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THE CHANGES IN CHEMICAL COMPOSITION AND PROPERTIES OF SUBFOSSIL OAK DEPOSITED IN HOLOCENE SEDIMENTS

Tomáš Kolář, Michal Rybníček
Mendel University in Brno, Faculty of Forestry and Wood Technology,
Department of Wood Science
Brno, Czech Republic

Marie Střelcová, Josef Hedbávný
Mendel University in Brno, Faculty of Agronomy Department of Chemistry and Biochemistry
Brno, Czech Republic

Jan Vít
Czech Geological Survey, Branch Brno
Brno, Czech Republic

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ABSTRACT

The study deals with the influence of chemical composition changes on subfossil wood properties in comparison to recent wood in the conditions of the Czech Republic, in dependence on the specific geological sediments the wood was deposited in. Chemical constituents (including individual elements) were established in order to determine what type of fossilization proceeds in the specific geological conditions. As regards properties, attention focuses on density, shrinkage, compression strength parallel to grain and hardness. We ascertained that the proportions of ash and calcium in subfossil wood increase as well as the proportion of lignin which increases at the expense of polysaccharides. The differences in chemical composition cause differences in behaviour of wood, e.g. shrinkage increases or mechanical properties deteriorate. The results indicate that the influence of the environment in which the wood was deposited on the changes in chemical composition and thus mechanical properties prevails over the effect of time.

KEYWORDS: Chemical components, fossilization, oak, physical and mechanical properties, subfossil wood.

INTRODUCTION

The main organic macromolecular components of sound wood, which make 90–99 % of its weight, are cellulose, hemicelluloses and lignin (Fengel and Wegener 1989). Types of these substances and their proportions have an essential impact on the behaviour and basic properties of wood (Lewin and Goldstein 1991). The ratio of the crystalline and the amorphous region of cellulose is an essential characteristic affecting chemical, physical and mechanical properties of wood (Fengel and Wegener 1989). Hemicelluloses are bound to the cellulose especially by hydrogen bonds (Lewin and Goldstein 1991). They are easily hydrolyzable, they usually have an amorphous structure and affect mainly sorption. Lignin gives the cell walls their characteristics with regard to e.g. strength, density or swelling properties (Fengel and Wegener 1989). Lignin increases mechanical strength of wood, mainly compression strength (Clarke 1937). Besides the main components, there are also extractives, which can be important for some properties and quality of wood processing (Fengel and Wegener 1989). There is also a small amount of mineral compounds, which are usually expressed as ash content in wood arisen from burning (Hägglund 1928). The main ash components are compounds of potassium, magnesium (Bodig and Jayne 1993) and especially calcium (700–770 $mg.kg^{-1}$ in recent wood) (Krutul et al. 2010). Furthermore, there is a considerably lower proportion of Mn, Na, P and Cl compounds (Tsoumis 1991) and of trace elements (e.g. Ba, Al, Fe, Zn, Cu, Ti, Pb, Ni, V, Co, Ag and Mo) – their content is lower than 50 $\mu g.g^{-1}$ (Fengel and Wegener 1989).

If a tree is submerged under water or soil, fossilization begins in the absence of oxygen, which will finally leads to petrifaction depending on the conditions of submersion into this anaerobic environment (Christiernin et al. 2009). Historic, archaeological or subfossil wood samples have different chemical compositions, primarily in dependence on the conditions they were deposited in (Passialis 1997); in other words, the conditions determine the mechanisms and rates of degradation of wood. Time plays only a secondary role in the destruction process (Krutul and Kocoń 1982). Generally, chemical analyses of old and fossilized woods show a decrease in polysaccharides and an increase in the non-hydrolyzable residue (Fengel and Wegener 1989). During fossilization, the types of inorganic substances that replace organic substances depend on the burial environment (Florian 1990). Fengel and Wegener (1989) and Fengel (1991) distinguish two types of fossilization of wood in dependence on environmental conditions: Silicification and carbonization (Fengel and Wegener 1989), Morávek (1997) mentions silicification and e.g. Carrión, 2003 (Plešák 2006) describes the processes of silicification and calcification.

A change in chemical composition of wood has a significant influence on its physical properties (Bednar and Fengel 1974), for example physical mechanical strength characteristics can be altered to variable degrees by loss of structural chemicals or tissue integrity (Florian 1990). In comparison with recent oak the density of subfossil oak wood is approximately the same or slightly smaller (Borgin et al. 1979, Sinković et al. 2009). However, Horský and Reinprecht (1986) state that there is a more marked increase in density mainly in surface layers, where a higher degree of fossilization is assumed and neither an influence of chemical changes can be ruled out, e.g. thickening of the cellulose crystalline structure. The most significant difference between subfossil and recent wood occurs in the dimensional changes. If this wood is allowed to dry without special treatment, it may go through extensive dimensional changes and distortions (Schniewind 1990). Horský and Reinprecht (1986), Wagenführ (2000) and Sinković et al. (2009) present approximately double values of percentage shrinking of subfossil oak in comparison with recent oak. Wood dimensional changes are primarily a result of water addition to the amorphous region of the cellulose microfibrils (Bodig and Jayne 1993).

In dependence on the degree of degradation, also the values of mechanical properties of subfossil oak wood deteriorate (Schniewind 1990). Compression strength parallel to the grain of subfossil oak reaches about 70–80 %, in some cases even only 50 % of the strength of recent oak (Bednar and Fengel 1974, Horský and Reinprecht 1986). The modulus of elasticity in compression of subfossil oak displays an even larger decrease than the strength values (Horský and Reinprecht 1986). As regards the other mechanical properties, such as bending or tensile strength, we can see very similar dependencies (Bednar and Fengel 1974, Horský and Reinprecht 1986, Govorčin and Sinković 1995).

MATERIAL AND METHODS

The research was conducted in the area of Moravia, which is located in the eastern part of the Czech Republic. For the purpose of the research a sample of the Pedunculate Oak (*Quercus robur* L.) in a recent stand, forest district Valtice, near Lednice (N48°48.238, E16°47.362′; 161 a.s.l.) and a sample of the Sessile Oak (*Quercus petraea* (Matt.) Liebl.) in a recent stand in the Training Forest Enterprise Masaryk Forest Křtiny in Útěchov (N49°17.220, E16°36.534′; 480 a.s.l.) were taken. Further, five samples were extracted from subfossil oak trunks in the catchment basin of the Morava River. Three trunks were sampled in the gravel pit Tovačov, district Přerov (N49°24.264, E17°17.469′; 200 a.s.l.) (Tovačov 1, 2, 3), one trunk in the river bed of the Bečva River near the municipality of Osek nad Bečvou, district Přerov (N49°29.837, E17°31.271′; 218 a.s.l.) (Osek nad Bečvou – river bed) and one in the gravel pit Osek nad Bečvou (N49°29.459, E17°31.531′; 218 a.s.l.) (Osek nad Bečvou – gravel pit). All samples were dated by radiocarbon dating (Tab. 1). Based on a microscopic analysis, all samples of subfossil oak were identified as the Pedunculate Oak (*Quercus robur* L.) (Kolář et al. 2012). For this reason, the ascertained results will be further compared with the recent oak of the same species mainly.

Tab. 1: Radiocarbon dating of subfossil trunks.

Sample	^{14}C age (yr BP)	Cal. age range 95.4 % conf. intervals (yr AD/BC)
Tovačov 1	3870 ± 60	2490–2190 BC
Tovačov 2	2150 ± 45	265–50 BC
Tovačov 3	1973 ± 76	168 BC–214 AD
Osek nad Bečvou – river bed	2600 ± 110	945–405 BC
Osek nad Bečvou – gravel pit	2017 ± 76	208 BC–137 AD

Geographical and geological description of the sites

Tovačov

The site has been revealed due to the exploitation of gravels in deposit Tovačov, in its western part which is located approximately 2.3 km to the south of the centre of Tovačov. From the geomorphologic perspective, the site is located in the depression Hornomoravský úval (Upper Moravian Depression). Moreover, the site is located at the very western edge of a large confluence area of the Morava and Bečva Rivers (alluvial plain), which is about 12 km broad here and can be flooded entirely (as it was e.g. in 1997).

While the Morava River deposits its sediments in the western edge, the sediments of the Bečva River form a flat fluvial cone between Přerov – Troubky and Chropyně, which forces the space of the Morava River to the west. In this area, the basal layer is formed by an insecure

Quaternary subgrade covered in at least 14 m thick fluviolacustrine sediments from the beginning of the Middle Pleistocene (Macoun and Růžička 1967). This tectonically fixed filling is covered in up to 7 m thick gravel layer, with some places of sand, which is again covered in up to 2 m thick layer of sands, changing into flood loam towards the overlying layer. The gravels are medium to coarse, formed predominantly by pebbles of quartz (about 60 %), and to a lesser extent by gneiss and granitoids (about 20 %), rocks of the Lower Carboniferous sediments (about 15 %), quartzites (about 3 %) and Cretaceous sandstones (about 2 %). These sediments contain erosion cuts of the current riverbeds or lower floodplain levels with a total depth of up to 5 m.

Osek nad Bečvou

This site is located 1.6 km to the south-west of the centre of Osek nad Bečvou and the trunks partially come from a pile created during a local extraction of gravel but also from a newly formed riverbed of the Bečva River. From the geomorphologic perspective, this site is a part of the depression Moravská brána (the Moravian Gate). The Bečva River floodplain is nearly 3 km broad here but the part actually flooded (1997) is smaller due to the alluvial fans at its edges reaching 1.2 km. Historical maps clearly show that the riverbed has changed substantially in this area.

Thanks to the fact that the riverbed has cut about 5 m into the surrounding floodplain, we can deliver a more detailed litological description of the site. The topmost, about 3 m thick layer is formed by light brown sandy silt, in places interrupted by layers of fine grained gravels to a thickness of 20 cm. This layer of "flood loam" can be completely missing in places where the "lower flood plain terrace" is developed or there are channels filled with loamy gravel up to 1 m thick. The age of the accumulation of flood loam in this area is unknown; it is assumed that the main accumulation of flood loams, which currently cover nearly the entire surface of the floodplain, is of subrecent age and is related to colonization efforts in submontane and montane regions. It reached the highest intensity at the end of the Middle Ages and continued uninterrupted until the modern stream regulation efforts (Opravil 1983).

The change of flood loams to subgrade gravel is relatively abrupt and the following alternation of sands and fine gravels is at a depth of about 70 cm replaced with sandy middle to coarse gravel, with semi-rounded or rounded pebbles predominantly of graywackes (Lower Carboniferous) sized 5–10 cm, exceptionally up to 20 cm. Some parts of this position display pebbles with a markedly red patina. A majority of the available trunks came from this layer.

Chemical analysis

The samples of the recent Pedunculate Oak and Sessile Oak and the five subfossil oak trunks of different ages were subjected to a chemical analysis. All the samples were divided into 3 zones along their radius – the inner part, the middle part and the outer part of the radius next to the cambium. The wood of each section was milled to sawdust and fraction of 0.5–1 mm was sorted out for the analysis. Dry matter was obtained by drying the sample in a hot-air drying kiln at 103°C until constant weight was achieved. The average of three independent measuring sessions was used as the result.

Detergent fibre was established by means of Abeson K surfactant, modification of Van Soest's method (Goering and Van Soest 1970). As a part of pentosans and hemicelluloses transferred to the solution during the analysis, the amount of hemicelluloses has not been established. By hydrolysing the detergent fibre by 72 % sulphuric acid the remnants of hemicelluloses and the cellulose were released. The matter remaining after the hydrolysis was used to ascertain the amount of lignin (Goering and Van Soest 1970). The amount of lignin was also ascertained by the

standard method TAPPI T-13m (Klason's method modified by Ritter) (Melcer et al. 1977) using randomly chosen samples to check the results. Results of both methods proved to be comparable.

The cellulose content was established by means of nitration according to Kürschner–Popik (Kačík and Solár 1999). The sawdust was preliminarily processed by mercerisation (using KOH at 0°C). The cellulose obtained in this way is nearly pure as also a large part of the hemicelluloses transfers to the solution with nitrolignin. The method is suitable for all hardwoods. The cellulose was extracted for 4 hours by ethanol (EtOH) and after that for 6 hours by a 2:1 mixture of benzene – EtOH. The ash content was ascertained by a careful pyrolysis (with temperature gradually increased to 600°C) and annealing until constant weight was achieved at 600°C (Melcer et al. 1977). The amount of detergent fibre, cellulose and lignin was converted to absolutely dry, non-extracted wood.

The amounts of silicon (Si), cadmium (Cd), lead (Pb), chrome (Cr) and nickel (Ni) were found out by electrothermal atomization – atomic absorption spectrometry (ETA – AAS) at pertinent wavelengths (Si – λ = 251.6 nm; Cd – λ_{max} = 228.8 nm; Pb – λ_{max} = 217.0 nm; Cr – λ_{max} = 357.9 nm; Ni – λ_{max} = 232.0 nm). The inert gas used for the electrothermal atomization was N2 (99.999 % pureness).

Calcium (Ca), magnesium (Mg), copper (Cu) and zinc (Zn) were established by the AAS in the absorption mode at pertinent wavelengths (Ca – λ = 422.7 nm; Mg – λ = 285.2 nm; Cu – λ_{max}= 324.8 nm, Zn – λ_{max} = 213.9 nm) in the flame C_2H_2 – air. To suppress emissions, Sr^{2+} (c = 1000 mg.l^{-1}) in a measured sample was used.

Sodium (Na) and potassium (K) were established by the AAS in the emission mode at pertinent wavelengths (Na – λ_{max} = 589.0, K – λ_{max} = 766.5 nm) in the flame C_2H_2 – air.

Physical and mechanical wood properties

Wood density is defined as weight per unit volume with specific moisture. For the actual measuring, we used samples of 20 × 20 mm in transversal dimensions and 25 ± 5 mm in length. Their weight was taken with an accuracy of 0.01 g and dimensions were measured with an accuracy of 0.1 mm. The density of each sample was calculated using the following formula:

$$\rho_0 = m_0/V_0 \qquad (kg.m^{-3}) \tag{1}$$

where: m_0 - wood mass at 0 % moisture (kg),
V_0 - wood volume at 0 % moisture (m^3).

Wood shrinking is a process when wood dimensions are reduced as a consequence of a loss of bound water. For the actual testing, we used testing samples of 20 × 20 mm in transversal dimensions and 30 mm in length. The samples previously measured were dried at a temperature of 103 ± 2°C until the moisture content was 0 % and then weighed again. The content of moisture in a sample is 0 % when there is no weight difference greater than 0.02 g between two processes of weighing within the interval of 2 hours. The obtained results were used to calculate the shrinkage of subfossil wood using the following formula:

$$\beta_{imax} = ((i_{iw1} - i_{iw2})/i_{iw1})*100 \qquad (\%) \tag{2}$$

where: i_{iw1} - dimensions of a sample being dried in the radial and tangential directions (mm) and the volume of the sample (mm^3),
i_{iw2} - dimensions of a sample with 0 % moisture content in the radial and tangential directions (mm) and the volume of the sample (mm^3).

Mechanical properties were examined for normalized moisture of 12 %. To examine compression strength parallel to the grain we used conditioned samples of 20 × 20 × 30 mm. The samples were loaded using a universal testing device ZWICK Z050 evenly at a constant speed. The compression strength (σp) and modulus of elasticity (E) parallel to the grain were expressed in MPa following these formulas:

$$\sigma_p = F_{max}/(a*b) \qquad (MPa) \tag{3}$$

where: F_{max} - maximum load (N),
a, b - transversal dimensions of the sample (mm).

Results were rounded off to the nearest 0.5 MPa.

$$E = \sigma/\varepsilon \qquad (MPa) \tag{4}$$

where: σ - stress per unit area ($N.mm^{-2}$),
ε - unit deformation ($mm.mm^{-1}$).

The static hardness of wood was examined using Janka method. We used conditioned samples with dimensions of 50 × 50 × 50 mm and ZWICK Z050 universal testing device. A steel ball (an indenter) with a radius of 5.64 mm was forced into the depth of 5.64 mm, which created an indented area of 1 cm^2. The force necessary for indenting the ball directly provides the hardness per 1 cm^2, which was converted to MPa. As we assumed the material will be more fragile, we only forced the ball into the half depth – 2.82 mm. Then the static hardness is to be calculated using this formula:

$$HJ = 4\,F / (3 * \pi * r^2) \qquad (MPa) \tag{5}$$

where: F - the force necessary for ball indentation,
r- the radius of the indenter.

The static hardness of the recent oak and subfossil trunk from the river bed in Osek nad Bečvou was not established due to an insufficient amount of available material for the production of the hardness testing samples.

RESULTS

Chemical analysis

The contents of some of the basic components which have been established differ when subfossil and recent wood is compared. The content of fibre in the subfossil wood is higher than in recent wood in all the zones along the trunk radius; the highest content of fibre has been found in the middle zone in both subfossil and recent oaks. The total proportion of fibre is 6–16 % higher in the subfossil wood than in recent oak. The proportion of the cellulose does not change considerably in spite of the different age of the trunks. The proportion of lignin is 23–41 % higher than in recent oak. The comparison of the proportions of fibre, cellulose and lignin along the trunk radius or the comparison of samples from the same sediments does not display any specific dependency.

The greatest difference in the chemical composition between subfossil and recent oak has been found in the amount of ash, which grows from the trunk centre to its most exposed parts. The amount of ash of subfossil oak is severalfold higher than of recent oak. The ratio of ash content in subfossil oak to recent oak reaches up to 5:1 in the outer zone and up to 16:1 in the middle zone. The proportion of silicon in the heartwood of recent oak grows in the direction from the pith to the trunk perimeter but then drops again in the sapwood. The highest proportion of silicon in subfossil oak is usually in the outer zones of the trunk, or rather of the heartwood as sapwood is seldom maintained (Tab. 2).

Tab. 2: Chemical analysis results of recent and subfossil oaks of different age (Vavrčík et al. 2008).

Components	**Zone of wood**	**Tovačov 1**	**Osek nad Bečvou – river bed**	**Tovačov 2**	**Osek nad Bečvou – gravel pit**	**Tovačov 3**	***Quercus robur* L.**	***Quercus petraea* (Matt.) Liebl.**
		2490–2190 BC	**945–405 BC**	**265–50 BC**	**208 BC – 137 AD**	**168 BC – 214 AD**	**recent**	**recent**
Fibre (%)	inner	76.67	85.68	79.35	84.94	73.05	72.65	72.96
	middle	75.04	79.08	77.39	78.74	70.05	67.44	68.10
	outer	75.45	77.62	67.61	78.55	71.94	61.69	70.78
	total	75.72	80.79	74.78	80.74	71.68	67.26	70.61
Lignin (%)	inner	33.72	25.62	21.45	24.39	22.73	18.16	18.06
	middle	25.27	20.48	23.67	25.38	23.37	14.78	18.85
	outer	27.58	19.96	24.30	27.95	25.03	18.15	19.54
	total	28.86	22.02	23.14	25.91	23.71	17.03	18.82
Cellulose (%)	inner	36.91	45.57	45.62	46.12	39.58	45.00	44.65
	middle	40.66	48.84	43.44	43.21	36.86	42.48	47.45
	outer	40.28	44.40	39.39	41.62	39.67	42.54	44.30
	total	39.28	46.27	42.82	43.65	38.70	43.34	45.47
Ash (%)	inner	2.61	1.37	1.14	1.90	1.81	0.19	0.35
	middle	1.61	1.53	1.27	1.33	2.10	0.13	0.36
	outer	1.57	2.15	2.62	2.47	2.45	0.55	0.59
	total	1.93	1.68	1.68	1.90	2.12	0.29	0.43
Silicon ($mg.kg^{-1}$)	inner	802.3	200.6	129.7	575.2	123.2	119.5	168.1
	middle	91.3	114.3	285.3	307.5	302.9	333.7	533.3
	outer	380.6	633.5	499.1	950.8	1005.5	24.5	187.7
	total	425	316	305	611	477	159	296.4

Subfossil oak trunks go through a process of fossilization (Fengel and Wegener 1989). Based on literature, we assumed that the process going on in our samples will be a process of silicification. Therefore, a chemical analysis of silicon was conducted in all the samples. However, the amount of silicon we found out was rather small. Based on this result we were able to rule out the process of silicification. As a consequence of this finding, we decided to conduct an analysis of ten inorganic elements using a selected sample, the greatest attention being devoted to the amount of calcium. Tab. 3 shows that this element really has the highest proportion. Based on this, we can assume that the samples have gone through a process of calcification.

Tab. 3: Chemical analysis results of ten elements in a selected subfossil sample.

Chemical element	Na	K	Mg	Ca	Cu	Zn	Cd	Pb	Cr	Ni
Unit	mg.kg^{-1}									
Tovačov 2	93.6	80.2	326.3	3594	1.39	10.48	0.067	2.88	1.063	3.038

Physical and mechanical properties

The results in the tables and the following figures are ordered from the oldest subfossil wood to the recent oak. The density of subfossil oak slightly decreases in comparison with recent oak (Fig. 1). The density of most samples increases with the increasing proportion of latewood, an exception is compression samples of Tovačov 3 (Tab. 5). The radial, tangential and volumetric shrinkage of subfossil wood reaches double values of recent wood and the value increases with the increasing age (Fig. 2, Tab. 4).

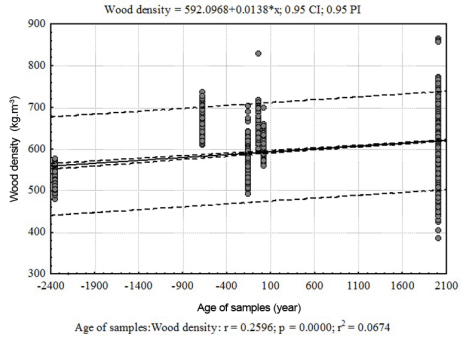

Fig. 1: The correlation of density and age of samples (results of the recent wood from Vavrčík et al. 2008). (CI = Confidence interval, PI = Prediction interval, r = Pearson's correlation, p = p-value of significance test of regression model, r^2 = coefficient of determination).

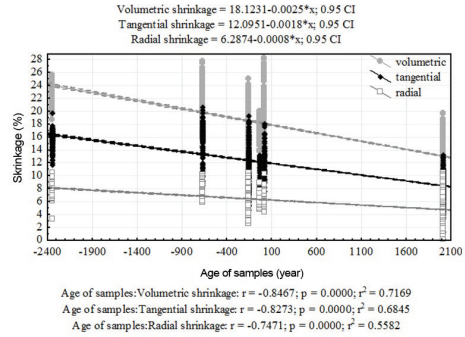

Fig. 2: The correlation of shrinkage and age of samples (results of the recent wood from Vavrčík et al. 2008). (CI = Confidence interval, r = Pearson's correlation, p = p-value of significance test of regression model, r^2 = coefficient of determination).

The values of mechanical properties of subfossil oak are lower than those of recent oak. Compression strength parallel to the grain reaches 55–75 % of the recent oak strength (Fig. 3, Tab. 5). The values of the modulus of elasticity are even lower, decreasing down to 36 % of the values of recent oak (Tab. 5). The compression strength parallel to the grain increases with an increasing wood density both for subfossil and recent oak; however, recent oak displays a higher correlation between the variables (Fig. 4).

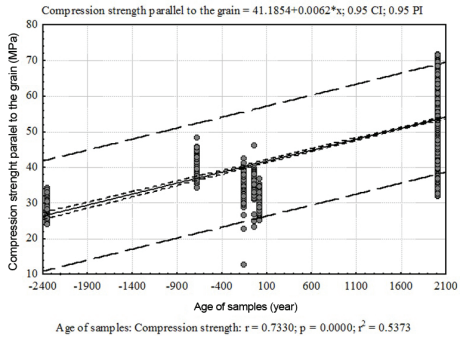

Fig. 3: The correlation of compression strength parallel to the grain and age of samples (results of the recent wood from Vavrčík et al. 2008). (CI = Confidence interval, PI = Prediction interval, r = Pearson's correlation, p = p-value of significance test of regression model, r^2 = coefficient of determination).

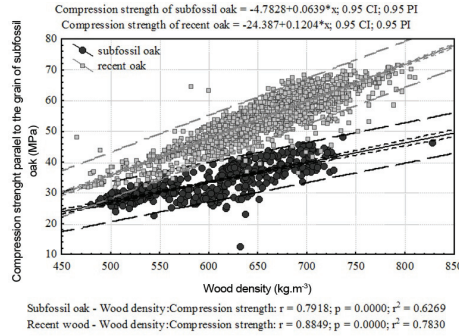

Fig. 4: The correlation of compression strength parallel to the grain and density of subfossil and recent oak wood (results of the recent wood from Vavrčík et al. 2008). (CI = Confidence interval, PI = Prediction interval, r = Pearson's correlation, p = p-value of significance test of regression model, r^2 = coefficient of determination).

Tab. 4: The results of the analysis of shrinkage of subfossil and recent oak wood. The table shows samples in the order from the oldest one to the youngest one (M = mean, Mdn = median, Min = minimum, Max = maximum, SD = standard deviation, CV = coefficient of variation, N = number).

Sample			Tovačov 1	Osek nad Bečvou – river bed	Tovačov 2	Osek nad Bečvou – gravel pit	Tovačov 3	*Quercus robur* L. (Vavrčík et al. 2008)
Age			2490–2190 BC	945–405 BC	265–50 BC	208 BC–137 AD	168 BC–214 AD	recent
Tangential	%	M	15.82	15.52	12.23	11.03	11.92	8.10
		Mdn	16.15	16.11	12.51	11.69	11.93	8.48
		Min	11.64	8.53	5.92	7.79	4.05	0.10
		Max	19.75	20.64	17.18	13.23	19.55	13.29
		SD	1.30	2.71	2.73	1.61	2.71	1.03
		CV	8.22	17.47	22.28	14.64	22.70	12.24
		N	198	117	75	51	119	2966
Radial	%	M	7.40	8.24	7.03	6.56	6.54	4.71
		Mdn	7.30	8.38	6.92	6.53	6.55	4.69
		Min	3.32	6.00	4.15	4.83	2.98	0.05
		Max	10.53	10.23	10.48	8.97	10.26	10.41
		SD	0.80	0.91	1.34	0.79	1.02	0.66
		CV	10.83	11.09	19.02	12.07	15.63	14.11
		N	198	117	75	51	119	2966
Volumetric	%	M	22.70	22.82	17.85	17.52	20.56	12.99
		Mdn	22.80	23.83	18.42	18.28	20.58	13.04
		Min	18.63	14.50	7.43	13.76	10.68	4.94
		Max	25.63	27.82	25.07	20.10	31.77	19.68
		SD	1.22	3.00	4.05	1.87	3.59	1.31
		CV	5.38	13.14	22.68	10.66	17.45	10.07
		N	198	117	160	51	119	2966

Tab. 5: The results of the analysis of compression strength parallel to the grain of subfossil and recent oak wood. The table shows samples in the order from the oldest one to the youngest one (M = mean, Mdn = median, Min = minimum, Max = maximum, SD = standard deviation, CV = coefficient of variation, N = number).

Sample			Tovačov 1	Osek nad Bečvou – river bed	Tovačov 2	Osek nad Bečvou – gravel pit	Tovačov 3	*Quercus robur* L. (Vavrčík et al. 2008)
Age			2490–2190 BC	945–405 BC	265–50 BC	208 BC–137 AD	168 BC–214 AD	recent
Density at 0 % moisture	$kg.m^{-3}$	M	526.4	668.5	581.8	647.9	606.6	618.2
		Mdn	524.4	670.0	579.8	634.9	604.9	620.2
		Min	479.5	609.8	491.5	596.4	559.8	384.3
		Max	575.8	737.5	703.6	828.4	699.9	863.9
		SD	19.0	32.7	48.6	44.2	26.4	61.1
		CV	3.6	4.9	8.3	6.8	4.4	9.9
		N	177	117	50	44	69	2966
F_{max}	MPa	M	29.31	40.07	33.07	35.32	29.43	53.95
		Mdn	29.23	39.87	32.43	35.54	29.17	54.47
		Min	24.17	34.14	12.68	23.11	25.18	31.88
		Max	34.39	48.28	42.47	46.17	36.79	71.86
		SD	1.77	3.11	4.75	3.96	2.48	8.20
		CV	6.05	7.76	14.36	11.20	8.41	15.19
		N	177	117	50	44	69	1601
Modulus of elasticity	MPa	M	4830	9510	4490	10342	7124	12351
		Mdn	4009	9211	4360	8999	5879	11438
		Min	1224	3707	1306	3717	1650	1988
		Max	10821	15819	10120	25188	21188	33599
		SD	2359	3457	1928	5169	3535	5201
		CV	49	36	43	50	50	42
		N	177	117	50	44	69	1601
Average tree-ring width	mm	M	1.45	2.61	3.29	1.79	1.17	2.11
		Mdn	1.39	2.24	2.44	1.90	1.07	1.86
		Min	1.08	1.63	1.98	1.15	0.92	0.69
		Max	2.23	5.06	5.95	2.19	2.70	5.94
		SD	0.21	0.84	1.33	0.31	0.32	0.98
		CV	14.45	32.05	40.51	17.13	27.05	46.56
		N	177	117	50	44	69	601
Latewood proportion	%	M	51.25	64.45	62.93	64.24	40.05	64.65
		Mdn	50.81	64.17	59.69	63.52	38.56	64.97
		Min	41.23	54.30	45.00	58.64	33.89	33.99
		Max	66.32	74.98	80.89	73.11	61.37	89.58
		SD	5.07	4.73	8.15	3.46	5.33	9.29
		CV	9.90	7.34	12.94	5.39	13.31	14.37
		N	177	117	50	44	69	601

Considering the fact that the process of fossilization includes deposition of hard minerals to the structure of wood, an investigation into wood hardness in individual directions is interesting. Also hardness depends on wood density – the highest correlation is indicated in radial direction (Fig. 6). The lowest hardness values were measured for the oldest sample (Tovačov 1), then the values increase with the decreasing age of samples (Fig. 5, Tab. 6).

Tab. 6: The results of the analysis of hardness of subfossil and recent oak wood. The table shows samples in the order from the oldest one to the youngest one (M = mean, Mdn = median, Min = minimum, Max = maximum, SD = standard deviation, CV = coefficient of variation, N = number).

Sample			Tovačov 1	Tovačov 2	Osek nad Bečvou – gravel pit	Tovačov 3
Age			2490–2190 BC	265–50 BC	208 BC–137 AD	168 BC–214 AD
Density at 0 % moisture	$kg.m^{-3}$	M	557.6	619.9	625.2	734.0
		Mdn	556.2	620.4	613.4	747.1
		Min	531.3	544.7	566.1	667.1
		Max	585.9	671.8	766.0	854.9
		SD	12.3	36.0	40.1	138.7
		CV	2.2	5.8	6.4	18.9
		N	43	39	45	35
Longitudinal	MPa	M	45.19	48.62	51.05	61.17
		Mdn	45.27	48.85	51.05	62.14
		Min	38.09	33.08	39.58	44.17
		Max	53.76	58.85	64.61	72.33
		SD	3.62	5.32	5.38	8.35
		CV	8.02	10.94	10.54	13.65
		N	43	39	45	35
Tangential	MPa	M	18.86	23.35	25.05	34.29
		Mdn	18.41	23.10	25.69	34.38
		Min	15.48	14.86	14.31	23.81
		Max	22.26	28.85	34.56	46.64
		SD	1.77	3.66	4.92	6.26
		CV	9.40	15.70	19.66	18.27
		N	43	39	45	35
Radial	MPa	M	24.53	30.72	31.62	42.54
		Mdn	24.18	31.77	30.60	43.46
		Min	20.47	18.49	22.25	28.29
		Max	30.04	41.62	45.93	64.66
		SD	2.09	6.47	5.25	11.28
		CV	8.53	21.07	16.59	26.51
		N	43	39	45	35
Average tree-ring width	mm	M	1.57	3.14	1.54	1.96
		Mdn	1.56	3.13	1.47	1.83
		Min	1.41	2.16	1.17	0.99
		Max	1.83	4.29	2.17	3.42
		SD	0.11	0.73	0.32	0.58
		CV	6.99	23.14	20.88	29.51
		N	43	39	45	35
Latewood proportion	%	M	52.66	65.86	56.20	57.44
		Mdn	52.55	67.01	54.43	56.51
		Min	47.33	53.99	47.48	47.93
		Max	60.16	74.42	71.33	65.58
		SD	2.78	5.73	6.10	4.59
		CV	5.29	8.70	10.86	7.99
		N	43	39	45	35

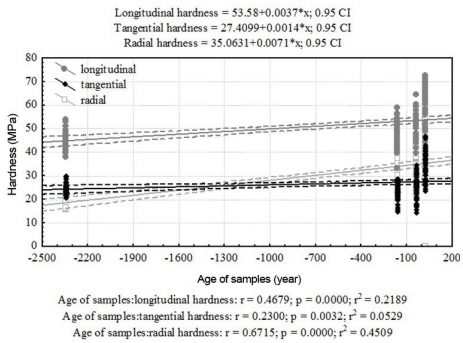

Fig. 5: The correlation of hardness and age of samples of subfossil oak wood (CI = Confidence interval, r = Pearson's correlation, p = p-value of significance test of regression model, r^2 = coefficient of determination).

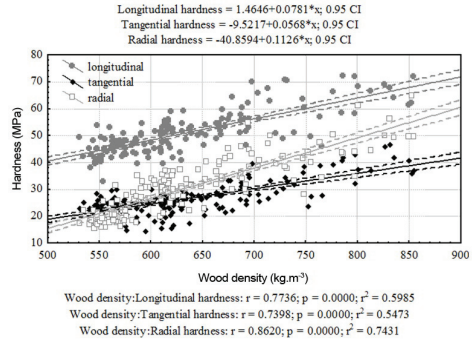

Fig. 6: The correlation of hardness and density of subfossil oak wood (CI = Confidence interval, r = Pearson's correlation, p = p-value of significance test of regression model, r^2 = coefficient of determination).

DISCUSSION

During the past years dozens of subfossil oak trunks were found in the territory of the Czech Republic. Many of them have been dated by dendrochronological or radiocarbon methods. Five of the dated trunks were used for a chemical analysis and an establishment of selected physical and mechanical properties of wood. The same tests were applied to two recent oaks – the Pedunculate Oak (*Quercus robur* L.) and the Sessile Oak (*Quercus petraea* (Matt.) Liebl.). All the analysed subfossil oak trunks were identified as the Pedunculate Oak (*Quercus robur* L.), therefore, for the purpose of comparison, the attention has mainly been devoted to the recent oak of the same species.

The subfossil oak trunks were found to come from three different periods. One sample from Tovačov dates back to the 3rd millennium BC, another from Osek nad Bečvou river bed is from 945–405 BC. The remaining three samples are from the turn of the era. We assumed that the age span of nearly five thousand years can sufficiently express and capture the changes in wood properties and chemical composition in time.

Besides our research, subfossil and recent wood has been compared by a number of studies, however, not all authors reached the same conclusions. Subfossil oak from the geological conditions as described in our study manifests a considerable relative increase in the proportion of fibre and lignin (up to 41 % increase). Literature dealing with this comparison usually states an increase of 31–33 % (Krutul et al. 2010) or even 35 % (Horský and Reinprecht 1986) in lignin. The highest increase observed in subfossil oak wood when compared with recent wood regarded ash, whose amount was 16 times higher in subfossil wood. According to Prądzyński and Cichocka (2002), it can be even 18 times higher. Although the amount of silicon has increased as well, its proportion in the total amount of ash is nearly negligible. The proportion of cellulose remained approximately the same. Based on an analysis of three subfossil trunks of the same age and one recent tree, Krutul et al. (2010) concluded that the amount of cellulose is 30 % lower in subfossil wood. On the contrary, Kúdela and Reinprecht (1990) ascertained a 5 % increase in cellulose in subfossil wood and Horský and Reinprecht (1986) a 1–7 % increase. Subfossil wood has a higher

proportion of fibre in comparison with recent wood. A more substantial increase was found in the samples from Osek nad Bečvou. Considering growing or constant proportions of wood components we can conclude that the proportion of hemicelluloses, mainly pentosans, will be considerably lower in subfossil wood than in recent wood. The same conclusion was reached, among others, by Bednar and Fengel (1974), Hedges (1990), Govorčin and Sinković (1995) or Wagenführ (2000). All chemical constituents were investigated in three different zones along the trunk diameter. The amounts of ash and silicon decrease in the direction from the more exposed parts of the trunk to its centre. Concerning the basic chemical components, we cannot express any clear trend which would manifest itself along the trunk diameter (Tab. 2).

One of the aims of the study was to confirm the hypothesis based on some literary sources that the process appearing in subfossil wood is the process of silicification. However, as has been stated, no considerable increase in the amount of silicon has been found. The subsequent chemical analysis of sample Tovačov 2 indicated that the main petrifaction process going on in our subfossil wood was calcification. The amount of calcium in subfossil wood is five times higher (Tab. 3) than in recent oak (Krutul et al. 2010). The reason is a substantially higher content of Ca than Si in ground water which participates in the fossilization of trunks. According to the data from the database of hydrogeological objects of the Czech Geological Survey, the proportion of CaO in the ground water of the surroundings of the explored site is 60-130 $mg.l^{-1}$ with a 68 % probability, whereas the proportion of SiO_2 is 6-17 $mg.l^{-1}$. These values are common also at the regional level. This is caused by a markedly higher mobility of calcium carbonate (the main carrier of calcium) in the current climatic conditions and its ability to bind into the structure of a buried trunk. Finding the specific source of $CaCO_3$ would be highly speculative; however, besides solution of some calcareous sandstones which are found in the sedimentary filling, an important source could be Baden calcareous clays which form the immediate subgrade of gravels in some places and the ground water is thus in contact with them.

The presented results confirm that the time of deposition is not the main determinant affecting the chemical composition. What seems to be the key factor is the conditions of deposition (Florian 1990, Hedges 1990). It becomes obvious that it is not possible to express changes in the chemical composition of wood in time generally. And as wood properties are directly dependent on its chemical composition, the same applies to them.

The density of subfossil oak wood is not substantially different from the density of recent wood (Tab. 5, Fig. 1). An important role here is played by e.g. the degree of degradation or the amount of minerals settled in the wood structure. However, the compression sample Tovačov 3 shows an opposite – in comparison with samples from the same site, they have the lowest ring width, the lowest latewood proportion, very low strength but the highest density. This sample contains a high proportion of ash, a relatively small proportion of lignin and the lowest proportion of cellulose of all investigated samples. It means this sample contains a very low amount of the components responsible for wood strength (Tab. 2).

Mechanical properties of subfossil wood have lower values than those of recent wood. Compression strength parallel to the grain ranges between 55 % and 75 % of the strength of recent oak (Fig. 3, Tab. 5). Bednar and Fengel (1974) presented 70–80 % and Horský and Reinprecht (1986) even 50 % only. The strength of subfossil oak has lower correlation with density than the strength of recent oak (Fig. 4). Comparing the results of hardness presented by Ugolev (1975) for recent oak at a moisture of 12 % (67.5 MPa longitudinal direction, 56.0 MPa radial direction and 49.0 MPa tangential direction), this decrease is even more substantial. The values of subfossil oak hardness we found out to achieve 67–90 % in the longitudinal direction, 44–76 % in the radial direction and 38–70 % in the tangential direction of the values of recent oak (Tab. 6).

Hardness decreases with age (Fig. 5) and also with density in all directions (Fig. 6). We can see an interesting relation between longitudinal and transversal directions. While in recent wood the values of transversal directions reach 73–83 % of the values of the longitudinal direction, in the youngest subfossil oak sample the relation was only 56–70 % and in the oldest subfossil sample it was 42–54 %. Moreover, the difference in hardness between the radial and the tangential directions extends as well. The value of hardness in recent oak in the tangential direction reaches 87 % of the value of hardness in the radial direction, whereas in subfossil oak this value is 76–80 %. Generally, the values of mechanical properties of subfossil oak wood reach 38–90 % of the values of recent oak. Although we expected some decrease, this range is substantial and besides the degree of degradation it depends on the way and direction of wood loading. The lowest decrease in the values when compared with recent oak was found for longitudinal hardness, more significant effects were observed in compression strength and radial hardness; the highest manifestation of the change was found in tangential hardness (Tab. 6). These results can be explained at submicroscopic and chemical level. The structure of the crystalline cellulose, which has an essential effect on mechanical loading, has covalent bonds in the longitudinal direction as opposed to weaker hydrogen bonds in the transversal direction. Also hemicelluloses are bound to the cellulose by hydrogen bonds (Lewin and Goldstein 1991). A lower content of hemicelluloses in subfossil wood can be caused by their hydrolysis (Bednar and Fengel 1974), which provides free binding sites (hydroxyl groups on the cellulose) where other ligands, mainly water, can be bound by means of hydrogen bonds. This way of disruption of the structure explains the higher decrease in the mechanical strength in the transversal directions, mainly the tangential one. The higher values in the radial direction are caused by pith rays in wood. The same theory can also be used for the explanation of the marked manifestation of shrinkage and warping. The values of radial, tangential and volumetric shrinking of subfossil wood are about double in comparison with recent wood (Fig. 2, Tab. 4). Govorčin and Sinković (1995) or Wagenführ (2000) arrived at the same results. The frequent warping of subfossil wood could be explained by a collapse of cell walls in consequence of a fast removal of water from wood.

CONCLUSIONS

The behaviour and properties of subfossil oak wood are highly specific, affected by the long-term effect of the environment it has been deposited in. The results present and clarify the occurring changes at the submicroscopic and chemical levels and the effect these changes have on mechanical and physical properties of subfossil wood. Further, the study has revealed other issues which are still to be resolved. The unanswered questions provide topics for further, more practical, research. The first issue to be solved from a practical point of view is a reduction of significant dimensional changes – one of possible ways could be thermal modification. Still another issue is the determination of a suitable gentle way of drying so that the frequency and size of cracks can be reduced. The cracks impair the material and prevent its use for manufacture of any products.

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Tomáš Kolář, Michal Rybníček
Mendel University in Brno
Faculty of Forestry and Wood Technology
Department of Wood Science
Zemědělská 3
613 00 Brno
Czech Republic
Phone +420 545 134 546
Corresponding author: koldatom@gmail.com

Marie Střelcová, Josef Hedbávný
Mendel University in Brno
Faculty of Agronomy
Department of Chemistry and Biochemistry
Zemědělská 1
613 00 Brno,
Czech Republic

Jan Vít
Czech Geological Survey,
Branch Brno
Leitnerova 22
658 69 Brno
Czech Republic