Characterization of archaeological waterlogged wooden objects exposed on the hyper-saline Dead Sea shore

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ABSTRACT

Archaeological waterlogged wood objects exposed on the Dead Sea shore exhibit little visual evidence of degradation when first exposed, and after prolonged exposure and dehydration. An investigation on the state of preservation of this material was recognized as a necessary step towards its long-term conservation. Micromorphological observations, ATR FTIR, ash content, and physical tests showed that deterioration is limited and is mostly non-biological in nature. Natural bulking and impregnation with lake minerals and salts appear to play a significant role in the physical stability of these woods when dried, and apparently inhibit microbial colonization and subsequent degradation. In contrast, archaeological wood examined from a typical Mediterranean marine environment showed advanced stages of degradation by bacteria, with the wood structure extensively compromised.

1. Introduction

The Dead Sea is a hyper-saline inland desert lake located at the lowest terrestrial place on Earth (Fig. 1). The lake and its surroundings have a harsh desert climate, extremely rugged terrain, and rich mineral resources.

The archaeological record of the Dead Sea basin is extremely long and diverse, indicating a continuous human presence at least from the Neolithic Period (9750–4500 BCE) to the present time (Nissenbaum, 1993; Taute, 1994; Gichon, 2000: 93–101; Recchi and Gopher, 2002; Hirschfeld, 2006; Barkai et al., 2007; Schaub and Chesson, 2007; Schyle, 2007; Vardi and Cohen-Sasson, 2012). This human presence was associated with the exploitation of the region’s rich natural resources, e.g., salt, bitumen (natural asphalt), and flint, as well as the cultivation of dates and aromatic plants at several lakeshore oases.

A severe and ongoing drop in the lake water level since the 1960’s (Klein, 1982; Bookman et al., 2006: 167–168) has led to the exposure of vast areas of the former lakebed, and with it a diverse collection of ancient and historical objects. Of particular importance are several well preserved anchors made of stone, waterlogged wood and rope, dating from the 8th century BC to the 12th century AD (Hadas, 1992, 1993; Hadas et al., 2005; Oron et al., 2008). Together with cargo remains, shoreline finds and other types of evidence, these anchors add significantly to our knowledge of the basin’s history and illuminate the lake’s unique maritime cultural landscape (Oron et al., 2015a, 2015b).

Waterlogged wood finds from the Dead Sea may be found while still wet or damp near the waterline, or completely dry, having been exposed for several years, or even decades, such as the anchors in Fig. 2a and b. Both appear visually and physically intact, with their three-dimensional integrity little changed. This seemingly un-degraded condition is unusual, and contrasts with similar finds from other marine environments, which are normally found chemically and biologically degraded, and prone to rapid disintegration upon uncontrolled drying (Hoffmann and Jones, 1990; Blanchette and Hofmann, 1994; Gelbracht et al., 2008; Björdal, 2012).

The excellent state of preservation of wooden finds from the Dead Sea raises questions regarding their physical and chemical nature. The aim of the study was to characterize the deterioration found in archaeological waterlogged wooden objects and other waterlogged wood found in and along the shoreline of the Dead Sea, using protocols commonly used for the evaluation of archaeological waterlogged wood...
This information is fundamental to the development of suitable long-term conservation methods for the lake’s waterlogged cultural remains. For comparative purposes, waterlogged archaeological wood from the Late Byzantine Tantura F shipwreck found in the Mediterranean Sea (hereafter termed ‘Tantura F’) was also studied (Barkai and Kahanov, 2007; Barkai et al., 2010; Liphschitz, 2012).

2. Materials and methods

2.1. Study material

The rarity and intact nature of the archaeological wooden objects from the Dead Sea restricts their sampling to minute segments of wood suitable mainly for tree species analysis and density measurements. Data for the study were thus collected either in-situ directly from these objects when possible, or otherwise from readily available archaeological waterlogged driftwood found along the lake shore that could be destructively tested (Fig. 3). The latter originates from the densely forested banks of the Jordan River and from other freshwater sources around the lake (Zohary, 1962: 144–152, 165–177). Its presence in the lake is linked with powerful flash floods common to the region, and from the erosion of the soft marl banks of the Jordan River, which result in the washing of large amounts of this vegetation into the lake every year. Waterlogged objects and driftwood finds exposed by the receding shoreline are often found heavily encrusted with layers of lake minerals (Fig. 4).

Fig. 1. Map of research area showing the eastern Mediterranean (inset) and the Dead Sea region (A. Oron).

Fig. 2. Composite anchors. a) Composite anchor (Anchor A, Oron et al., 2008, sample DS 8, 14C dating: cal 898–1048 CE [97.9%] made of stone, wood and rope as found still wet at the waterline. b) Composite anchor (Samar Springs anchor C, Oron et al., 2008, 14C dating: cal 1032–1160 CE [100.0%] made of stone, wood and rope as found fully dehydrated after several years of exposure (scale 20 cm, photos A. Oron).
Eleven samples of waterlogged archaeological wood were collected for this study at several locations along the western shores of the lake's northern basin (Fig. 5). Their dating was established by radiocarbon analysis (Table 1). The research sample group from the Dead Sea was supplemented by a sample of a related tree species obtained from the Tantura F (Barkai and Kahanov, 2007; Barkai et al., 2010; Liphschitz, 2012). Non-degraded modern wood samples of identical tree species were also collected within the research zone as references. Information about the different samples is summarized in Table 1.

The study material was subjected to wood species analysis, micro-morphological characterization, physical analysis, ash content measurements and ATR FTIR analysis.

2.2. Identification of wood species

Wood samples of 0.5–1 cm³ were taken from each wood piece for microscopic examination. Radial, longitudinal and tangential sections were prepared for each sample with a sharp razor blade. The species level identification of the samples was based on microscopic comparison between the three-dimensional structure of the wood and illustrations of anatomical characteristics of wood of modern trees and shrubs from reference books (Fahn et al., 1986; Schweingruber, 1990).

2.3. Micro-morphological characterization

Small segments of the wood samples from the Dead Sea and from the Tantura F were cut and prepared for scanning electron microscopy. Samples were infiltrated with TBS™ Tissue Freezing medium™...
using low vacuum, mounted on brass stubs at $-20$ °C in an OM 2488 Minotome (International Equipment Company, Needham Heights, MA, USA), and cut to produce a transverse section of the wood segment. Samples were then thawed, air-dried for 48 h, mounted on stubs and coated with gold in an EMS 76M sputter coater (Ernest F. Fullam, Inc., Schenectady, NY, USA). Prepared samples were examined and digital photographs obtained using a Hitachi S3500N (Hitachi, Tokyo, Japan) scanning electron microscope.

2.4. Physical analysis

The physical analyses comprised maximum water content (MWC), basic density ($D_b$), residual basic density (RBD), loss of wood substance (LWS), linear shrinkage ($\beta_t$, $\beta_r$, $\beta_l$) cross-sectional shrinkage ($\beta_{cs}$) and Anti-Shrinkage Efficiency (ASE). The formulas used in these calculations are presented in Table 2, and the results in Table 3.

The sampling methods used in the physical analyses were adapted to the availability of original material and the inherent restriction of sampling intact cultural heritage material. Three sampling procedures were followed in order to collect as much information as possible within these restrictions (see Table 1 for the procedure used for each sample):

1) Small prismatic sections measuring 0.5–1.5 cm longitudinally, and 0.5 cm radially and tangentially, were used for samples from small driftwood stems and archaeological objects.

2) Cross-sectional slices across medium-sized driftwood stems measuring 2–8 cm in diameter and 2 cm thick (Fig. 3a).

3) In situ shrinkage measurements on three timbers from an intact wooden anchor (Mazin A in Oron et al., 2008) found on the lake shore.
2.4.1. Basic density (Db) and maximum water content (MWC)

Before taking measurements, wood samples from the Dead Sea were stored in Dead Sea lake water and Tantura F samples in tap water. To prevent possible biased water content and density (MWC, Db) values due to the high mineral content of the Dead Sea sample group, samples used for these analyses were first desalinated. Desalination was done by gradual dilution of the initial storage water with de-ionized water at 20% increments at regular time intervals. The process was monitored with a calibrated conductivity meter, and was considered completed when conductivity readings reached a constant value of ≤50 μS/cm. In order to achieve maximum water content, samples were then placed in a vacuum chamber for 30 min at 30 kPa. This cycle was repeated twice. The samples were then weighed after careful blotting of the excess water from their surface. The weight (Ms) of each sample was measured five times on a calibrated analytical scale (accuracy 0.001 g), and the average value was calculated. The volume (Vs) of each sample was then determined by the water displacement method by the procedure of Jensen and Gregory (2006: 554–557), using a wide-mouth 25 ml Hubbard Carmick pycnometer on the same analytical balance. Following these measurements, samples were dried in an oven at 103 ± 2 °C to a constant weight, and their oven-dry weight (Mo) recorded after cooling in a desiccator. The results were used for the calculation of basic density (Db), maximum water content (MWC) and related parameters.

2.4.2. Shrinkage

The initial small size of some of the samples used for the study limited the shrinkage measurements to few larger cut samples and to several in-situ shrinkage measurements taken directly from three timbers of the intact wooden anchor (DS 8). Measurements were made using stainless steel pins inserted into the wood across its radial (r), tangential (t), and longitudinal plane (l). Measurements were taken at full saturation and after slow air-drying in a controlled environment at 20 °C and 50% relative humidity (RH). Three measurements were taken using digital calipers (accuracy

### Table 1

<table>
<thead>
<tr>
<th>Sample</th>
<th>Wood species</th>
<th>Object</th>
<th>Age in YBP</th>
<th>Origin</th>
<th>Sampling method</th>
</tr>
</thead>
<tbody>
<tr>
<td>DS8</td>
<td>Ziziphus spina-christi</td>
<td>Composite anchor (Mazine A)</td>
<td>953</td>
<td>Dead Sea</td>
<td>1, 3</td>
</tr>
<tr>
<td>D512</td>
<td>Ziziphus spina-christi</td>
<td>Carved wooden bowl</td>
<td>1647</td>
<td>Dead Sea</td>
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<tr>
<td>D7a</td>
<td>Tamarix (×5)</td>
<td>Driftwood (collected by diving in the lake)</td>
<td>136</td>
<td>Dead Sea</td>
<td>1, 2</td>
</tr>
<tr>
<td>D11</td>
<td>Tamarix (×5)</td>
<td>Drift wood (collected by diving in the lake)</td>
<td>855</td>
<td>Dead Sea</td>
<td>1</td>
</tr>
<tr>
<td>S10</td>
<td>Tamarix (×5)</td>
<td>Driftwood</td>
<td>667</td>
<td>Dead Sea</td>
<td>1</td>
</tr>
<tr>
<td>S11</td>
<td>Tamarix (×5)</td>
<td>Driftwood</td>
<td>1263</td>
<td>Dead Sea</td>
<td>1</td>
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<td>Tamarix (×5)</td>
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<td>Dead Sea</td>
<td>1</td>
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<td>Driftwood</td>
<td>2745</td>
<td>Dead Sea</td>
<td>1–2</td>
</tr>
<tr>
<td>S20a</td>
<td>Tamarix (×5)</td>
<td>Driftwood</td>
<td>1271</td>
<td>Dead Sea</td>
<td>1–2</td>
</tr>
<tr>
<td>Tantura F</td>
<td>Tamarix smyrensis</td>
<td>Frame</td>
<td>1239</td>
<td>Mediterranean wreck site</td>
<td>1–2</td>
</tr>
<tr>
<td>S14</td>
<td>Populus euphratica</td>
<td>Driftwood</td>
<td>124</td>
<td>Dead Sea</td>
<td>1</td>
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<tr>
<td>S15</td>
<td>Populus euphratica</td>
<td>Driftwood</td>
<td>852</td>
<td>Dead Sea</td>
<td>1</td>
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<tr>
<td>Reference 1</td>
<td>Tamarix (5)</td>
<td>Branch</td>
<td>Modern</td>
<td>Dead Sea basin</td>
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</tr>
<tr>
<td>Reference 2</td>
<td>Ziziphus spina-christi</td>
<td>Branch</td>
<td>Modern</td>
<td>Dead Sea basin</td>
<td>1</td>
</tr>
<tr>
<td>Reference 3</td>
<td>Populus euphratica</td>
<td>Branch</td>
<td>Modern</td>
<td>Dead Sea basin</td>
<td>1</td>
</tr>
</tbody>
</table>

### Table 2

Methods used for physical characterization of waterlogged wood samples.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Abbreviations</th>
<th>Method</th>
</tr>
</thead>
<tbody>
<tr>
<td>Maximum water content (%)</td>
<td>MWC</td>
<td>MWC = 100 × Dbl/Mo</td>
</tr>
<tr>
<td>Basic density of archaeological sample at MWC (g/cm³)</td>
<td>Db</td>
<td>Db = Dbl/Mo</td>
</tr>
<tr>
<td>Basic density of non-degraded (fresh) wood from the literature (g/cm³)</td>
<td>Dbl</td>
<td>Data from literature</td>
</tr>
<tr>
<td>Residual basic density (%)</td>
<td>LWS</td>
<td>LWS = 100 × Dbl/(100 – Dbl)</td>
</tr>
<tr>
<td>Linear shrinkage (%)</td>
<td>β</td>
<td>β = 100 × (Dbl – Dbl)/(100 × Dbl)</td>
</tr>
<tr>
<td>Cross sectional shrinkage (%)</td>
<td>βcs</td>
<td>βcs = 100 × (l1 – l0)/(100 × l0)</td>
</tr>
<tr>
<td>Anti-shrinkage efficiency (%)</td>
<td>ASE</td>
<td>ASE (%) = (100 × Dbl/Mo) × 100</td>
</tr>
</tbody>
</table>

**Abbreviations**

- Ms: mass of waterlogged wood (g) at MWC
- Mo: mass of oven-dry wood (g)
- Vs: volume of sample (cm³) at MWC
- Ms: mass of waterlogged sample (g)
- M0: mass of oven-dry sample (g)
- Ash Des: ash desalinated = ash content after desalination
- l0: distance between pins in wet state at MWC
- l1: distance between pins after drying
- [β, βt, βr, βl]: linear shrinkage in tangential, radial and longitudinal directions (%)
They were then heated to 500 °C for 4 h in a muf (Ash) and desalinated samples (Ash desal.) were dried at 105 °C over-

sums were used to calculate cross-sectional shrinkage (\(S_{\text{avg}}\)). The total average sums were used to calculate cross-sectional shrinkage (\(S_{\text{avg}}\)). The total average sums were used to calculate cross-sectional shrinkage (\(S_{\text{avg}}\)).

In order to evaluate the impact of the high mineral content of the samples from the Dead Sea on their dimensional stability, a second set of samples was prepared from each of the cut samples (D7b S19b, D20a S21a [×5]). Their soluble mineral content was then removed by desalination following the protocol described above. After desalination, the dimensions of the samples in the radial and tangential planes were measured as above. The differences in shrinkage rates between this set of samples and the mineral saturated wood were used for the calculation of anti-shrinkage efficiency (ASE).

### 2.5. Ash content analysis

Ash content was measured by the standard loss-on-ignition method (Soil and Plant Analysis Council, 1999). Un-desalinated wood samples (Ash) and desalinated samples (Ash desal.) were dried at 105 °C overnight and cooled in a desiccator. Samples were then weighed in pre-weighted crucibles on an analytical balance to the nearest 0.0001 g. They were then heated to 500 °C for 4 h in a muffle furnace, cooled in a desiccator, and weighed again to determine ash content.

### 2.6. FTIR ATR

Five sub-samples approximately 4 × 4 mm were removed from each initial designated sample with a scalpel. Each sub-sample was placed on the diamond attenuated total reflectance (ATR) accessory of a Thermo Scientific Nicolet iS 10 spectrometer. The inner surface of the sub-sample was placed on the ATR crystal. The pressure tower on top of the sampling plate applied a constant pressure on the sample to ensure good contact between the sample and the ATR crystal. The laboratory in which the measurements were performed was maintained at 65 ± 2% RH and 24 ± 1 °C. FTIR spectra were recorded at a spectrum resolution of 4 cm\(^{-1}\) between 650 cm\(^{-1}\) and 4000 cm\(^{-1}\), and averaged from 32 scans. A background scan of a clean diamond crystal was acquired before scanning each sample. Smoothing (3rd order Savitzky-Golay filter with 51 points) was applied to each spectrum to minimize absorbance bands to ambient water vapor. Smoothing was followed by baseline correction using the procedure developed by Mazet et al. (2005) (with a second order asymmetric truncated quadratic function) and normalization with the Vector Normalization procedure used by Pizzo et al. (2015):

\[
S_{\beta} = \frac{S - S_{\text{avg}}}{\sum(S - S_{\text{avg}})}
\]

where S is the original spectrum, S_{\text{avg}} is the spectrum mean, and \(S_{\beta}\) the normalized spectrum. The sum is on the spectral range considered, in the present case the 700–1800 cm\(^{-1}\) interval. Finally, the spectra of the five sub-samples were averaged, and these average spectra were used for the analysis reported below.

### 3. Results and discussion

#### 3.1. Wood species

The samples examined were identified as *Ziziphus spina-christi* (Ziziphus spina-christi [Christ thorn; Jujube]), *Tamarix* (×5) [Tamarisk with 5 sepals, 5 petals and 5 stamens in the flower], *Tamarix smyrnensis* (*Tamarix* and *Populus euphratica* [Euphrates poplar]) (Table 1). Of these four species, only *Tamarix smyrnensis* is not native. It originates in Izmir and Antalya on the Turkish coast, and was used as hull construction timber for the Tantura F ship (see Liphschitz, 2012). The other three species are native to the Dead Sea region. They were used for the anchor and the carved wooden bowl found on the Dead Sea shore, and were identified amongst the driftwood located along the shore.

<table>
<thead>
<tr>
<th>Wood species and Db value* (\text{g/cm}^3)</th>
<th>Cited sources</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Populus euphratica</em></td>
<td>0.505</td>
</tr>
<tr>
<td><em>Tamarix spp. (smyrnensis and aphylia)</em></td>
<td>0.635</td>
</tr>
<tr>
<td><em>Ziziphus spina-christi</em></td>
<td>0.65</td>
</tr>
</tbody>
</table>

### 3.2. Micromorphological analysis

#### 3.2.1. Findings

Sound modern wood was sectioned to compare its micromorphological characteristics with the various woods from the Dead Sea, and with the Tantura F sample. Transverse sections of two woods, *Tamarix* (×5) and *Ziziphus spina-christi* are shown in Fig. 6a, b. Wood from the anchor, sample DS8 (Ziziphus spina-christi), appeared sound, and its structural integrity was intact. Sections of wood from below the surface layer showed some occluded vessel elements, and in general, cells were free of cell wall degradation (Fig. 6c and d). Sections of wood near the surface of the wood showed some cells with altered morphology (Fig. 6e). Secondary walls in some fiber cells were slightly eroded, and others had detached secondary walls. The compound middle lamellae between cells were not affected, and most cells retained normal cell structure. The areas where cell wall alterations occurred were localized...
near the wood surface. Wood cells in Sample D7 (*Tamarix* (×5)) were heavily occluded (Fig. 6f). Salts and other substances filled vessel elements and coated the fiber cell walls. At the edge of this wood, cells were separated and defibrated. The compound middle lamellae between cells were degraded, and swollen secondary walls were detached from one another. This pattern of detached cells also occurred in wood at the outer surface of many other wood samples. More pronounced defibration was evident in sample S12 (*Tamarix* (×5), Fig. 7a and b), and large groups of cells were detached with no detectable compound middle lamellae remaining between cells. Cells at wood surfaces were defibrated and separated into individual strands of secondary wall material. Some samples, such as S14 (*Populus euphratica*), had large depositions of crystalline compounds within vessel elements and fiber cells, but did not display significant defibration or disruption of the wood cells (Fig. 7c). There was substantial degradation in wood from Sample S11 (*Tamarix* (×5), Fig. 7d), with large areas of eroded wood cells and voids. Large groups of cells remained unaltered between the degraded areas. Some large voids in the radial plane appeared to follow the ray parenchyma cells. This sample was thus a mixture of intact zones of cells, localized areas of defibrated cells, and relatively large voids containing remnants of degraded cell walls.

In contrast to the deterioration found in wood samples from the Dead Sea, the Tantura F samples showed extensive decay (*Tamarix smyrnensis*, Fig. 7e). Cells appeared much defibrated, and the remaining wood cells were greatly distorted during sample preparation and drying. Increased magnification showed wood cells with advanced stages of bacterial degradation (Fig. 7f). Some cells had secondary cell walls that were completely degraded, leaving only the compound middle lamellae; while others had swollen and very porous secondary walls.

### 3.2.2. Discussion

In certain environments, high concentrations of salts in wood can cause serious damage to wood. This occurs when wood absorbs moisture and salts from the surrounding environment, and evaporation causes salt to be deposited in the wood. Over time, without rainfall to wash out the salts, the salt concentrations can become exceedingly high. Archaeological wood found in dry deserts, and historical woods along coastal areas in Antarctica and the Arctic, have been found with severe wood defibration caused by high salt contents (Blanchette et al., 1994, 2002, 2008; Ortiz et al., 2014). This deterioration, however, is not caused by the physical formation of salt crystals in cell lumina. Although the process is not well understood, salts cause a chemical reaction that affects the compound middle lamellae between cells, causing secondary walls to separate. With time, the surface wood cells continue to defibrate, causing a white fibrous appearance and a slow corrosion of the wood. The rate and extent of deterioration apparently depends on
the environment. For example, wood only a few decades old may become extensively defibrated if it has a high salt content (Blanchette et al., 2002, 2004; Ortiz et al., 2014); while much older wood with high salt content in the Dead Sea region suffers limited attack. This may be due to the type of salts and the waterlogged condition of the wood. The latter prevents the occurrence of wet and dry cycles, which most probably accelerate this form of degradation.

The high contents of salts and other compounds in the wood found along the Dead Sea shore are probably responsible for inhibiting microbial degradation. There are very few environments where microbial decay does not take place when wood is found together with moisture. The Dead Sea appears to be one of these locations. In less salty sea water, such as the Mediterranean, archaeological wood is found with extensive microbial degradation. In this study, wood from the Tantura F showed an advanced stage of decay caused by bacterial degradation.

3.3. Physical analysis

3.3.1. Maximum water content

The maximum water content (MWC) values of the Dead Sea material range between 72% (DS12) and 211% (S11). A significantly higher MWC (854%) was measured in the Tantura F sample. This latter value corresponds well with MWC data from other waterlogged shipwrecks in the Mediterranean (Capretti et al., 2008: Table 7; Pizzo et al., 2010: Table 2). A classification system proposed by Christensen (1970) and De Jong (1977), and commonly cited in the conservation literature, relates maximum water content to the degree of wood degradation. Plotting the research wood sample MWCs according to this classification system (Fig. 8) defines the Tantura F sample as Class I (400% and higher) – ‘highly degraded’ wood; while the Dead Sea samples are at the lower end of Class II (185%–400%) – ‘moderately degraded’ wood, ranging between 189% (S12) and 211% (S11); and Class III (less than 185%) – ‘non-degraded wood’, ranging between 72% (DS12) and 176% (D7a).

The relatively low MWC values of the Dead Sea samples indicate lower deterioration levels than the MWC data from the Mediterranean. There seems to be no correlation between the age of the samples from the Dead Sea and their level of decay based on MWC values ($R^2 = 0.0077$) (see Fig. 1 in Supplementary online). For example, the MWC values of the two oldest samples in the group (S19a, 2745 YBP, MWC = 161% and S12, 2580 YBP, MWC = 189%) are not much different from the MWC values of the most recent samples (D7a, 136 YBP, MWC = 176% and S14, 124 YBP, MWC = 198%). This lack of correlation within the Dead Sea sample group may suggest the presence of micro-environments within the lake in which different rates of decay may
occur (Ionescu et al., 2012), or possibly variation in the pre-depositional conditions of some of the wood used in the study.

3.3.2. Density measurements

Basic density ($D_b$) measurements quantify the degradation state of waterlogged wood. The amount of change or difference between the basic densities of the degraded wood and literature references of recent (modern) wood of the same species ($D_{bl}$) is then expressed as residual basic density (RBD) and loss of wood substance (LWS). Table 3 shows that, with the exception of sample DS12, $D_b$ values are lower than the average values of their fresh wood counterpart ($D_{bl}$). This suggests that various degrees of degradation have occurred in all the samples.

$D_b$ values of the Dead Sea samples range between 0.369 g/cm$^3$ (S11) and 0.747 g/cm$^3$ (DS12), whereas the Tantura F sample shows a significantly lower $D_b$ value (0.108 g/cm$^3$), indicating its advanced level of degradation. The highest basic density values amongst the Dead Sea samples occurred in *Ziziphus spina-christi*, which also has a higher basic density value when fresh (0.650 g/cm$^3$). Natural variations in wood density between different tree species and even within the same species, stemming from growth rates, position of sample within the tree and other factors (Schniewind, 1990:90–91; Hacke et al., 2001; Westoby et al., 2002; Chave et al., 2006), mean that calculations based on average basic density are prone to some error. Nevertheless, it is likely that the values presented here for the archaeological wood vary from the actual basic density of non-degraded wood, due to varying levels of wood degradation. The level of material loss in each of the samples relative to the average basic density of non-degraded (fresh) wood is expressed as % RBD.

In practice, RBD should be less than 100%, and LWS should have a positive value. In some samples the basic density of archaeological wood was higher than the value for non-degraded wood, i.e. the RBD was higher than 100% (DS12). Thus the LWS values were negative. These values were not taken into consideration.

Residual basic density (RBD) values vary due to the level of degradation of each sample, but also because of the initial difference in the basic density between the different wood species. Using loss of wood substance (LWS) on the other hand allows a comparison of the percentage decay rates of different tree species. The highest loss of wood substance (the greatest decay) within the research group occurred in the sample from the Mediterranean Tantura F (82.9%), the loss of wood substance of the research material from the Dead Sea (excluding DS12) is significantly lower, ranging from 9.6% (DS8) to 41.8% (S11), and averaging 28.1%.

As the deterioration of waterlogged wood proceeds, the loss of wood substance causes a drop in its basic density accompanied by increased absorption of water. These linked processes are shown by the strong correlation between MWC and $D_b$ values ($R^2 = 0.9151$) (see Fig. 2 in Supplementary online).

Sample DS12 — a carved wooden bowl fragment dated to the Late Roman period — has unusually high $D_b$ (0.747 g/cm$^3$) and low MWC (72%) values. These values, which indicate very low degradation levels, may point to a non-waterlogged origin for this object. This could be an eroding archaeological land site from which the bowl may have been washed onto the lakeshore; or a change in the physical properties of the wood caused during the production or use of this object.

3.3.3. Shrinkage

Loss of cell wall material – reflected in reduced density and increased water content – leads to a considerable loss of original strength in archaeological waterlogged wood. Upon drying such wood will thus shrink, warp and crack, depending on the level of material loss.

Shrinkage rates of a limited selection of wood samples were measured (Table 3 and Fig. 3b).

The cross-sectional shrinkage ($\beta_{cs}$), expressing the total of linear shrinkage, or expansion in some cases, of the Dead Sea samples after slow air-drying, is 2%. Radial (r) shrinkage within this group averages 0.2%; tangential (t) 1.8%; and longitudinal (l) 0.1%. Higher shrinkage rates in the tangential plane than in the radial and longitudinal planes are a common characteristic of fresh wood, and occur to varying degrees in archaeological waterlogged wood, as is the case here (De Jong, 1977:298–299; Table 1; Stamm, 1977; Schniewind, 1990:94–98). Shrinkage along the longitudinal plane in fresh and archaeological waterlogged wood is usually very small, and is often ignored. In the sample from the Dead Sea where such a measurement was possible (DS8), its value was 0.1%.

In general, the shrinkage rates of the air-dried samples from the Dead Sea are extremely low when compared to waterlogged wood finds from other marine environments. A good example of the latter is...
the highly degraded Mediterranean sample from the Tantura F. In this sample, cross-sectional shrinkage (βcs) is 53.4%, and the radial and tangential shrinkage are 34.6% and 28.8% respectively. While these values derive only from one sample, they are widely corroborated by data from other studies of waterlogged wood finds from marine sites (Schniewind, 1990: Table 4; Macchioni, 2003: Table 3).

The small number of samples available for shrinkage measurements shows that shrinkage rates, although minimal amongst the Dead Sea samples, increase with the increase of the degree of wood degradation indicated by the MWC samples (Fig. 9).

3.3.4. Ash content, mineral build-up and anti-shrinkage efficiency (ASE)

Whereas most sound woods have an ash content of less than 1 wt%, the ash content in waterlogged archaeological wood may be 10% or more (Grattan and Mathias, 1986; Fig. 9; Hoffmann, 1982: Table 2; Mikolajchuk et al., 1989: Table 1; Hedges, 1990: 137; Hoffmann and Jones, 1990: Table 2; Bettazzi et al., 2005: Tables 3–4; Babiński et al., 2014: Table 3).

At the Dead Sea, the mineral content of waterlogged wood is greatly increased by the high mineral content of the lake (ca. 30% dissolved salts), and is clearly visible in micromorphological examination of the ash content analysis of the wood samples from the Dead Sea (Table 3) indicates an average mineral content (Ash) five times higher (32.5%) than that measured in the reference samples (6.5%).

Most of these minerals migrate into the wood during its submersion in the lake, as indicated by the ash content of samples D7a (22.2%) and D11 (34.4%); both collected during dives in the lake. Additional deposition of minerals probably takes place during the exposure of the wood on the shore, similarly to the mechanism reported above (3.2.2) in coastal regions of the Ross Sea in Antarctica and the high Arctic.

The dimensional stability of the finds from the Dead Sea afforded by the soluble minerals in the wood during drying may be expressed as anti-shrinkage efficiency (ASE). This measures the effect of a specific conservation treatment on the shrinkage of waterlogged wood (Grattan and Clarke, 1987: 197–198). The ASE was obtained by comparing the average air-dried shrinkage of the wood samples from the Dead Sea with that of a set of samples from which the soluble mineral content had been removed by gradual desalination down to an average ash content (Ash Desal. 3.3%) almost to the level of the desalinated reference samples (2.9%).

The differences in the shrinkage rates between the two sets of samples after slow drying are apparent visually (Fig. 3b) and through measurements of dimensions (Fig. 10). Average shrinkage rates were much higher in the desalinated samples than in the mineral-laden material: in the radial plane — 25.0% against 0.4%; in the tangential plane — 28.9% against 2.2%; and in total average cross-sectional shrinkage — 44.8% against 2.6%. An average ASE value was 96%. This indicates that the soluble mineral content within these wood samples suppressed 96% of the shrinkage which would have been expected had it not been present in the wood.

It is generally agreed that a successful conservation treatment should attain a minimum ASE value of 75% (Morgos and Imazu, 1993: 289). For example, the ASE value measured on the Bremen Cog hull timbers after its prolonged PEG treatment was 92% (Hoffmann, 2001).

The high ASE values of the mineral saturated wood samples from the Dead Sea highlights the central role played by the mineral content of the finds on their dimensional stability upon drying.

3.4. FTIR ATR analysis

3.4.1. Dead Sea versus Mediterranean Sea

Fig. 11 shows the normalized average spectra of all the Tamarix samples. The ‘modern’ sample was dry, which explains the much lower absorbance in the 1600–1700 cm\(^{-1}\) range. Comparing the spectra of the ‘modern’ sample with that of the archaeological finds reveals the disappearance of the 1733 cm\(^{-1}\) and 1235 cm\(^{-1}\) bands in all archaeological spectra. These absorbance bands are associated with xylan C=O (Kuo et al., 1988; Bjarnestad and Dahlman, 2002; Chen et al., 2010; Lionetto et al., 2012). The absence of the 1733 cm\(^{-1}\) band in the spectra of archaeological finds was also reported by Pizzo et al. (2015). Comparison between the spectra of the Dead Sea finds and the spectrum of the Tantura F sample shows the relative decrease of all the bands associated with cellulose and polysaccharides (897, 1027, 1050, 1107, 1158 cm\(^{-1}\)) and the corresponding relative increase of all the absorbance bands associated with lignin (1120, 1230, 1266, 1327, 1460 cm\(^{-1}\)) (Petrou et al., 2009; Pizzo et al., 2013, 2015) in the latter. Lignin content relative to polysaccharides is a good indicator of the degree of bacterial attack, since bacteria predominantly decompose polysaccharides, so that the relative lignin content increases with the degree of bacterial attack (Gelbrich et al., 2008; Hoffmann et al., 1986; Troya et al., 1989a, 1989b; Kim, 1990; Blanchette et al., 1991). The results show that the Dead Sea environment greatly reduced microbial degradation of wood, compared to the more common kind of marine burial environment of the Tantura F sample. This observation is corroborated by the micromorphological analysis. In particular, other than xylan (1733 cm\(^{-1}\) and 1235 cm\(^{-1}\) bands), the polysaccharide content of the Dead Sea sample from 2597 BP (S19a) was virtually indistinguishable from that of the ‘modern’ sample.

![Fig. 10. Shrinkage. Average anti-shrinkage efficiency (ASE), and linear and cross-sectional shrinkage of wood samples after slow air-drying with and without soluble mineral content (measured at 50% RH).](image-url)
The change in the xylan shown by the ATR FTIR analysis is important in understanding the condition of the waterlogged wood. Xylan is a group of hemicelluloses found in plant cell walls. Along with lignin it fills the interstices between the cellulose microfibrils (Florian, 1987: 27–28). The chemical alterations of the hemicellulose affect the lignocellulose cell wall matrix, and are probably closely linked with the extreme shrinkage that characterizes degraded waterlogged wood (Schniewind, 1990: 95). This alteration may explain the separation of cells observed in the Dead Sea wood samples and its significant shrinkage after desalination.

3.4.2. Dead Sea — different wood types

Due to the limited number of samples, it is difficult to reach definite conclusions regarding differences between the various finds from the Dead Sea area. Fig. 12a shows the average spectra of all 11 finds.

In order to identify ranges in which the spectra of the various finds exhibited consistent significant differences, we applied principal component analysis (PCA) to all the individual spectra (rather than to the average spectra). PCA is a mathematical procedure for analyzing high-dimensional data such as mid-IR spectra (e.g. Jackson, 1991; Brereton, 2003). The information contained in the original data is condensed into a small number of ‘scores’, which are the projections of the original data onto new reference axes. Most of the information (variance) contained in the original data is reflected in the first few scores, and similarity/dissimilarity in the original data can be investigated by plotting these scores against each other and identifying score clusters.

The only spectral range found to give consistent results was 1160–1300 cm⁻¹. As shown in the Fig. 12a insert, absorbance in Ziziphus spina-christi (DS8 and DS12) is stronger at 1266 cm⁻¹ than at 1230 cm⁻¹, while in the Populus euphratica spectra (S14 and S15) the two absorbances are similar. For Tamarix (D7a, D11, S10, S11, S12, S19a, S20a), the absorbance at 1230 cm⁻¹ is stronger than at 1266 cm⁻¹, except for D11. This is verified by the three distinct clusters of PCA scores in the scatter plot in Fig. 12b. Although it would be tempting to associate the spectral differences with the wood type, this could not explain the results observed for D11. At this point, we cannot explain the observed differences, and further investigation using other measurement techniques is required.

4. Conclusions

Micromorphological, physical and chemical analyses showed less sign of biological and chemical degradation in waterlogged wood samples from the Dead Sea than in similar material from less highly saline marine environments.

The increased shrinkage rates of the wood samples from the Dead Sea after their desalination are a result of the high mineral content of the Dead Sea, the latter acts not only as an inhibitor of wood biodegradation processes, but also as an important factor contributing to the physical stability of waterlogged wood finds from the lake during their exposure and subsequent drying.

The deposition of wooden cultural heritage material in the Dead Sea, and its subsequent exposure on shore, is a two-phase process.

In the first phase, starting at the submersion of the wood in the Dead Sea, all pre-burial biodegradation processes and new microbial colonization are halted by the hyper-saline water. Although little or no biological degradation seems to have occurred in this phase, some degradation did occur, possibly through non-biological chemical reactions. This degradation is indicated by the reduced Db values, loss of wood substance (LWS), increased MWC and shrinkage rates, as well as by the absence of bands associated with xylan from ATR FTIR spectra. The latter may be linked to the separation of cells, observed by micromorphological examination, possibly through the chemical breakdown of the lignin-hemicellulose matrix. This phase is also characterized by the migration of lake minerals into the wood cells and lumens.

In the second phase, starting with the exposure of objects on shore, slow dehydration begins, and with it a gradual crystallization of the dissolved minerals within the cell walls and lumens. This process reduces or entirely prevents the shrinkage of the degraded wood as it dries. The small volume increase observed in some of the wood samples upon drying may be related to an increase in the volume of the minerals within the wood, due to their crystallization. This process seems to bring about chemical alteration of wood cells and internal cracks observed in the micromorphological analysis. Post-burial mechanical and chemical degradation processes may be continued by repeated wet and dry cycles on the lake shore, or due to uncontrolled environmental conditions in storage or display areas.

The degradation of waterlogged wood finds from the Dead Sea and the process by which they were impregnated by the lake minerals should be taken into account when they are retrieved, stored and conserved. Parameters, such as wood density and maximum water content, commonly used as guidelines in the planning of a specific conservation treatment of a waterlogged wood object, should be considered together with other data, such as the object’s mineral content and storage environment. An attempt to wash the minerals out of waterlogged wood finds from the lake intentionally or accidently by storing them in low
salinity water – a common practice when dealing with newly retrieved marine finds – will remove the salts from the wood and eliminate its stabilizing properties. On the other hand, leaving the minerals in the wood may lead to gradual breakdown through mechanical and chemical processes driven by uncontrolled storage and display environments.

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Fig. 12. Spectra. a) Average normalized spectra of all archaeological finds. Solid lines correspond to Tamarix samples, dashed lines correspond to Populus samples, and dotted lines correspond to Ziziphus samples (see Table 1 for details of each sample). The insert shows the 1100–1300 cm$^{-1}$ region in more detail. b) Scatter plot of the PCA scores of all the spectra. PCA was applied to the 1160–1300 cm$^{-1}$ interval.


