PNAS Nexus, 2023, 2, 1–9
https://doi.org/10.1093/pnasnexus/pgad344
Advance access publication 21 October 2023
Research Report

A key to wine conservation lies in the glass–cork interface

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Edited By: Adelia Bovell-Benjamin

Abstract

This study investigates the evolution of the oxygen barrier properties of the bottleneck–stopper system under conditions simulating the conservation of wine in the bottle (presence of model wine, storage position, and temperature) over a long aging period of 24 months. The results highlighted that the oxygen diffusion coefficient of the stopper alone is not modified regardless of the storage conditions. At 20°C, the presence of model wine favors oxygen transfer at the glass–cork interface, accounting for nearly 75% of total oxygen transfer in comparison to cork studied without model wine. Yet, the position of the bottle during storage, vertical (i.e. cork in contact with the vapor phase of the model wine) or horizontal (i.e. cork in contact with the liquid phase), does not influence the oxygen transfer. At higher storage temperatures (35 and 50°C), the barrier properties of the bottleneck–cork system remain stable up to 9 and 3 months, respectively. After this period, an alteration of the barrier properties is observed with an increase of the transfer at the glass–cork interface.

Keywords: gas transfer, oxidation, agglomerated cork, interface, aging

Significance Statement

The shelf-life of bottled wines, intimately linked to cork-based closures, is a major concern in the wine industry. Premium wines reach organoleptic optimum after aging periods ranging from a few months to likely several years or decades. This work demonstrates that the glass–cork interface is a major pathway for oxygen entry into the bottled wines. Neither the temperature nor the position of the bottle—horizontal or vertical—has an impact on the intrinsic oxygen diffusion property of microagglomerated corks after 24 months of storage. However, high storage temperature strongly increases the oxygen transfer at the glass–cork interface.

Introduction

The aging potential of wine in bottle is firstly related to its intrinsic molecular composition and, in particular, its antioxidant metabolome (1). The bottle is secured by wine stoppers, used to protect the wine from oxidation. However, controlled low oxygen intakes are usually required for the wine to evolve and reach its optimal organoleptic characteristics (2). While the detrimental effects of excessive exposure are well established, determining the amount of oxygen required for a given type of wine would still represent a considerable step toward improving wine quality (3). The aging potential of wines is intimately conditioned by storage environmental parameters, particularly the temperature (4). Various studies have demonstrated that an increase in temperature tends to accelerate chemical reactions associated with wine aging, such as anthocyanin degradation, ester hydrolysis, or the formation of oxidative aromas (5, 6). Empirically, it is considered that wines should be stored at temperatures around 12–16°C. Yet, there are different situations where bottles of wine can experience much higher temperatures, such as inside shipping containers where fluctuations up to 20°C can lead to noticeable changes in the wine (7–9). In addition, recent studies have shown that vibrations experienced during bottle transport can also impart sensory modifications (10). Furthermore, the relative humidity of the environment is thought to have a particular influence on the aging of wine in the bottle, although its effect is still not fully understood. It indeed acts on the mechanical and barrier properties of the cork (11), and although relative humidity above 50% is required for good elasticity of cork-based closures (12), a relative humidity above 80% has been found to increase risk of mildew formation on the outer surface of cork (13). The light exposure of the wine through the bottle also induces substantial changes to the wine (14, 15). Green-colored bottles provide a greater protection to the wine than the uncolored bottles, although they do not totally prevent color change induced by light (16, 17). Extreme storage conditions, in contrast to the traditional conservation of wine in bottle, also lead to a particular evolution of wines. This was demonstrated with bottles of Champagne wine from a shipwreck that had been immersed in the sea. The analyses performed revealed a

Competing Interest: The authors declare no competing interest.
Received: July 22, 2023. **Accepted:** October 1, 2023

good preservation of the organoleptic quality of Champagne over nearly two centuries, thus highlighting the intrinsic qualities of a vibration-free, anoxic, and isothermal marine environment for the long-term preservation of wine (18).

Historically, natural corks extracted directly from the outer bark of the cork oak have served to secure wine bottles, with the earliest evidence of cork being used as a sealing agent dating back to Roman ages (19). Today, natural cork stoppers still account for nearly half of the wine closure market (20). In addition, a variety of stoppers are now available on the market including cork-based, synthetic, and glass stoppers as well as screw caps, each type offering different oxygen barrier properties (11, 21, 22). The transfer of oxygen from the outside environment to the wine in the bottle can be broken down into different variables: a transfer through the stopper alone and a transfer at the interface between the cork stopper and the glass bottleneck. An additional contribution to oxygen transfer also originates from the internal structure of the cork due to its compression after bottling. A recent study has highlighted that the interface between the cork stopper and the glass bottleneck plays a significant role in the transfer of oxygen inside the wine bottle (23). This transfer at the glass–cork interface is subject to several parameters, such as the mechanical properties of the stopper (i.e. the force applied by the stopper on the glass surface), the geometry of the stopper and the bottleneck, the surface roughness of both the stopper and the glass, and the presence of a coating on the stopper surface. This surface treatment is an essential parameter in the control of oxygen transfer because it significantly reduces the transfer at the glass–cork interface to the same level as a stopper alone (23). Moreover, the storage conditions (temperature, humidity, storage position, alcohol content, and initial oxygen concentration) likely have an influence on the aging of the cork stopper and its surface treatment.

This raises the question of how the oxygen transfer through the bottleneck–cork system will evolve over time and under different storage conditions. While a few studies on this topic are available in the literature (24–26), no comprehensive, long-term investigations have been conducted to our knowledge. Therefore, a systematic study on the evolution of oxygen transfers through microagglomerated stoppers was carried out over a long period of 24 months and under very diverse conditions. It allowed to differentiate the evolution of oxygen flow over time through the stopper and at the glass–stopper interface. This work provides answers to practical questions (influence of the presence of model wine, storage position, or temperature), which are of interest to both the producer and the consumer, and is based on scientific concepts that were not yet explored in this field.

Results and discussion

Initial barrier properties of cork

Prior to the aging test, the initial oxygen diffusion coefficients through the cork and through the glass bottleneck–cork system were determined. The results are displayed in Supplementary material S1. The values of the oxygen diffusion coefficient for a 6-mm compressed wafer alone ($D_{stopper}$) ranged from 10^{-10} to 10^{-12} m^2 s^{-1}, with an average value around 1.6×10^{-11} ($\pm 0.5 \times 10^{-11}$) m^2 s^{-1}. This value lies in the same range as that already reported in previous work on similar agglomerated stoppers (23). In the case of a wafer compressed in a bottleneck, i.e. considering the gas transfer at the glass–cork interface, the experimental values of the oxygen diffusion coefficient (D_{total}) also lie between 10^{-10} and 10^{-11} m^2 s^{-1}, with an average value around 2.3×10^{-11} ($\pm 0.7 \times 10^{-11}$) m^2 s^{-1}. It is noteworthy that the oxygen diffusion coefficient of the stopper compressed in the glass bottleneck is significantly higher than that of the compressed stopper alone (Supplementary material S1). Therefore, this result suggests that part of the oxygen transfer initially takes place at the interface between the stopper and the bottleneck, corresponding to more than 30% of the total oxygen transfer.

Effect of aging on the oxygen transfer through the cork stopper alone

The oxygen diffusion coefficient through the cork stopper alone was determined for the five storage conditions after 3, 6, 9, 12, 18, and 24 months (Fig. 1). The mean values of the oxygen diffusion coefficient are also reported in Supplementary material S1. These values refer to the oxygen transfer occurring through the cork stopper alone, without considering the transfer at the interface between the cork stopper and the glass bottleneck. Ninety-five percent of the oxygen diffusion coefficients measured on wafers alone ($D_{stopper}$) over 24 months for all the conditions studied lies within the shaded area in Fig. 1. It is remarkable that, regardless of the storage conditions, the values of the oxygen diffusion coefficient through the cork stopper alone remain similar over the 24-month period. The average value is around 1.3×10^{-11} ($\pm 0.6 \times 10^{-11}$) m^2 s^{-1}. Thus, even after 24 months of storage, the oxygen barrier properties of the cork stopper alone are unchanged. There is no significant effect of the presence of model wine, the storage position, or the storage temperature on the diffusion coefficient of oxygen. A slightly higher diffusion coefficient value can be noticed, however, for the samples stored without model wine on average (Fig. 1, violet bars). This difference may nevertheless be attributed to the intrinsic variability of the material, as the data were similar to those of the initial reference and remained within the 95% data distribution. This highlighted the remarkable stability of the stoppers over time, at least in terms of their intrinsic oxygen barrier properties, under all storage conditions.

It may be noted that, concerning the samples stored at 50°C (Fig. 1, green bars), the measurements were stopped after 6 months of storage because the model wine contained in the bottleneck had completely evaporated and thus no longer reflected the initial storage conditions.

Impact of aging on the oxygen transfer at the glass–cork interface

Evolution of the barrier properties in the absence of wine

The effect of aging was then evaluated focusing on the cork compressed in a bottleneck without model wine. Oxygen transfers occurring both through the cork and at the glass–cork interface were considered. After 3, 6, 9, 12, 18, and 24 months of storage, the corresponding global oxygen diffusion coefficients for the cork compressed in the bottleneck were similar to that of the initial reference (Fig. 2, violet bars). The observed variations were mostly related to the variability of the raw material itself rather than to aging. An average value of all the diffusion coefficients in a single distribution over the period of 24 months was thus used thereafter as the reference for the condition without model wine, both for the intrinsic cork value and for the total value (cork + glass–cork interface). This gave an oxygen diffusion coefficient for the stopper alone and for the cork stopper compressed in the bottleneck of 1.9×10^{-11} ($\pm 0.6 \times 10^{-11}$) m^2 s^{-1} and 3.0×10^{-11} ($\pm 0.9 \times 10^{-11}$) m^2 s^{-1}, respectively. These values remained in the same range

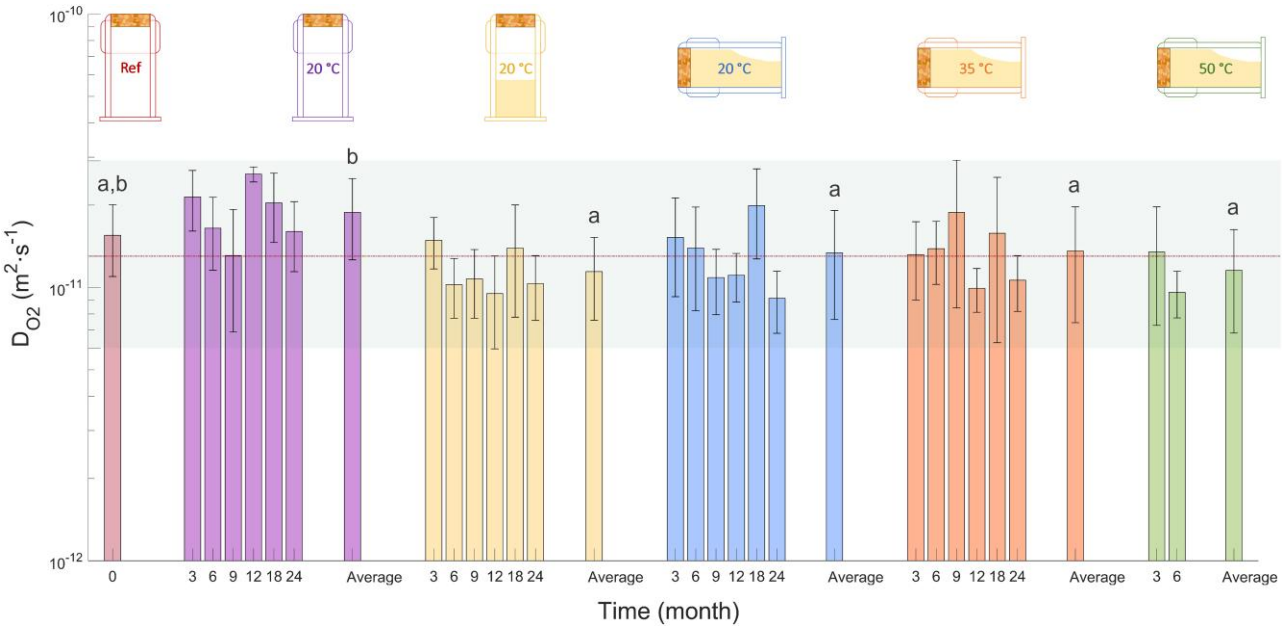

Fig. 1. Evolution of the oxygen diffusion coefficient through compressed cork alone after storage in the different conditions over 24 months determined by experimental data measured on 6-mm compressed cork wafers. Red: reference without model wine. Violet: storage at 20°C without model wine. Yellow: storage at 20°C with model wine and vertical position. Blue: storage at 20°C with model wine and horizontal position. Orange: storage at 35°C with model wine and horizontal position. Green: storage at 50°C with model wine and horizontal position. Shaded area: 95% distribution corresponding to all conditions. One-way ANOVA test was carried out on the average values for each condition. Significant differences ($P < 0.05$) are indicated with different letters (a, b).

as that of the reference at time 0. Moreover, the oxygen diffusion coefficient measured on the stopper compressed in the glass bottleneck was higher than that of the compressed stopper alone (without considering the transfer occurring at the interface with the glass bottleneck). This indicates, again, that part of the oxygen transfer occurred at the glass–cork interface. It shows a significant contribution of the oxygen transfer at the interface, accounting for 35% of the total transfer (Supplementary material S1). This proportion of the transfer occurring at the glass–cork interface remains globally unchanged over time for this condition without model wine.

Influence of the presence of wine and of storage position

Thereafter, the effect of the presence of model wine and of the storage position of the wine bottles (vertical position or horizontal position) on the gas transfer through the glass bottleneck–cork system was determined at a storage temperature of 20°C over 24 months (Fig. 2, yellow and blue bars). In the presence of model wine, the total oxygen diffusion coefficient for the bottleneck–stopper system was significantly higher after 3 months of storage. The values obtained for vertical and horizontal storage with model wine (6.7×10^{-11} and 4.6×10^{-11} $m^2\ s^{-1}$, respectively) are nearly doubled compared with the condition without model wine (3.0×10^{-11} $m^2\ s^{-1}$). As reported previously, the oxygen diffusion coefficient through the cork alone did not change whatever the storage conditions. Thus, between 0 and 3 months of storage, the presence of model wine favored the oxygen transfer at the interface between the stopper and the bottleneck. However, after 3 months, there was almost no change in the oxygen diffusion coefficient for samples stored at 6, 9, 12, and 18 months. Although the 24-month vertically stored samples seem to show a higher value of the total oxygen diffusion coefficient, it is noteworthy that it remained within the same log, contrary to the unambiguous effect of temperature, as further described. Such an increase of the oxygen diffusion coefficient after 3 months in the presence of model wine could be attributed to the sorption of water and ethanol in the cork, which could favor the surface diffusion between the polymer chains composing the cork (27–29). This phenomenon could also be due to a modification of the mechanical properties of the cork, promoting the transfer at the glass–cork interface. Indeed, the cork stoppers used were initially relatively dry (stored at 20°C and 50% relative humidity), and they became progressively hydrated once placed in contact with the model wine, whether in the vapor or in the liquid phase. Cork hydration has been shown to impact its mechanical properties, with a significant decrease in the Young's modulus to half of the initial value between 50 and 100% relative humidity. For high water sorption rates, water molecules aggregate around hydrophilic sites to form clusters that tend to plasticize the material (12, 30). Consequently, it can be assumed that the force applied to the glass surface walls of the bottleneck by the stopper decreases as the material is hydrating, thus resulting in an increase in the oxygen transfer at the glass–cork interface. Once the sorption equilibrium of water and ethanol on the cork is reached, a relative stability of the diffusion coefficient should then be observed over the following months.

Moreover, two positions for storage were studied: "vertical storage," corresponding to the stopper in contact with the vapor phase, and "horizontal storage," corresponding to the stopper in contact with the liquid phase. The values of the diffusion coefficient of total oxygen D_{total} for the two different storage positions were similar on average. Therefore, the storage position of the bottle had no significant influence on the oxygen transfer, neither through the cork (as previously reported) nor through the glass–cork interface. These observations prevailed for all durations measured (3 to 24 months) for these two conditions. In the literature, the question of the impact of the storage position of the bottles (vertical or horizontal storage) was not settled, with studies

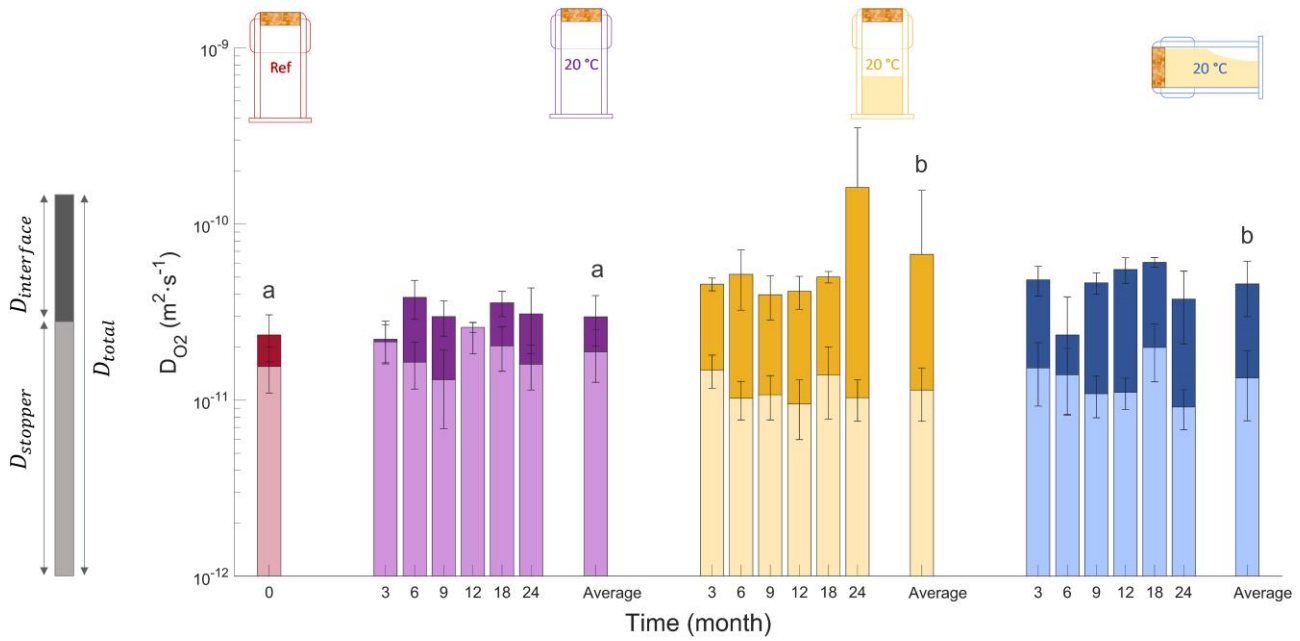

Fig. 2. Evolution of the oxygen diffusion coefficient through compressed cork alone ($D_{stopper}$) and through cork compressed in a bottleneck (D_{total}) over 24 months, determined by experimental data measured on 6-mm compressed cork wafers alone and compressed in the glass bottleneck. Red: reference without model wine. Violet: storage at 20°C without model wine. Yellow: storage at 20°C with model wine and vertical position. Blue: storage at 20°C with model wine and horizontal position. Data are displayed as the sum of the diffusion coefficient through the cork alone (light color) and the diffusion coefficient at the interface (dark color). One-way ANOVA test was carried out on the average values of D_{total} for each condition, and significant differences ($P < 0.05$) are indicated with different letters (a, b).

giving divergent results (24, 31, 32). Using a colorimetric method, Lopes et al. followed the oxygen transfer through bottles corked with different stoppers, stored either in vertical or in horizontal position. After 24 or 36 months of storage, depending on the storage position, their results showed that there was no significant effect of the storage position on oxygen transfer. These results agreed with those obtained in a more recent study by Hirlam et al. (8) where similar values of oxygen transmission rate (OTR) were reported for bottles corked with microagglomerated stoppers and stored either vertically or horizontally. Conversely, another study by Venturi et al. on red wines stored in bottles showed that the different storage conditions affected

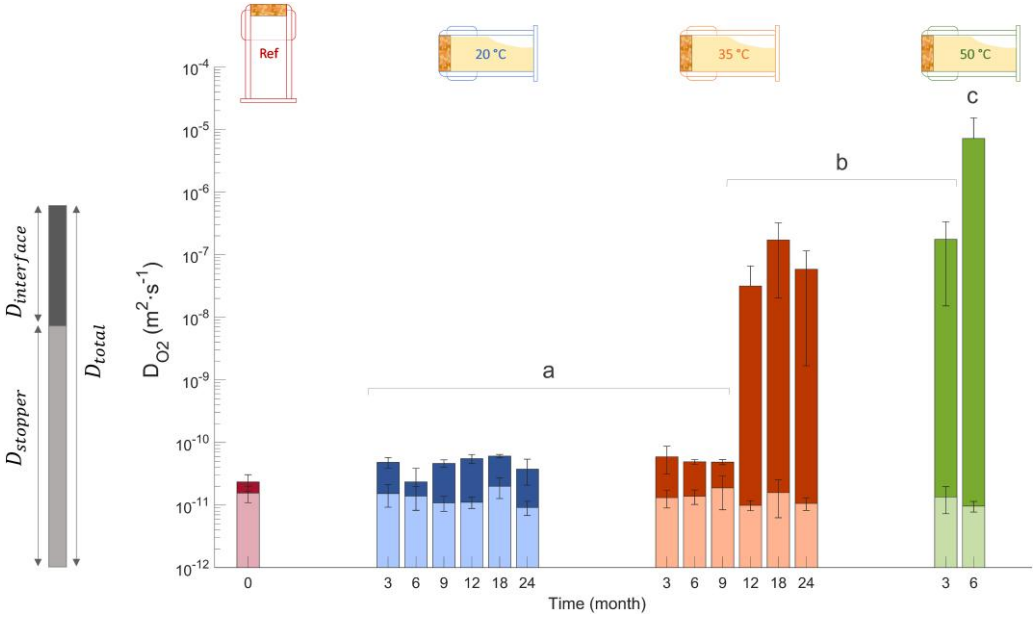

Fig. 3. Evolution of the oxygen diffusion coefficients through cork alone ($D_{stopper}$) and through cork compressed in a bottleneck (D_{total}) over 24 months determined by experimental data measured on 6-mm compressed cork wafers alone and compressed in the glass bottleneck. Red: reference without model wine. Blue: storage at 20°C with model wine and horizontal position. Orange: storage at 35°C with model wine and in horizontal position. Green: stored at 50°C with model wine and horizontal position. Data are displayed as the sum of the diffusion coefficient through the cork alone (light color) and the diffusion coefficient at the interface (dark color). Kruskal–Wallis test was carried out on the D_{total} values for each condition and at each time, and significant differences ($P < 0.05$) are indicated with different letters (a, b, and c).

the quality of the wine. These results showed that there was a slowing of the oxidation of the red wine during the bottle storage in horizontal position for a period of 12 months. The present study clearly established through a systemic approach that the storage position of the wine bottles during a 24-month aging period at 20°C did not have an impact on the oxygen transfer through the bottleneck–cork system, neither through the cork itself nor at the interface with the glass.

Effect of temperature

The effect of storage temperature was studied with samples where the model wine was in contact with the cork stopper (horizontal position). At 20°C, the oxygen diffusion coefficients D_{total} and $D_{stopper}$ remained unchanged from 3 months up to 24 months of storage (Fig. 3, blue bars). At 35°C, these two diffusion coefficients were similar to those measured at 20°C but only for up to 9 months of storage. At 12 months, a sharp increase of the total oxygen diffusion coefficient was observed (from 5.2×10^{-11} to 3.5×10^{-8} m^2 s^{-1}) while the diffusion coefficient through the stopper $D_{stopper}$ remained unchanged. Such an increase is thus obviously due to a significant transfer at the glass–stopper interface. Finally, for the samples stored at 50°C, a tremendous oxygen transfer occurring at the glass–cork interface was noticeable, even from 3 months, with a value for the total diffusion coefficient around 1.8×10^{-7} m^2 s^{-1} and a diffusion coefficient through the stopper which was not modified. This phenomenon was further accentuated after 6 months, until reaching a value (D_{total} $= 7.2 \times 10^{-6}$ m^2 s^{-1}) approaching the diffusion coefficient of oxygen in the air ($D = 2.0 \times 10^{-5}$ m^2 s^{-1}), which indicated the presence of leakage at the glass–cork interface (33).

The appearance of leakage at the glass–cork interface could be attributed to a change in the mechanical properties of the stopper, leading to a weaker force applied by the stopper on the glass of the bottleneck. Another hypothesis that can also be suggested to explain an oxygen transfer very close to a leakage would be related to the behavior of the surface treatment product. A high storage temperature of 50°C could induce the partial melting of the surface treatment agent applied to the external surface of the cork stopper. Indeed, this coating is composed of paraffin and silicon. Complementary measurements carried out by differential scanning calorimetry (Supplementary material S2) showed a first endothermic peak around −42°C and a second large peak starting around 20°C and ending around 70°C during the first heating cycle. The first thermal event can be attributed to the melting of the silicone oil contained in the surface treatment product (34). The second thermal event was composed of a first peak at around 45°C and a second one with a maximum at 64°C (35). This corresponds to the melting of the different paraffins contained in the product (36). In addition, the liquid:solid ratio can be determined according to the temperature. At a storage temperature of 20°C, the liquid:solid ratio of the coated product was estimated as 6%, whereas at 35°C, it increased up to 19 and 41% at 50°C. At storage temperatures of 35 and 50°C, the partial melting of the coating agent on the surface of the stopper could therefore favor oxygen transfer at the interface between the cork stopper and the bottleneck. Lastly, a change in the mechanical properties over time could also be a factor promoting capillary rise of wine at the glass–cork interface.

Conclusion

The evolution of the oxygen barrier properties of microagglomerated cork-based stoppers was studied over a long period of storage of 24 months mimicking various conditions of the conservation of wine in bottle. It is first remarkable that, even after 24 months of aging, the oxygen diffusion coefficient of the cork wafer alone was not modified, whatever the storage conditions. Temperature, storage position, and the presence of model wine did not impact the barrier properties of the cork stopper alone. In contrast, the total oxygen transfer, which includes not only the oxygen transfer through the stopper but also the oxygen transfer at the glass–cork interface, was modified by the presence of model wine. The total diffusion coefficient increased from 2.3×10^{-11} to 4.7×10^{-11} m^2 s^{-1} after the three initial months of storage at 20°C, considered here as ambient temperature in the case of bottles kept on shelves (for example, in supermarkets). This leads to a transfer at the glass–cork interface accounting for nearly 70% of the total oxygen transfer. The storage position ("vertical storage" corresponding to the stopper in contact with the vapor phase or "horizontal storage" for the stopper in contact with the liquid phase) did not modify the oxygen transfer. Once the sorption equilibrium of cork with water and ethanol was reached within the three first months of storage (which corresponds to the first analysis period in this study), the barrier properties of the bottleneck–cork system did not change during the following months. Finally, temperature also had a strong impact on the oxygen transfer of the stopper in the bottleneck. At a storage temperature of 20°C, the oxygen barrier properties remained unchanged over 24 months of aging. However, at 35°C, a temperature easily reached during bottle shipping, while total oxygen transfer did not increase significantly for up to 9 months; beyond this duration of storage, a significant transfer at the glass–cork interface started to occur. This could be attributed to a partial melting of the surface treatment agent or to a modification of the mechanical properties of the stopper. At 50°C, this shift already occurs within the first 3 months of storage.

Altogether, our results provide unprecedented representation of the impact the glass–cork interface on the shelf-life of bottled wines, in controlled conditions. Before transferring these results to real wine bottles and get a comprehensive model of oxygen transfer in real situation, other parameters need to be more deeply investigated, including the hydration state of the full-length stopper, the evolution of its mechanical properties, and the relation with the diffusion mechanisms involved. However, a comprehensive description of the aging capability of genuine bottled wine still requires that the oxidative stability, which is its intrinsic capacity to withstand oxygenation while developing to an organoleptic optimum, is characterized.

Materials and methods

Cork stoppers

Microagglomerated cork stoppers (of the type Diam 5) were produced by Diam Bouchage (Céret, France) by a molding process using cork particles associated with binding agents. The stoppers used for the experiments were 24.2 mm in diameter and 49 mm long. They were coated with a single-layer surface treatment product composed of an emulsion of paraffin and silicone.

Model wine

A model wine solution was prepared with the following composition: DL-malic acid (2.5 g L^{-1}), potassium sulfate (0.1 g L^{-1}), magnesium sulfate (0.025 g L^{-1}), and acetic acid (0.1 g L^{-1}) (37). This model wine was adjusted to an ethanol concentration of 12.5% (v/v). It was then set to a pH of 3.5 with a potassium hydroxide

solution (2 mol L^{-1}). It was inerted using nitrogen bubbling to remove dissolved oxygen before use.

Sample preparation

For the experiment, miniaturized bottle systems were designed. To that purpose, full-length stoppers were first inserted in a "CETIE" glass bottleneck (CevaQoe, France), using a professional bottling machine with four stainless steel jaws (GAI 4040WL, France). Bottlenecks were obtained from wine bottles cut at 70 mm from the top of the bottleneck. Prior to bottling, each bottleneck profile was measured to ensure they complied with the corresponding standard (38). Cork stoppers were then pulled 43 mm out of the bottleneck using a TAX-HD+ texturometer (Swantech). They were cut to keep a 6-mm-thick cork wafer inside the bottleneck. This thickness allowed the time of the permeation experiment to be reduced while still being representative of a microagglomerated stopper (39). The surface treatment was therefore located on the periphery of the cork and on the surface in contact with the model wine.

Final sample preparation steps were performed in an inert atmosphere (Atmosbag, Sigma-Aldrich) using argon (Alphagaz 1, Air Liquide). Corked bottlenecks without model wine were directly closed with a circular glass plate (glued with an epoxy adhesive, Araldite 2011 bicomponent, Huntsman) to prevent gas transfer between the bottom of the bottleneck and the glass plate. For cork samples in contact with the model wine, 10 mL of model wine was added before closing the bottom part of the bottleneck with the glass plate. In this closed system, the residual oxygen pressure in the bottleneck was initially between 5 and 7 hPa for all samples. Seven miniaturized systems were prepared for each condition and for each analysis time.

Storage conditions

The selected conditions for the aging of the samples are summarized in Fig. 4A. To evaluate the effect of the wine on the oxygen barrier properties of the cork material, the stoppers were stored in the absence or in the presence of the model wine solution. In addition, the bottle position was varied to mimic vertical or horizontal bottle storage (either in contact with the vapor phase of the model wine or in contact with the liquid phase, respectively). To assess the effect of the storage temperature during aging, three storage temperatures were also studied: 20, 35, and 50°C. The two higher temperature conditions were applied for the samples in the "horizontal" position only. This aging test was performed over 24 months. An external relative humidity of 50% was chosen for aging under controlled hygrometry conditions. This corresponds to a storage under ambient conditions for temperate countries. The different storage conditions, with the corresponding scheme, are presented in Fig. 4B.

The total number of individuals for this study was nearly 150, with an average of five measurements for each analysis time and storage condition. It included six different times of analysis (3, 6, 9, 12, 18, and 24 months) and five different storage conditions (without wine model at 20°C, with wine model at 20°C stored vertically, with wine model at 20°C stored horizontally, with wine model at 35°C stored horizontally, and with wine model at 50°C stored horizontally).

Oxygen permeation

Oxygen permeation measurements were performed in two trials: first, on the cork wafer inserted in the bottleneck and then, second, on the cork alone. For the first experiment, the bottleneck was inserted into a metal ring, and the part between the ring and the bottleneck was glued with Araldite 2011. For the second experiment, the cork wafer alone was placed into a metal ring, and the interface between the cork and the metal was glued to prevent any gas transfer at the interface. The homemade equipment and the protocol used for oxygen transfer measurement have been detailed in previous works (27, 39, 40). In brief, the oxygen flow was measured through a sample separating two chambers. First, an oxygen purge was performed in the measuring chamber equipped with a pressure sensor.

The pressure of the measuring chamber was then set to an initial value depending on the experiment while the other chamber was kept under dynamic vacuum (0.1 hPa). In the first experiment with the cork wafer compressed in the bottleneck, the initial oxygen pressure was set to 600 hPa, to prevent the cork wafer from coming out of the bottleneck. For the second experiment with the cork wafer alone, the initial pressure was fixed at 900 hPa. The decrease in oxygen pressure in the measuring chamber, caused by the transfer of oxygen through the sample, was monitored over time. The temperature was kept constant at 20°C (±1°C) by water circulation surrounding the measuring chamber. The pressure sensitivity was ±0.1 hPa. The oxygen permeation measurements were performed on at least four replicates per condition and per analysis time. The measurements were destructive and carried out on different samples for each time of analysis.

It is noteworthy that the determination of oxygen transfer by such a manometry method does not allow an in situ measurement of the oxygen diffusion coefficient through the samples during the storage. The measurements were carried out on samples after removal of the glass plate and the model wine (i.e. on samples which were not in equilibrium with saturated water and ethanol vapors anymore). However, since the desorption rates of water and ethanol were quite slow, the conditions for measuring the diffusion coefficients could be considered very close to those of storage (28, 29).

Model used for oxygen transfer

From oxygen permeation experiments, effective diffusion coefficients were determined.

Oxygen diffusion through the cork stopper alone

The phenomenon of permeation is classically described as a three-step mechanism: (i) firstly, sorption of gas molecules on the surface of the material; (ii) secondly, diffusion through the material according to the concentration gradient; and (iii) lastly, instantaneous desorption from the other surface of the material.

Considering the gas as ideal, the surface molar flow of oxygen passing through the cork wafer, $J_{stopper}$ (mol m^{-2} s^{-1}) is given by Eq. 1:

$$J_{stopper} = -\frac{1}{S_w}.\frac{dn}{dt} = -\frac{V}{S_w.R.T}.\frac{dp}{dt}, \quad (1)$$

with n the amount of oxygen (mol), p the pressure (Pa) in the measuring chamber along time t (s), V the volume of this chamber (m^3), S_w the surface of the wafer (m^2), R the ideal gas constant (8.314 J mol^{-1} K^{-1}), and T the temperature (K). According to the first Fick law, the surface molar flow of oxygen passing through the cork wafer, once the steady state is established, is also given by Eq. 2:

$$J_{stopper} = -D_{stopper}.\nabla C^a \approx D_{stopper}.\frac{C^a}{e}, \quad (2)$$

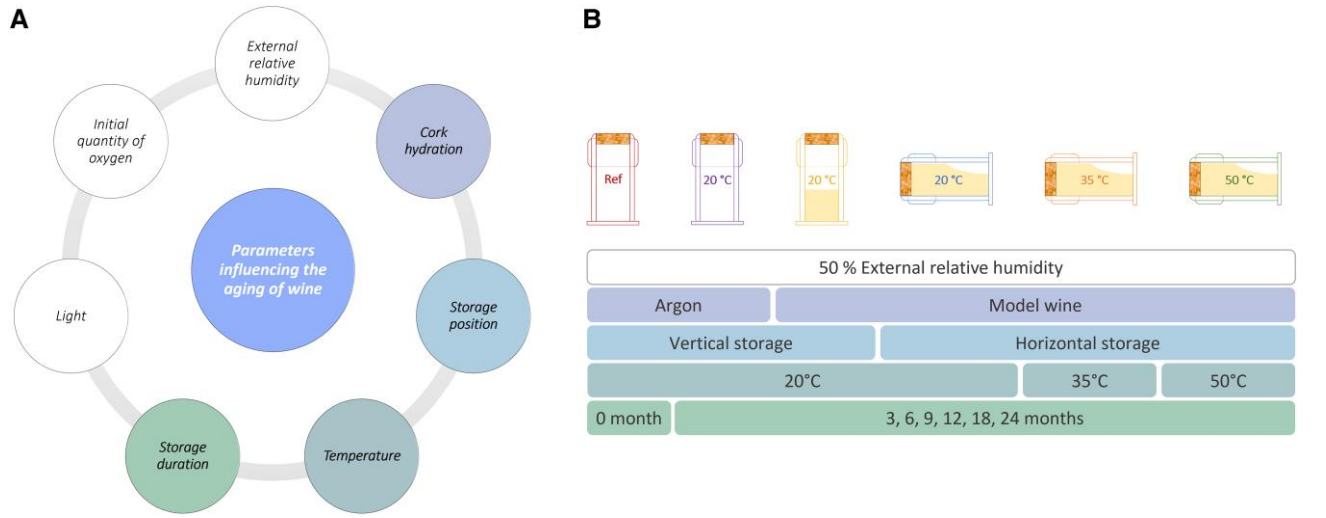

Fig. 4. A) Main parameters influencing the wine aging in bottle. B) Overview of the different conditions investigated for the aging study and corresponding classification used for the five types of samples compared with the initial reference.

with $D_{stopper}$ the diffusion coefficient ($m^2\ s^{-1}$) of oxygen inside the wafer, e the thickness of the wafer (m), and ∇C^a (mol m^{-4}) the concentration gradient of oxygen adsorbed on both sides of the wafer. C^a (mol m^{-3}) is also related to the concentration of the gas C^g (mol m^{-3}) by Eq. 3:

$$C^a = \psi . C^g = \psi . \frac{P}{R.T}, \tag{3}$$

with ψ, the separation factor or partitioning coefficient. ψ is obtained from the sorption isotherm of oxygen on cork, which has been determined in previous work on natural cork (40). For the measurements carried out on the cork wafer alone, the partition coefficient used for the calculation is 0.9, which corresponds to the pressure gradient applied of 900 hPa.

By combining Eqs. 1–3, and after integration over time, the following Eq. 4 is obtained:

$$\ln\left(\frac{p_{t=0}}{p_t}\right) = \frac{D_{stopper}.\psi.S_w}{e.V}.t. \tag{4}$$

Thus, the diffusion coefficient of oxygen through the cork wafer $D_{stopper}$ is determined from the slope of the plot $\ln\left(\frac{p_{t=0}}{p_t}\right) = f(t)$ considering that the steady state of the oxygen transfer is established.

Oxygen diffusion through the cork stopper compressed in the bottleneck

The total flow J_{total}, going through the system comprising the cork wafer inserted in the glass bottleneck, is expressed by the following:

$$J_{total} = -\frac{1}{(S_w + S_{interface})}.\frac{dn}{dt} = -\frac{V}{S_w.R.T}.\frac{dP}{dt}. \tag{5}$$

Here, we assume that the surface section defined by the glass–cork wafer interface, $S_{interface}$, is negligible compared with the one of the cork wafer, S_w. Moreover, it is supposed that oxygen sorption can occur at the interface between the cork wafer and the glass bottleneck. Thus, the partition coefficient ψ is also considered in the determination of the total effective diffusion coefficient D_{total}.

$$J_{total} = -D_{total}.\nabla C^a = D_{total}.\psi.\frac{P}{R.T}. \tag{6}$$

For the measurements carried out on the cork wafer compressed in a bottleneck, the partition coefficient used for the calculations is 0.7, corresponding to the pressure gradient applied of 600 hPa. As mentioned above, by combining Eqs. 5 and 6, we obtain the following:

$$\ln\left(\frac{p_{t=0}}{p_t}\right) = \frac{D_{total}.\psi.S_w}{e.V}.t. \tag{7}$$

The slope of the plot $\ln\left(\frac{p_{t=0}}{p_t}\right) = f(t)$ once the steady state is established gives the total diffusion coefficient D_{total}.

Statistical analysis

Statistical analyses were carried out on oxygen diffusion coefficient values for the different conditions. All statistical analyses were performed on the logarithm of the oxygen diffusion coefficient values in order to enable comparison between samples. First, Student's t tests ($P < 0.05$) were carried out between the diffusion coefficient through the cork alone and the diffusion coefficient through the closure system (cork compressed in bottleneck) for the same storage condition and analysis time. Then, one-way ANOVA test with a Tukey test was performed ($P < 0.05$) to compare the mean oxygen diffusion coefficients through the cork wafer alone under all storage conditions. One-way ANOVA was also applied to compare the mean oxygen diffusion coefficient values through the wafer compressed in a bottleneck for the different samples stored at 20°C (without or with model wine, stored horizontally or vertically). In the two previous cases, the conditions for the application of a one-way ANOVA test have been satisfied, i.e. the normality of residuals, the homogeneity of variance of residuals, and the independence of measurements. Finally, to compare the oxygen diffusion coefficient values through the wafer compressed in a bottleneck for the samples stored horizontally at 20, 35, and 50°C (with model wine), a Kruskal–Wallis test was performed ($P < 0.05$), as the conditions for conducting a one-way ANOVA test were not satisfied (nonnormality and heterogeneity

of variance of residuals). Statistical tests were realized on MATLAB (MathWorks, R2019b).

Characterization of the surface treatment product

The evolution of the thermal properties of the stoppers' surface treatment product after evaporation of the solvent was studied using Q20 calorimeter (TA instruments, New Castle, DE, United States). The samples were weighed and sealed in aluminum capsules (T-Zero, TA instruments, New Castle, DE, United States) before being subjected to a double heating–cooling cycle at 10°C min^{-1} under nitrogen atmosphere. The temperature range was from −20 to 120°C.

Acknowledgments

The authors would like to thank the DIVVA platform for access to the analytical equipment, as well as Alabeurthe and GAI for the loan of the professional bottling machine. The authors also wish to thank Laurence Dujourdy for the very fruitful discussion on the statistical analysis.

Supplementary Material

Supplementary material is available at *PNAS Nexus* online.

Funding

We would like to thank Diam Bouchage as well as the Association Nationale de la Recherche et de la Technologie (ANRT) for their financial support and J.C.'s PhD grant (CIFRE 2018-1278).

Author Contributions

J.C., R.D.G., J-P.B., and T.K. designed research; J.C., J-P.B., and T.K. performed research; J.C., R.D.G., J-P.B., and T.K. analyzed data; J.C., R.D.G., J-P.B., and T.K. wrote the paper.

Data Availability

The data underlying this article are available within the article and in its online supplementary material.

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