alteration at a molecular level. In particular, the detection of 3-methoxy-1,2-benzenediol (#52) with relatively high abundances with respect to the other samples has been reported in the literature as a marker of the action of brown rot fungi (Martínez et al., 2011). Nevertheless, the drastic reduction of monomers, indicating an alteration of the lignin side chains, means it is not possible to exclude the action of white rot fungi also for these samples. These examples underline the importance to evaluate the distribution of lignin pyrolysis products, in order to integrate and sometimes correct the information obtained by the H/L ratio.
The distribution of holocellulose categories of pyrolysis products was also investigated, as shown in Figure 62.

The two categories of pyrolysis products which underwent the most relative changes were anhydrosugars and cyclopentenones. The distribution of holocellulose pyrolysis products varied significantly among the sound wood samples. In fact, hemicelluloses can have different compositions depending on wood species (Hedges, 1990; Saka, 2001). Since the pyrolysis products of cellulose and hemicelluloses cannot be distinguished, the relative abundances of holocellulose (both cellulose and hemicelluloses) pyrolysis products are expected to vary significantly depending on the composition of hemicelluloses in the various wood species.

For all the other samples an increase in anhydrosugars and a decrease in cyclopentenones were detected with respect to the corresponding sound wood samples. It has to be considered that the analysis was performed using two different pyrolysers and it is known that the pyrolysis yield of carbohydrates strongly depends on pyrolytic conditions (Moldoveanu, 1998, 2010). In addition, the Egyptian samples showed relevant differences with respect to those from Biskupin site, which could have played an important role:

- the extensive loss of lignin for the Egyptian samples could have resulted in the cleavage of the lignin-carbohydrate bonds and left a residue of unaltered polysaccharides in these wood samples, thus resulting in a higher abundance of anhydrosugars in the pyrolytic profile;
- white rot fungi can depolymerise the carbohydrates, not necessarily metabolising them (Blanchette, 2000, p. 14; Martinez, 2005, p. 23]. The pyrolytic yield of levoglucosan formation as a function of cellulose depolymerisation has been monitored in the literature and it was observed to increase together with the degree of depolymerisation in some cases (Moldoveanu, 1998).

The results for sample EG-SOH-1 highlighted no significant differences in the distribution of holocellulose pyrolysis products with respect to the sound Tamarix, indicating a good preservation of the holocellulose component. Similar results were obtained for pine wood samples EG-SOH-2 and EG-SOH-3.
Figure 62: Distribution of categories of holocellulose pyrolysis products expressed as percentages for all the samples from Egypt and the corresponding sound wood samples.

The second hypothesis could also explain the behaviour of samples EG-SAQ-4 and EG-UNKNOWN, which showed the same trend as the other samples, despite lignin resulted relatively well preserved for these samples.
7.5 Discussion:

All the techniques revealed a high variability in the state of preservation of the samples, and the interpretation of the results was very complex. Complementary information was obtained by the various techniques, and it was clear from the comparisons that misleading information may be obtained if only one approach is used to investigate such samples. In fact, our results highlighted how the decay patterns for some samples were very different from those usually encountered for waterlogged wood. The loss of holocellulose was not the most common result in these samples, thus suggesting that several other mechanisms of degradation had affected them. This section discusses the results in a more comprehensive way, highlighting various trends.

7.5.1 Faidherbia albida - samples EG-SAQ-1 and EG-SAQ-7 from the Khendjer pyramid site (ca. 1760 BC)

SEM analyses revealed an altered structure for these samples, with evident fungal and bacterial activity in sample EG-SAQ-7. The results obtained by WCA and Py(HMDS)-GC/MS were not in direct agreement. In fact, a comparable amount of lignin with the sound wood was obtained for both samples by WCA, however Py(HMDS)-GC/MS highlighted that lignin was highly altered. In addition, a relative decrease in holocellulose was observed by WCA analysis, but the relative abundances of holocellulose pyrolysis products were higher than the sound wood. WCA also revealed an extremely high content of substances that are soluble in water, and Py(HMDS)-GC/MS showed that the residual holocellulose was depolymerised. The FTIR spectra acquired before and after the extraction procedure explained the reason for the disagreement between the results. In fact, a major fraction of these soluble substances contained carboxylate groups and pointed to the presence of oligo-sugars (perhaps due to the opening of the glucose ring). These were produced during cellulose degradation and were partially solubilised during the extraction process in hot water accounting as extractable material in the WCA analysis. However, they accounted as holocellulose pyrolysis products using Py(HMDS)-GC/MS, as no pre-treatment of the sample was performed.

Such high values of soluble substances are never found in the analysis of waterlogged archaeological wood (Pizzo, Giachi, & Fiorentino, 2013), where the material is leached during...
its long-term immersion in water. In contrast, when the material (like the one analysed here) is preserved in dry conditions, these depolymerisation products are not leached and thus remain within the wood tissue. The presence of carboxylate groups also suggested the action of brown rot fungi (Kirk et al., 1991).

7.5.2 *Ficus sycomorus* - samples EG-SAQ-3, EG-SAQ-4, EG-SAQ-5 and EG-SAQ-6 from the Khendjer pyramid site (*ca.* 1760 BC) and sample EG-DAK-1 from Dakhla oasis (332 BC – 395 AD)

Despite being from the same wood species, four different degradation pathways were identified for these samples. For samples EG-SAQ-3 and EG-SAQ-6, a significant reduction in lignin was the main finding. This was also found in sample EG-DAK-1, but was accompanied by a partial depletion of holocellulose. This was the only sample showing a comparable degradation of lignin and holocellulose, probably reflecting its particular geographical/chronological origin. Sample EG-SAQ-5 revealed a high depletion of holocellulose and sample EG-SAQ-4 showed a relatively good preservation state of the wood components.

Generally, a good agreement was observed between the FTIR and Py(HMDS)-GC/MS results. In fact, the residual lignin appeared to be highly altered in all samples (except for sample EG-SAQ-4), whereas minor cellulose depolymerisation was observed. High amounts of soluble substances were obtained especially in sample EG-DAK-1. However, the FTIR spectra highlighted minor differences before and after extraction, which was taken as an indication that both oligo-sugars from partially depolymerised holocellulose and water-soluble lignin aromatic units were present in the extracted material, confirming the comparable degradation of lignin and holocellulose. All this was also consistent with an attack by white rot fungi.

In sample F4, the detection of the demethylation product 3-methoxy-1,2-benzenediol (#52) with such a relative high abundance should be underlined. In fact, this has been reported in the literature as a marker of the action of brown rot fungi (Martínez et al., 2011).
7.5.3  *Taxus baccata* - sample EG-SAQ-8 from the Khendjer pyramid site (*ca.* 1760 BC)

The results obtained for this sample fall under the category of a predominant depletion of lignin and alteration of the residual cellulose. In this case, the formation of conjugated diketones observed by FTIR was taken as a further indication of attack by white rot fungi.

7.5.4  *Tamarix* sp. - sample EG-SOH-1 - and *Pinus sylvestris* – samples EG-SOH-2 and EG-SOH-3 – from the city of Jerja (*ca.* 1787 AD)

The results obtained by all the techniques agreed with a good preservation of the wood components, which showed only slight changes with respect to the corresponding sound wood samples. These were also the most recent wood samples, which is probably why they showed the best preservation state.

7.6  Causes of degradation

Although fungal activity was clearly observed in most of the degraded samples, the definitive cause of degradation was difficult to interpret. Some results suggest the possibility of the degradation by two factors simultaneously whereas, for other samples, the chemical analysis results suggest a specific cause of decay or biological attack when the microscopic examinations do not support these outcomes directly. The experiments were repeated at least 3 times to get results as accurate as possible. Moreover, FTIR and microscopic investigations were repeated in the University of Melbourne after performing them in IVALSA-CNR in Florence as discussed in Chapter 4. Some Py(HMDS)-GC/MS studies have demonstrated that attack by white rot fungi results in an increase in lignin pyrolysis products with a shortened side chain with respect to the original phenylpronane units (del Rio et al., 2001; Terron et al., 1995; van Kuijk et al., 2016), as well as a small increase in dihydroxybenzenes, because of the demethylation reactions of the methoxy groups on the aromatic rings (Vane, 2003). Consequently, the lignin degradation observed in most samples would suggest an attack by white rot fungi. However, this was not always clear in the SEM images and was suggested by WCA only when there was a decrease in lignin.
On the other hand, indications of an attack by brown rot fungi were obtained for samples EG-SAQ-2, EG-SAQ-5 and EG-SAQ-7. Samples EG-SAQ-2 and EG-SAQ-7 also appeared to show degradation features ascribable to the combined effect of both white and brown rot fungi. However, it is impossible to ascertain whether the attack started in the burial environment, or after excavation.

The effects of time in terms of hydrolytic and oxidative degradation of wood components must also be considered. In fact, if we consider the chronological line, the worst preserved samples were among the most ancient ones (EG-SAQ-2, EG-SAQ-5 and EG-SAQ-7) from the Khendjer pyramid site - ca. 1760 BC). However, very different degradation pathways were observed within the same archaeological site and within the same wood species, which prevents trends from being highlighted in relation to the geographical origin and the type of wood. Despite the speculative aspect of these hypotheses, these results nevertheless highlight how complex the evaluation of the preservation state of archaeological dry wood is compared to waterlogged wood.

Other techniques than those used here would be helpful in terms of providing additional information on the extent and nature of degradation. Gel permeation chromatography (GPC) could give more precise results on the depolymerisation of cellulose and lignin, and on the preservation of the lignin-carbohydrate complexes (Salanti et al., 2012). 2D-HSQC and $^{31}$P NMR analyses also have the potential to semi-quantitatively evaluate the different types of inter-monomeric bonds present in lignin and to quantify the amounts of the different types of phenolic, alcoholic and acidic groups, respectively (Colombini et al., 2007). These techniques have been applied to archaeological waterlogged wood, proving their suitability (Zoia, Salanti, & Orlandi, 2015; Zoia et al., 2017), but only seldom to dry archaeological wood (Crestini et al., 2009), making this an interesting subject for future research.

### 7.7 Conclusions

The analyses of samples of dry archaeological wood from Egyptian sites by wet chemical analysis (WCA), FTIR, EDS and Py(HMDS)-GC/MS highlighted that different degradation pathways had often simultaneously occurred even in the same burial environment and within the same wood species. This shows that in order to correctly evaluate the causes of decay and
reliably assess the state of preservation of the samples a higher complexity of interpretation is required for dry archaeological wood than for waterlogged archaeological wood.

The preferential loss of lignin, the preferential loss of holocellulose, the comparable loss of lignin and holocellulose, and the relatively good preservation of wood components were all detected in this group of samples. Additionally, the WCA analysis highlighted a high content of water soluble substances, which is not usually present in waterlogged wood, as water progressively solubilises the depolymerised wood components. FTIR analyses performed before and after extraction with water and organic solvents shed light on the composition of the soluble substances. These were preferentially composed of oligo-sugars sometimes in combination with low molecular weight compounds derived from lignin. Carboxylates and diketone salts were also observed and taken as an indication of fungal activity. Py(HMDS)-GC/MS revealed a high degree of alteration of lignin and holocellulose in most samples. These results provide new insights into the chemical processes taking place during the degradation of dry archaeological wood and show the limitations of the techniques used, when applied alone rather than in conjunction. In fact, simply estimating the H/L ratio, one of the most common parameters to describe wood degradation, was not sufficient in most cases. The H/L ratio is a good indicator of the preservation state of archaeological wood if one component is preferentially degraded with respect to the other, as is usually the case for waterlogged wood. However, it fails as an indicator when both components are involved in degradation at comparable levels. In addition, the preferential loss of one wood component does not necessarily mean that the other component is not degraded. Chemical changes in the structure of residual wood components need to be considered by complementary approaches, such as FTIR strategies and/or the evaluation of the distribution of pyrolysis products.
Chapter 8

This chapter is a rewritten version of the publication Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture: A Case Study (Appendix B)

Statement of co-authorship:

- **Professor Robyn Sloggett**, the Grimwade Centre for Cultural Materials Conservation, University of Melbourne
  **Role:** Supervision

- **Mostafa Abdelfatah**, Ministry of Antiquities, Egypt.
  **Role:** Participated in the treatment and the conservation procedure

- **Mahmoud Youssif Mohammed**, the Grimwade Centre for Cultural Materials Conservation, University of Melbourne
  Conservation Department, Faculty of Archaeology, Fayoum University, Egypt
  **Role:** Sampling, data collection, data analysis, treatment and conservation and writing of the article.
8 Chapter 8: Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture: A Case Study

8.1 Abstract

This paper describes conservation of an ancient Egyptian polychrome statuette, discovered in Saqqara in 1984 and registered as Object 18241. It discusses documentation, sampling, investigation of the wooden substrate, microorganism identification, ground and pigment analysis, and issues of previous restoration. Analysis was conducted with light microscopy, powder X-Ray diffraction (PXRD), Fourier transform infrared (FTIR), and scanning electron microscope equipped with energy dispersive X-ray analysis (SEM-EDS). *Rhizopus stolonifer* and *Aspergillus niger* were indicated as the main fungi, calcium carbonate as the main compound of the ground layer, and polyvinyl acetate (PVA) in a previous intervention. The pigments Egyptian blue, graphite and dark yellow ochre were identified. Conservation treatment entailed consolidation; cleaning; filling and reconstruction; and stabilisation with cotton, Paraloid® B-72 (ethyl methacrylate/methyl acrylate co-polymer) and micro-balloons. Assessment and treatment indicated the success of cotton as a filling material, as well as emphasising the importance of comprehensive analysis prior to treatment.

8.2 Introduction

Saqqara is the largest part of the necropolis of the ancient Egyptian capital Memphis (Men-nefer), located south of modern Cairo and is renowned for its archaeological sites (Shaw & Nicholson, 2002]. The label on the polychrome statuette identifies the object as excavated in AD1984 by Said Amer Elfeky in the Unas excavation; no other details are available. The figure represents a form of servant statuette, produced for burial with the deceased to serve the household in the next life (Saleh & Sourouzian, 1978) and depicts a kneeling woman grinding cereal. Examples of this servant statuette, executed in both wood and stone, are found in museums around the world including the Rosicrucian Egyptian Museum, San Jose; Glencairn Museum, Pennsylvania; Museum of Fine Arts, Boston; Egyptian Museum, Cairo; Alexandria National Museum; and others. Most of these sculptures can be dated to the Old Kingdom from the 3rd millennium BC.
Object 18241 consists of several pieces of wood connected with wooden dowels and mounted on a rectangular wooden base; a method often noted in similar statuettes. Dowel joins are evident in objects from the First Dynasty, ca.3100 – 2890 BC (Lucas, 1948, p. 513), and constitute the main joining technique used in this statuette. Investigation into the construction of the statuette indicated that the head, main body and legs were carved from one piece of wood. The arms and feet were carved separately and were connected by dowels to the shoulders and body. The body was fastened to the base by a small hidden dowel, which extended from the middle of the statuette to the base. The figure is leaning forward in order to perform the task of grinding cereal and is fastened by mortise and tenon joints to the wooden grinding piece. The hands are produced from calcium carbonate (CaCO$_3$), which is also used for the ground layer. This ground layer covers the wooden substrate, providing a base onto which the decorative elements of the surface were applied. This is a basic method of production of Egyptian statuettes from this era (Sliwa, 1996), providing a suitable foundation for painting the finer anatomical details of the body (Killen, 1994, p. 16). Details of the figure are painted, with dark yellow ochre used for the skin, black for the hair, white for the skirt and blue for the wristband.

The statuette was in poor condition. The paint and the ground layers were extremely brittle, precluding any handling of the object. This paper describes the assessment of the materials and composition of the statuette, the degraded nature of the materials, and the subsequent conservation decision-making and treatment undertaken on Object 18241. Both SEM, which identified the black pigment as graphite, and FTIR investigation of the black deposition from the skirt, informed treatment decision-making. Further identification of materials assisted with decisions regarding cleaning the statuette to remove dust and dirt and the existing restorations. Final treatment consisted of consolidation of flaking paint, filling gaps and reconstruction of the various constituent parts.

8.3 Materials Identification and Analytical Methodology

Simple visual examination and condition reporting revealed information about the colours, dimensions, structure and design elements used to construct this object (Miller, 2007, p. 22). One wooden block was carved to form the body, the head and the legs, with dowels attaching the arms and feet. The figure is mounted on a rectangular wooden base. Its height from head to the knees is 40.5 cm and depth from the front to back (forehead to the feet) is 40 cm. The
The wooden base measures 61.5 x 20 x 5 cm. The arms measure 24.5 cm in length. With one foot being longer than the other; the right measuring 14.5 cm and the left 13.5 cm. The statuette does not display the quality of work evident in similar statuettes from archaeological sites associated with royalty or the wealthy. It was in poor condition, loss of adhesion resulted in the separation of appendages. All body parts were put in place without proper adhering using a metal wire. A longitudinal crack was visible in the wood substrate, in the chest and the abdominal areas. Below this crack and just above the skirt, a dark spot indicating biological growth was noted.

The average thickness of the ground layer was 5 mm. Both the ground and paint layers exhibit substantial loss, most obviously on the chest and abdominal area and sections on the arms. The extensive flaking of the paint layer is due in part to the delamination of the ground layer, which created problems with handling. This delamination may have been exacerbated by the dry environment in Saqqara, causing the wooden substrate, ground layer and paint layer to shrink in different ways and the adhesion between the wood, ground and paint layers to fail. On the back and shoulders, there was a remnant film suggesting a previous consolidation. While this film had successfully stabilised the areas, they were darker than the surrounding paint and ground, and sand particles had adhered to the film (Fig. 63).
In order to best determine a treatment methodology for the statuette, samples were collected. Areas sampled include the pigment flakes on the wooden base, a very small wooden specimen from the groove of the left foot from the previous restoration material; and from the dark spots on the abdomen.

Powder X-ray diffraction (PXRD) is one of the most popular techniques with which to identify inorganic pigments (Stuart, 2007, p. 253), due to its ability to determine the lattice constants value of the material crystals (Janssens, 2004, p. 189). A Philips PW1840 with Cu tube anode, generator tension of 40 kV and generator current of 25 mA was used to identify the ground layer and pigment samples.

A scanning electron microscope with energy dispersive spectrometry, SEM-EDS, was used to confirm the identification of the black pigment as graphite and to investigate the wooden sample. Examination was performed using a PHILIPS (FEI) XL30 ESEM TMP with a beam of 15kV and spot size 6. Gold was used for coating under high vacuum. A JEOL-JSM-5400LV was also used to investigate the wooden substrate. The binder was identified using a Bruker Alpha-P FTIR spectrometer equipped with a diamond ATR window (Bruker Optik GmbH, Ettlingen, Germany). All spectra recorded were in the range of 4000–400 cm⁻¹ with 32 co-added scans at a spectral resolution of 4 cm⁻¹. (Nel et al., 2010). A number of comparative samples, including carbon with gum Arabic, carbon with egg yolk and control samples of egg yolk, gum Arabic, PVA and rabbit skin glue, were produced in order to test for any likely binder material. FTIR was also used to examine the black colour on the skirt to clarify if it is an original pigment, an additional deposition resulting from poor storage, or some other cause. Light microscopy and USB digital microscopy (micro capture version - 1.3 ml) were used to identify the microorganisms on the wooden substrate. Test samples were cultivated in agar gel for mould identification.

8.4 Results and Discussion

8.4.1 Pigments

Four pigments were identified using PXRD; graphite, Egyptian blue, dark yellow ochre and calcite. All contained calcite (CaCO₃), being contamination from the ground layer.
Black pigment: PXRD analysis indicated that the black pigment is graphite. This was unexpected given the suggestion that the statuette is dated to the Old Kingdom (as documented by the excavation team), and that most studies of Egyptian objects from this period identify carbon black as the main source of black pigment (Lucas, 1948; Afifi 2011; Abd EL Aal, 2010; Lee & Quirke, 2000). This result was confirmed by SEM, which revealed the flaky and irregular outlines of the particles of the graphite (Winter & West FitzHugh, 2007, p. 25) (Figs. 64-65).

Blue pigment: The blue sample contains quartz (SiO$_2$), Egyptian blue (=Cuprorivaite CaCuSi$_4$O$_{10}$), with calcite (CaCO$_3$) as the main compound (Fig. 66).

Dark yellow pigment: The dark yellow pigment contains yellow ochre (=Ferrihydrite 5Fe2O3.9H2O), in addition to calcite and quartz (Fig. 67).

White pigment: Calcite CaCO$_3$ was the main compound identified in the white pigment.

![Figure 64: SEM-EDS of the black sample. A and B are SEM images. C is the EDS pattern.](image)

![Figure 65: PXRD spectrum of black pigment with a crystalline phase of calcite, graphite and quartz](image)
Figure 66: PXRD spectrum of blue pigment with a crystalline phase of calcite, Egyptian blue and

Figure 67: PXRD spectrum of dark yellow pigment with a crystalline phase of calcite, yellow
8.4.2 Ground layer

PXRD analysis of the ground or preparation layer indicated calcite $\text{CaCO}_3$ and quartz $\text{SiO}_2$ (Fig. 68)

![PXRD spectrum of the ground layer with a crystalline phase of calcite and quartz.]

8.4.3 Binder

FTIR was used to compare control standards with the binder used in the paint on the statuette. FTIR analysis did not provide a definitive answer as the calcium carbonate, the major compound of the ground, dominated the reflectance result. Despite this, the FTIR did detect some areas that identified the binder as egg yolk. The FTIR absorption peaks for the binder were recorded at 1730, 1619, 1214 and 600 (Fig. 69).

8.4.4 Old restoration material

FTIR analysis of the sample from the previous restoration indicated the material used in restoration was almost identical to the PVA control standard. This confirms the assumption
that previous interventions were undertaken on the object, and that the material used for this restoration is likely to be PVA (Fig. 70).

8.4.5 Black colour on skirt

FTIR analysis showed a match for the ground layer and the black sample from the skirt, and indicated that no evidence of any binder exists, suggesting the black is not a pigmented layer. These results were confirmed using SEM, and visual analysis of the black deposition. Comparison with a range of similar figures from this period indicated white skirts in Egyptian
art (Watson & Cassin-Scott, 1987; Roth, 2002, p. 104) with no indication of black decoration similar to the black colouration on the skirt. A decision was therefore made to remove this carbon deposition, which was possibly due to bad storage or some other reason (Fig. 71).

![FTIR spectrum of the black deposits on the skirt, ground layer and black pigment.](image)

**Figure 71:** FTIR spectrum of the black deposits on the skirt, ground layer and black pigment.

### 8.4.6 Wood

SEM photomicrographs showed the weakened nature of the wooden substrate with deformation of the cell walls. This loss of strength and tendency towards brittleness and fragility may be attributed to chemical changes resulting from weathering and the reduction of cellulose, crystallisation and depolymerisation of hemicellulose (Obataya, 2009, p. 22). As a

![SEM of the wooden support (Ficus sycomorus). It shows good integrity of the microstructure and the ultrastructure of the cell wall. No signs of biological attack were obvious.](image)

**Figure 72:** SEM of the wooden support (Ficus sycomorus). It shows good integrity of the microstructure and the ultrastructure of the cell wall. No signs of biological attack were obvious.
result, there was a need to consolidate the support. The decision was made not to remove the substantial section of the wood required for proper identification, by weighing up the loss of original material against the potential gain of information (Rivers & Umney, 2003, p. 391). It is clear, however, that it is hardwood. Sycamore fig (*Ficus sycomorus*) may be a possible source in line with the description given by Johnson et al (1995, p. 78), and its popularity in ancient Egypt (Gale et al., 2000) (Fig. 72).

**8.4.7 Moulds**

Cultivating samples from the mould infested area enabled identification as indicated below in Table 13. The aspergillus species was dominant. All mould was contained to the surface of the wood and had no impact on the mechanical properties of the support*.

<table>
<thead>
<tr>
<th>N</th>
<th>Organisms</th>
<th>No. of colonies</th>
<th>Rate of appearance %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust</td>
<td><em>Aspergillus niger</em></td>
<td>4</td>
<td>27</td>
</tr>
<tr>
<td>Total</td>
<td><em>Asperillus flavus</em></td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td><em>Alternaria alternata</em></td>
<td>2</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td><em>Aspergillus verrucose</em></td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td><em>Rhizopus stolonifer</em></td>
<td>5</td>
<td>33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>15</td>
<td>100%</td>
</tr>
</tbody>
</table>

**8.5 Conservation Treatment**

**8.5.1 Documentation**

The statuette was documented using a standard condition report, photographic images, and analytical documentation. The condition and stability of the statuette was identified as poor with very fragile and brittle ground and paint layers. As a result, the decision was made to clean and consolidate each separated part; being the body, arms, feet and the delaminating areas of the ground layer. After cleaning, treatment involved reconstructing and reattaching these separated sections (Figs. 73, a and b).

* The collection of samples performed under aseptic condition and were stored aseptically.
8.5.2 Cleaning

A fine layer of dust covered the surface of the statuette. This was removed gently with a soft goat-hair brush and a flicking motion (Norton, 1990). Several areas were too delicate to be cleaned in this way, including the paint layer on the grinding piece, which was too flaky to be touched. It was therefore necessary to consolidate the flaking paint (described below) prior to cleaning. As the ground layer was completely missing from the abdominal area, it was possible to mechanically remove the staining from the mould outbreaks on this area. It was removed using bristle brushes, a 1:1 mixture of distilled water and ethanol (99%) was then applied to the surface with cotton swabs to gently clean any residual deposits. This procedure was also undertaken on the skirt. The same mixture, commencing with 2:1 deionised water: ethanol (99%) and gradually increasing to a ratio of 1:1, was used to remove the PVA film. This treatment satisfactorily removed both the dirt and the PVA. Pure ethanol (99%) was used to inhibit any reoccurrence of mould.

Figure 73: The object 18241 during the documentation and in the first stages of conservation. It documents in more details the condition of the statuette (a) and its size compared to real human body (b).
8.5.3 Consolidation

Often archaeological material is too degraded to be handled without treatment (Rodgers, 2004, p. 41). This was the case here and fragile sections required initial consolidation. Paint flakes were consolidated with Paraloid® B-72 in acetone from an initial 10% concentration which gradually increased to 20%, and applied by syringe and pipette. Where both the ground and light paint required consolidation, Klucel® G (hydroxypropyl cellulose) 2% in ethanol was used (Lokma, 2010, p. 158). This ensured that the relatively light colour of the ground and the pigments in the paint layer were not darkened. Klucel® G demonstrates long-term stability, low shrinkage percentage and retains flexibility after exposure to high temperature and light (Johnson et al., 1995, 76); all necessary in the environment at Saqqara. Paraloid® B-72 2% in acetone was used to consolidate the dark coloured layers (black and dark yellow). The wood substrate was consolidated using Plexisol® P550 2% in an acetone and toluene mixture (40:60) increasing to 4% where necessary and applied with a syringe.

8.5.4 Structural repair

After consolidation of the detached and delaminating sections, the final task of reconstruction was able to be completed. First the wooden dowels, originally used to fasten the arms and the feet, were strengthened. The dowels were wrapped with cotton wool then reinserted into the existing dowel-holes after these were injected with Paraloid® B-72, initially at 10% increasing to 20% where necessary. Gaps remaining between

Figure 74: Structural consolidation for the object 18241 showing the areas where the cotton wool was used (arrows)
The dowel and body of the statuette were filled with a mortar comprising micro-balloons in Paraloid® B-72 20% in acetone; pigmented with red and yellow ochre. Stabilisation of the space between the support stand under knees and the knees was achieved using the same fill procedure.

The use of cotton as a filling material has been very successful (Lokma, 2010), and further use was made of cotton to fill the crack in the chest and abdomen, as well as the gaps left after the reconstruction process. First a spatula was used to insert cotton wool into cracks and gaps, which were then consolidated by injecting the cotton wool with Paraloid® B-72 10% in acetone, increased gradually to 20%. Remaining surface losses were finished using micro-balloons in Paraloid® B-72 20% in acetone, mixed with an appropriate pigment which was usually yellow and red ochre (Fig 74).

The loss of the gesso layer on the arm was filled with a mortar of Paraloid® B-72 20% in acetone and micro-balloons, mixed with red and yellow ochre, and laid as a continuous layer on the surface (Fig. 74).
8.6 Conclusion

Investigation and treatment of the statuette, Object 18241, confirmed the success and simplicity of using cotton wool as a filling material. Like wood, cotton is cellulose-based, providing suitable flexibility and compression where needed. This technique is easily reversible by removing the finishing layer, injecting the Paraloid® B-72/cotton fill with acetone, and removing the cotton once the adhesive has dissolved sufficiently. This paper also confirms the necessity of understanding the condition of the object and ascertaining previous treatments prior to the commencement of treatment. FTIR spectra were dominated by the calcite making them difficult to read. Isolating the binder prior to FTIR analysis is preferable but the brittle condition of the paint and associated binder loss made this impossible. Unlike the spectra associated with the paint layers, the result on the skirt displayed no binder peaks, indicating that this was not part of the original pigmented layer and could be safely removed.

For more documenting photographs please have a look at Appendix C.
8.7 References


Science + Business Media Inc.


Manuelian, P. and Jacquet-Gordon, H. (Tr.). Cairo: The Organization of Egyptian
Antiquities.

The American University in Cairo Press.

pg7

Wiley & Sons Ltd.

New York: Chelsea House Publications.


**Materials used for the treatment process:**

Paraloid® B-72 (ethyl methacrylate/methyl acrylate co-polymer):
Lascaux Colours & Restauro Barbara Diethelm AG
Züriichstrasse 42, CH-8306 Brüttisellen
Phone +41 44 807 41 41. Fax +41 44 807 41 40
info@lascaux.ch

Klucel® G (Hydroxypropylcellulose):
C.T.S Srl
Via G Fantoli n. 26
00149 Roma (RM) - Italy
Phone: +39 06 55301779. Fax: +39 06 5592891
cts.roma@ctseurope.com
www.ctseurope.com

Plexisol® P550 (Butyl methacrylate) and pigments (inorganic oxides):
Kremer Pigmente GmbH & Co. KG
Hauptstrasse 41-47, D 88317 Aichstetten
Phone: +49 7565 91120. Fax +49 7565 1606
Cotton wool, Acetone and Ethanol:
Novartis Pharma S.A.E
PO Box 1893. El Sawah Street, 11511 Amiria, Cairo, Egypt
Phone: +202 24 567 200. Fax: +20 2 257 4616
http://www.novartis.com.eg
Summary, conclusion and further work:

This thesis presents a comprehensive investigation of the deterioration mechanisms of dry cultural heritage wood, in order to correlate the chemical composition of the degraded wood with its properties, such as changes in the anatomical features and density. These results are compared with the data obtained for waterlogged archaeological wood reported in the literature. Compared to waterlogged wood, the degradation pathways for dry heritage wood have not been extensively studied in the past. Therefore, detailed information about the degradation of dry archaeological wood is essential for the development of techniques to conserve and preserve historical treasures. As a result of a dry environment the factors driving deterioration and degradation factors are different than for waterlogged wood. Because the changes in the wood properties are related to the changes in the chemical composition of wood, the chemical modification resulting from various environmental or biological factors will affect the other anatomical, physical and mechanical properties.

Different techniques were implemented to study the degradation of dry wood samples, some of which were applied for the first time to dry archaeological wood. The experimental study included three main parts to assess the anatomical, physical and chemical properties of cultural heritage wood, which contributed to the comprehensive understanding of the deterioration mechanism of dry cultural heritage wood:

- microscopic and morphological investigation
- physical measurements
- chemical analysis and assessment

The samples used in this study were principally from Egypt and were chosen to cover a wide range of geographical regions and eras. The samples have no aesthetic or religious value and the decision was made after discussion with employee at the place that they were collected from. Therefore samples could be collected for this study. The Egyptian samples included samples from ancient Egypt, the Graeco-Roman period, the Islamic period and the Modern era. In addition to this, for selected experiments, samples from Italy and Australia were examined for comparison.
Identification of most samples was possible. *Ficus sycomorus* (sycamore fig) wood was the dominant species among the ancient Egyptian samples. Also, generally, hardwoods (angiosperms), were more common in the ancient Egyptian samples, whereas the softwoods (gymnosperms) were the main wood types of the Islamic and Modern era samples.

Two samples were identified as *Faidherbia albida* (White Acacia), which both belong to samples collected from Saqqara and dated to the Second Intermediate Period, as the site suggests. The older samples had the worst state of preservation, while some of the Islamic samples were found to be almost as intact as the recent wood, however, it is impossible to ascertain whether the attack started in the burial environment, or after excavation. SEM Microscopic investigation showed that most of the ancient Egyptian samples had signs of biological decay, including fungi and bacteria. SEM images revealed the decay characteristics of brown rot, white rot, and soft rot in some samples. It was not possible to attribute the signs of decay to a specific type of fungi due to the non-selective decay characteristics, in addition to the absence of a suitable environment to grow these microorganisms. For example, in the case of the sample collected from El-Dakhla oasis (EG-DAK-1/ *Ficus sycomorus*) SEM images of the transverse and the radial sections showed voids in the cell wall, which is a typical feature of white rot fungi. However, this geographic location is known for its very arid weather conditions around the year with no presence of moisture, which is not an encouraging environment for these fungi to grow. The most noticeable degradation was found in sample EG-SAQ-8 (*Ficus sycomorus*) from Saqqara. The transverse section images showed apparent detachment and axial cavities of the secondary cell wall layers, which can be attributed to the soft rot or white rot fungi. Bacterial attack was also observed by the different alterations and scratches of the cell wall seen in the radial section of sample EG-SAQ-7 (*Faidherbia albida*) from Saqqara.

The physical measurements of the samples showed a correlation with the microscopic investigations. Samples from ancient Egypt, the Graeco-Roman period, the Islamic era and the Modern era were measured and compared with samples from Italy, Australia and reference samples of the same taxa. The results revealed the decline in the density of the ancient Egyptian samples, which was more pronounced than in the other samples, resulting from the aging process and the impact of the microbiological attack, in particular in the samples collected from Saqqara, Egypt. Densities of some of these samples from ancient Egypt (samples EG-SAQ-1, EG-SAQ-3 and EG-SAQ-5) had declined to about 50% of the density of the reference sample.
All these affected samples showed evident signs of microbiological attack, which contributed to the physical state of the material. On the other hand, one of the samples (EG-SAQ-6) that did not show signs of any attack by fungi or bacteria, had a higher density than that measured for the reference sample or recorded in the literature. The ash content value might contribute to this high value as inorganic mineral which has penetrated inside the wood structure can increase its mass.

Comprehensive analysis of the chemical micro-structure (main constituent’s proportions such as holocellulose, lignin, ash and extraneous substances proportions) and the chemical ultra-structure (molecular compounds of the constituents) of the cultural heritage wooden samples did not reveal a unique degradation pattern across all samples (unlike waterlogged wood). Some samples exhibited more degradation of the lignin, whereas in other samples a preferential loss of holocellulose was found. Some samples also had a comparable degree of loss of lignin and holocellulose (such as sample EG-DAK-1 from Dakhla Oasis) and others had good state of preservation compared to recent or fresh wood. The differences were evident amongst both wood samples collected from the same burial site and samples of the same species.

The experimental work done in this thesis emphasises the importance of the preliminary scientific studies before and during the conservation process. Results of the wet chemical analysis (WCA), Fourier transform infrared (FTIR), Energy-dispersive X-ray Spectroscopy (EDS) and analytical pyrolysis gas chromatography mass spectrometry with in situ silylation (Py(HMDS)-GC/MS) examinations (Chapter 7) required analysis and interpretation together in order to arrive at a clear explanation of the data acquired. The results showed the significant differences between the degradation of waterlogged archaeological wood and the dry wood, both in the chemical modification and in the other properties that occurred subsequently. The main differences were evident in the holocellulose to lignin ratio (H/L), which is considered as one of the most reliable indicators of the degree of the decay of archaeological wood. The H/L of the waterlogged wood is significantly lower whereas in the dry wood samples studied it varies. Furthermore, the ash content and extractable substances are present in significant levels in the dry wood, while in the waterlogged wood they had almost vanished or substantially leached because of the depolymerised wood components. These anomalous results could not have been satisfactorily explained without complex analysis using data from different analytical techniques simultaneously.
FTIR analyses performed before and after extraction with water and organic solvents revealed that the soluble substances are preferentially composed of oligo-sugars sometimes in combination with low molecular weight degradation products from lignin. Carboxylates and diketones were also observed and taken as an indication of fungal activity. Py(HMDS)-GC/MS revealed a high degree of alteration of lignin and holocellulose in most samples.

This study showed the importance of using different techniques to assess the chemical processes taking place during the degradation of dry heritage wood and not to relying on WCA alone to understand the degradation processes and mechanisms. As dry wood can have degradation and loss of all its components at a comparable level, and, therefore, estimating the hemicellulose/lignin ratio by WCA alone does not provide a clear assessment of the chemical modification of the wood.

While the state of preservation correlated with the age of the wood sample, different degradation pathways were observed in the samples belonging to the same site, era or species. It was evident that the oldest samples from ancient Egypt (EG-SAQ-2, EG-SAQ-5, EG-SAQ-7 and EG-SAQ-8 from the Khendjer pyramid site - 1760 BC) were in the worst state of preservation, but showed different degradation pathways. The interpretation of the cause of the degradation using the data gained by SEM and the different chemical analysis techniques was very complicated, which made the process of determining the cause of degradation very difficult. Most of the samples studied by Py(HMDS)-GC/MS have shown lignin degradation, suggesting that they were attacked by white rot fungi. These samples were characterised by an increase in lignin pyrolysis products with a shortened side chain with respect to the original phenylpronane units (del Río et al., 2001; Terron et al., 1995; van Kuijk et al., 2016) or a small increase in dihydroxybenzenes, resulting from demethylation of the methoxy groups on the aromatic rings (Vane, 2003). However, apart from sample EG-SAQ-8, which showed some clear signs of attack by white rot or soft rot fungi, the microscopic investigations did not reveal definite signs of this attack. Indications of brown rot attack were observed in some samples, such as EG-SAQ-5 (*Ficus sycomorus*) from Saqqara, where the demethylation product 3-methoxy-1,2-benzenediol was found in relatively high abundance.

In some instances, the results obtained from the WCA and the Py(HMDS)-GC/MS appeared to contradict each other. This disagreement could be explained by the fact that FTIR spectra were either acquired before and after the extraction, as in the case of sample EG-SAQ-2
(Faidherbia albida) from the Khendjer pyramid site. This finding again clearly emphasises the importance of not relying on one technique alone to analyse and assess dry cultural heritage wood.

The thesis makes an important contribution to the understanding of the deterioration mechanisms and the changes in the properties of dry cultural heritage wood, and of the difference between these deterioration mechanisms and changes and those found in waterlogged wood.

Further studies are clearly required to provide a deeper understanding of the nature of degradation and the different degradation results, in comparison with the waterlogged archaeological wood studies in the literature. Techniques such as gel permeation chromatography (GPC) could give more precise data on the depolymerisation of cellulose and lignin, and on the preservation of the lignin-carbohydrate complexes (Salanti et al., 2012). In addition, the 2D-HSQC and $^{31}$P Phosphorus NMR analyses could be used to semi-quantitatively evaluate the different types of inter-monomeric bonds present in lignin and to quantify the amounts of the different types of phenolic, alcoholic and acidic groups, respectively (M.P. Colombini et al., 2007). These techniques have been applied to archaeological waterlogged wood, proving their suitability (Zoia et al., 2015; Zoia et al., 2017), but only seldom to dry archaeological wood (Crestini et al., 2009), making this an interesting subject for future research. Further studies on the mechanical changes of dry cultural heritage wood are also required to reveal how the mechanical properties, in particular the modulus of elasticity and the storage modulus, are influenced by chemical composition.
References:


NMR and GPC techniques. *Microchemical Journal, 85*(1), 164-173
doi: [http://doi.org/10.1016/j.microc.2006.05.001](http://doi.org/10.1016/j.microc.2006.05.001)


http://www.paulmitchell.co.uk/, 2014


*Need Protection from a Biological Perspective* Paper presented at the The Art and Joy of Wood conference, Bangalore, India.


Troy, L. (2013). Did You Know .Secret history of didgeridoos. In (pp. 50-50): Y.


Appendices

Appendix A

List of ancient Egyptian samples codes used in the thesis and in the publications

The thesis has a published work. Some of the samples studied in the published work has different codes than what has been used here in the thesis. The thesis used the prefixes of the country followed by the location and then the number of the samples from this location. For examples sample EG-SAQ-1 is sample number 1 collected from Saqqara, Egypt and sample EG-SOH-3 is sample number 3 collected from Sohag, Egypt. A complete list of the samples examined in the publication and their alternatives used in the thesis is in Table 12 below.

Table 14: List of the samples examined in the publication and their alternatives in the thesis

<table>
<thead>
<tr>
<th>Sample code used in the thesis</th>
<th>Sample code used in the publication</th>
<th>Origin of the sample</th>
</tr>
</thead>
<tbody>
<tr>
<td>EG-SAQ-2</td>
<td>F1</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-3</td>
<td>F2</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-4</td>
<td>F3</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-5</td>
<td>F4</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-6</td>
<td>F5</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-SAQ-7</td>
<td>F8</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>Code</td>
<td>Location</td>
<td>Description</td>
</tr>
<tr>
<td>------------</td>
<td>----------</td>
<td>---------------------------</td>
</tr>
<tr>
<td>EG-SAQ-8</td>
<td>F9</td>
<td>Saqqara-Khendjer Pyramid site (ca. 1760 BC)</td>
</tr>
<tr>
<td>EG-DAK-1</td>
<td>F6</td>
<td>El Dakhla Oasis (Mut) (332 BC-395 AD)</td>
</tr>
<tr>
<td>EG-SOH-1</td>
<td>F11a</td>
<td>Jerja, Sohag- El Seiny Mosque (1787 AD)</td>
</tr>
<tr>
<td>EG-SOH-2</td>
<td>F11b</td>
<td>Jerja, Sohag- El Seiny Mosque (1787 AD)</td>
</tr>
<tr>
<td>EG-SOH-3</td>
<td>F11c</td>
<td>Jerja, Sohag- El Seiny Mosque (1787 AD)</td>
</tr>
</tbody>
</table>
Appendix B

Chapter 8 in press work.

This appendix shows the version before the final corrections of the paper: “Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture: A Case Study” which is in press and will be published online on the ICOM-CC website.

The manuscript starts in the next page.
17

Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture: A Case Study

Mahmoud Youssif Mohammed*, 2, Mostafa Abdelfatah1 and Robyn Sloggett2

1Conservation Department, Faculty of Archaeology, Fayoum University, Egypt
2The Centre for Cultural Materials Conservation, University of Melbourne, Australia
1Saqqara Conservation Department, Ministry of Antiquities, Egypt

*Author for correspondence: m.youssif@animelb.edu.au

Abstract

This paper describes conservation of an ancient Egyptian polychrome statuette, discovered in Saqqara in 1984 and identified as Object 18241. It discusses documentation, sampling, investigation of the wooden substrate, microorganism identification, ground and pigment analysis, and issues of previous restoration. Analysis was conducted with light microscopy, powder X-Ray diffraction (PXRD), Fourier transform infrared (FTIR), and scanning electron microscope equipped with energy dispersive X-ray analysis (SEM-EDS). Rhizopus stolonifer and Aspergillus niger were indicated as the main fungi; calcium carbonate as the main compound of the ground layer, and polyvinyl acetate (PVA) in a previous intervention. The pigments Egyptian blue, graphite and dark yellow ochre were identified. Conservation treatment entailed consolidation; cleaning; filling and reconstruction; and stabilisation with cotton, Paraloid® B-72 (ethyl methacrylate/methyl acrylate co-polymer) and micro-balloons. Assessment and treatment indicated the success of cotton as a filling material, as well as emphasising the importance of comprehensive analysis prior to treatment.

Keywords

Egyptian statuary; Saqqara artefact; polychrome cleaning; materials analysis; polychrome stabilisation; conservation treatment

17.1 Introduction

Saqqara is the largest part of the necropolis of the ancient Egyptian capital Memphis (Men-nefer), located south of modern Cairo and is renowned for its archaeological sites [Shaw and Nicholson 2002]. The label on the polychrome statuette that is the focus of this paper identifies the object as excavated in AD1984 by Said Amer Elfeky in the Unas excavation; no other details are available. The figure
represents a form of servant statuette, produced for burial with the deceased to serve the household in the next life (Saleh and Sourouzian 1978) and depicts a kneeling woman grinding cereal. Examples of this servant statuette, executed in both wood and stone, are found in museums around the world including the Rosicrucian Egyptian Museum, San Jose; Glencairn Museum, Pennsylvania; Museum of Fine Arts, Boston; Egyptian Museum, Cairo; Alexandria National Museum; and others. Most of these sculptures can be dated to the Old Kingdom from the 3rd millennium BC.

Object 18241 consists of several pieces of wood connected with wooden dowels and mounted on a rectangular wooden base; a method often noted in similar statuettes. Dowel joins are evident in objects from the First Dynasty, c.3100 – 2890 BC (Lucas 1948, 513), and constitute the main joining technique used in this statuette. Investigation into the construction of the statuette indicated that the head, main body and legs were carved from one piece of wood. The arms and feet were carved separately and were connected by dowels to the shoulders and body. The body was fastened to the base by a small hidden dowel, which extended from the middle of the statuette to the base. The figure is leaning forward in order to perform the task of grinding cereal and is fastened by mortise and tenon joints to the wooden grinding piece. The hands are produced from calcium carbonate (CaCO3), which is also used for the ground layer. This ground layer covers the wooden substrate, providing a base onto which the decorative elements of the surface were applied. This is a basic method of production of Egyptian statuettes from this era (Sliwa 1996), providing a suitable foundation for painting the finer anatomical details of the body (Killen 1994, 16). Details of the figure are painted, with dark yellow ochre used for the skin, black for the hair, white for the skirt and blue for the wristband.

The statuette was in poor condition. The paint and the ground layers were extremely brittle, precluding any handling of the object. This paper describes the assessment of the materials and composition of the statuette, the degraded nature of the materials, and the subsequent conservation decision-making and treatment undertaken on Object 18241. Both SEM, which identified the black pigment as graphite, and FTIR investigation of the black deposition from the skirt, informed treatment decision-making. Further identification of materials assisted with decisions regarding cleaning the statuette to remove dust and dirt and the existing restorations. Final treatment consisted of consolidation of flaking paint, filling gaps and reconstruction of the various constituent parts.

17.2 Materials Identification and Analytical Methodology

Simple visual examination and condition reporting revealed information about the colours, dimensions, structure and design elements used to construct this object (Miller 2007, 22). One wooden block was carved to form the body, the head and the legs, with dowels attaching the arms and feet. The figure is mounted on a rectangular wooden base. Its height from head to the knees is 40.5 cm and depth from the front to back (forehead to the feet) is 40 cm. The wooden base measures 61.5 x 20 x 5 cm. The arms measure 24.5 cm in length. With one foot being longer than the other; the right measuring 14.5 cm and the left 13.5 cm. The statuette does not display the quality of work evident in similar statuettes from archaeological sites associated with royalty or the wealthy. It was in poor condition loss of adhesion resulted in the separation of appendages. A longitudinal crack was visible in the wood substrate, in the chest and the abdominal areas. Below this crack and just above the skirt, a dark spot indicating biological growth was noted.

The average thickness of the ground layer was 5 mm. Both the ground and paint layers exhibit substantial loss, most obviously on the chest and abdominal area and sections on the arms. The extensive flaking of the paint layer is due in part to the delamination of the ground layer, which created problems
with handling. This delamination may have been exacerbated by the dry environment in Saqqara, causing the wooden substrate, ground layer and paint layer to shrink in different ways and the adhesion between the wood, ground and paint layers to fail. On the back and shoulders, there was a remnant film suggesting a previous consolidation. While this film had successfully stabilised the areas, they were darker than the surrounding paint and ground, and sand particles had adhered to the film (Fig 1).

Figure 1. Object 18241 prior to conservation treatment.
In order to best determine a treatment methodology for the statuette, samples were collected. Areas sampled include the pigment flakes on the wooden base, a very small wooden specimen from the groove of the left foot from the previous restoration material; and from the dark spots on the abdomen.

Powder X-ray diffraction (PXRD) is one of the most popular techniques with which to identify inorganic pigments (Stuart 2007, 253), due to its ability to determine the lattice constants value of the material crystals (Janssens 2004, 189). A Philips PW1840 with Cu tube anode, generator tension of 40 kV and generator current of 25 mA was used to identify the ground layer and pigment samples. A scanning electron microscope with energy dispersive spectrometry, SEM-EDS, was used to confirm the identification of the black pigment as graphite and to investigate the wooden sample. Examination was performed using a PHILIPS (FEI) XL30 ESEM TMP with a beam of 15kV and spot size 6. Gold was used for coating under high vacuum. A JEOL-JSM-5400LV was also used to investigate the wooden substrate. The binder was identified using a Bruker Alpha-P FTIR spectrometer equipped with a diamond ATR window (Bruker Optik GmbH, Ettlingen, Germany). All spectra recorded were in the range of 4000–400 cm⁻¹ with 32 co-added scans at a spectral resolution of 4 cm⁻¹. (Nel et al. 2010). A number of comparative samples, including carbon with gum Arabic, carbon with egg yolk and control samples of egg yolk, gum Arabic, PVA and rabbit skin glue, were produced in order to test for any likely binder material. FTIR was also used to examine the black colour on the skirt to clarify if it is an original pigment, an additional deposition resulting from poor storage, or some other cause. Light microscopy and USB digital microscopy (micro capture version - 1.3 MB) were used to identify the microorganisms on the wooden substrate. Test samples were cultivated in agar gel for mould identification.

17.3 Results and Discussion

17.3.1 Pigments

Four pigments were identified using PXRD; graphite, Egyptian blue, dark yellow ochre and calcite. All contained calcite (CaCO₃), being contamination from the ground layer.

*Black pigment*: PXRD analysis indicated that the black pigment is graphite. This was unexpected given the suggestion that the statuette is dated to the Old Kingdom, and that most studies of Egyptian objects from this period identify carbon black as the main source of black pigment (Lucas 1948, Afifi 2011, Abd EL Aal 2010, Lee and Quirke 2000). This result was confirmed by SEM, which revealed the flaky and irregular outlines of the particles of the graphite (Winter and West FitzHugh 2007, 25) (Fig 2, 3).

*Blue pigment*: The blue sample contains quartz (SiO₂), Egyptian blue (Cu₂SiO₄(OH)₂), with calcite (CaCO₃) as the main compound (Fig 4).

*Dark yellow pigment*: The dark yellow pigment contains yellow ochre (5Fe₂O₃·9H₂O), in addition to calcite and quartz (Fig 5).

*White pigment*: Calcite CaCO₃ was the main compound identified in the white pigment.
Figure 2. PXRD spectrum of black pigment with a crystalline phase of calcite, graphite and quartz (if long use: PXRD spectrum of the black pigment and the same with following).

Figure 3. SEM-EDS of the black sample. A and B are SEM images. C is the EDS pattern.
Figure 4. PXRD spectrum of blue pigment with a crystalline phase of calcite, Egyptian blue and quartz.

Figure 5. PXRD spectrum of dark yellow pigment with a crystalline phase of calcite, yellow ochre, halite and quartz.

Mohammed, M.Y. et al. Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture
17.3.2 Ground layer

PXRD analysis of the ground or preparation layer indicated calcite CaCO3 and quartz SiO2 (Fig 6).

![Image](image_url)

Figure 6. PXRD spectrum of the ground layer with a crystalline phase of calcite and quartz.

17.3.3 Binder

FTIR was used to compare control standards with the binder used in the paint on the statuette. FTIR analysis did not provide a definitive answer as the calcium carbonate, the major compound of the ground, dominated the reflectance result. Despite this, the FTIR did detect some areas that identified the binder as egg yolk. The FTIR absorption peaks for the binder were recorded at 1730, 1619, 1214 and 600 (Fig. 7).

17.3.4 Old restoration material

FTIR analysis of the sample from the previous restoration indicated the material used in restoration was almost identical to the PVA control standard. This confirms the assumption that previous interventions were undertaken on the object, and that the material used for this restoration is likely to be PVA (Fig. 8).
Figure 7. FTIR spectrum of a binder in black pigment.

Figure 8. FTIR Spectrum of the previous restoration material compared to the PVA control.

Mohammed, M.Y. et al  Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture
17.3.5 Black colour on skirt

FTIR analysis showed a match for the ground layer and the black sample from the skirt, and indicated that no evidence of any binder exists, suggesting the black is not a pigmented layer. These results were confirmed using SEM, and visual analysis of the black deposition. Comparison with a range of similar figures from this period indicated white skirts in Egyptian art (Watson and Cassin-Scott 1987, Roth 2002, 104) with no indication of black decoration similar to the black colouration on the skirt. A decision was therefore made to remove this carbon deposition, which was possibly due to bad storage or some other reason (Fig 9).

![FTIR spectrum](image)

Figure 9. FTIR spectrum of the black deposits on the skirt, ground layer and black pigment.

17.3.6 Wood

SEM photomicrographs showed the weakened nature of the wooden substrate with deformation of the cell walls. This loss of strength and tendency towards brittleness and fragility, may be attributed to chemical changes resulting from weathering and the reduction of cellulose, crystallization and depolymerisation of hemicellulose (Obataya 2009, 22). As a result there was a need to consolidate the support. The decision was made not to remove the substantial section of the wood required for proper identification, by weighing up the loss of original material against the potential gain of information (Rivers and Umney 2003, 391). It is clear, however, that it is hardwood. Sycamore fig (*ficus sycomorus*) may be a possible source in line with the description given by Johnson et al (1995, 78), and its popularity in ancient Egypt (Gale et al. 2000) (Fig 10).
17.3.7 Mould

Cultivating samples from the mould infested area enabled identification as indicated below in Table 1. The aspergillus species was dominant. All mould was contained to the surface of the wood and had no impact on the mechanical properties of the support.

<table>
<thead>
<tr>
<th>N</th>
<th>Organisms</th>
<th>No. of colonies</th>
<th>Rate of appearance %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dust</td>
<td>Aspergillus niger</td>
<td>4</td>
<td>27</td>
</tr>
<tr>
<td></td>
<td>Aspergillus flavus</td>
<td>3</td>
<td>20</td>
</tr>
<tr>
<td></td>
<td>Alternaria alternata</td>
<td>2</td>
<td>13</td>
</tr>
<tr>
<td></td>
<td>Aspergillus verrucose</td>
<td>1</td>
<td>7</td>
</tr>
<tr>
<td></td>
<td>Rhizopus stolonifer</td>
<td>5</td>
<td>33</td>
</tr>
<tr>
<td>Total</td>
<td></td>
<td>15</td>
<td>100%</td>
</tr>
</tbody>
</table>

Table 1. Mould species identified from the samples.

Mohammed, M.Y. et al  Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture
17.4 Conservation Treatment

17.4.1 Documentation

The statuette was documented using a standard condition report, photographic images, and analytical documentation. The condition and stability of the statuette was identified as poor, with very fragile and brittle ground and paint layers. As a result, the decision was made to clean and consolidate each separated part; being the body, arms, feet and the delaminating areas of the ground layer. After cleaning, treatment involved reconstructing and reattaching these separated sections (Fig 11).

Figure 11. The object 18241 during the documentation and in the first stages of conservation
17.4.2 Cleaning

A fine layer of dust covered the surface of the statuette. This was removed gently with a soft goat-hair brush and a flicking motion (Norton 1990). Several areas were too delicate to be cleaned in this way, including the paint layer on the grinding piece, which was too flaky to be touched. It was therefore necessary to consolidate the flaking paint (described below) prior to cleaning. As the ground layer was completely missing from the abdominal area, it was possible to mechanically remove the staining from the mould outbursts on this area. It was removed using bristle brushes, a 1:1 mixture of distilled water and ethanol (99%) was then applied to the surface with cotton swabs to gently clean any residual deposits. This procedure was also undertaken on the skirt. The same mixture, commencing with 2:1 deionized water: ethanol (99%) and gradually increasing to a ratio of 1:1, was used to remove the PVA film. This treatment satisfactorily removed both the dirt and the PVA. Pure ethanol (99%) was used to inhibit any recollection of mould.

17.4.3 Consolidation

Often archaeological material is too degraded to be handled without treatment (Rodgers 2004, 41). This was the case here and fragile sections required initial consolidation. Paint flakes were consolidated with Paraloid® B-72 in acetone from an initial 10% concentration which gradually increased to 20%, and applied by syringe and pipette. Where both the ground and light paint required consolidation, Klucel® G (hydroxypropyl cellulose) 2% in ethanol was used (Lokma 2010, 158). This ensured that the relatively light colour of the ground and the pigments in the paint layer were not darkened. Klucel® G demonstrates long-term stability, low shrinkage percentage and retains flexibility after exposure to high temperature and light (Johnson et al 1995, 76); all necessary in the environment at Saqqara. Paraloid® B-72 2% in acetone was used to consolidate the dark coloured layers (black and dark yellow). The wood substrate was consolidated using Plexisol® P550 2% in an acetone and toluene mixture (40:60) increasing to 4% where necessary and applied with a syringe.

17.4.4 Structural repair

After consolidation of the detached and delaminating sections, the final task of reconstruction was able to be completed. First the wooden dowels, originally used to fasten the arms and the feet, were strengthened. The dowels were wrapped with cotton wool then reinserted into the existing dowel-holes after these were injected with Paraloid® B-72, initially at 10% increasing to 20% where necessary. Gaps remaining between the dowel and body of the statuette were filled with a mortar comprising micro-balloons in Paraloid® B-72 20% in acetone; pigmented with red and yellow ochre. Stabilisation of the space between the support stand under knees and the knees was achieved using the same fill procedure.

The use of cotton as a filling material has been very successful (Lokma 2010), and further use was made of cotton to fill the crack in the chest and abdomen, as well as the gaps left after the reconstruction process. First a spatula was used to insert cotton wool into cracks and gaps, which were then consolidated by injecting the cotton wool with Paraloid® B-72 10% in acetone, increased gradually to 20%. Remaining surface losses were finished using micro-balloons in Paraloid® B-72 20% in acetone, mixed with an appropriate pigment which was usually yellow and red ochre (Fig 12).
Figure 12. Structural consolidation for the object 18241 showing the areas where the cotton wool was used.
The loss of the gesso layer on the arm was filled with a mortar of Paraloid® B-72 20% in acetone and micro-balloons, mixed with red and yellow ochre, and laid as a continuous layer on the surface.

17.4.5 Fumigation

The decision regarding fumigation of the statuette is pending subject to further assessment of suitable options (Fig 13).

![Figure 13. The object 18241 after treatment.](image)
17.5 Conclusion

Investigation and treatment of the statuette, Object 18241, confirmed the success and simplicity of using cotton wool as a filling material. Like wood, cotton is cellulose-based, providing suitable flexibility and compression where needed. This technique is easily reversible by removing the finishing layer, injecting the Paraloid® B-72/cotton fill with acetone, and removing the cotton once the adhesive has dissolved sufficiently. This paper also confirms the necessity of understanding the condition of the object and ascertaining previous treatments prior to the commencement of treatment. FTIR spectra were dominated by the calcite making them difficult to read. Isolating the binder prior to FTIR analysis is preferable but the brittle condition of the paint and associated binder loss made this impossible. Unlike the spectra associated with the paint layers, the result on the skirt displayed no binder peaks, indicating that this was not part of the original pigmented layer and could be safely removed.

Acknowledgments

The authors are indebted to Ms. Abeer Fouad Hagrasy, Conservation Department, Faculty of Archaeology, Fayoum University for her assistance in fungi identification, and Mr. Ashraf Fahmi, Saqara Conservation Department, Ministry of Antiquities, for his support for this project.

References


*Mohammed, M.Y. et al* Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture


Materials

Paraloid® B-72 (ethyl methacrylate/methyl acrylate co-polymer):
Lascaux Colours & Restauro Barbara Diethelm AG
Zürichstrasse 42, CH-8306 Brüttisellen
Phone +41 44 807 41 41. Fax +41 44 807 41 40
info@lascaux.ch

Klucel® G (Hydroxypropylcellulose):
C.T.S Srl
VIA G Fantoli n. 26
00149 Roma (RM) - Italy
Phone: +39 06 55301779, Fax: +39 06 5592891

Mohammed, M.Y. et al. Treatment and Conservation of a Polychrome Egyptian Wooden Sculpture
Plexisil® P550 (Butyl methacrylate) and pigments (inorganic oxides):
Kremer Pigmente GmbH & Co. KG
Hauptstrasse 41-47, D 88317 Aichstetten
Phone: +49 7565 91120. Fax +49 7565 1606
kremer-pigmente@t-online.de
www.kremer-pigmente.de

Cotton wool, Acetone and Ethanol:
Novartis Pharma S.A.E
PO Box 1893, El Sawah Street, 11511 Amiria, Cairo, Egypt
Phone: +202 24 567 200. Fax: +202 2 257 4616
http://www.novartis.com.eg

Please use the following when citing this paper:

Disclaimer:
This paper is published and distributed by the International Council of Museums – Committee for Conservation (ICOM-CC), with authorization from the copyright holders. The views expressed do not necessarily reflect the policies, practices, or opinions of ICOM-CC. Reference to methods, material's, products or companies, does not imply endorsement by ICOM-CC.
Appendix C
Photograph documentary of the case study examined in Chapter 8 before and after conservation.

<table>
<thead>
<tr>
<th>Before the conservation treatment</th>
<th>After and during the conservation treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td><img src="image1" alt="Before conservation" /></td>
<td><img src="image2" alt="After conservation" /></td>
</tr>
<tr>
<td><img src="image3" alt="Before conservation" /></td>
<td><img src="image4" alt="After conservation" /></td>
</tr>
</tbody>
</table>
Author/s:
Mohammed, Mahmoud

Title:
Changes in the chemical composition of archaeological wood caused by exposure to different environments and its relation with the other properties.

Date:
2018

Persistent Link:
http://hdl.handle.net/11343/222000

File Description:
Thesis

Terms and Conditions:
Terms and Conditions: Copyright in works deposited in Minerva Access is retained by the copyright owner. The work may not be altered without permission from the copyright owner. Readers may only download, print and save electronic copies of whole works for their own personal non-commercial use. Any use that exceeds these limits requires permission from the copyright owner. Attribution is essential when quoting or paraphrasing from these works.