

“Alexandru Ioan Cuza” University of Iași
Faculty of Geography and Geology
Doctoral School of Geoscience
Specialization - Environmental Science



In-depth studies on the modifying effects of natural aging on the chemical structure of wood and wood-water relations

Supervisor

Prof. Dr. Ion SANDU

PhD Candidate

Amir GHAVIDELESFAHLAN

2021

Acknowledgements

First of all, I want to thank my supervisor, Prof. Dr. Ion SANDU for his support during the entire work; for helping me through difficult times with patience, understanding and encouragement.

A special thanks to Dr. Viorica VASILACHE, for sharing her broad knowledge and expertise on the analysis.

I would like to thank International and Erasmus office of the Alexandru Ioan Cuza University of Iasi for financial support and scholarships in Erasmus internships.

I also would like to thank Prof. Dr. Holger MILITZ (Department of Wood Biology and Wood Products, Georg-August-Universität Göttingen), Dr. Reza HOSSEINPOURPIA (Department of Forestry and Wood Technology of Linnaeus University), Dr. Miklos BAK (Institute of Wood Science, Sopron University) for supporting during Erasmus practicing mobility.

I am grateful to Dr. Tamas HOFMMAN from Sopron University, Dr. Jana GELBRICH from material testing institute of Bremen for their profound technical help and advice in wet chemical and biological analysis of the samples.

Finally, I would like also to acknowledge all colleagues in the Laboratory of Scientific Investigation and Cultural Heritage Conservation Department, Alexandru Ioan Cuza University for their support and encouragement, I enjoyed working alongside such talented young researchers and being able to exchange ideas on some of my work.

Furthermore, I would like to thank my family for supporting me during the last years.

Content

<u>Introduction.....</u>	<u>6</u>
Chapter One Introductory Overview.....	11
1.1.General overview of wood.....	11
1.1.1. Nature of structural components, type of support.....	14
1.1.2. The wood cell wall.....	15
1.1.3. movement of moisture in wood	17
1.2. Aging of wood.....	18
1.2.1. Natural aging.....	18
1.2.2. Properties of archaeological wood.....	20
1.2.2.1. Changes in chemical composition.....	20
1.2.2.2 Colour.....	23
1.2.2.3. Changes in the microstructure.....	25
1.2.2.4. Hygroscopic behaviour.....	25
1.3. Accelerated aging.....	26
Chapter Two Materials and methods.....	28
2.1. Raw Materials.....	28
2.1.1. Fresh-cut wood samples.....	28
2.1.2. Archaeological wood samples.....	28
2.1.2.1. European Oak (<i>Quercus robur</i> L.).....	29
2.1.2.2. European White Elm (<i>Ulmus laevis</i> P.).....	29
2.1.2.3. Black Poplar (<i>Populus nigra</i> L.).....	31
2.1.2.4. European Spruce (<i>Picea abies</i> L.).....	32
2.1.2.5. Silver Fir (<i>Abies alba</i>).....	33
2.2. Methods.....	34
2.2.1. Cyclohexane-ethanol extract.....	34

2.2.2. Holocellulose content.....	34
2.2.3. α -Cellulose content.....	35
2.2.4. Kürschner-Hoffer cellulose content.....	35
2.2.5. Lignin content.....	36
2.2.6. Ash content.....	36
2.2.7 Energy-dispersive X-ray (EDX) spectrometry.....	37
2.2.8 Characterization by scanning electron microscope (SEM).....	37
2.2.9 ATR-FTIR analysis.....	37
2.2.10 X-ray photoelectron spectroscopy (XPS) analysis.....	37
2.2.11 XRD analysis.....	38
2.2.12 Microscopic imaging.....	39
2.2.13 DVS analysis.....	39
2.2.14 Statistical analysis of the results.....	40
Chapter Three Results and discussion.....	41
3.1. Chemical analysis.....	41
3.1.1 Wet chemical analysis.....	41
3.1.1.1. Oak	41
3.1.1.2. Elm	43
3.1.1.3. Poplar	45
3.1.1.4. Spruce	45
3.1.1.5. Fir	46
3.1.2 FTIR analysis.....	47
3.1.2.1. Oak	48
3.1.2.2. Elm	49
3.1.2.3. Poplar	51
3.1.2.4. Spruce	52
3.1.2.5. Fir	54

3.1.3 XPS analysis.....	56
3.1.3.1. Oak	56
3.1.3.2. Elm	58
3.1.3.3. Poplar	60
3.1.3.4. Spruce	62
3.1.3.5. Fir	65
3.1.4 XRD.....	67
3.1.5 Energy-dispersive X-ray (EDX) spectrometry.....	71
3.2 structural properties.....	73
3.2.1 Scanning Electron Microscope (SEM).....	73
3.3 Microscopic examinations.....	77
3.4 Physical properties.....	83
Conclusion	88
References.....	94
APPENDIX 1.....	113

Introduction

In this report, a large number of investigations were undertaken to provide valuable knowledge on the properties of archaeological wood. This has been undertaken in conjunction with a rigorous review of literature that has enabled a greater understanding of chemical changes during ageing and their effect on wood behaviour.

Wood is a natural and renewable material with many uses. Due to its natural structure, it is susceptible to biological degradation. Due to biological degradation, the structure of wood changes, which results in a significant reduction in the economic and practical value of this material; therefore, the importance and necessity of wood protection against destructive factors are well defined [Verma *et al.*, 2009].

On the other hand, wood is considered to be one of the oldest construction materials, used traditionally for buildings and different constructions all over the world [Nilsson and Rowell, 2012]. Nevertheless, as an available, strong and versatile material, people have utilized wood throughout history as a base material in everything from art to construction [Timar *et al.*, 2014]. During utilization or storage, wood is exposed to a wide variety of abiotic and biotic factors, including weathering, moisture fluctuation, fungi, insects or termites [Kim and Singh, 2016]. Among these factors, moisture changes are a key factor, as this phenomenon has influence on all the other factors. The moisture in wood occurs in two distinct forms: as free water stored as a liquid in the wood's pores or vessels themselves, and as bound water trapped within the cell walls. Only once all the free water has been lost will the wood reach what is referred to as the fiber saturation point (FSP). All polymers of the cell wall are hydroscopic (cellulose, hemicellulose, and lignin). Each cell wall polymer's sorption of moisture depends not only on its hydrophilic nature but also on the water accessibility of the hydroxyl groups of the polymer [Rowell, 2012]. If the wood stays at stable RH for long periods of time, an equilibrium moisture content (EMC) will be achieved [Brunauer, 1943; Fengel, 1991].

Because of the biodegradable nature of the wood, the effect of the degradation factors leads to different degradation processes. Storage of wooden objects in water or soil under waterlogged environments is the most severe form of moisture-induced degradation. As the conditions might vary from site to site, chemical changes in the material tends to vary that

leads to the diverse chemical composition of archaeological wood. Findings indicate lower cellulose content and higher lignin content in archaeological oak wood relative to fresh-cut wood. The presence of excessive water is always a key factor during the chemically and especially the biologically induced degradation of wood [Björðal *et al.*, 2000; Colombini *et al.*, 2009; Krutul *et al.*, 2010; Łucejko *et al.*, 2012; Bader *et al.*, 2013; Kolář *et al.*, 2014]. In addition to the degradation of the cell wall macromolecules, the deposition of inorganic substances during fossilization also occurs. This process is highly dependent on the sub-surface environment [Fengel, 1991; Fengel and Wegener, 1986; Florian, 1990]. The variations in chemical composition cause inconsistencies in wood behaviour [Kolář *et al.*, 2014], among them the wood-water relations as well.

As can be seen from the above examples, the study of archaeological woods is important. Therefore, in this study, several methods, techniques and equipment are used to investigate the physical properties and wood-water relations, as well as chemical and structural properties in fresh-cut and archaeological samples.

The present study aims to fill this scientific gap and to contribute to the knowledge about the ageing process of wood. The main objectives were:

- describe the ageing process and its effect on the wood properties;
- delivering a complete characterisation of archaeological wood;
- providing the necessary parameters to model the diffusion processes to determine the allowable climate fluctuations;
- reviewing of the assumptions and contradictions in earlier publications.

In this study, five species of archaeological and fresh-cut samples were investigated. The archaeological European Oak (*Quercus robur* L.) was originally used in street pavements as fences sample and belong to the 14th century.

In this study, we had three different samples of archaeological European White Elm (*Ulmus laevis* P.) wood that were marked with A, B and C. The archaeological elm A was extracted from sand mines and its age varies from 1800 to 2000 years. The type of usage is unclear. The archaeological sample B belonged to an old house in the monastic village. The house was built between 1641 and 1643. The archaeological sample C was from a historical building in the Iasi city. The building was built about 350 years ago.

Another sample studied in this investigation belonged to a boat in freshwater. The wood of this boat was made from Black poplar (*Populus nigra* L.) wood and the boat was

kept for a long time in the History Museum of Iasi in Romania. The approximate age of this boat is 1000 to 1200 years.

Also, two samples of European Spruce (*Picea abies* L.) wood marked with A and B were studied. The sample A was sourced from an outdoor part of a building constructed in the 17th century in the Brăila Naval Shipyard on the Danube, Romania. Samples of archaeological European spruce B were obtained from a furniture item located in a historical building from the 18th century in Iasi, Romania.

Samples of archaeological silver fir (*Abies alba*) was taken from a historical furniture item from the 18th century in the same building in Iasi, Romania. This sample was located on an outside part of the furniture.

All of fresh-cut and archaeological samples were compared in terms of extractive, chlorite holocellulose, α -cellulose, lignin, and ash contents. All of the samples underwent complement of analytical techniques using Scanning Electron Microscope (SEM) coupled with Energy Dispersive X-ray diffraction (EDX) for imaging wood morphology structures and elemental analysis, Fourier Transform Infrared (FTIR) for examining functional groups, Optical Microscopic (OM) for investigation of biological degradation, X-ray photoelectron spectroscopy (XPS) for characterization of wood surfaces elemental compositions, X-ray diffraction (XRD) for determining the crystallinity of partially crystalline of cellulose and Dynamic vapour sorption (DVS) for identification of sorption and desorption behaviour of both fresh-cut and archaeological wood samples.

The obtained results using these multidisciplinary devices from both the fresh-cut and archaeological samples were compared and matched according to similarities in morphological, elemental, spectral and chemical markers for identification purposes.

The results obtained from the comparison between the archaeological and fresh-cut samples were able to answer several questions about the chemical, morphological, structural, biological and physical changes during the ageing process.

An overall elaboration of the study was described in Chapter 1, which included general description of the wood, ageing process etc. as well as full details on the approach, purpose and importance of the study, concluded the chapter with bibliographical review on the latest current state of knowledge in the field related.

The experimental part starts from Chapter 2, where a demonstration for the instrumental and analytical methods that were utilized for analysing the fresh-cut samples and the archaeological samples. In this section, all the details related to the archaeological samples studied in this research are explained. The information of all devices is also mentioned.

The results of all analysis, microscopic experiments and imaging, chemical, physical and structural changes are fully described in Chapter 3.

Finally, the data collected from this research that includes analytical stages of wet chemical analysis, FTIR, SEM-EDX, optical microscopy, XPS, XRD and DVS analysis as part of multi analytical techniques approach, was summarized in the conclusion section.

This collection has 41 images and 18 tables. Also, 217 references have been used in this collection. The work of this thesis has been covered with four published articles in ISI Publications and three published articles in non-ISI journals. Also, two articles in international workshops and conferences have been published. Also, three articles submitted by ISI Publications are under review.

This research was conducted in collaboration with four universities of Alexandru Ioan Cuza of Iasi in Romania, University of Sopron in Hungary, George-August-University-Göttingen in Germany and Linnaeus University in Sweden.

Chapter One

INTRODUCTORY OVERVIEW

1.1.General overview of wood

Wood and wood-based products are similarly to the mainly man-made alternatives limited in their ability to remain functional over time [Hill, 2006]. The wood and wood products are inherently prone to biodegradation under natural conditions of the ecosystem cycle and due to this condition of the wood, uses are impacted to some extent. The risk of wood degradation mainly depends on the usage conditions [Borgin *et al.*, 1975a,b]. For

example, decay fungi are ubiquitous and can grow everywhere as long as the environmental conditions are suitable. The growth of fungi requires wood substances as nutrient source – so they will decrease the strength of wood materials – and a moisture source. The risk or hazard of a wooden product regarding fungal degradation depends on typical organisms thriving under dry up to continuous wet circumstances, identified as use classes defined as such in EN 335 (2013). Performance related to service life is depending on the durability or material resistance against degrading fungi. Wood or timber species have been classified for natural durability using a service life approach by means of graveyard type field testing.

1.1.1. Nature of structural components, type of support

The structure of wood has a significant impact on the physical properties and behavior of wooden materials. As a result, it's critical to comprehend the fundamentals of this framework. Wood is a non-homogeneous and anisotropic material. Wood comes from two types of tree species: softwood (or coniferous) and hardwood (or deciduous). The various properties of these two groupings, needles and leaves, can be used to distinguish them. Cells of various shapes and sizes make up every portion of the tree. The cambium, which is a layer of live cells between the wood and the bark, divides to generate cells. The tree expands by adding new cells to the wood's surface. Hardwoods are less uniform than softwoods. The majority of a softwood tree (90-95 percent) is made up of long, hollow, tubular fibres (called tracheids) that are mostly vertical. Their length is usually between 2.5 and 7 mm, and their breadth is around a hundredth of that [Martensson, 1992].

1.1.2. The wood cell wall

The cellulose skeleton, hemicellulose matrix, and lignin exciting material (considered the second most common ingredient in the wood) that binds the cells together and gives the cell wall stiffness are the three principal polymer components of the wood cell wall. Furthermore, extractives are found in wood. cellulose accounts for 40 to 50 percent of the timber's weight, hemicellulose for 20 to 30 percent, lignin for 25 to 30 percent, and extractives for 0 to 10%. (e.g. resin).

1.1.3. Movement of moisture in wood

The movement of moisture in wood can be divided into two main parts: the movement of liquid water above the fibre saturation point and the movement of bound water and water vapour below the fibre saturation point (hygroscopic moisture). Different approaches, reported in the literature, for describing moisture transport processes are presented. Moisture Transfer Mechanisms The most common method of describing quantitative aspects of moisture movements in wood is to assume that the rate of moisture exchange is increased by diffusion (molecular diffusion) processes. The transport equation's diffusion coefficient is used to describe the flow rate of migrating moisture.

1.2. Aging of wood

Wood, as a most widely used raw material in human's life, is mainly composed of cellulose, hemicelluloses and lignin polymers. In a biological life cycle, wood undergoes degradation when it exposed to a desired condition [Bjodal, 2000; Eriksson and Johnsrud, 1982]. Factors such as solar radiation, oxygen, water, heat, wind-blown particles, pollution, and microorganisms cause inter- and intra-molecular breakage in wood polymers, and thus degrade the wood structure. Solar radiation is the main reason for photochemical degradation on the wood surface. This type of degradation causes the lignin to decompose on the wood surface and therefore changes the colour of the wood surface. Changes in humidity over time are also another reason for wood degradation. These changes can be through outdoor rainfall or indoor water contact. This moisture is quickly absorbed by the surface of the wood and causes it to swell, and as the moisture decreases, the volume of the wood decreases. These stresses in the volume of wood over time may cause warping and cracking of the surface. Although heat is not as important as humidity and solar radiation, but the rate of photochemical and oxidative reactions increases with increasing temperature [Feist, 1990; Ghavidel *et al.*, 2020a,b].

Chapter Two

Materials and methods

2.1. Raw Materials

Aged woods investigated in this study came from different areas and providers. The usages and ages of the wood samples were different.

Given that historical samples were not identified in this study, in the first stage before the start of the analysis, the samples in collaboration with the University of Sopron in Hungary and the University of Hamburg in Germany were accurately identified. The samples identified in this study include five different species of wood.

The fresh-cut samples used in this study came from a Romanian and Iranian sawmill. The samples taken in Romania reflect the most relevant forest growth regions in Suceava, whereas the samples collected in Iran are from the forest region of northern Iran. Eight archaeological wood samples from five different species of wood were collected from the ARHEOINVEST laboratory and the historical museum of Iasi-Romania. Sample of archaeological oak wood was used in street pavements as fences and it belonged to the 14th century. The archaeological elm A, was extracted from sand mines in the city of Vetis county of Satu Mare- Romania and its age varies from 1800 to 2000 years. Elm Sample B, belonged to an old house in the monastic village in the area of Neamt county-Romania. The house was built between 1641 and 1643. The archaeological elm C, was from a historical building in the Iasi-Romania and it was 350 years old. The archaeological poplar sample was part of a boat in a freshwater lake or river and the age of the sample is approximately 1000 to 1200 years. Two samples of archaeological spruce wood were investigated in this research. Sample A was sourced from an outdoor part of a building constructed in the 17th century in the Baila Naval Shipyard on the Danube, Romania and sample B obtained from a furniture item located in a historical building from the 18th century in Iasi, Romania. The archaeological fir wood sample was collected from a historical building from the 18th century in Iasi, Romania.

2.2. Methods

All the analyses used in this study are shown schematically in Figure 2.7.

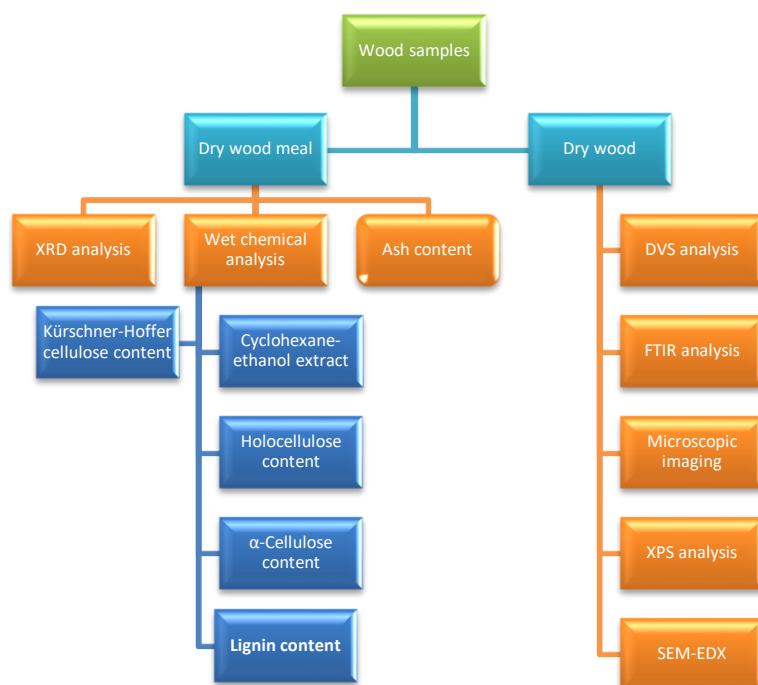


Fig. 2.7. Flow diagram of the analysis of this study

Chapter Three

Results and discussion

Oak wood

Oak wood is highly tolerant to the impact of biotic influences and is therefore frequently found in archaeological excavations. After lying in wet conditions for several years, the wood turns black as a consequence of reaction with iron compounds. Archaeological oak is an essential raw material. The research results from this study on fresh-cut oak wood (*Quercus* spp.) and archaeological oak wood show that the contents of cyclohexane-ethanol extract and hemicellulose in the fresh-cut oak wood are significantly

higher than those of the archaeological oak, which was explained by the degradation of hemicelluloses and the leaching of native wood extractives during soil contact. The amount of lignin in the archaeological oak wood increased relatively compared to the fresh-cut oak wood; however, no significant difference was found between cellulose levels. Both Kürschner-Hoffer and chlorite holocellulose assays/ α -cellulose assays proved to be suitable to assess the cellulose content of the samples. Data can be used as archaeometric characteristics of the samples. The ash content of the archaeological oak wood was remarkably higher, due to the deposition of inorganic elements from the soil into the wood. The amount of iron was remarkably higher in the archaeological oak wood due to the long-term soil contact of the oak material. This high amount of iron element in the archaeological oak wood caused the color change in the historical oak wood ash, and possibly the color change of the archaeological oak wood material itself as well. Among inorganic components, higher amounts of calcium, magnesium, sulfur, iron and aluminum were found in the archaeological wood. These above elements, as well as potassium, were found as deposition components in the cell lumens. These depositions were clearly visible in the SEM images as well.

According to the FTIR results, the O-H peaks between 3180/3590 in the archaeological oak wood because of aging, decreased. An absorption band was observed in the carbonyl group region of wood samples at 1743 cm^{-1} , showing a reduction in the peak intensity due to the aging, caused by degradation of hemicelluloses.

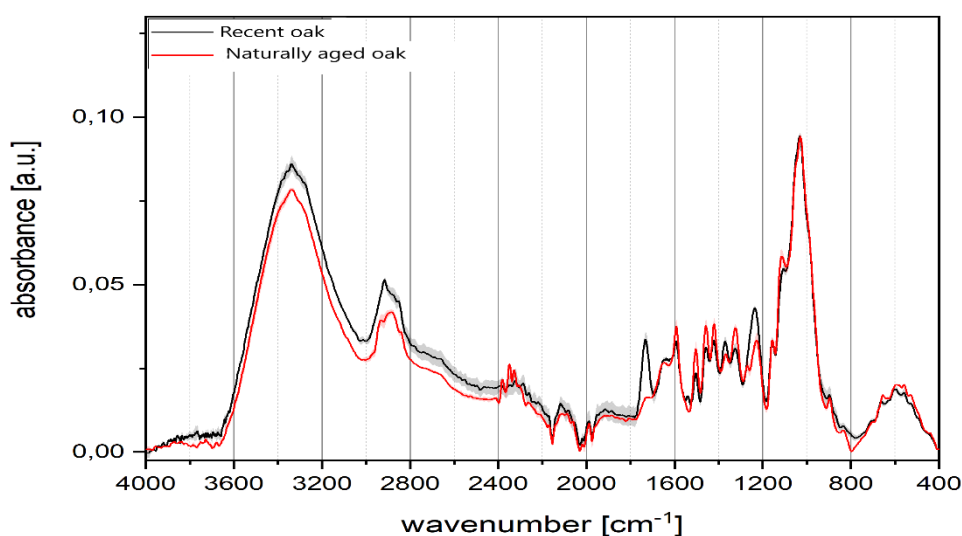


Fig. 3.1. Fourier transform infrared spectroscopy (FTIR) spectra of fresh-cut and archaeological oak wood

XPS result shows the C1 sub-peak area significantly increased and C2 sub-peak significantly decreased in the archaeological oak wood sample. The absorption in C3 peak in the archaeological oak sample is decreased after the ageing process. Both atomic ratio and Cox/Cunox in the archaeological oak wood were lower compared to the fresh-cut sample. The O2 sub-peak reflects an oxygen atom linked to a carbon atom by a single bond in the archaeological oak was significantly lower compared to the fresh-cut sample.

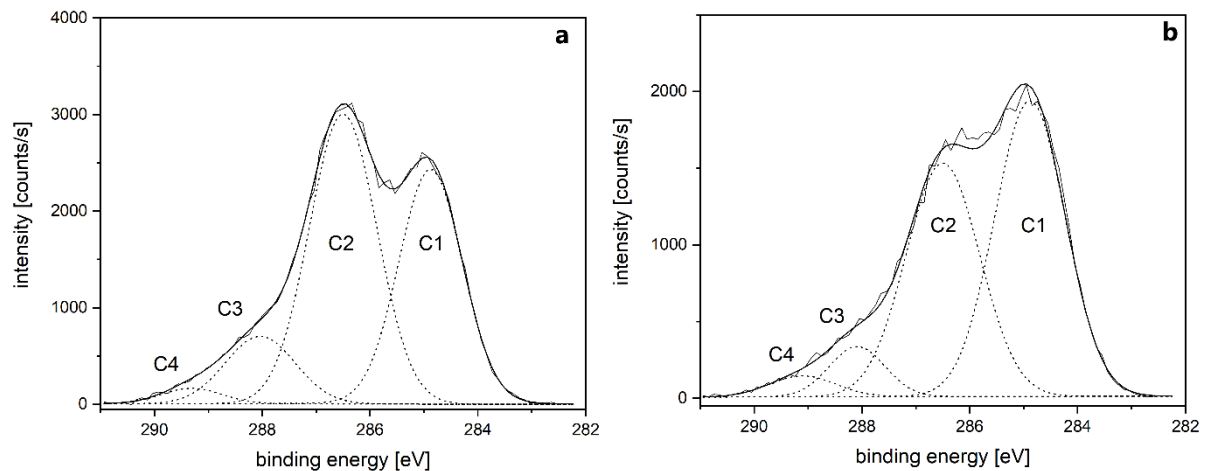


Fig. 3.6. High-resolution spectra of the C1s energy level of fresh-cut (a) and archaeological (b) oak samples

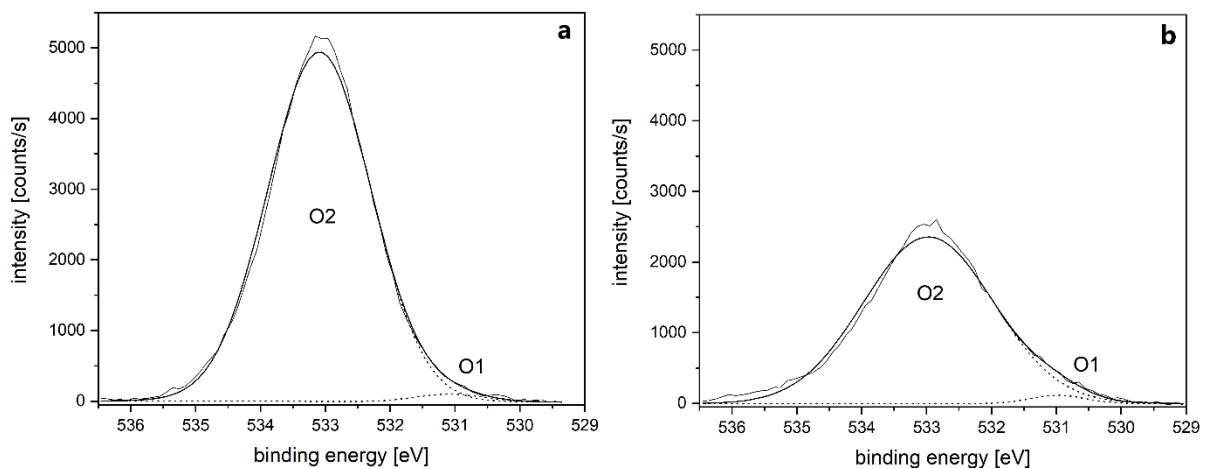


Fig. 3.7. High-resolution spectra of the O1s energy level of (a) fresh cut, (b) archaeological oak

According to the XRD measurements, the crystallinity and crystallite size of the celluloses in the archaeological oak sample were not significantly lower than the fresh-cut sample. This low decreasing in crystallinity and crystallite size could be due to the high durability of oak, which reduces degradation of wood by wood-destroying bacteria and fungi. According to the microscopic and SEM images of the archaeological oak specimen, it can be clearly seen that the rate of biological degradation was low.

Also, the amount of water absorption and desorption in wood depends on the amorphous areas of the wood, considering that the degree of crystallinity of archaeological oak wood was high, the isotherm and sorption hysteresis curves of fresh-cut and archaeological oak, the isotherm curve of archaeological oak was not significantly different compared to the fresh-cut oak. This finding can be justified by chemical analysis and biological experiment of the archaeological oak sample.

Elm wood

Current research study on fresh-cut and historic elm (*Ulmus* spp.) shows that the contents of chlorite holocellulose assays / α -cellulose, and hemicellulose in the fresh-cut wood were significantly higher than that of the archaeological ones, which was explained by the degradation of native wood hemicelluloses during soil contact by erosion bacteria and most likely in the low oxygen amount. Compared to the fresh-cut elm wood, the amount of lignin in the all archaeological elm wood grew comparatively. This data can be used for archaeometric purposes. Due to the incorporation of inorganic elements from the soil into the wood, the ash and cyclohexane–ethanol extract contents of the archaeological elm wood were significantly higher. The following bands, 1121, 1051, 1028 cm^{-1} , mainly attributable to CO vibrations in hemicelluloses, decrease significantly for the all of archaeological elm samples and between 1645 and 1237 cm^{-1} adsorbed OH bands, β -glucosidic bonds or conjugated C = O groups display high intensity for the archaeological specimen, according to the ATR FTIR spectrum. Such results indicate that cellulose and hemicellulose are the main elements to be degraded during storage completely buried and that the percentage amount of lignin increases with their degradation. For several metabolic reactions, wood-degradation fungi are known to use molecular oxygen as an electron acceptor. On the other hand, a variety of bacteria involved in the primary degradation and humification of organic matter can colonize wood that is exposed to soil and low oxygen. Considering that archaeological elm specimens were stored in the soil to a depth of 10 meters and the possibility of being in low oxygen conditions, the tendency of destruction by erosion bacteria is higher than wood-degradation fungi. Bacterial degradation of archaeological elm wood resulted in a decrease in the chlorite holocellulose content and thus, an increase in the relative percentage of lignin by residual enrichment.

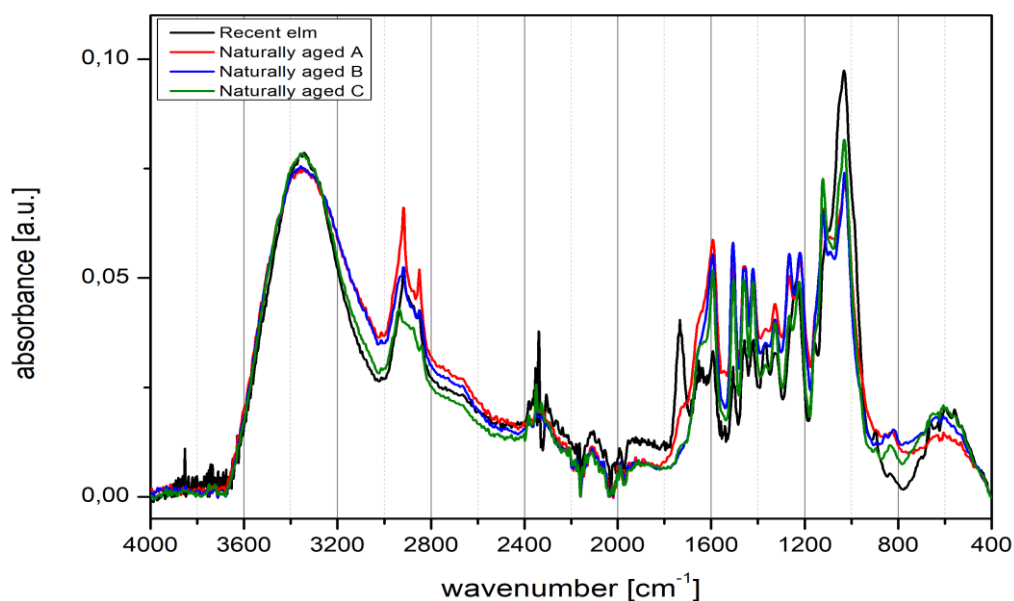


Fig. 3.2. Fourier transform infrared spectroscopy (FTIR) spectra of fresh-cut and archaeological elm wood samples

According to EDX results, carbon and oxygen had the highest amount in all of archaeological specimens. Also, the amount of iron was remarkably higher in the archaeological elm woods due to the long-term soil contact of this sample. This high content of iron element in the archaeological elm wood caused the colour change in elm wood samples. The main elements of soil such as calcium, potassium, magnesium, sulfur, and iron were higher in the archaeological wood samples.

Depolymerization, oxidation and hydrolysis reactions occurred in the archaeological samples, as indicated by lower ratios of C_{ox}/C_{unox} and O/C than fresh sample. The crystalline structure of all elm samples were also considerably decreased due to the ageing conditions. Accordingly, higher EMC values during adsorption and desorption processes were obtained in the archaeological samples as compared to the fresh one. The greater sorption hysteresis in archaeological elm samples than the fresh specimen are expected to be due to the inability of the cell wall to rearrange during the desorption run, because of the severe degradation process. Slight differences were observed in the microstructure of archaeological elm samples, which are mainly related to their condition of exposure and degradation mechanisms.

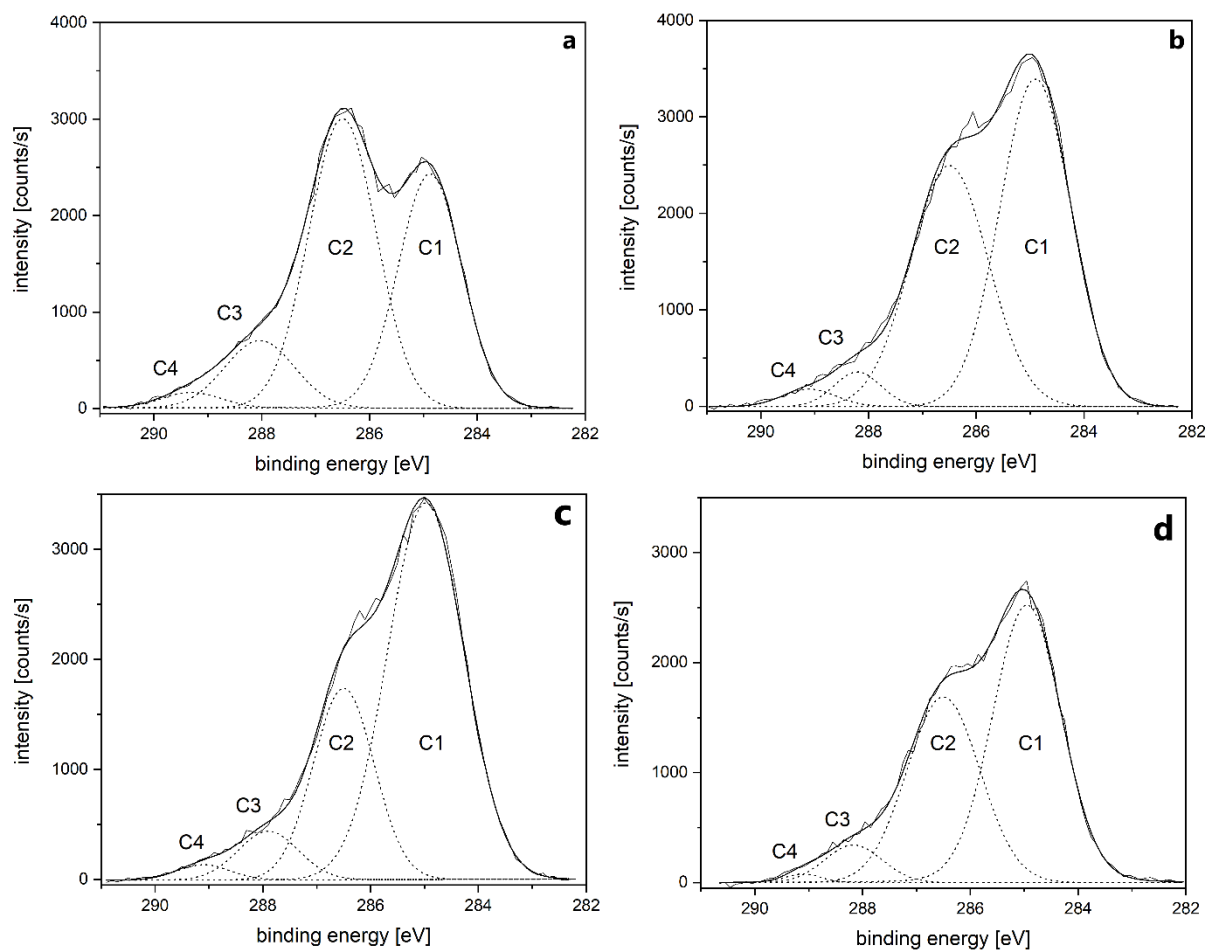


Fig. 3.8. High-resolution spectra of the C1s energy level of fresh cut (a), archaeological [A] (b), archaeological [B] (c) and archaeological [C] (d) elm samples

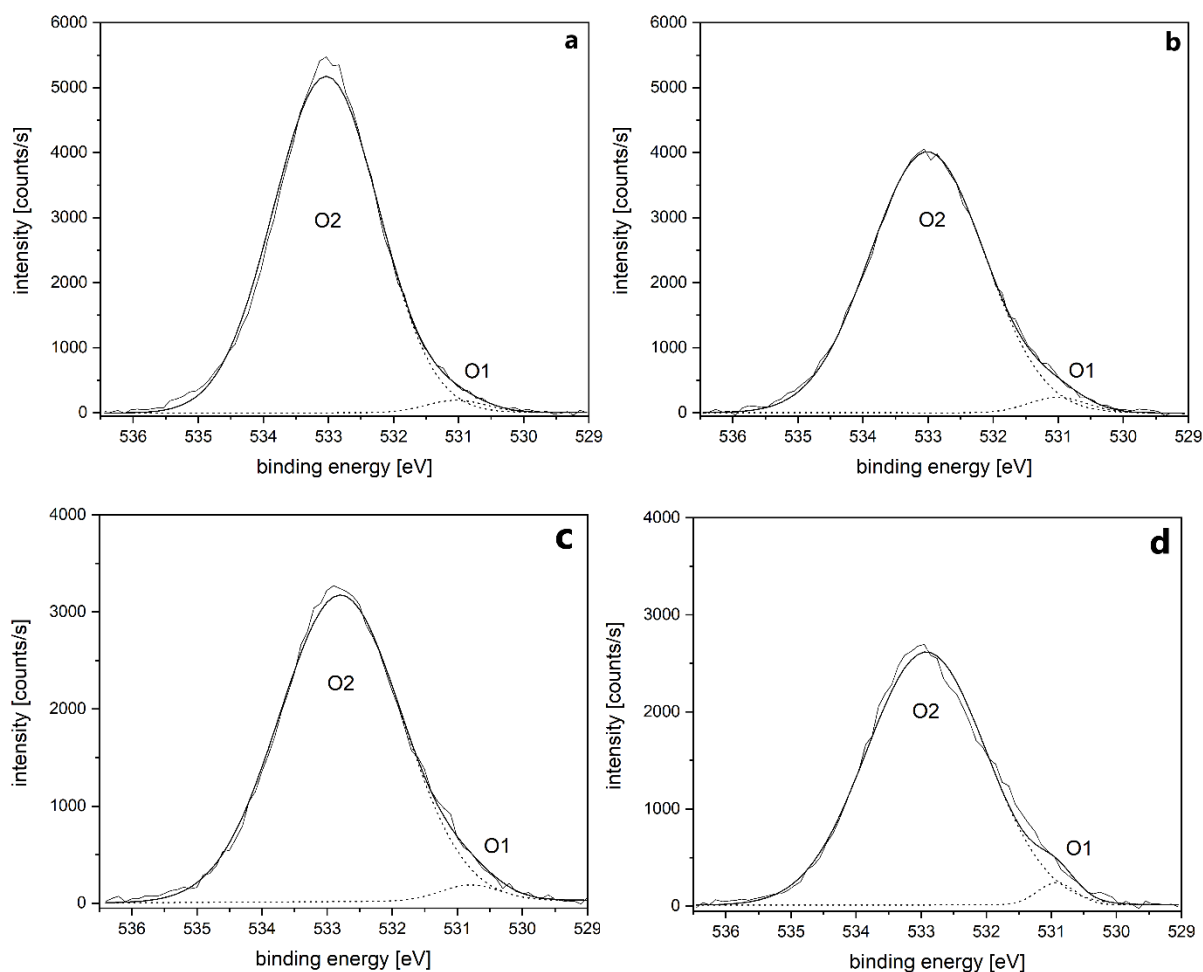


Fig. 3.9. High-resolution spectra of the O1s energy level of (a) fresh-cut, (b) archaeological elm [A], (c) archaeological [B] and (d) archaeological [C] elm

Poplar wood

The results showed that the chlorite holocellulose assays, α -cellulose, and hemicellulose in the fresh-cut wood samples were considerably higher than those of the archaeological one, which was explained by the degradation of native wood hemicelluloses during being in the low oxygen level environmental such as being in the water in the poplar sample. It is known that as the amount of holocellulose decreases the percentage of lignin also increases. According to the results in this study, this has been proven. Also, due to the presence of external and inorganic elements during the aging period by contact with soil and water, the amount of cyclohexane–ethanol extract and ash in archaeological samples were significantly higher than fresh-cut samples.

According to the FTIR analysis, the spectrum obtained for the archaeological samples revealed that the intensity in the region 1505-1593 cm^{-1} related to stretching vibrations of C=C and C=O in lignin significantly increased. On the other hand, the bands which are mainly attributed to stretching vibrations of C-O and C-C, glycosidic symmetric vibrations of C-O-C and asymmetric stretch of C-O and C-C and are related to cellulose and hemicellulose, significantly decreased due to the bacterial and fungi degradation in archaeological poplar sample.

As seen in the SEM images, the structure of archaeological poplar sample, during water contact, heavily degraded. Since the quality and resolution of SEM images are hi

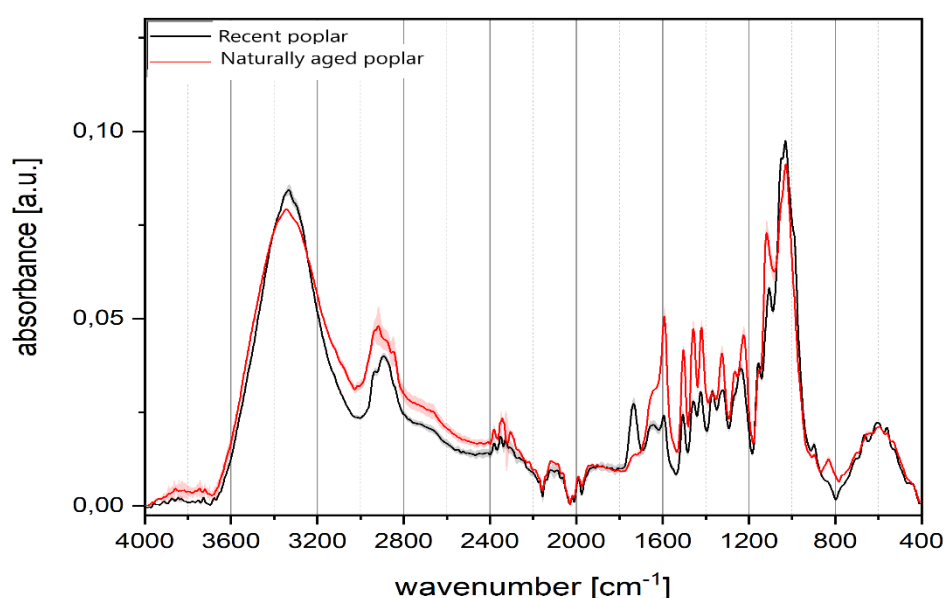


Fig. 3.3. Fourier transform infrared spectroscopy (FTIR) spectra of fresh-cut and archaeological poplar woods

gher than microscopic images and given that the samples were in low oxygen environments, it can be clearly explained that the main cause of destruction by EB and fungi.

According to EDX results, carbon and oxygen had the highest amount in archaeological specimen.

According XPS analysis, both of C_{ox}/C_{unox} and O/C ratio were lower in the archaeological poplar sample comper to the fresh-cut one. This decreasing can be due to the depolymerization, oxidation and hydrolysis reactions in archaeological wood. Also, XRD masurmantes of archaeological and fresh-cut poplar showed that the crystallinity and crystallite size of the celluloces in the archaeological poplar due to the biological degradation during aging process significatly lower then fresh-cut sample. Also, due to the decrease in the crystallinity region of cellulose and the increase in the amount of amorphous regions, the

amount of water absorption in the archaeological sample was higher than the new sample. These changes in sorption, desorption and hysteresis curves are well shown.

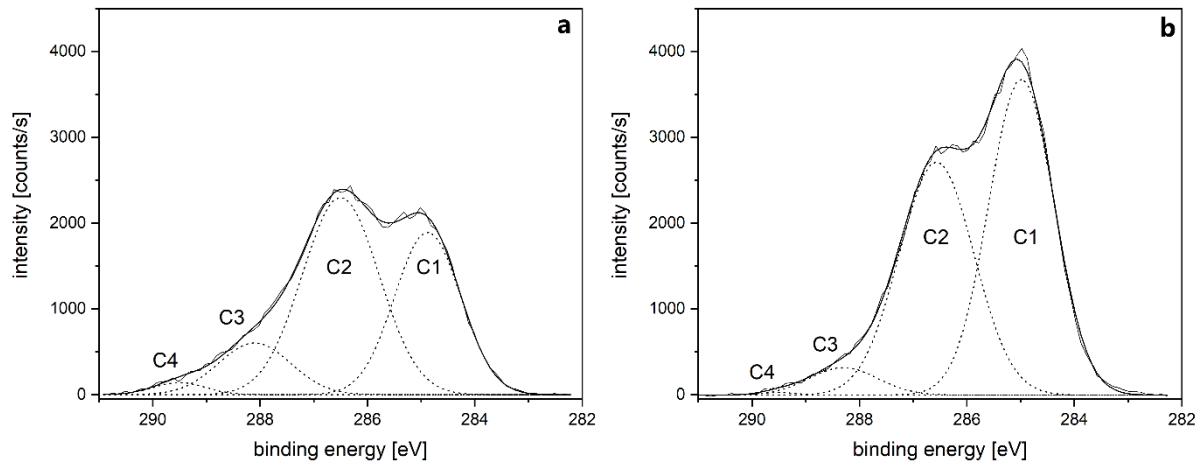


Fig. 3.10. High-resolution spectra of the C1s energy level of fresh-cut (a) and archaeological (b) poplar samples

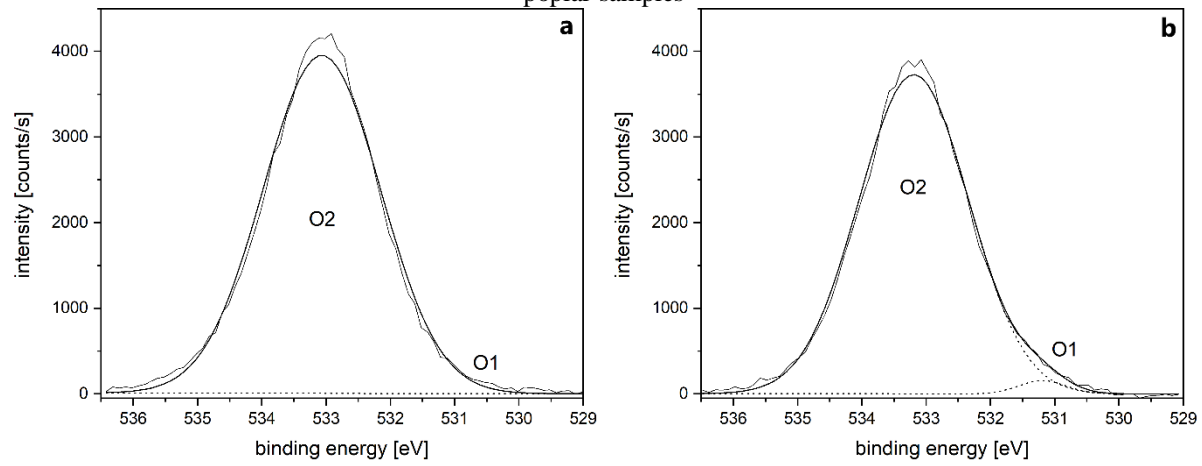


Fig. 3.11. High-resolution spectra of the O1s energy level of (a) fresh-cut, (b) archaeological poplar

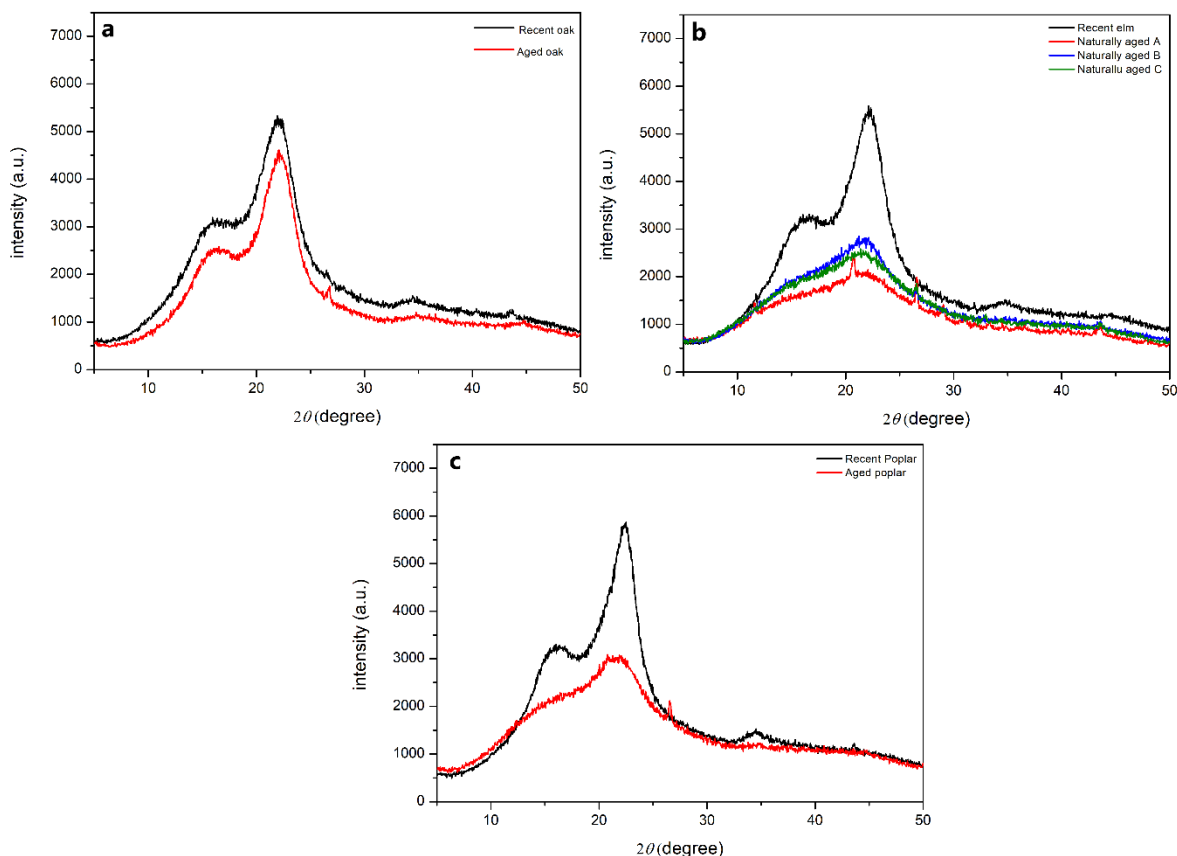


Fig. 3.16. X-ray diffractograms from fresh-cut and archaeological oak (a), elm (b), and poplar (c) wood samples

Spruce and fir woods

The wet chemical analysis on spruce and fir samples show that the contents of holocellulose and α -cellulose of archaeological spruce which located outside, due to the environmental factors such as UV ray, weathering and aging process, were significantly lower than the aged samples that was located inside of the building and also the fresh-cut spruce.

According to the FTIR analysis, the main age-induced changes in fir are the degradation of C-O and C=O groups in hemicellulose. For spruce, degradation of cellulose and hemicelluloses was observed with a greater effect seen in the sample aged indoor.

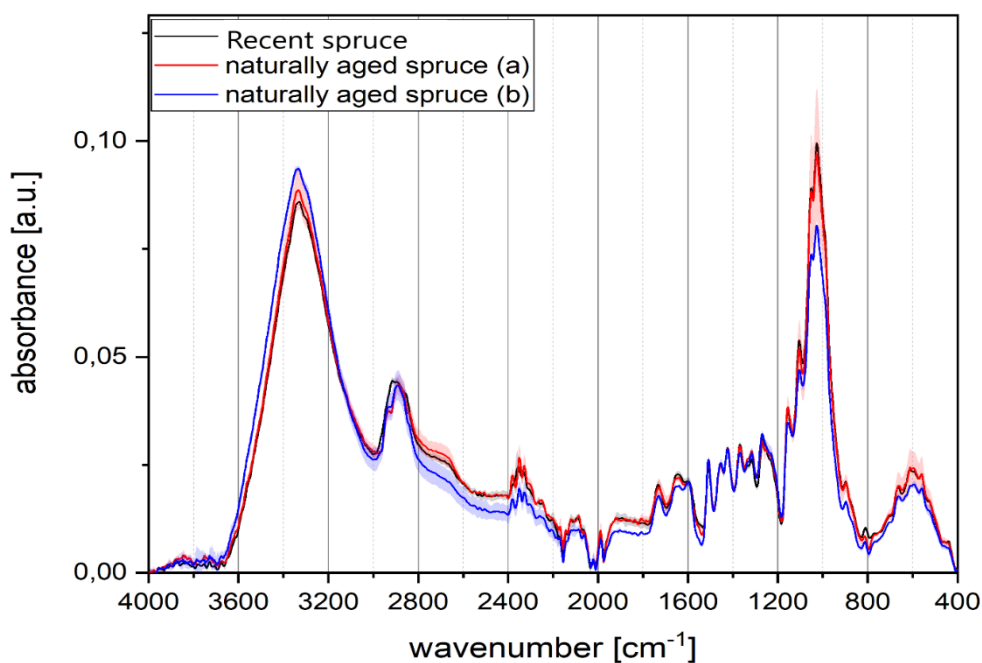


Fig. 3.4. FTIR spectra of fresh-cut and archaeological spruce wood samples

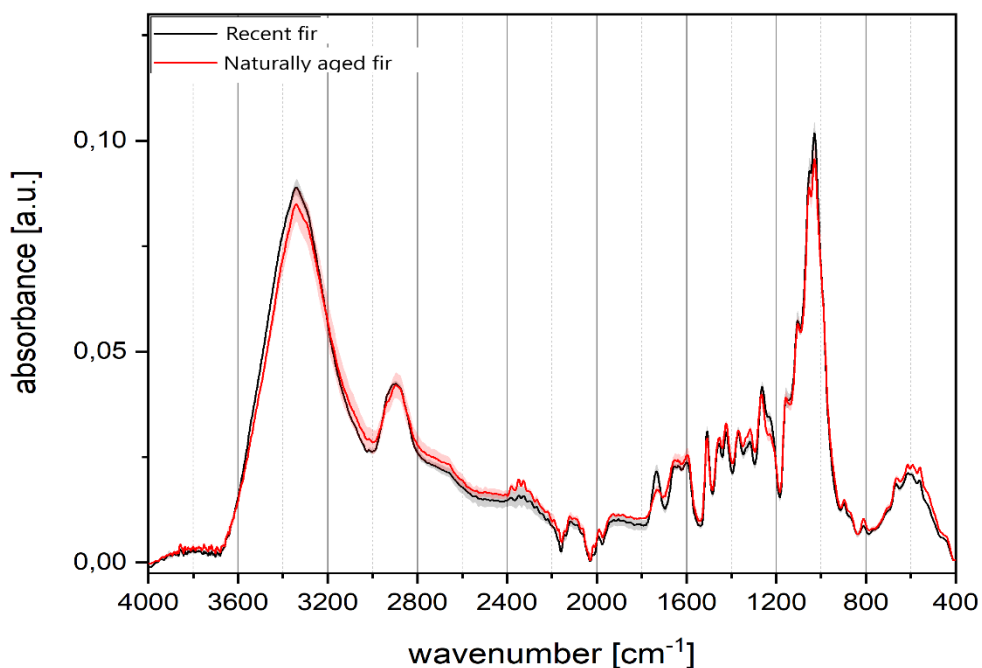


Fig. 3.5. FTIR spectra of fresh-cut and archaeological fir wood samples

XPS analysis indicated that depolymerization, oxidation and hydrolysis reactions occurred on the aged wood surfaces, exhibiting higher C_{ox}/C_{unox} and O/C ratios in aged wood. These ratios for the indoor-aged sample were higher than for the one aged outdoor showing the influence of weathering on the surface sample. The XPS results differed from the IR spectroscopy data due to different information depths of the two techniques. It was observed

that the wood surface is oxidised while no or little oxidation effects are seen deeper into the sample.

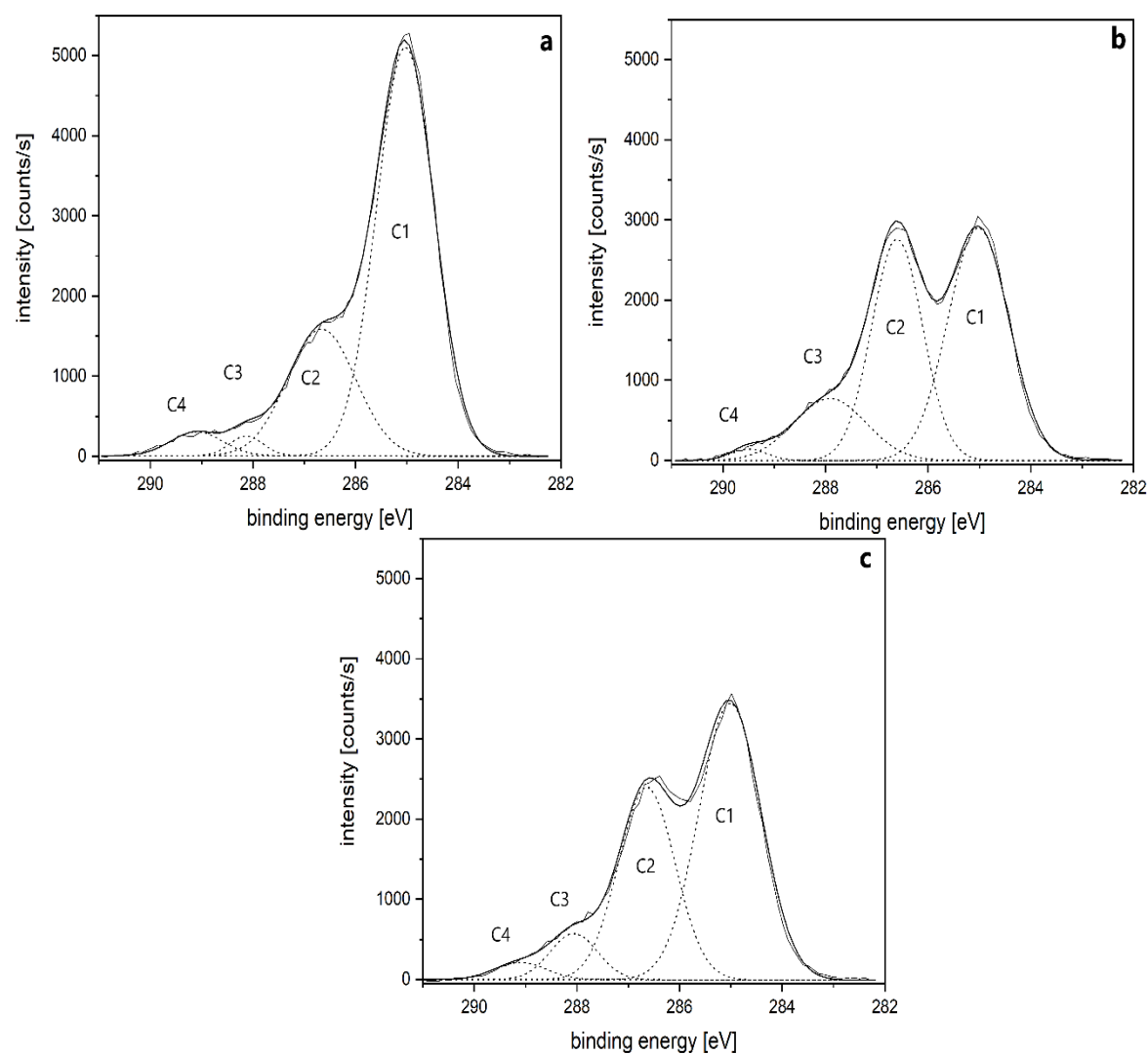


Fig. 3.12. High-resolution spectra of the C1s energy level of new spruce (a), archaeological spruce [A] (b), archaeological spruce [B] (c)

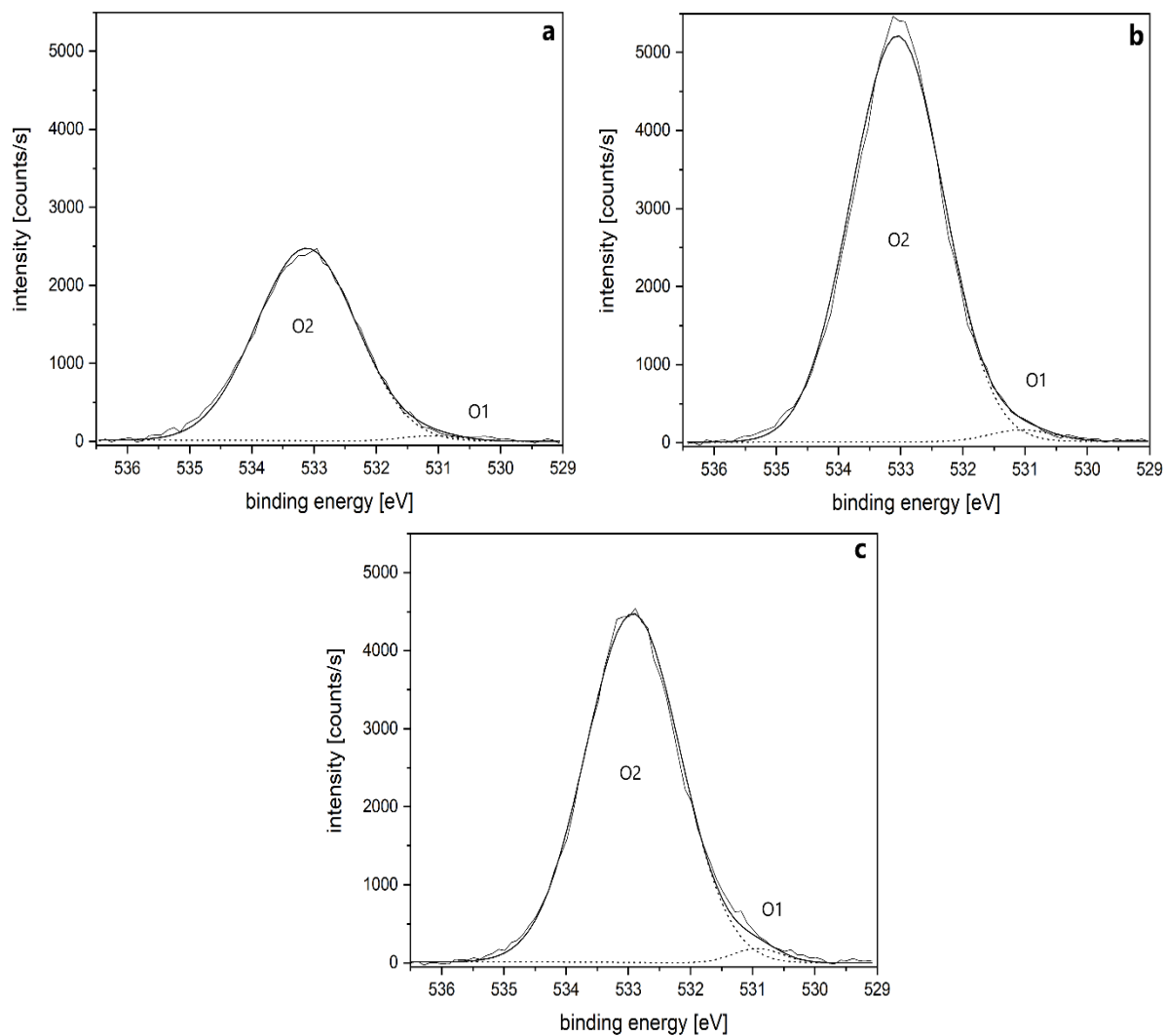


Fig. 3.13. High-resolution spectra of the O1s energy level of new spruce (a), archaeological spruce [A] (b), archaeological spruce [B] (c)

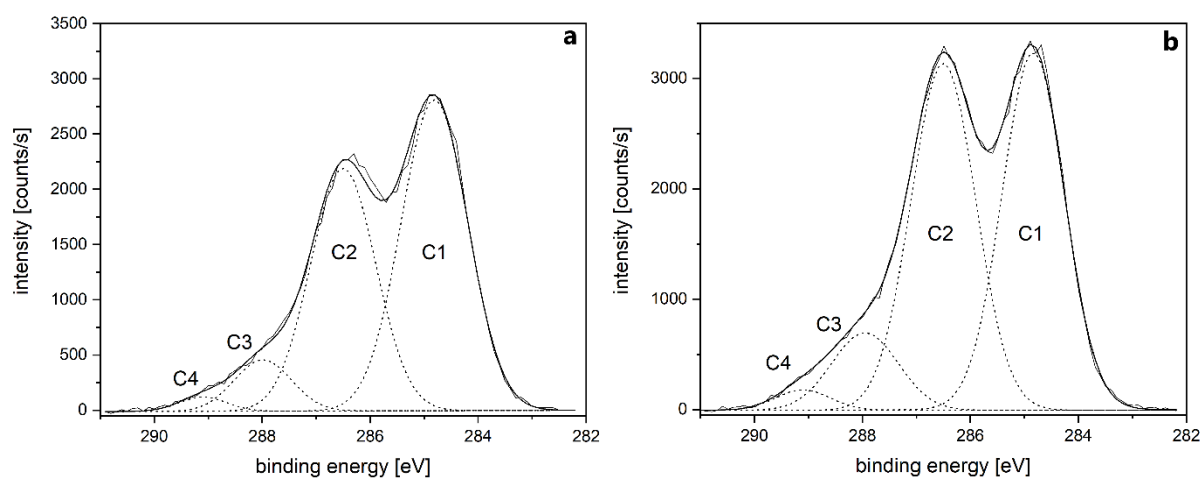


Fig. 3.14. High-resolution spectra of the C1s energy level of new fir (a) and archaeological fir (b)

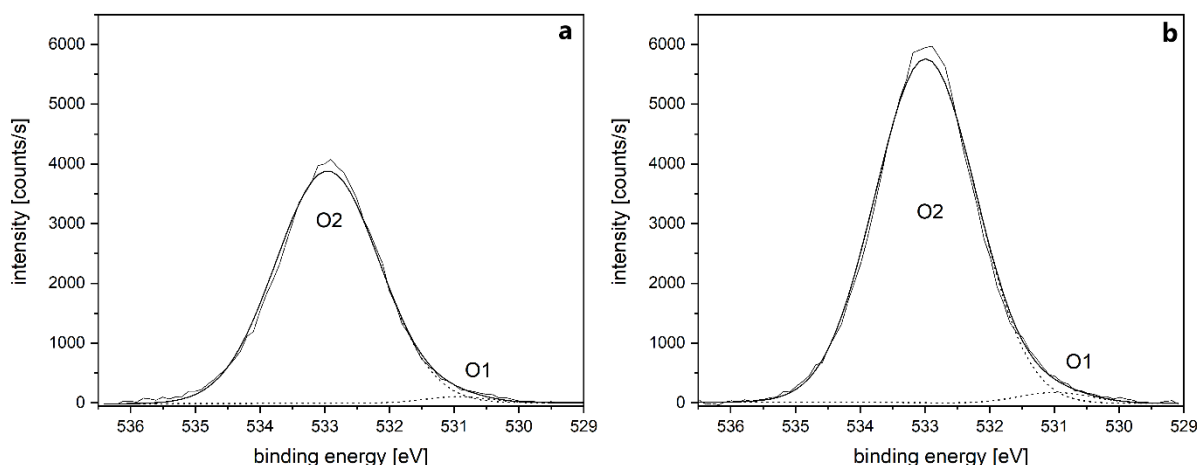


Fig. 3.15. High-resolution spectra of the O1s energy level of fresh-cut fir (a) and archaeological fir (b)

XRD measurements revealed that the aged fir and spruce (b) wood exhibited both lower crystallinity index and crystalline peak intensities. However, in aged spruce (a) the crystallinity index and crystalline peak intensity were higher due to the decomposition of the amorphous regions in cellulose and hemicelluloses and the crystallisation of amorphous cellulose caused by weathering.

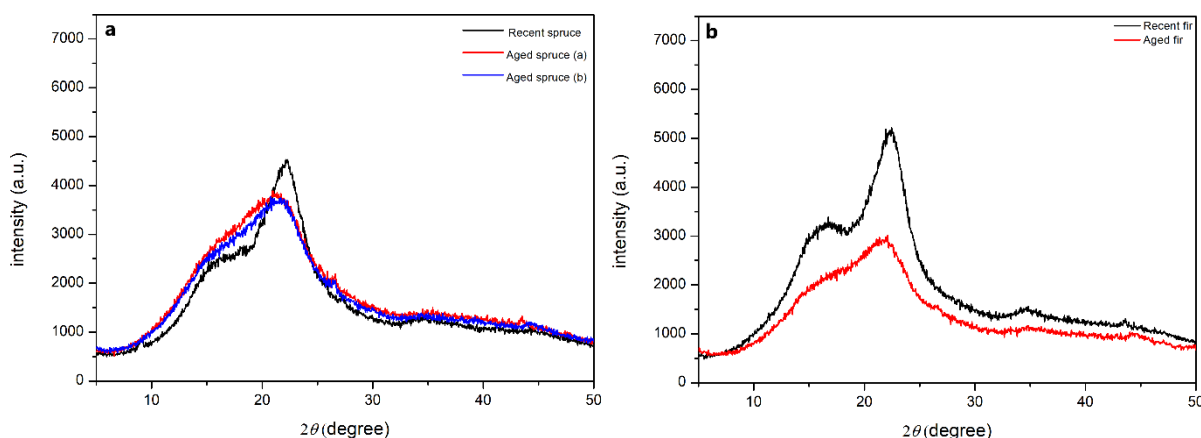


Fig. 3.17. X-ray diffractograms from fresh-cut and archaeological spruce (a) and fir (b)

According to the microscopy and SEM images of both archaeological and fresh-cut spruce samples, there is no significant changes between archaeological and fresh-cut samples. Also, the two samples of spruce and fir in this study had no signs of biological degradation.

Conclusion

Critical assessment for this research and

suggestions for future research

Based on the results obtained, during the research for the compilation of the doctoral dissertation, new perspectives were opened for the development of this field. Most of them were not included in this study due to the unavailability of the required devices and equipment as well as the lack of sufficient time during the research process.

To better understand the changes in archaeological woods, the following tests and analysis are recommended for other researchers in this field:

One of the factors that increase the amount of water absorption and Desorption is the amount of pores in the wood. In order to investigate more accurately the cause of water absorption and desorption in archaeological woods, analyzes related to pores are recommended. There are many analyzes in this field, but the most widely used are: the Brunauer–Emmet–Teller (BET) theory and The Barrett–Joyner–Halenda (BJH) method.

To obtain possible phase transitions in the cell wall polymers also, determine the maximum water holding capacity of the cell walls, using differential scanning calorimetry (DSC) or other suitable and accurate method are suggesting for the future research.

Also, for a more detailed analysis of chemical changes in archaeological woods, Confocal Raman microscopy is recommended. The Raman effect is based on light interacting with the chemical bonds of a sample. Due to vibrations in the chemical bonds the interaction with photons causes specific energy shifts in the back scattered light that appear in a Raman spectrum. The Raman spectrum is unique for each chemical composition and can provide qualitative and quantitative information of the material. Also, to determine the chemical changes in the cell wall scale (i.e. primary wall, S1, S2 and S3 layer, middle lamella), Raman microscopy is suggested.

For further investigation on changes in elemental compounds on archaeological woods, experiment with the Nuclear magnetic resonance spectroscopy (NMR) and High-performance liquid chromatography (HPLC) is particularly useful.

Also, for more detailed investigation of biological degradation and high magnification imaging with high-resolution, Transmission electron microscopy (TEM) is recommended. In addition, it is possible to identify bacteria and fungi in the species by culturing DNA of them. However, it should be noted that this method is awfully expensive and there is no definite guarantee for accurate identification of bacteria and fungi in archaeological wood because of the possibility of loss of DNA during the aging process and also changes in the conditions.

In the end, the author hopes that this work will be able to provide useful information in the field of archaeological wood so that it can be used for future research or by individuals and organizations responsible in this field for their research.

Selected References

1. Andrade, J.D.; Gregonis, D.E.; Smith, L.M., (1985), **Polymer surface dynamics. In: Surface and Interfacial Aspects of Biomedical Polymers**, Vol. 1. Surface Chemistry and Physics. Plenum Press, New York.
2. Arnold, M.; Sell, J.; Feist, W.C., (1991), *Wood weathering in fluorescent ultraviolet and xenon arc chambers*. **Forest Products Journal**, **41**(2): 40-44.
3. Ayadi, N.; Lejuene, F.; Charrier, F., (2003), *Color stability of heat-treated wood during artificial weathering*. **Holz als Roh- und Werkstoff**, **61**: 221–226.
4. Baar, J.; Paschová, Z.; Hofmann, T.; Kolář, T.; Koch, G.; Saake, B.; Rademacher, P., (2019), *Natural durability of subfossil oak: wood chemical composition changes through the ages*. **Holzforschung** **74**(1): 47–59, <https://doi.org/10.1515/hf-2018-0309>
5. Bader, T.K.; de Borst, K.; Fackler, K.; Ters, T.; Braovac, S., (2013), *A nano to macroscale study on structure-mechanics relationships of archaeological oak*, **Journal of Cultural Heritage**, **14**:377–388. <https://doi.org/10.1016/j.culher.2012.09.007>
6. Back, E.L. (1991), *Oxidative activation of wood surfaces for glue bonding*, **Forest Products Journal**, **41**(2): 30–36.
7. Back, E.; Sandström, E., (1982), *Critical aspects on accelerated methods for predicting weathering resistance of wood based panels*. **Holz als Roh-und Werkstoff** , **40**: 61–75. <https://doi.org/10.1007/BF02612224>
8. Barry, A.O.; Zoran, Z., (1990), *Surface analysis by ESCA of sulfite post-treated CTMP*, **Journal of Applied Polymer Science**, **39**: 31–42.
9. Beyer, M.; Kranitz, K.; Bremer, M.; Peters, J.; Fischer, S.; Bues, C.T.; Niemz, P., (2018), *Effect of natural aging on the chemical composition of Norway spruce, fir, and European oak wood*. **Pro Ligno**, **14**: 3-19.
10. Bjurhager, I.; Ljungdahl, J.; Wallström, L.; Gamstedt, E.K.; Berglund, L.A., (2010), *Towards improved understanding of PEG-impregnated waterlogged archaeological*

wood: a model study on recent oak, **Holzforschung**, **64**:243–250. <https://doi.org/10.1515/hf.2010.024>

11. Björdal, C.G.; Nilsson, T.; Daniel G.F., (1999), *Microbial decay of waterlogged archaeological wood found in Sweden – applicable to archaeology and conservation*, **International Biodeterioration and Biodegradation**, **43**: 63-71.
12. Björdal, C.; Daniel, G.; Nilsson, T., (2000), *Depth of burial, an important factor in controlling bacterial decay of waterlogged archaeological poles*, **International Biodeterioration and Biodegradation**, **45**(1-2): 15-26. DOI: 10.1016/S0964-8305(00)00035-4
13. Bjodal, C.G., (2000), *Waterlogged archaeological wood, biodegradation and its implications for conservation*, **PhD Thesis**, Swedish University of Agricultural Science, Uppsala, Sweden.
14. Blanchette, R.A.; Hoffmann, P., (1993), *Degradation processes in waterlogged wood*. In: Hoffmann, P. (ed) **Proceeding of the 5th ICOM Group on Wet Organic Archaeological Materials Conference**, Portland, Maine, 111-137.
15. Boutelje, J.B.; Bravery, A.F., (1968), *Observations on the bacterial attack of piles supporting a Stockholm building*. **J. Inst. Wood Sci.** **4**:47-57.

Appendix 1

The work of this thesis has been covered in the following publications and communications:

Publications ISI:

1. A. GHAVIDEL; M. BAK; T. HOFMANN; R. HOSSEINPOURPIA; V. VASILACHE; I. SANDU, *Comparison of chemical compositions in wood and bark of Persian Silk tree (Albizia julibrissin Durazz.)*. **Wood Material Science and Engineering**, 2021 <https://doi.org/10.1080/17480272.2021.1953141>
2. A. GHAVIDEL; M. BAK; T. HOFMANN; V. VASILACHE; I. SANDU, *Evaluation of some wood-water relations and chemometric characteristics of recent oak and*

archaeological oak wood (*Quercus Robur*) with archaeometric value, **Journal of Cultural Heritage**, 2021, 51, pp. 21-28.

3. **A. GHAVIDEL**, R. HOSSEINPOURPIA, H. MILITZ, V. VASILACHE, I. SANDU, *Characterization of archaeological european white elm (*Ulmus laevis* p.) and black poplar (*populus nigra* l.)*, **Forests** 2020, 11(12), Article Number: 1329.
4. **A. GHAVIDEL**, A. SCHEGLOV, V. KARIUS, C. MAI, A. TARMIAN, W. VIOEL, V. VASILACHE, I. SANDU, *In-depth studies on the modifying effects of natural ageing on the chemical structure of European spruce (*Picea abies*) and silver fir (*Abies alba*) woods*, **Journal of Wood Science** 2020 66, 2020, Article Number: 77.
5. **A. GHAVIDEL**, T. HOFMANN, M. BAK, I. SANDU, V. VASILACHE, *Comparative archaeometric characterization of recent and historical oak (*Quercus spp.*) wood*, **Wood Science and Technology**, **46**(1–3), 2020, pp.153–177. <https://doi.org/10.1007/s00226-020-01202-4>.
6. **A. GHAVIDEL**; J. GELBRICH; A. KUQO; V. VASILACHE; I. SANDU, *Investigation of archaeological European white elm (*Ulmus laevis*) for identifying and characterizing the kind of biological degradation*, **Heritage** (ISSN 2571-9408), **3**(4), 2020, pp. 1083-1093. <https://doi.org/10.3390/heritage3040060>.
7. **A. GHAVIDEL**; R. HOSSEINPOURPIA; J. GELBRICH; M. BAK; I. SANDU, *Identification of biological degradation in archaeological White Elm (*Ulmus laevis* P.) and Poplar (*Populus spp.*)*, **Molecules** 2021, (Submitted)

Publications non-ISI (BDI):

1. **A. GHAVIDEL**, I. SANDU, V. VASILACHE, *Decay resistance of beech wood against white rot fungus*, **Acta Chemica Iasi**, **28_2**, 2020, pp. 175-182. DOI: 10.2478/achi-2020-0012.
2. **A. GHAVIDELESFAHLAN**, I. SANDU, V. VASILACHE, *Evaluation of colour changing of saturated woods surface with nanosilver*, **Pro Ligno**, **15**(4), 2019, pp. 284-287.
3. **A. GHAVIDELESFAHLAN**, I. SANDU, V. VASILACHE, *Evaluation of some chemometrics characteristics with archaeometric value from the variation of water balance for wood*, **Pro Ligno**, **15**(4), 2019, pp. 288-294.

Communications at international workshops and conferences:

1. D.-E. COLBU, A. GHAVIDELESFAHLAN, I. SANDU, V. VASILACHE, I.C.A. SANDU, *Intervenții de preservare prin tratarea obiectelor de artă cu radiații ionizante*, **EUROINVENT - INTERNATIONAL WORKSHOP, Scientific, Technological and Innovative Research in Current European Context**, 12th edition, 21 May 2020, Iasi, **Topics: Scientific Inquiries through Elective Elaborations**, (Editors: I.G. Sandu, I. Sandu and A.S. Ciornei), Ed. PIM, 2020, pp. 94-111.
2. **GHAVIDELESFAHLAN**, I. SANDU, V. VASILACHE, *Evaluation of Wood Chemometrics Characteristics With Archaeometric Value from the Variation of Water Balance*, **12th edition of the International Conference “Wood Science and Engineering in the Third Millennium” – ICWSE 2019**, Ed. Universității Transilvania din Brasov, ISSN 1843-2689, 2019, pp. 57-63.
3. **GHAVIDELESFAHLAN**, I. SANDU, V. VASILACHE, *Evaluation of Colour Changing of Saturated Woods Surface with Nanosilver*, **12th edition of the International Conference “Wood Science and Engineering in the Third Millennium” – ICWSE 2019**, Ed. Universității Transilvania din Brasov, ISSN 1843-2689, 2019, pp. 52-66.
4. **GHAVIDELESFAHLAN**, V. VASILACHE, A.V. SANDU, **I. SANDU**, *The Archaeometric and Chemometric Characteristics Acquired Over Time of Wood Artifacts by Changing the Normal Range Variation of Hygroscopic Balance*, **The Fourth International Conference New Trends in Environmental and Materials Engineering (TEME)** 25-27 October 2017, GALAȚI, ROMANIA, Poster Session, 28.10.2017, P70, **Book Abstracts**, GUP Galati University Publishing Press, 2017, p. 91.

