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Original article

Micro-morphological, physical and thermogravimetric analyses of waterlogged archaeological wood from the prehistoric village of Gran Carro (Lake Bolsena-Italy)

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A B S T R A C T

Oak disks from pile dwellings of the prehistoric site of Gran Carro (lake Bolsena, Italy) were analysed in order to estimate wood degradation. Micro-morphological observations showed that the microbial decay could be mainly attributed to erosion bacteria. The most important physical properties, i.e. Maximum Water Content (MWC), Residual basal Density (RDb), and the calculation of the Lost Wood Substance (LWS) highlighted that heartwood (HW) was moderately preserved, with MWC values slightly higher or comparable to that of recent oak, whereas sapwood (SW) was very degraded. Thermogravimetric analysis (TGA) was tested as an alternative method for the chemical characterisation of archaeological wood. The TGA profiles were critically discussed taking into account the results of the physical and micro-morphological analyses. Potentialities and drawbacks of TGA were underlined.

1. Introduction

The definition "waterlogged archaeological wood" includes all wooden remains recovered from submerged archaeological sites (in lakes, rivers, wetlands and the sea) or from terrestrial waterlogged sites. At these sites, wood is subjected to slow biodegradation depending on the oxygen concentration, which influences the types of micro-organisms involved in the process (erosion bacteria, tunnelling bacteria and/or soft-rot fungi) [1–3]. These microorganisms mostly degrade cellulose and hemicellulose, however partial deterioration of lignin has also been reported [4–8]. Selective degradation of cellulose and hemicellulose leads to increased lignin content in wood and considerable loss in mechanical flexibility and a general change in other physical properties [4,9].

Over the last number of years, the characterisation of waterlogged archaeological wood has assumed a significant importance in correct conservation and restoration practices. This topic is becoming more and more significant because of the recent problems with wooden pilings in certain European cities, like Venice and Amsterdam (e.g. [10]). Guidelines for wood characterisation established by European Technical Standards [11] define a diagnostic protocol for wood conservation, including microscopic, physical and chemical analyses. Physical and chemical characterisation of wood, which is one of the main tasks when planning the appropriate methods for conservation and/or restoration, is sometimes very time-consuming. Chemical techniques using classic extraction systems, for instance, require specialised equipment and are usually associated with considerable consumption of chemicals and time [12–14]. Recently, several spectroscopic and chromatographic techniques, like FT-IR, GC-MS-Py, SEM-EDX, NMR, and UV-microspectrophotometry (UMSP) have been applied to refine data on wood degradation [6,15–20]. Furthermore, they are very helpful for the chemical identification of

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wood remnants. Usually, application of one method is not sufficient; hence, it is convenient to combine several different techniques to gain as much information as possible. All these methods are micro-destructive and yield detailed results, but a number of them are quite expensive and the obtained data are not always easily comparable to each other and to the data collected by traditional techniques [13]. Thermogravimetry (TGA) is a well-known thermal analysis procedure, which provides information about the residual components of wood. TGA analyses are not expensive, can be performed at high speed, and require only a small amount of material. In the field of archaeological wood, TGA has been previously applied primarily to demonstrate the effectiveness of wood consolidation [21,22], but few examples have been seen regarding characterisation of wood degradation in waterlogged wood [23–25].

The major aim of the present study was to define the state of degradation of pile-dwelling poles from the lake Bolsena in Italy. A peculiarity of the studied samples is that the majority of the poles contained both sapwood (SW) and heartwood (HW) so it was possible to compare the performance of these two tissues, which usually have different resistances to decay. The second goal was to test the potential of TGA as a technique in the characterisation of decayed waterlogged wood. To establish the effectiveness of the technique, the obtained results were evaluated taking into account those of physical and micro-morphological analyses routinely conducted to assess the state of preservation of waterlogged wood.

2. Materials and methods

2.1. Site description

The wood analysed in the present work was sampled from the underwater archaeological site of Gran Carro. The site lies at a depth of 4–5 m, about 100 m off the Point of Grancarro on the east coast of the volcanic lake Bolsena (42°35′ N 11°59′ E) (Fig. 1A, B). It was studied for approximately twenty years, since 1959, by a group of volunteers coordinated by Alessandro Fioravanti [26–30] and by institutions including the University of Pennsylvania and the Superintendence of Southern Etruria (excavation campaigns: 1965–66, 1981). Extended research, started in 2012, has allowed in-depth examination of the structure of the village [31] and seeks to establish an accurate chronology.

The site consists of two predominant remains: the “Aiola” and the residential area. The former, dated from the Bronze Age, is an elliptical mound (60 × 80 m) of unknown function that was built with different sized stones. The residential area, located farther south, covers an area of 8000 m^2 and consists of the remains of a Villanovan village dating from the 9th century B.C. It was discovered by A. Fioravanti in 1959 based on the presence of ceramic and metallic finds, bones, wooden remains and more than 400 poles pounded into the lake bottom, in most cases almost completely buried into the sediment (Fig. 1C). The poles, 17–22 cm in diameter, are arranged in parallel and placed at intervals of 3 m in the area facing the lake while having an irregular distribution in the part of the site nearest to dry land. This arrangement has led to the hypothesis that the village was made of quadrangular houses located alongside the ancient lake bank in a first phase, while at a later stage of the settlement, pile dwellings were constructed to confront rising water levels (from 297 to 304 m altitude) [30,32]. Since the first excavation, two main shapes of pole-tops have been evident – flat and pointed. The latter is probably the result of axe cutting [30].

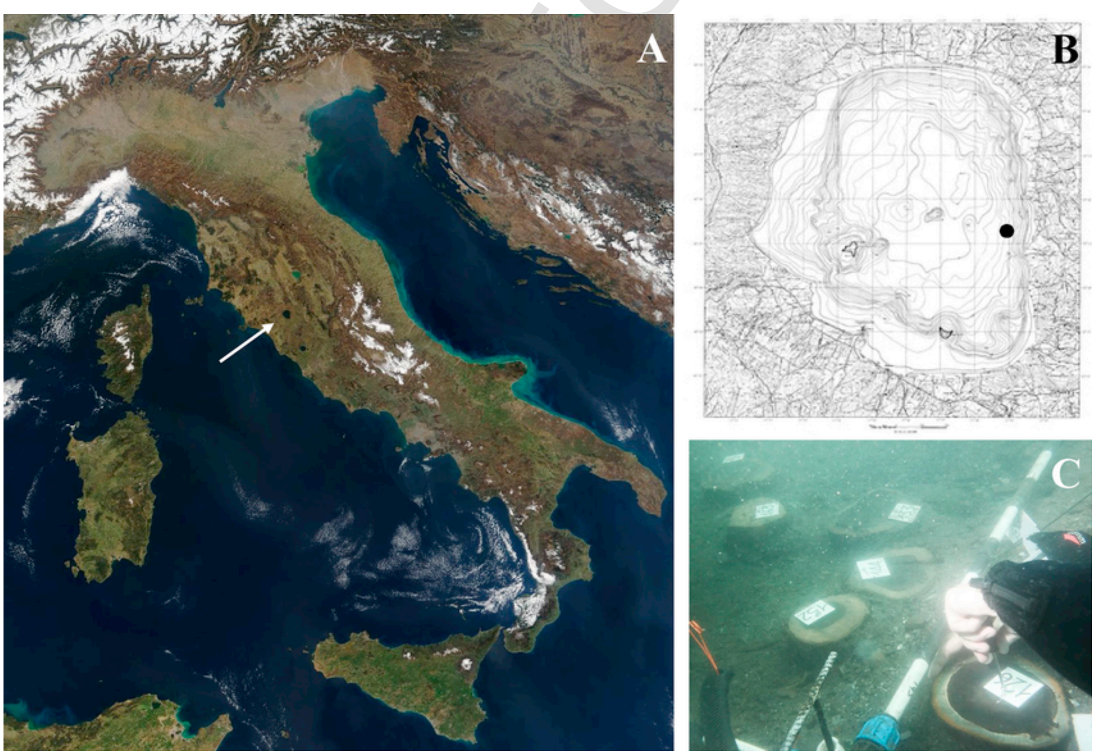

Fig. 1. The archaeological site of Gran Carro, Italy. A. Location of Lake Bolsena (white arrow) (satellite image from NASA). B. Bathymetric map of the lake (1:40,000); the black dot indicates the position of the site (photo from Istituto italiano di Idrobiologia). C. Underwater photo of the poles of the village taken after cleaning operations.

2.2. Sampling

During the excavations in 2011–12, eight of the poles from the village were selected as representative of the site by the Superintendence for the Archaeological Heritage of Latium and Southern Etruria. The tops of the poles were cleaned up from the sediments and a cross-section (ca. 5–10 cm thick) (Fig. 2A, B) was cut from each pole. The Identification Number (ID) of the samples was the same that was assigned to the poles by the underwater archaeologists (125, 126, 133, 144, 146, 152, 163, and 183). Samples were stored in fresh water to prevent drying and shipped to the laboratory for the analyses. A diametric parallelepiped (Fig. 2C) was cut from each sample (removing the top part). A different number of blocks was acquired from each parallelepiped depending on its dimension. Blocks were cut separating sapwood (SW) from heartwood (HW), when both were present, following the orthotropic wood direction. The smallest blocks (approximately 1 cm cubed and marked with a number) were used for micro-morphological analyses. The biggest ones (marked by a capital letter), with variable size depending on the state of preservation of wood (Fig. 2D), were employed for physical characterisation and for thermogravimetric analyses.

2.3. Identification of wood species and micro-morphological characterisation

Identification of wood species and micro-morphological investigations were carried out using transmission light microscopy (DMRB, Leitz) on thin sections (10–20 μm) cut in the three anatomical planes: cross, longitudinal-radial and longitudinal-tangential. Samples were cut either by hand with a razor blade or by cryo-microtome (Cryostat CM 1900, Leica). Wood in too bad a state of preservation was previously embedded in a glycerol-based medium (Glycerol Gelly, BDH) to improve its consistency and elasticity [33]. In many cases, sections were stained with an aqueous solution of 1% w/v methylene blue in 50% lactic acid in order to highlight the occurrence of micro-organisms. Wood species were determined using identification keys and comparing the observed features with the reports in the literature [34–36]. Microbial attacks were evaluated using both bright-field and polarized light microscopy in order to identify decay patterns and demonstrate the loss of crystalline cellulose.

2.4. Physical characterisation of wood

After the recovery from the lake, the blocks to be used for physical investigations were left completely soaked to maintain the state of maximum water content. They were then weighed and their volume was defined by the water displacement method. Weight was measured again after the sample was dried in an oven at 103°C ± 2°C up to a constant weight. The physical parameters used to evaluate the decay of waterlogged wood were calculated as follows:

- basic density, Db ($g \times cm^{-3}$): Ratio between anhydrous mass (M_0) and volume at maximum water content (V_f);
- maximum water content, MWC (%): Percentage ratio of the difference between mass at maximum water content (M_f) and anhydrous mass over anhydrous mass, MWC (%) : $(M_f – M_0)/M_0$;
- residual density, RDb (%): Ratio between basic density of decayed wood (Db_d) and basic density of non-decayed wood (Db) as assessed by reference;
- lost wood substance, LWS (%): 100 − RDb.

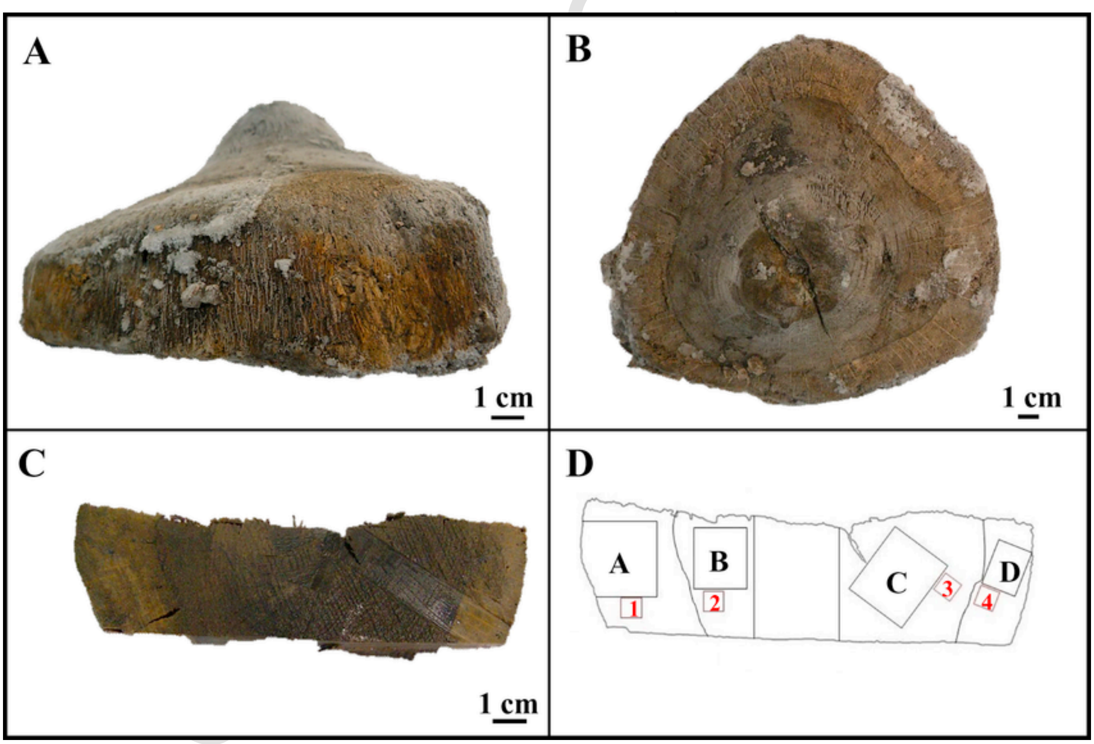

Fig. 2. Example of sampling. A, B. Lateral and top view of the cross-section of one of the studied poles. C. Diametral parallelepiped obtained from the cross-section. D. Graphic representation of the position of the blocks in the parallelepiped, the biggest blocks were used for the physical and thermogravimetric analyses (marked by letter), the smallest ones, marked by a number, were used for micro-morphological studies.

2.5. Chemical characterisation of wood

A TGA 2050 thermogravimetric analyser (TA Instruments, New Castle, DE) was used to evaluate the degradation of archaeological waterlogged wood according to the increasing of temperature. The wood previously used for the physical characterisation (blocks of ca 2 cm side) was grinded (granulometry less than 0.2 mesh) and 10 mg of mixed wood flour were used for each replication of the thermogravimetric analysis. They were heated at a rate of 20°C/min in an air atmosphere (flow of 50 cm^3 min^{-1}) after equilibration at 100°C; the weight loss expressed as its derivate was recorded as a function of temperature (the DTG curve). At the end of the process, the thermogravimetric residual at 650°C was assessed as the inorganic fraction (ash). The protocol parameters were selected after preliminary tests: the sample quantity and the airflow were carefully selected to have a thermo-oxidative condition without combustion.

In order to compare TGA results obtained for archaeological wood with the values of sound wood, three samples of oak from central Italy belonging to the sect. *robur* were sampled and they were subjected to the TGA analysis, using the same protocol applied for archaeological wood. The profiles of thermal breakdown of SW and HW of both archaeological and sound wood were described and compared.

3. Results and discussion

3.1. Wood species and micro-morphological characterisation

Basing on the observed anatomical features, all the examined wood samples were identified as deciduous oak *Quercus* sect. *robur* except for Q. sect. *cerris* for the sample 183. The wood of the identified species generally has medium-to-high density and robust mechanical properties. Its HW has a strong decay resistance [37], but durability is variable according also to density values. *Q. cerris* is ranked as moderately durable (DC 2), *Q. robur* with a density of 650–670 kg/m^3 is ranked from durable to slightly durable (DC 2–4), and *Q. robur* with a density of 710–760 kg/m^3 is ranked from very durable to durable (DC 1–2) according to EN 350: 2017. Thanks to these characteristics and its solid workability, oak wood has been one of the most important building materials (e.g. piles and various constructions) since prehistoric ages. Furthermore, different species belonging to the genus *Quercus* were identified in a wide range of archaeological discoveries (e.g., boats, tools, coffins, combs, dishes, wheels, water pipes and other hydraulic structures) [38–41].

Oak is a taxon with brown HW clearly distinguishable from the light-coloured SW. In waterlogged wood, HW turns black and can be well differentiated from grey-brown coloured SW [9]. In the examined poles, SW and HW could be distinguished based on colour differences but also considering different states of preservation because SW, when present, was soft and spongy to the touch while HW exhibited a better consistency. This difference was estimated by micro-morphological observations and quantified by means of physical and chemical analyses. Micro-morphological investigation of xylem tissue, carried out with optical microscope, allowed identifying microbial decay as mostly accredited to erosion bacteria. Observation through the bright-field view highlighted the presence of the typical “mosaic” pattern: apparently sound cells having a well-preserved cell wall among clusters of severely degraded ones, where secondary cell walls had shrunken and collapsed, detaching from the middle lamella. In the advanced degradation stages, cell walls transformed into an amorphous residual consisting of wood and products of bacterial decomposition (Fig. 3A). Polarized light aided in distinguishing sound cells, which still maintained a birefringence of crystalline cellulose, from the decayed ones in which the crystalline structure almost completely disappeared (Figs. 3A and B). In addition to the signs of bacterial degradation, which, as is known, occurs in very long time even in conditions of complete anaerobiosis, evidences of inchoate fungal colonisation were observed. The well-preserved aspect of the hyphae and the presence of spores make ones think of a development that occurred during the recovery and the storage of wood in water.

3.2. Results of physical analyses

The results of the physical tests are reported in Tables 1 and 2 for the SW and HW samples, respectively. The reference value of Db for oak (*Quercus robur, Q. petrea*) used in the calculation of RDb is 0.67 g × cm^{-3} [37]. All the SW samples exhibited a high level of degradation as the MWC ranged from 586% (183-A) to 957% (144-A) with an average value of 730% [42,43]. RDb varied between a minimum of 14.6% (183-A) to a maximum of 22.9% (144-A), confirming the patterns obtained by MWC results.

The SW of pole 144 was the most decayed with an average MWC of ca. 950% and an average RDb ca. 15%, corresponding to 85% of LWS. Microscopic observations confirmed a large degree of degradation, featuring detachments, collapse, thinning or complete loss of secondary cell walls. Where a thin layer of the secondary wall was still preserved, we noted a weak birefringence (Figs. 3A and B). The SW of pole 183 was apparently the best preserved, although with MWC values over 600% and an LWS approaching 80%, there was clearly a high level of degradation. In this case, microscopic analyses revealed the presence of clusters of better-preserved cells in severely decayed ground tissue. In addition, widespread occurrence of mineral inclusions was observed.

As expected, HW samples were considerably better preserved with respect to SW. Indeed, MWC ranged between 76% (133-D) and 292% (146-C) with an average value of 170%. Based on the MWC data, the samples could be classified into two groups corresponding to low and medium degrees of decay [43] with a corresponding LWS of 24% and 53%, respectively. On the whole, the best-preserved HW was that of pole 183 – all MWC values were lower than 185%. The poles with the greatest MWC values were 146 and 152. Pole 133 was cut at the height of a bifurcation of the tree trunk and so it had a double pith. The D, E and F blocks had MWC values lower than 100% while block B had an MWC of ca. 200%. This result can be referred to the position of this block that was near one of the piths but in the outer part of the pole, and so it was more exposed to decay than the other blocks. At a microscopic level, block B exhibited a superb preservation of secondary cell walls without detachments or collapses. The polarized light showed there to be a high birefringence, provided by the presence of crystalline cellulose (Figs. 3C and D).

The MWC values obtained for HW samples are comparable to those of sound or slightly degraded oak, ranging between 100 and 130% [9,12,44], and are in line with the oak durability previously mentioned . MWC and RDb values for the poles of Gran Carro are comparable to those reported for waterlogged oak archaeological findings [12,13,45]. To be noted as preservation is much better than in case of 4500–5500 years old poles from the Ljubljansko barje pile dwellings [6,9].

In Fig. 4, the relationship between Db and MWC is depicted. The regression model proposed well fits the data accounting for 98% of the variance. Basing on the regression results it can be observed that SW (blue dots) and HW (orange and grey dots) samples are divided into two groups. SW values are dispersed in a narrow range on the

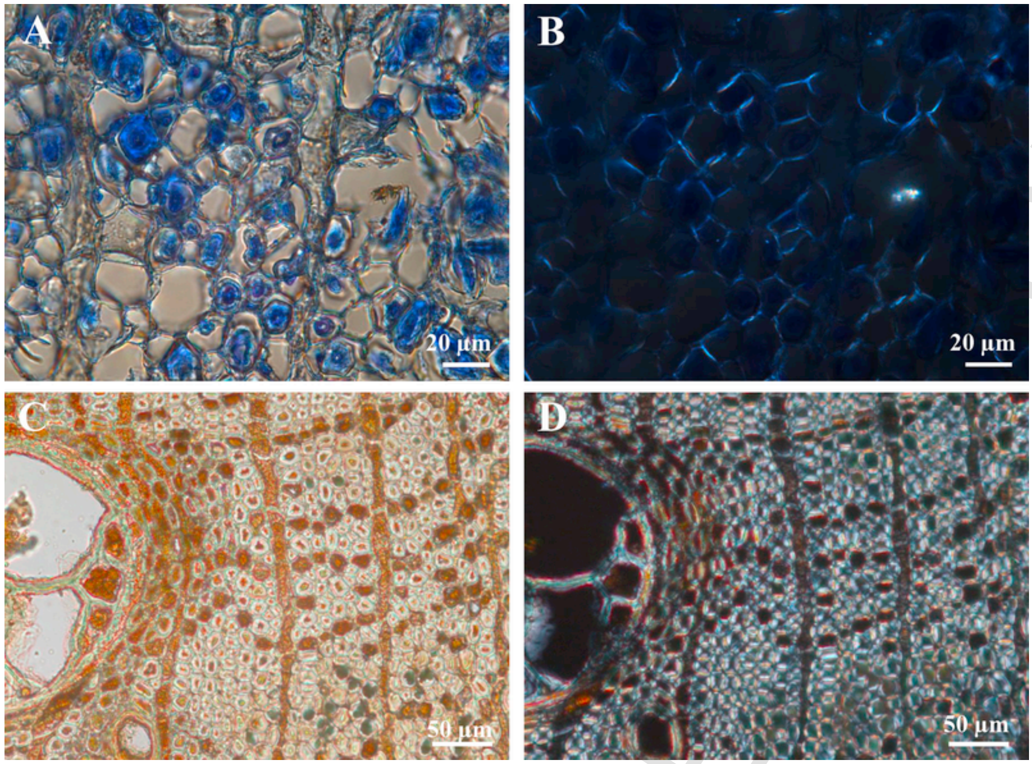

Fig. 3. Micro-morphological characterisation of wood on thin sections. A, B. Sample 144: Severely degraded wood in which the detachment or complete loss of secondary cell walls can be seen with light microscopy after staining with methylene blue and lactic acid (A) while there is only a weak birefringence of the thin remaining layer of the secondary wall (B). C, D. Sample 133: well-preserved secondary cell walls under light microscopy (C) and extensive presence of cellulose birefringence under polarised light (D).

Table 1
Results of physical analyses and ashes content of archaeological wood samples – SW.

Sample	Block	Db ($g \cdot cm^{-3}$)	MWC (%)	RDb (%)	LWS (%)	Ash (weight %) (650 °C)
133	A	0.124	787	18.24	81.76	5.5
144	A	0.098	957	14.6	85.37	5.1
	D	0.099	939	14.8	85.22	5.5
146	A	0.141	605	21	78.96	4.3
163	A	0.124	698	18.6	81.43	3.5
	B	0.130	665	19.3	80.67	2.6
	C	0.132	657	19.7	80.30	4.0
	D	0.120	751	17.9	82.14	2.2
	E	0.121	722	18	81.95	2.1
	F	0.132	693	19.7	80.33	2.4
	G	0.125	734	18.7	81.34	3
183	A	0.154	586	22.9	77.06	5.6
	G	0.131	693	19.5	80.45	6.5

Db: basic density; MWC: maximum water content; RDb: residual density; LWS: lost wood substance.

Bd axes (values comprises between 0.09 and 0.15) but are more dispersed on the MWC axes (between 586 and 957). On the other side, HW values cover a narrower range of MWC (between 76 and 292) but a wider interval of Bd (between 0.27 and 0.59). Based on the data yielded, two MWC thresholds can be identified distinguishing the samples into three classes of degradation. According to the guidelines of the English Cultural Heritage [42], the best-preserved wood has MWC values < 150%, which corresponds to a RDb > 70%. The second threshold can be established at MWC ≥ 500%, in fact above this value, all RDb values are < 25%, indicating quite severely degraded wood. The intermediate class of decay corresponds to 150% < MWC < 500% and RDb values ranging between 70 and 25%.

Table 2
Results of physical analyses and ashes content of archaeological wood samples – HW.

Sample	Block	Db ($g \cdot cm^{-3}$)	MWC (%)	RDb (%)	LWS (%)	Ash (weight %) (650 °C)
125	A	0.516	116	77	23.05	3.9
	B	0.550	119	82	17.97	2.7
	C	0.310	262	46.3	53.73	3.6
126	A	0.564	113	84.2	15.76	2.7
	B	0.493	139	73.6	26.4	4.5
133	B	0.325	204	48.5	51.54	3.8
	D	0.590	76	88.1	11.87	2.4
	E	0.553	86	82.6	17.40	1.6
	F	0.533	97	79.6	20.42	1.4
144	B	0.340	230	50.7	49.25	3.1
	C	0.609	100	90.9	9.10	2.7
146	B	0.296	271	44.2	55.82	5.6
	C	0.280	292	41.8	58.21	6.5
152	D	0.275	289	41	59.01	6.4
	E	0.376	195	56.2	43.83	4.3
183	B	0.471	148	70.4	29.63	3.8
	C	0.468	150	69.9	30.11	3.3
	D	0.480	141	71.7	28.31	2.6
	E	0.409	177	61	39.03	3.6

Db: basic density; MWC: maximum water content; RDb: Residual density; LWS: lost wood substance.

3.3. Results of chemical analyses

In Figs. 5A and B, the three DTG curves of the HW and SW of the reference sound oak samples are portrayed; the profiles are quite comparable, especially for the holocellulose fraction, with the results obtained through TGA on oak wood by different authors, even if in

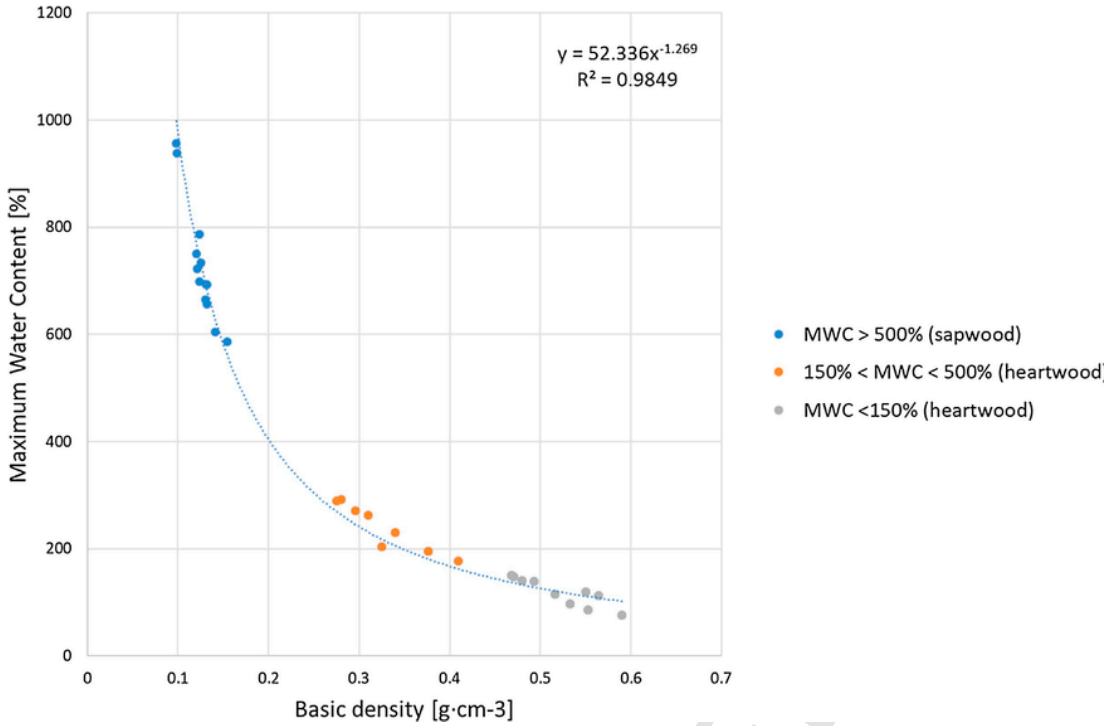

Fig. 4. Relationship between Db and MWC in SW and HW.

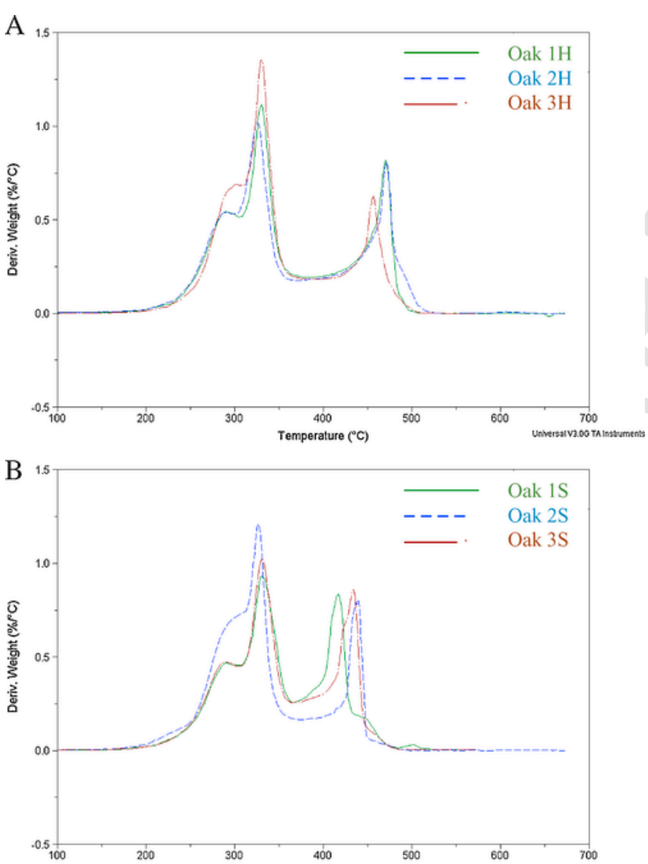

Fig. 5. DTG curves of sound oak references. A. HW; B. SW.

their researches the applied experimental conditions were rather different [23,46].

With respect to HW samples, two major peaks were present. They could be attributed, respectively, to the decomposition of crystalline cellulose (ranging between 220 and 370°C), comprising a shoulder (between 280 and 300°C) ascribable to hemicelluloses and amorphous fraction of cellulose, and to the decomposition of lignin and related compounds containing phenol and catechol structures (ranging between 420 and 530°C). The first peak might include also signals produced by low molecular weight extractives that can be present in oak wood [47]. It must be taken into account that even if the peaks attributable to the maximum weight loss of cellulose and lignin are well distinguished, the thermal degradation of hemicelluloses, cellulose and lignin starts at ca. 200°C, thus between 200°C and 400°C, signals of degradation are partially overlapped [22,48]. Above 400°C, only the phenolic compounds undergo thermal decomposition. In oak HW, these are represented by lignin and other phenolic substances typical of wood extractives, among which the most abundant are tannins. Their chemical composition and concentration in wood is exceptionally variable and related to several factors, such as the wood age, species, wood provenance, etc. [49–52]. The different composition and/or amount of phenolic extractives in HW of different trees could be the reason for the observed shifting of the second peak.

In SW, the main peak of cellulose had a maximum of weight loss at the temperature almost coincident with that of HW and it spanned in a slightly wider range of temperature (180–360°C). The shoulder was wider as it should comprise not only hemicelluloses and, as already said, the amorphous cellulose, but possibly also the starch present in the SW. The second peak, in SW, was significantly shifted to lower temperatures (ranging between 370 and 480°C), probably because of the different amount or the lack of phenolic extractives. Although a certain shifting in the maximum degradation temperature was observed among the oak samples, it can be related to the natural variability in the sapwood composition.

DTGA profile of archaeological wood has some basic characters to show (Fig. 6A and B).

Fig. 6A shows the DTG curves of three HW archaeological specimens (133-D, 152-E and 146-C), characterised by MWC values of 76, 195 and 292%, respectively, compared with one curve of the reference oak samples. For these samples, a first peak was clearly visible. It almost perfectly corresponded to the peak attributed to crystalline cellulose of the reference oak for samples 133-D and 152-E, while it was slightly shifted to lower temperatures for the most degraded sample (146-C) where reasonably also the crystalline fraction of cellulose started depolymerizing.

In the archaeological samples, the shoulder at temperatures lower than 300°C was significantly diminished or quite absent (133-D). When present, it could not be attributed only to the hemicellulose because in waterlogged wood hemicellulose usually is the first component lost because of its water solubility and its highest susceptibility to biological degradation [53]. The shoulder most likely should be attributed to degradation products of wood, probably both of cellulosic and phenolic nature. In support of this hypothesis, in the best-preserved sample of this group (133-D) this shoulder was not evident: in this case, probably hemicelluloses were lost and no degradation products were present (Fig. 6A). It is noteworthy that the relative intensities of the two peaks described above changed in the most degraded archaeological samples, i.e. the main peak decreased while the shoulder increased. This could be attributed to the lower quantity of crystalline cellulose present in the most degraded wood and to the greater amount of degradation products.

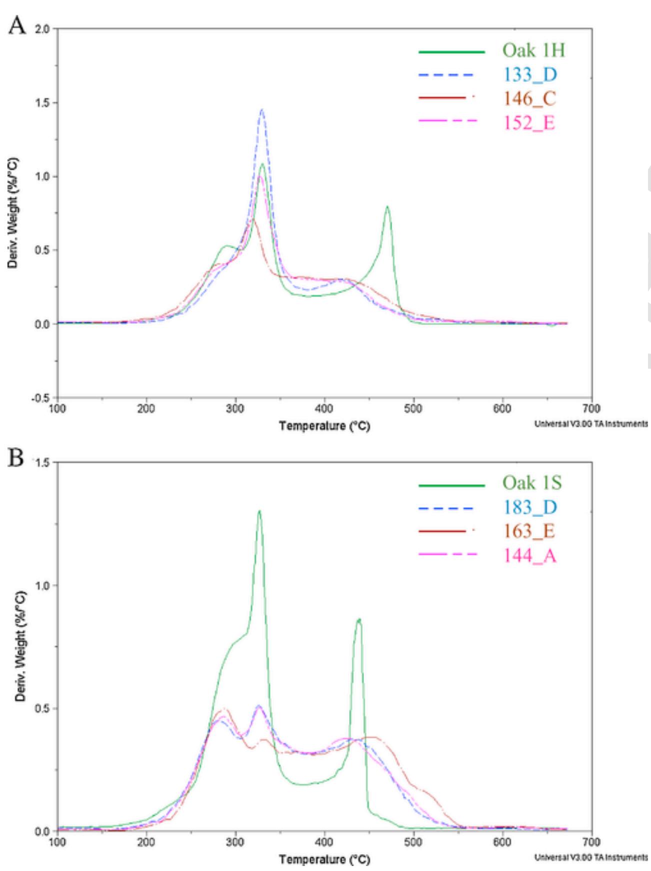

Fig. 6. DTG curves of archaeological specimens compared with one of the reference oaks. A. HW. B. SW.

In the three archaeological specimens, the second peak (attributable to lignin and/or other phenolic compounds) was less defined with respect to the reference and had a broader temperature range (with a maximum at ca. 425°C). This could be credited not only to the original structure of lignin but also to phenolic compounds deriving from its degradation [54] and probably also to the breakdown of phenolic compounds related to wood extractives (like tannins).

Fig. 6B presents the DTG curves of three archaeological samples of SW (144-A, 163-E, and 183-D), representing three different degradation states (MWC values of 957, 722 and 586%, respectively) compared with one reference curve. Three main peaks were here visible; the first two had a maximum at ca. 280 and 330°C. As for HW, these two peaks could be attributed to the degradation products and to the residue crystalline cellulose respectively.

The peak attributable to phenol compounds was widened for all three samples (spanning from 375 to about 550°C) and not easily interpretable. The part of the peak at lower temperature could be based on the contribution of lignin being partially depolymerized by natural oxidative processes, which foster degradation at lower temperatures [54]. On the other hand, it is quite difficult to explain the part of the peak at temperatures higher than 480–500°C. A possible hypothesis of this occurrence could be the formation of condensed compounds produced by the degradation of lignin at high temperatures [55]. Furthermore, degraded wood has a lower cellulose content, and therefore fewer oxygen atoms. This suggests that pyrolytic phenomena may be accentuated over those of the oxidative type, leading to a shift to higher temperature as was shown in tests carried out under nitrogen where graphitization phenomena were also observed [56].

Ashes weight values for the archaeological samples are reported in Tables 1 and 2. SW values ranged from 2.1 to 6.5% with an average of 4.0% while HW residues varied between 1.4 and 6.5% with an average of 3.6%. This low amount of ashes could not have influenced the MWC values unlike cases where this quantity is significantly higher [57]. The amount of ash is usually higher in the most degraded wood [53], whereas in the samples analysed in this study, the values were comparable between SW and HW. It could be hypothesised that TGA residues not only depend on the preservation state of waterlogged wood, but also on other chemical characteristics of wood, like the proportion of inorganic compounds. The presence of these inorganics might have influenced the thermal degradation of wood, most of all the oxidative phenomena concerning cellulose, but the use of a low airflow reduced this effect.

4. Conclusions

The oak wood poles from the prehistoric village of Gran Carro (lake Bolsena) have, in general, very degraded SW (586% < MWC < 957%) and moderately preserved HW (76% < MWC < 292%). In spite of the conditions of temperate climate that favour the degradation phenomena, the oak heartwood confirmed its durability and strong decay resistance. Micro-morphological observations highlighted that the microbial decay could be mainly attributed to erosion bacteria and only few evidences of an inchoate fungal colonisation were observed.

As said, one of the aims of this work was to test TGA as an alternative method, which is faster, easier to implement, and less cost effective than existing chemical techniques routinely used for the characterisation of waterlogged archaeological wood. The obtained results highlighted that the application of this technique to the characterisation of wood is not so easy. For the reference oak while the results obtained for holocellulose are quite reliable, those concerning the phenolic compounds are more variable. This can be related to the fact that the analysed wood was not extracted, but this condition was necessary in order to make comparisons with the archaeological wood. The application to archaeological wood allowed affirming that an easily interpretable qualitative difference can be observed only for clearly distinct classes of degradation (MWC < 300% and MWC > 500%). This is especially true with regard to the temperature range between 200 and 400°C. Here for slightly degraded samples the crystalline cellulose peak is still well distinguishable from the shoulder attributable to low molecular weight products of degradation. However, in highly degraded samples, the shoulder at temperatures below 300°C turns into a real peak with a variable relative intensity compared to the cellulose peak. The part related to the phenolic compounds has, as mentioned, a high variability even for the sound wood so it is not very reliable for the assessment of the state of preservation of archaeological wood.

In conclusion, it can be said that the TGA could become a more useful and reliable method after further studies that, thanks to a comparison with the results obtained with different techniques on archaeological wood, will allow obtaining a calibration of thermogravimetric analyses.

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