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Conservation of waterlogged archaeological corks using supercritical CO_2 and treatment monitoring using structured-light 3D scanning

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ABSTRACT

Archaeological waterlogged cork is one the most unpredictable archaeological materials to conserve. Over the years, various techniques designed to conserve waterlogged wood have been applied to cork with less than satisfactory results. These techniques include freeze drying with or without consolidant, air-drying and silicone oil treatment. Alternatively, recent studies demonstrated that methanol exchange followed by supercritical CO_2 drying can overcome most of the limitations of the latter techniques when applied to organic waterlogged materials. In 2005, a joint research project was initiated between the Warren Lasch Conservation Center (WLCC) and Parks Canada to evaluate the use of supercritical CO_2 drying on significant archaeological corks and composite artifacts from several shipwrecks. This paper will discuss the drying process of the various corks and the techniques employed to monitor their appearance and dimensions, namely conventional measurement techniques and structured-light 3D scanning combined with three-dimensional inspection.

1. Introduction

Waterlogged archaeological organic materials have been reported to be challenging to conserve due to the critical step of drying the artifacts [1–3]. Conservation of waterlogged wood has been extensively reported, however, only few accounts have discussed successful stabilization of archaeological cork without extensive shrinkage upon drying [2,4].

As hygroscopicity increases, the cellular wall structure of cork becomes waterlogged and starts to deteriorate making it susceptible to shrinkage and collapse from drying stresses during stabilization. In addition to the water-saturation, deterioration due to microbial action is known to occur, rendering conservation even more challenging. As long as the waterlogged material is kept wet, it will retain its shape. If air dried, it cannot redistribute the internal moisture properly due to capillary tension engendering collapse and shrinkage of the material. In addition, degraded waterlogged wood and cork exhibit strength loss due to decomposition of the main polymeric structural components. Therefore, stabilization treatments must be tailored to not only control dimensional changes due to collapse and shrinkage but also to improve strength and stiffness of the material. Most of the time, conservation of waterlogged wood can be classified into two groups. One consists of dehydrating the wood prior to treating it with a consolidant. As the dehydration step commonly involves solvent exchange, treatment time increases with the artifact size. Therefore, such a process is limited to small artifacts. The second group, which is employed with larger objects, requires the injection of a consolidant prior to dehydration. Most consolidants utilized in the conservation field are oligomeric water soluble compounds which are introduced into the wood by diffusion, a time consuming process. Challenges in cork conservation have been attributed to its impermeability to consolidants [2,3]. The latter, such as polyethylene glycol (PEG), do not readily penetrate the cork's internal structure as they do in degraded waterlogged wood. Such difficulties in cork stabilization may be attributed to the elevated amount of highly hydrophobic suberin contained in cork cell walls.

As a part of the plant constitutive defense system, cork tissue is made of multiple corrugated cell layers. While effective at keeping wine inside a bottle, the most important function of cork in plants is to act as a diffusion barrier for water and other small, polar compounds. Cork cells are made impervious mostly by the deposition of suberin onto their walls. Indeed, the key compound for cork impermeability is suberin, a complex polymer comprising both poly(phenolic) and poly(aliphatic) domains [5–7]. The chemical composition of cork has been widely analyzed by chemical fractionation and showed to be quite different from that of wood [8,9]. Although the amounts of the different components can show significant variations [10,11], on average it contains 15% extractives (7.5% waxes and 7.5% tannins), 41% aliphatic suberin (referred to as

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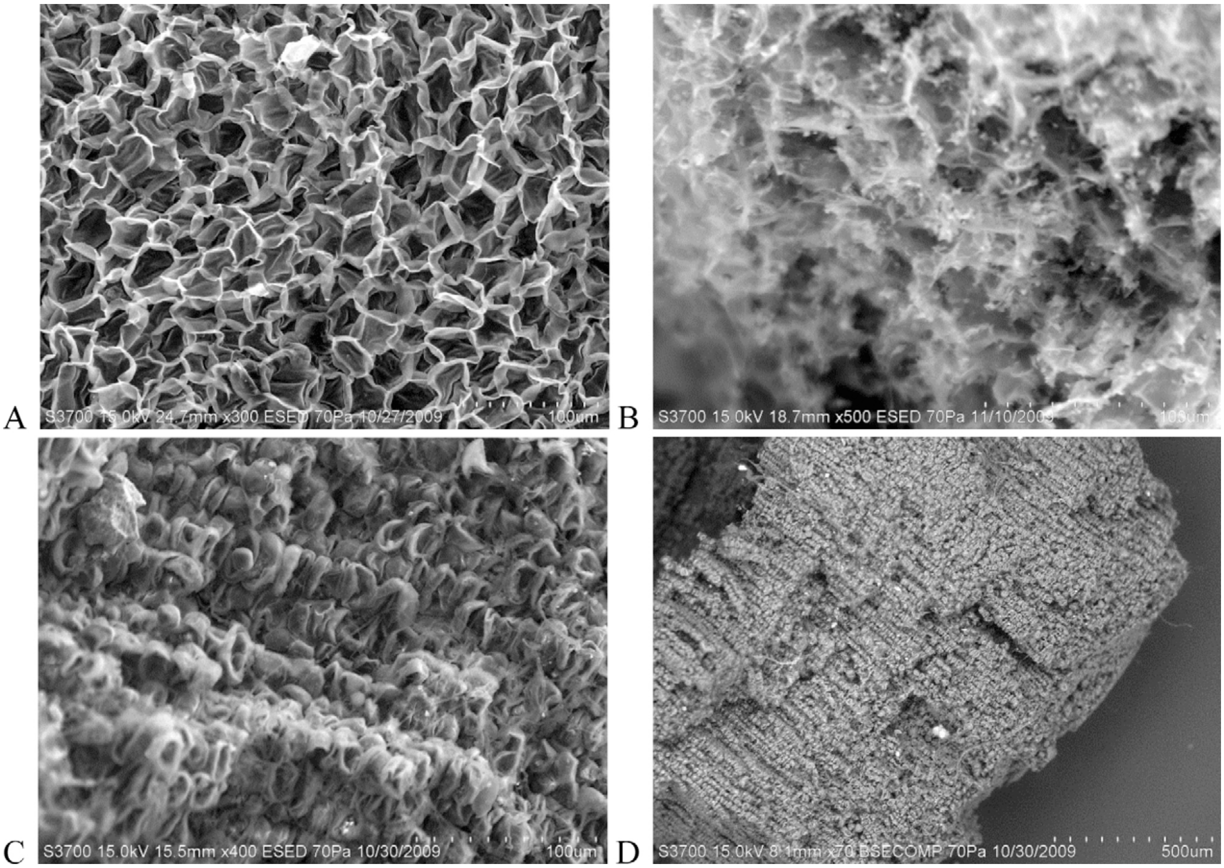

Fig. 1. Scanning electron micrographs of cork cell structure. (A) Non-degraded cork; (B) San Juan degraded cork fragment (wet state); (C and D) San Juan degraded cork fragment (dried).

suberin in cork tree literature), 22% aromatic suberin (referred to as lignin in cork tree literature), 20% polysaccharides, and 2% ash [10]. In addition, the cork internal structure, which has been described as an alignment of closed unit cells [12,13], could be another culprit for the unsuccessful diffusion of consolidants into cork as it can be observed in Fig. 1.

Over the years, various conservation techniques designed for waterlogged wood have been applied to cork with less than satisfactory results [2]. These techniques include air-drying with or without pretreatments at various concentrations of PEG, silicone oil, consolidation using acetone/rosin treatments, and vacuum freeze-drying with or without prior PEG consolidation. All these techniques have been investigated and have invariably resulted in unacceptable shrinkage and distortion [2–4]. Alternatively, recent studies demonstrated that methanol exchange followed by supercritical CO_2 drying – a process which will be simply referred to as SC-CO_2 drying in the following text – can overcome most of the limitations of these techniques when applied to organic waterlogged materials [3]. A joint research project was initiated between the WLCC and Parks Canada to evaluate the use of supercritical CO_2 drying on significant archaeological corks from several shipwrecks including the *Machault* (1760) [14] and the 16th century Basque whaler *San Juan* (1565), as shown in Fig. 2A and B, respectively. This successful collaboration was followed by the conservation of fragile waterlogged corks recovered from the Civil War era *H.L. Hunley* submarine (1864) and a waterlogged cork still encased in a glass bottleneck found during the *Queen Anne's Revenge* (1718) shipwreck excavation. This paper will discuss the drying process of the various corks, with a particular focus on the corks from the *San Juan*. In addition, monitoring of their appearance and dimensions was conducted using conventional measurement techniques and structured-light 3D scanning combined with three-dimensional inspection.

2. Materials and methods

2.1. Parks Canada experimental specimens

In 2005, Parks Canada provided eight wine bottle cork specimens from the site of the *Machault*, a French frigate that sank on July 8, 1760 at the mouth of the Restigouche River, at the far end of Baie des Chaleurs, Quebec, Canada [15]. Marine archaeologists from Parks Canada excavated the site between 1969 and 1972. The underwater environment surrounding the wreck was brackish water with temperatures ranging from 5 °C to 18 °C. The wreck was partially exposed and laid under about 2–8 m of water depending on the tides, which engendered extensive sediment movement on the site. For some 10 years after the excavation, the corks were stored in 1% phenol aqueous solution at room temperature in order to slow down microbiological activity. Subsequently, the corks were stored in water only, and kept refrigerated (±5 °C). The water in the storage containers was changed every five years. The cork specimens and their identification numbers are shown in Fig. 2A, as received from Parks Canada.

In 2007, Parks Canada provided eight additional cork artifacts excavated from the site of the *San Juan*, a Spanish Basque galleon that sank in the autumn of 1565 in Red Bay, Southern Labrador, Canada [16]. Marine archaeologists from Parks Canada excavated the site between 1979 and 1985. The whaler was discovered completely covered with sediment at a depth of approximately 10 m, in an excellent state of preservation. The underwater environment of the wreckage was sea water with temperatures ranging from