

Losses of Yeast-Fermented Carbon Dioxide during Prolonged Champagne Aging: Yes, the Bottle Size Does Matter!

G rard Liger-Belair,* Chlo  Khenniche, Clara Poteau, Carine Bailleul, Virginie Thollin, and Clara Cilindre



Cite This: *ACS Omega* 2023, 8, 22844–22853



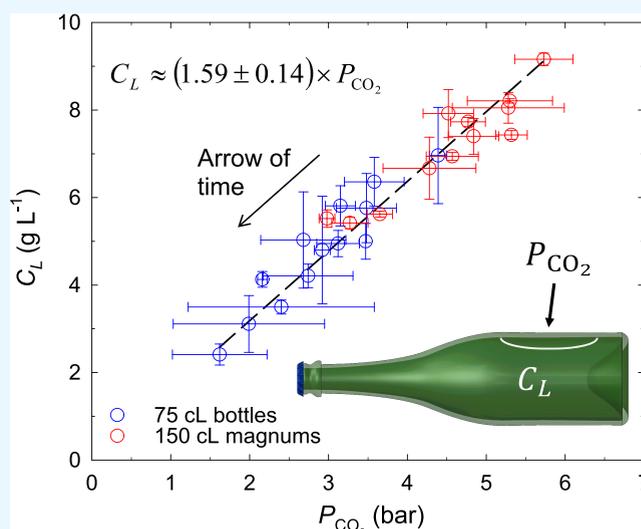
Read Online

ACCESS |

Metrics & More

Article Recommendations

ABSTRACT: When it comes to champagne tasting, dissolved CO₂ is a key compound responsible for the very much sought-after effervescence in glasses. Nevertheless, the slow decrease of dissolved CO₂ during prolonged aging of the most prestigious cuvees raises the issue of how long champagne can age before it becomes unable to form CO₂ bubbles during tasting. Measurements of dissolved CO₂ concentrations were done on a collection of 13 successive champagne vintages stored in standard 75 cL bottles and 150 cL magnums showing prolonged aging ranging from 25 to 47 years. The vintages elaborated in magnums were found to retain their dissolved CO₂ much more efficiently during prolonged aging than the same vintages elaborated in standard bottles. A multivariable exponential decay-type model was proposed for the theoretical time-dependent concentration of dissolved CO₂ and the subsequent CO₂ pressure in the sealed bottles during champagne aging. The CO₂ mass transfer coefficient through the crown caps used to seal champagne bottles prior to the 2000s was thus approached in situ with a global average value of $K \approx 7 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$. Moreover, the shelf-life of a champagne bottle was examined in view of its ability to still produce CO₂ bubbles in a tasting glass. A formula was proposed to estimate the shelf-life of a bottle having experienced prolonged aging, which combines the various relevant parameters at play, including the geometric parameters of the bottle. Increasing the bottle size is found to tremendously increase its capacity to preserve dissolved CO₂ and therefore the bubbling capacity of champagne during tasting. For the very first time, a long time-series dataset combined with a multivariable model indicates that the bottle size plays a crucial role on the progressive decay of dissolved CO₂ experienced by champagne during aging.



1. INTRODUCTION

Louis Pasteur (1822–1895), certainly one of the most internationally renowned French scientists, is a key figure in wine science. He contributed to the understanding of fermentation and proposed a process (known as pasteurization), which helped winemakers and brewers to considerably improve the quality of their yeast-fermented beverages.¹ Nevertheless, only since about three decades ago, many research efforts have been conducted to unveil every parameter involved in the bubbling process and the foaming properties of champagne and other sparkling wines.^{2–6}

From the physicochemical point of view, champagne wines can be viewed as multicomponent hydroalcoholic solutions with a surface tension of $\gamma \approx 50 \text{ mN m}^{-1}$ (i.e., reduced by about a third compared to that of pure water mainly due to ~12–13% ethanol by volume), a viscosity close to 1.5 mPa s

(~50% more than that of pure water), and a density close to unity.⁶ Moreover, champagne and other sparkling wines elaborated through the same method (called “m thode traditionnelle”) are saturated with dissolved carbon dioxide (CO₂) and formed together with ethanol during a second in-bottle fermentation process called “prise de mousse”. The prise de mousse is launched by adding selected yeasts and a certain amount of saccharose (classically approximately 22–24 g L⁻¹) inside bottles filled with a base wine and sealed with a crown

Received: March 17, 2023

Accepted: May 3, 2023

Published: June 12, 2023



cap or cork stopper. During this second alcoholic fermentation, which occurs in cool cellars, the bottles are sealed so that yeast-fermented gas-phase CO₂ cannot escape and progressively dissolves into the wine.⁶ The *prise de mousse* is generally completed within two months, and at the end of which, the pressure of gas-phase CO₂ in the bottle reaches approximately 6 bar (at 12 °C).⁶ CO₂ is indeed a key compound in champagne and in other sparkling wines (and more generally in carbonated beverages). When it comes to tasting, dissolved CO₂ is responsible for bubble nucleation and growth in the glass³ as well as for the very characteristic tingling sensation in the mouth.^{7,8} Moreover, the myriad of ascending bubbles release both gas-phase CO₂ and volatile compounds in the headspace above glasses, thus continuously modifying the chemical space perceived by the consumer.^{9–11}

With champagne, the second in-bottle fermentation is followed by a minimum aging period of 15 months (called “aging on lees”) during which the wine remains in contact with dead yeast cells.^{12–14} A misconception nevertheless lingers in the minds of many wine consumers that champagne wines should not age much after this minimum period of 15 months in contact with dead yeasts. It is indeed a common misconception especially when looking for the most prestigious cuvees.¹⁵ During prolonged aging on lees, champagne and other sparkling wines develop distinct and desirable flavors and aroma profiles attributed to the proteolytic processes characteristic of yeast autolysis as recently described in minute details by Gnoinski et al.¹⁶ Yeast autolysis usually begins between two and four months after the second in-bottle fermentation.¹⁷ Induced by a lack of nutrients combined with high levels of ethanol and dissolved CO₂, low pH (~3–3.5), and low temperature (12–14 °C) storage conditions, the irreversible degradation of several yeast cell-wall components occurs, such as glucans and mannoproteins for example.^{18–20} As a result of the subsequent cell-wall porosity, the release of degraded constituents into the wine is facilitated. Nevertheless, the slow rate of the enzymatic activity delays this autolytic process. Consequently, to fully benefit from positive autolytic effects, prolonged aging on lees is needed to bring complex and very much sought-after aromas to champagne.¹⁸ Old vintages of the finest champagne wines can even age on lees for several decades before finally being disgorged to expel the dead yeast sediment and then put on the market.¹⁵

Prolonged champagne aging nevertheless raises an issue, which may become problematic for prolonged maturation on lees. In fact, crown caps or cork stoppers used to seal the bottles during champagne aging are impermeable to liquids, but they are not 100% hermetic to gas transfers.^{21–28} Gaseous species present on both sides of the bottle closure system are thus able to slowly diffuse through the cap or through the cork along their respective inverse partial pressure gradients.²⁵ Because the pressure of gas-phase CO₂ in the sealed bottle reaches close to 6 bar at 12 °C at the end of the *prise de mousse* (a value much higher than the current 400 ppm level of CO₂ in ambient air), yeast-fermented CO₂ is therefore able to progressively escape from the bottle by slowly diffusing into ambient air across the bottle closure. Otherwise, because gas-phase and dissolved CO₂ experience thermodynamic equilibrium in the sealed bottle, both the CO₂ pressure and the level of dissolved CO₂ found in the sealed bottles slowly decrease with time during prolonged champagne aging. Now, the decrease of dissolved CO₂ from champagne during aging is far from insignificant when it comes to tasting. The decrease in the

concentration of dissolved CO₂ in champagne will have the direct consequence of reducing the number and size of bubbles in the glass²⁹ and the subsequent carbonation bite during tasting,³⁰ thus modifying the overall mechanisms behind the perception of aromas. Otherwise, should the concentration of dissolved CO₂ reach or fall under a critical value close to 2.5 g L⁻¹ (at 12 °C), bubble nucleation would simply become thermodynamically impossible, thus forbidding the presence of the very much sought-after effervescence during tasting.¹⁵ With effervescence being indeed the hallmark of champagne wines, the slow decrease of dissolved CO₂ during prolonged aging on lees therefore raises the issue of how long a champagne can age before it becomes unable to form bubbles during tasting. Keeping dissolved CO₂ as long as possible in champagne bottles during aging on lees is therefore a challenge of importance for old vintages likely to mature on lees for several decades.

In the current work, measurements of dissolved CO₂ concentrations were done on a collection of 13 old champagne vintages elaborated before the 2000s and showing prolonged aging on lees ranging from 25 to 47 years. The 13 successive vintages were aged in both standard 75 cL bottles and 150 cL magnums, which were all identically sealed with the same model of crown caps covered with a thin cork disc in force at the time. Based on the first Fick's law, a multivariable exponential decay-type model was proposed for the theoretical time-dependent concentration of dissolved CO₂ and the subsequent CO₂ pressure in the sealed bottles during champagne aging. The shelf-life of a champagne bottle was then examined in view of its ability to still produce CO₂ bubbles in a tasting glass. A formula was proposed for the shelf-life of a bottle having experienced prolonged aging on lees, which combines the various relevant parameters at play, including the geometric parameters of the bottle.

2. RESULTS AND DISCUSSION

2.1. Thermodynamic Equilibrium of CO₂ in the Sealed Bottles and Magnums. For each bottle and magnum aged on lees between 25 and 47 years, the dissolved CO₂ concentration found in champagne immediately after uncapping was plotted as a function of the pressure of gas-phase CO₂ measured in the sealed vessel before uncapping (Figure 1). Our dataset covers a wide range of CO₂ pressures and concentrations because the 13 successive vintages cover a range of differential aging of more than two decades with subsequent losses of CO₂, therefore logically increasing from vintage 1996 to vintage 1974. Figure 1 unambiguously indicates that dissolved and gas-phase CO₂ are linearly correlated. At equilibrium, this proportionality between the partial pressure P_i of a species in the gas phase and its concentration C_i in the solution is known as Henry's law (with the Henry's constant k_H , which is also called Henry's solubility, being the ratio of C_i to P_i).^{31,32} The Henry's constant for CO₂ in these old vintages aged on lees between 25 and 47 years can thus be approached through the slope of the regression line in Figure 1. At 20 °C, the average Henry's constant determined in this way for CO₂ in this collection of old vintages is $\overline{k_H} \approx 1.59 \pm 0.14 \text{ g L}^{-1} \text{ bar}^{-1}$.

The Henry's solubility of CO₂ in wines depends primarily on the temperature but also on several other factors such as the alcoholic degree and sugar level. Based on a series of dedicated experiments, Lonvaud-Funel and Matsumoto³³ proposed the

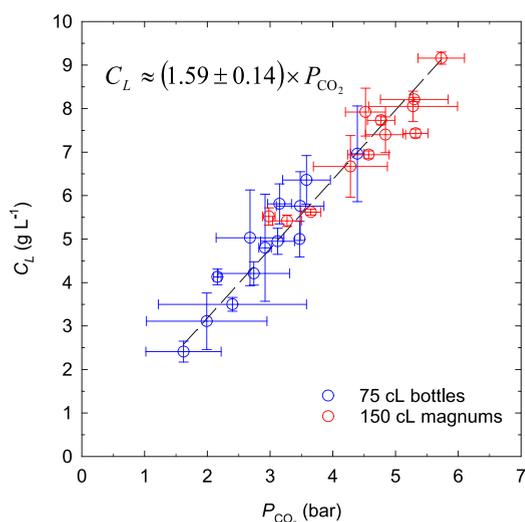


Figure 1. Dissolved CO₂ concentrations found in champagne immediately after uncapping plotted as a function of the pressure of gas-phase CO₂ measured in the sealed bottles (in blue) and magnums (in red) before uncapping.

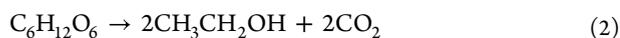
formula below, which makes it possible to deduce the Henry's constant of CO₂ in a wine according to its temperature, ethanol, and sugar content

$$k_H = 3.295 \times e^{(7 \times 10^{-5} a - 0.02905) T} \times e^{-(0.0179 a + 0.00111 b)} \quad (1)$$

with T being the wine temperature (in °C), a being the level of ethanol (in % vol), and b being the sugar concentration (in g L⁻¹).

After the second in-bottle fermentation was achieved in the collection of bottles and magnums, the level of ethanol reached nearly 12.5% by volume. Moreover, throughout the aging period, the concentration of sugar in wine remains very close to zero because fermentable sugar has been completely consumed by the yeasts. In such a wine without sugar and with 12.5% ethanol by volume, applying the empirical eq 1 leads to $k_H \approx 1.50 \text{ g L}^{-1} \text{ bar}^{-1}$ for the expected Henry's constant of CO₂ at 20 °C. The average Henry's constant for CO₂ in this collection of old vintages aged between 25 and 47 years approached from the respective measurements of their dissolved CO₂ concentration and CO₂ pressure is finally very close to what is expected from formula 1 for a sugar-free wine with 12.5% ethanol by volume. To the best of our knowledge, the solubility of CO₂ in a collection of old champagne vintages has never been approached before.

2.2. Thermodynamic Equilibrium of CO₂ at the End of the Prise de Mousse. To correctly understand and interpret the progressive losses of CO₂ through the crown caps during prolonged champagne aging, the initial concentrations of dissolved CO₂ and CO₂ pressure reached at the end of the prise de mousse (before aging) are to be precisely determined whether in bottles or magnums. The key metabolic process behind the production of CO₂ during the prise de mousse is alcoholic fermentation whose chemical equation is as follows.



By following the previous equation, 1 L of base wine added with nutrients and with 24 g of fermentable sugar (glucose + fructose) leads to the production of $n \approx 0.27$ mole of CO₂ after the prise de mousse is achieved (by considering a fermentation

efficiency close to 95%). Under the temperature and pressure conditions prevailing in a sealed bottle, the CO₂ is in the gaseous state. Nevertheless, bottles and magnums are sealed so that gas-phase CO₂ cannot escape and progressively dissolves into the wine according to Henry's thermodynamic equilibrium expressed hereafter

$$C_L = \frac{n_L}{V_L} = k_H P_G \quad (3)$$

with n_L being the mole number of dissolved CO₂ in wine, V_L being the volume of wine, k_H being the strongly temperature-dependent Henry's constant for CO₂ in wine, and P_G being the partial pressure of gas-phase CO₂ in the sealed bottle.

However, in the sealed bottles and magnums, a gas space with a volume V_G (the headspace, also commonly called "the bubble" in the Champagne region) cohabits with the volume V_L of wine, as exemplified in the scheme displayed in Figure 2.

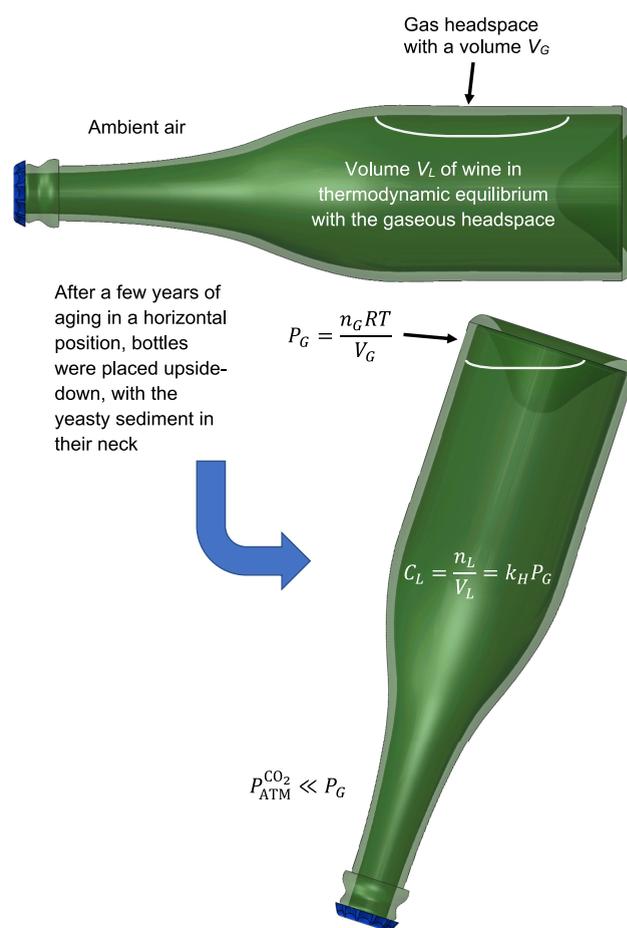


Figure 2. Scheme of a champagne bottle during prolonged aging on lees and compilation of the various relevant parameters involved in the thermodynamic equilibrium of dissolved and gas-phase CO₂ in the bottle sealed with a crown cap.

For the standard 75 cL bottle, $V_G \approx 2.5$ cL, whereas $V_G \approx 3.3$ cL for the 150 cL magnum. In the pressure range prevailing in the sealed bottles and magnums (typically a few bar), we may safely consider that the gaseous CO₂ of the bottle headspace is ruled by the ideal gas law. Thus, $P_G V_G = n_G RT$ with T being the wine temperature, n_G being the mole number of gas-phase CO₂ in the bottle headspace, and R being the ideal gas

constant ($8.31 \text{ J K}^{-1} \text{ mol}^{-1}$). Moreover, in the bottles hermetically sealed, the total mole number of CO_2 produced by yeasts during the prise de mousse ($n_T = nV_L$) is a conserved quantity, which is distributed between the bottle headspace (with n_G moles) and the wine (with n_L moles) according to $n_T = n_G + n_L$. Ultimately, by combining the previous equations, the concentration of dissolved CO_2 and the subsequent pressure of gas-phase CO_2 reached at the end of the prise de mousse (denoted C_{PDM} and P_{PDM} , respectively) can be related to the collection of various parameters according to the following relationships

$$\begin{cases} C_{\text{PDM}} \approx \frac{nk_{\text{H}}RTx_{\text{V}}}{k_{\text{H}}RTx_{\text{V}} + 1} \\ P_{\text{PDM}} \approx \frac{nRTx_{\text{V}}}{k_{\text{H}}RTx_{\text{V}} + 1} \end{cases} \quad (4)$$

with x_{V} being the dimensionless ratio of the wine volume to the gaseous headspace (i.e., $x_{\text{V}} = V_{\text{L}}/V_{\text{G}}$) and every other parameter being expressed in the international system of units (SI).

With the knowledge of the inherent volume ratio x_{V} for each bottle type, the previous system of equations therefore enables us to precisely determine the initial concentration of dissolved CO_2 (in mol m^{-3}) and the pressure of gas-phase CO_2 (in Pa) reached after the prise de mousse was achieved whatever the size of the bottle and the temperature of the system. Following eq 1, at a cellar temperature close to 12°C , the Henry's constant for CO_2 in a sugar-free wine with 12.5% ethanol by volume is $k_{\text{H}} \approx 1.88 \text{ g L}^{-1} \text{ bar}^{-1} \approx 4.3 \times 10^{-4} \text{ mol m}^{-3} \text{ Pa}^{-1}$. After a second in-bottle fermentation classically launched at 12°C in a base wine added with 24 g L^{-1} fermentable sugar, the dependence with x_{V} of both C_{PDM} (converted in g L^{-1}) and P_{PDM} (converted in bar) is displayed in Figure 3. For the standard 75 cL bottles with $x_{\text{V}} \approx 30$, $C_{\text{PDM}} \approx 11.5 \text{ g L}^{-1}$ and $P_{\text{PDM}} \approx 6.1 \text{ bar}$, whereas for the 150 cL magnums with $x_{\text{V}} \approx 45$, $C_{\text{PDM}} \approx 11.6 \text{ g L}^{-1}$ and $P_{\text{PDM}} \approx 6.2 \text{ bar}$. Interestingly, the higher the volume ratio x_{V} in a bottle, the higher the concentration of dissolved CO_2 and subsequent pressure of

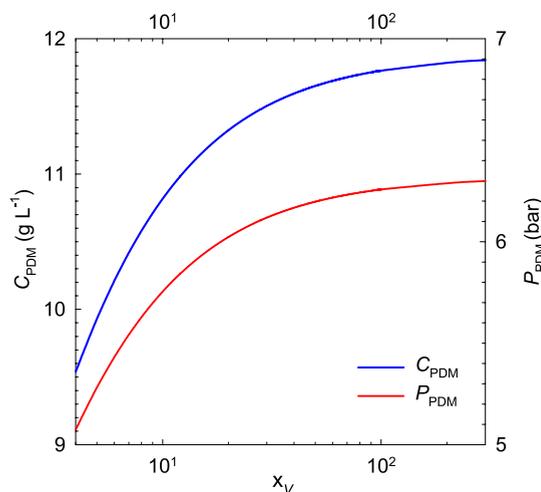


Figure 3. Concentration of dissolved CO_2 (blue line) and subsequent pressure of gas-phase CO_2 (red line) reached at the end of the prise de mousse plotted as a function of the dimensionless ratio of the wine volume to the gaseous headspace x_{V} .

CO_2 after the prise de mousse is achieved. Nevertheless, it is noteworthy to mention that there is a theoretical asymptotic concentration, namely, $C_{\text{PDM}}^{\text{max}} = n \approx 0.27 \text{ mol L}^{-1} \approx 11.9 \text{ g L}^{-1}$, and a subsequent maximum pressure of CO_2 within the bottle, namely, $P_{\text{PDM}}^{\text{max}} = C_{\text{PDM}}^{\text{max}}/k_{\text{H}} \approx 6.3 \text{ bar}$ (at 12°C), which can never be exceeded.

2.3. Highlighting the Losses of Dissolved CO_2 during Aging on Lees. The dissolved CO_2 concentrations recorded in the 13 successive vintages aged on lees whether in bottles and in magnums are displayed in Figure 4 together with their

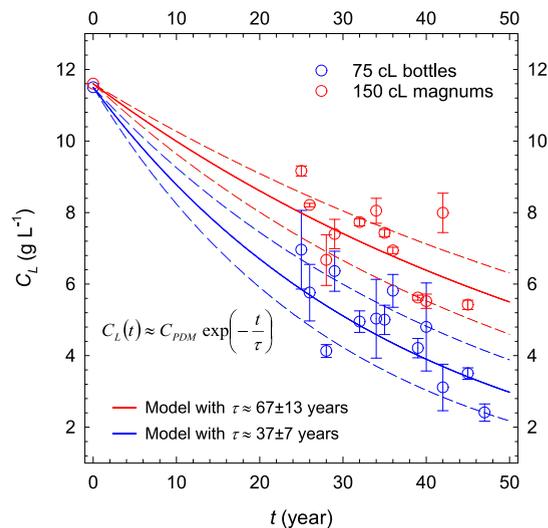


Figure 4. Dissolved CO_2 concentrations recorded in the 13 successive vintages having experienced prolonged aging on lees ranging from 25 years (for vintage 1996) up to 47 years (for vintage 1974); at $t = 0$, the initial dissolved CO_2 concentrations reached in bottles and magnums at the end of the prise de mousse also appear (as theoretically determined through eq 4 for a second in-bottle fermentation launched with 24 g L^{-1} of saccharose).

initial dissolved CO_2 concentrations reached at the end of the prise de mousse as theoretically determined through eq 4. As seen in Figure 4, a very significant decrease of the dissolved CO_2 is highlighted during champagne aging for both bottle types. The maximum recorded losses on the order of 9 g L^{-1} were experienced by the oldest vintage (1974) elaborated in the standard 75 cL bottles. Nearly 80% of the bottle's initial CO_2 content has escaped through the crown caps during the 47 years of aging. The same overall trend toward a gradual decrease of dissolved CO_2 is also observed in the 150 cL magnums, but this drop is less marked than for the successive vintages aged in standard 75 cL bottles. Very clearly, the vintages elaborated in magnums were found to retain their dissolved CO_2 more efficiently during prolonged aging than the same vintages elaborated in standard bottles.

For the very first time, a long time-series dataset indicates that the bottle size plays a crucial role on the progressive decay of dissolved CO_2 experienced by champagne during aging on lees. To better apprehend our experimental observations, a multivariable model for the decay of dissolved CO_2 is proposed hereafter.

2.4. Time-Series Dataset Versus the Model. After the prise de mousse of the 13 vintages of the present study was achieved, the partial pressures of gas-phase CO_2 reached close to 6 bar (at 12°C) whether in bottles or magnums (Figure 3). Yeast-fermented CO_2 will thus progressively escape from the

Table 1. Compilation of the Various Bottle, Wine, and Dissolved CO₂ Parameters, Including the Timescales of the Exponential Decay-Type Model and the Corresponding Ranges for the Respective Mass Transfer Coefficients *K* for Gas-Phase CO₂ through the Various Closure Systems as Approached through Eq 10^a

parameters of the bottle, wine, and closure system used to seal the various vintages during prolonged aging	75 cL bottles of the present study sealed with crown caps	150 cL magnums of the present study sealed with crown caps	75 cL bottles of a previous study sealed with traditional cork stoppers ¹⁵
<i>T</i> (°C)	12	12	12
<i>V_G</i> (cL)	2.5	3.3	2.5
<i>V_L</i> (cL)	75	150	75
<i>x_v</i> = <i>V_L</i> / <i>V_G</i>	30	45	30
neck diameter (mm)	29	29	26
closure system	crown caps with cork disc	crown caps with cork disc	premium cork stoppers
<i>C_{PDM}</i> (g L ⁻¹)	11.5	11.6	11.5
<i>P_{PDM}</i> (bar)	6.1	6.2	6.1
<i>k_H</i> (g L ⁻¹ bar ⁻¹)	1.88	1.88	1.88
<i>τ</i> (years)	37 ± 7	67 ± 13	47 ± 12
<i>K</i> (×10 ⁻¹³ m ³ s ⁻¹)	6.8 ± 1.1	7.4 ± 1.4	5.3 ± 1.4

^aTo correctly determine *K* in m³ s⁻¹, every parameter in eq 10 must be converted in SI units.

inner bottle to ambient air by crossing the crown caps (non-100% hermetic to gas transfers). During prolonged champagne aging in a sealed vessel, the thermodynamic balance of dissolved and gas-phase CO₂ is therefore revisited by taking into account the transfer of CO₂ through the crown caps. Molecular diffusion is indeed the mechanism behind the transfer of gas-phase CO₂ through the crown caps.

A simple model based on the first Fick's law will be used, which stipulates that the flux of a gas species through a non-hermetic closure system is proportional to its gradient concentration (and therefore its partial pressure gradient). By considering a global mass transfer coefficient *K* for gas-phase CO₂ through the cork disc of the crown caps used to seal the 13 successive vintages, the mole number of CO₂ escaping per unit of time from each bottle and magnum is therefore ruled by the following equation

$$\frac{dn_T}{dt} \cong -K \frac{(P_G - P_{ATM}^{CO_2})}{RT} \quad (5)$$

with *P_{ATM}^{CO₂}* being the partial pressure of the gas phase in the atmosphere of the cellar where bottles and magnums have aged for several decades.

The total number of CO₂ moles trapped in the whole bottle, which is denoted as *n_T*, is the sum of the mole number of dissolved CO₂ found in the liquid phase, which is denoted as *n_L*, and the mole number of gas-phase CO₂ found in the gaseous headspace, which is denoted as *n_G*. Because *P_{ATM}^{CO₂}* is completely negligible in comparison with the CO₂ pressure found in the bottles and magnums of the various vintages, the following equation therefore applies for the progressive losses of the total mole number of CO₂ through the crown caps during champagne aging:

$$\frac{dn_T}{dt} = \frac{dn_L}{dt} + \frac{dn_G}{dt} \approx -K \frac{P_G}{RT} \quad (6)$$

Combining the equation above with both the ideal gas law and Henry's law leads to the differential equation displayed hereafter:

$$\left(V_L + \frac{V_G}{k_H RT} \right) \frac{dC_L}{dt} \approx -K \frac{C_L}{k_H RT} \quad (7)$$

Finally, by considering the mass transfer coefficient *K* to be constant during aging, the resolution of this differential equation leads to the following multivariable exponential decay-type model for both the theoretical time-dependent concentration of dissolved CO₂ and the subsequent pressure of gas-phase CO₂ during champagne aging (in SI units)

$$\left\{ \begin{array}{l} C_L(t) \approx C_{PDM} \exp\left(-\frac{t}{\tau}\right) \\ P_G(t) \approx P_{PDM} \exp\left(-\frac{t}{\tau}\right) \\ \text{with } \tau = \frac{V_G + k_H RT V_L}{K} \end{array} \right. \quad (8)$$

where *C_{PDM}* and *P_{PDM}* are the concentration of dissolved CO₂ and the CO₂ pressure reached in the sealed vessels, respectively, after the prise de mousse was achieved, *t* is the aging time, and *τ* is the timescale of the exponential decay-type model (a multivariable that depends on the parameters of the bottle, the wine, and the crown cap).

Bottles and magnums of this collection of old vintages were all identically sealed with the same model of crown caps covered with a thin cork disc in force at the time. Under the same sealing conditions, we can logically imagine that the CO₂ mass transfer coefficients *K* are substantially identical for the sealed bottles and magnums. Therefore, the theoretical ratio between the two timescales describing the decay of dissolved CO₂ in a magnum and in a bottle, both sealed with identical crown caps, is finally expressed as follows:

$$\frac{\tau_M}{\tau_B} = \frac{V_G^M + k_H RT V_L^M}{V_G^B + k_H RT V_L^B} = 1.98 \quad (9)$$

As seen in Figure 4, the progressive losses of dissolved CO₂ during prolonged aging on lees are indeed well described by exponential decays but with very different exponential timescales whether it is champagne aged in standard bottles or in magnums. In the standard 75 cL bottles, *τ_B* ≈ 37 ± 7 years, whereas in the 150 cL magnums, the exponential timescale appears significantly longer with *τ_M* ≈ 67 ± 13 years. The higher the exponential timescales, the less the losses of dissolved CO₂ during prolonged champagne aging and therefore the longer a vintage could age while preserving its

precious dissolved CO₂ content, which guarantees the production of bubbles during tasting. Our experimental time-series dataset leads to $\tau_M/\tau_B \approx 1.81 \pm 0.69$, which is in good agreement with the theoretical ratio presented above. Moreover, approaching the exponential timescales of the time-dependent concentrations of dissolved CO₂ enables us to propose a reasonable range for the mass-transfer coefficient K for gas-phase CO₂ through the crown caps used to seal the various bottles and magnums according to the following relationship:

$$K = \frac{V_G + k_H RTV_L}{\tau} \quad (10)$$

Table 1 compiles the various bottle, wine, and bottleneck parameters for each time-series dataset, including the timescale of the exponential decay-type model and the mass transfer coefficients for gas-phase CO₂ through the closure system used to seal the various vintages as determined through eq 10. The CO₂ mass transfer coefficients through the crown caps covered with a thin cork disc are not significantly different depending on whether they have sealed the vintages aged in bottles or in magnums. It seems to be indeed self-consistent with the fact that the crown caps, which were used at that time to seal both the bottles and magnums, had globally the same permeability properties with regard to CO₂ leakage during aging on lees. A global average value $K \approx 7.1 \pm 1.3 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$ is finally proposed for the CO₂ mass transfer coefficient through the crown caps with a cork disc, which were commonly used in Champagne to seal the bottles prior to the 2000s.

Moreover, the losses of dissolved CO₂ through the crown caps with cork discs used to seal the various vintages of the present study were compared with a previous dissolved CO₂ time-series dataset recorded on seven successive vintages aged on lees from several months up to 35 years in standard 75 cL bottles sealed with premium traditional cork stoppers.¹⁵ It appears from these various time-series data recordings that the mass-transfer coefficient for CO₂ is slightly but significantly smaller through the premium cork stoppers (with a 26 mm neck diameter) than through the crown caps with cork discs (with a 29 mm neck diameter).

2.5. Toward the Shelf-Life Prediction of Old Vintages Depending on the Bottle Capacity. As described in minute details by Liger-Belair,⁵ the bubble formation in champagne and sparkling wine glasses is triggered by tiny pre-existing air bubbles trapped in particles or glass anfractuosités acting as bubble nucleation sites. Nevertheless, below the critical concentration of dissolved CO₂, that is, C_L^* , expressed hereafter (in SI units), the pre-existing air bubble becomes thermodynamically unable to nucleate CO₂ bubbles during tasting²⁸

$$C_L^* \approx k_H \left(P_0 + \frac{2\gamma}{r} \right) \quad (11)$$

with P_0 being the ambient pressure and r being the radius of curvature of the pre-existing air bubble.

Despite C_L^* depending on the champagne-tasting temperature, ambient pressure, and pre-existing bubble size, we will consider a familiar situation with a tasting at 12 °C under an ambient pressure of 1 bar and with pre-existing bubbles with $r \approx 5 \mu\text{m}$. Under such conditions, the critical concentration $C_L^* \approx 2.5 \text{ g L}^{-1}$. In a tasting glass, the concentration of dissolved CO₂ in champagne must necessarily exceed this critical concentration to be able to produce CO₂ bubbles. In 2010,

an outstanding collection of champagne bottles produced by the French Champagne house Veuve Clicquot Ponsardin was discovered in a shipwreck at the bottom of the Baltic Sea. These bottles, which were probably elaborated by Madame Clicquot herself in the early 1840s, spent 170 years under the seawater. As reported by Jeandet et al.,³⁴ several bottles that have been uncorked were unable to create bubbles. There is little doubt that, after such a long time under the sea, their dissolved CO₂ content fell much below the critical concentration needed to nucleate CO₂ bubbles. The shelf-life of old champagne and sparkling wine vintages could thus be examined in view of their ability to produce CO₂ bubbles once they have been served in a glass. Nevertheless, between the end of the aging on lees and the tasting glass, there are still two key stages that cause the champagne to lose additional dissolved CO₂, namely, disgorging and service.

Disgorging is the procedure developed to get the dead yeast cells out of the bottle. The neck of the bottle is frozen, creating a small ice plug that traps the sediment of dead yeast cells. The crown cap is then removed, and the plug of dead yeast cells next to the cap is ejected. However, the volume of gas-phase CO₂ under pressure in the bottle headspace is inevitably lost at this step. The partial pressure of gas-phase CO₂ falls, but the bottle is then quickly re-corked with a cork stopper. Dissolved and gas-phase CO₂ therefore quickly recover Henry's equilibrium but with a newly subsequent concentration of dissolved CO₂ (denoted C_{CB}) in the corked bottle, which was indeed slightly lower than that just before disgorging, C_L , and theoretically determined as follows³⁵

$$C_{CB} \approx C_L \left(\frac{k_H RTV_L}{V_G^{AD} + k_H RTV_L} \right) \quad (12)$$

with V_G^{AD} being the headspace volume of the re-corked bottle after disgorging.

Strictly speaking, the Henry's constant k_H in the two previous relationships may slightly differ from the one used earlier because a specific dosage consisting of a mixture of sugar and aged wine is added before recorking, which slightly decreases the Henry's solubility of CO₂.³³ Nevertheless, these old vintages are usually added with a very small amount of sugar (<10 g L⁻¹) with negligible consequences on the Henry's constant of CO₂. Moreover, because the cork is inserted 2.5 cm in the bottleneck, the headspace volume V_G^{AD} of the recorked bottle is reduced by a few cubic centimeters compared with the headspace volume V_G of the bottle sealed with a crown cap before disgorging.

If the old vintage is put on the market quickly after disgorging (usually after 2–3 months), its dissolved CO₂ concentration should not vary compared with the value defined previously by eq 12 because the permeability of the cork to CO₂ is very low and will hardly cause the champagne to lose CO₂ over such a short period of time.¹⁵ However, uncorking the bottle and serving the champagne in the glass, which is the very last step before tasting, induce substantial losses on the champagne dissolved CO₂ concentration.^{36–38} During the service stage, the relative losses of dissolved CO₂ depend on several parameters, such as the champagne temperature, glass shape and volume served and if the glass is tilted or not during service.^{36–38} If 100 mL of champagne is served at a tasting temperature close to 12 °C in a vertically oriented standard flute, the loss of CO₂ caused by the turbulences of the service is approximately 30% of the initial

concentration of dissolved CO₂ when the champagne was still in the bottle.³⁶ Therefore, by taking into account the service and disgorging steps, the critical concentration C_{SB}^* of dissolved CO₂ below which the champagne in the bottle still sealed with a crown cap will no longer be able to produce bubbles in a glass can be approached as follows:

$$C_{SB}^* \approx \frac{10}{7} \left(\frac{V_G^{AD} + k_H RT V_L}{k_H RT V_L} \right) C_L^* \quad (13)$$

Ultimately, predicting the shelf-life of old vintages (i.e., their aging period on lees beyond which their concentration of dissolved CO₂ could fall below C_{SB}^* once the champagne has been served in a glass) becomes possible by replacing $C_L(t)$ in eq 8 by C_{SB}^* and by developing. The shelf-life, which is denoted as t_B^* , beyond which bubbling would become thermodynamically impossible due to the lack of dissolved CO₂ to trigger bubble nucleation in the glass is

$$t_B^* \approx \tau \ln \left(\frac{C_{PDM}}{C_{SB}^*} \right) \approx \left(\frac{V_G + k_H RT V_L}{K} \right) \ln \left(\frac{C_{PDM}}{C_{SB}^*} \right) \quad (14)$$

Today, nearly one billion bottles of different sizes and capacities are aging in champagne cellars while waiting to be put on the market.³⁹ Among them, several hundreds of thousands of prestigious cuvees elaborated prior to the 2000s are potentially affected by prolonged aging on lees. Moreover, it turns out that, before the 2000s, the majority of bottles were sealed with crown caps covered with cork discs, and for which, the CO₂ mass transfer coefficient K was approached in situ (i.e., in the real aging conditions of a champagne cellar) in the present study. From eq 14, it then becomes possible to predict the shelf-life of a bottle according to its geometric characteristics. In champagne, the three main bottle formats (in numbers) potentially affected by prolonged aging on lees are the standard 75 cL bottle, 150 cL magnum, and 300 cL jeroboam. The diameter of the bottleneck is generally identical for 75 cL bottles and 150 cL magnums and equal to 29 mm. Nevertheless, the neck of the 300 cL jeroboam is larger with a 36 mm diameter. However, because the CO₂ leakage operates through the cork disc, which seals the bottleneck, the mass transfer coefficient of CO₂ is therefore proportional to the diameter of the neck. For the jeroboam sealed with a crown cap with a cork disc, the CO₂ mass transfer coefficient was thus approached as $K \approx (36/29) \times (7.1 \pm 1.3) \times 10^{-13} \approx (8.8 \pm 1.6) \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$.

For second in-bottle fermentations classically launched with 24 g L⁻¹ saccharose, Figure 5 presents the exponential decay-type models that predict the decrease of dissolved CO₂ concentrations during prolonged aging on lees at 12 °C whether champagne is elaborated in 75 cL bottles, 150 cL magnums, or 300 cL jeroboams (all identically sealed with crown caps covered with a thin cork disc in force prior to the 2000s). Moreover, Table 2 compiles and compares the various relevant parameters at play which gradually lead us to the estimation of the shelf-life t_B^* beyond which bubble formation would become impossible after disgorging and once champagne has been served in the glass. For a cellar master, having chosen a 300 cL jeroboam to produce his champagne nearly triples the possible duration of aging on lees compared to that of the standard 75 cL bottle. In view of their ability to produce CO₂ bubbles once they have been served in a glass,

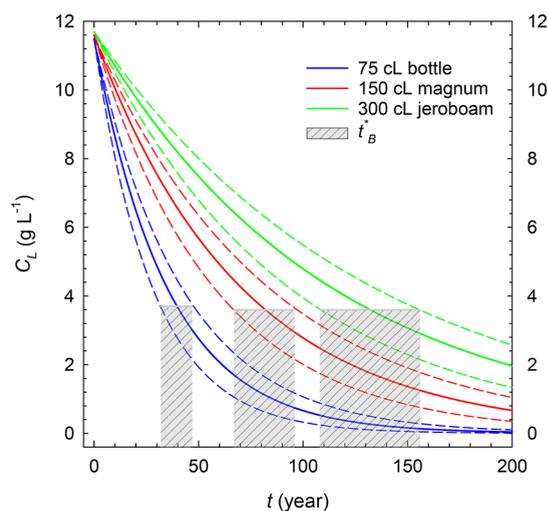


Figure 5. For second in-bottle fermentations classically launched with 24 g L⁻¹ saccharose, exponential decay-type models predicting the decrease of dissolved CO₂ concentrations during prolonged aging on lees, whether champagne is elaborated in 75 cL bottles, 150 cL magnums, and 300 cL jeroboams sealed with crown caps with cork disks in force prior to the 2000s; For each bottle format, the corresponding shelf-life range prediction appears beyond which bubble nucleation would become impossible during champagne tasting.

Table 2. For Prolonged Champagne Aging at 12 °C, in a 75 cL Bottle, a 150 cL Magnum, and a 300 cL Jeroboam Identically Sealed with Crown Caps Covered with a Thin Cork Disc, Comparison of the Various Relevant Parameters at Play which Gradually Lead Us to the Estimation of the Shelf-Life t_B^* beyond which Bubble Formation Would Become Impossible after Disgorging and Once Champagne Has Been Served in the Glass

parameters of the bottle, wine, crown cap, and subsequent theoretical CO ₂ parameters during prolonged aging	standard bottles (75 cL)	magnums (150 cL)	jeroboams (300 cL)
V_G (cL)	2.5	3.3	6
V_L (cL)	75	150	300
$\alpha_V = V_L/V_G$	30	45	50
neck diameter (mm)	29	29	36
k_H (g L ⁻¹ bar ⁻¹)	1.88	1.88	1.88
C_{PDM} (g L ⁻¹)	11.5	11.6	11.7
P_{PDM} (bar)	6.1	6.2	6.2
K ($\times 10^{-13} \text{ m}^3 \text{ s}^{-1}$)	7.1 ± 1.3	7.1 ± 1.3	8.8 ± 1.6
τ (years)	35 ± 7	70 ± 13	112 ± 20
V_G^{AD} (cL)	2.0	2.8	5.1
C_{SB}^* (g L ⁻¹)	3.7	3.6	3.6
$t_B^* \approx \tau \ln \left(\frac{C_{PDM}}{C_{SB}^*} \right)$ (years)	40 ± 8	82 ± 15	132 ± 24

the shelf-life of old champagne vintages is therefore definitely and strongly conditioned by the bottle size.

3. CONCLUSIONS

Measurements of dissolved CO₂ concentrations were done on a collection of 13 old champagne vintages elaborated before the 2000s and showing prolonged aging on lees ranging from 25 to 47 years. The 13 successive vintages were aged in both standard 75 cL bottles and 150 cL magnums, which were all identically sealed with the same model of crown caps covered

with a thin cork disc in force at the time. The vintages elaborated in magnums were found to retain their dissolved CO₂ more efficiently during prolonged aging than the same vintages elaborated in standard bottles. For the very first time, a long time-series dataset indicates that the bottle size plays a crucial role on the progressive decay of dissolved CO₂ experienced by champagne during aging on lees.

Based on the first Fick's law and by considering a constant CO₂ mass-transfer coefficient through the crown caps throughout the aging period, a multivariable exponential decay-type model was proposed for the theoretical time-dependent concentration of dissolved CO₂ and the subsequent CO₂ pressure in the sealed bottles during champagne aging. From our experimental time-series dataset, the CO₂ mass transfer coefficients through the crown caps were thus approached in situ with a global average value $K \approx 7 \times 10^{-13} \text{ m}^3 \text{ s}^{-1}$ of the same order of magnitude whether they have sealed the vintages aged in bottles or in magnums.

Moreover, with effervescence being the hallmark of Champagne wines, the slow decrease of dissolved CO₂ during prolonged aging on lees therefore raises the issue of how long the most prestigious cuvees can age before they become unable to form bubbles during tasting. The shelf-life of a champagne bottle was thus examined in view of its ability to still produce CO₂ bubbles in a tasting glass. A formula was proposed for the shelf-life of a bottle having experienced prolonged aging on lees, which combines the various relevant parameters at play, including the geometric parameters of the bottle. Increasing the bottle size is found to tremendously increase its capacity to preserve dissolved CO₂ and therefore the bubbling capacity of champagne during tasting.

It is also noteworthy to mention the universal nature of the model developed in the present study whatever the closure system used to seal the bottle during aging. Indeed, the precise knowledge of the CO₂ mass transfer coefficient K for each closure system then makes it possible to predict the shelf-life of a champagne bottle depending on the crown cap or the cork stopper that was used by the cellar master to seal the bottle at the time of the *prise de mousse*.

4. EXPERIMENTAL SECTION

4.1. Collection of Old Vintages Aged Upside-Down in Bottles and Magnums. Our industrial partner (Champagne Castelneau, Reims, France) made available an outstanding vertical collection of 13 old vintages (namely, 1996, 1995, 1993, 1992, 1989, 1987, 1986, 1985, 1982, 1981, 1979, 1976, and 1974), showing therefore prolonged aging on lees ranging from 25 years (for vintage 1996) up to 47 years (for vintage 1974). The successive vintages were elaborated with various blends of Chardonnay, Pinot noir, and Meunier base wines (i.e., the three main grape varieties grown in the Champagne vineyard). To examine the influence of the content, we chose to compare the 13 identical successive vintages elaborated in both 75 cL standard bottles and 150 cL magnums except for vintage 1974, which was only bottled in standard 75 cL bottles. Bottles and magnums showed bottlenecks of identical and standard diameters of 29 mm.

During the *prise de mousse* and throughout their aging in the cellar, bottles and magnums were sealed with identical and standard crown caps made with thin aluminum shells filled with dishes made with agglomerated cork. Before the 2000s, the crown caps with cork discs were certainly the most common closure types for champagne and sparkling wines

elaborated through the *méthode traditionnelle*. To seal the bottles and magnums, a 16-head pneumatic crown-capper, applying a force between approximately 440 and 480 daN, was used. Bottles and magnums of the 13 various vintages were all aged in the same cellar (at a typical temperature close to 12 °C). During the second in-bottle fermentation and the first years of aging, bottles and magnums were in a horizontal position in order to maximize the contact surface between the yeasts and the wine. After several years of aging in the horizontal position, the bottles and magnums were then put in the upside-down position with the yeasty sediment in their necks, as illustrated in the scheme displayed in Figure 6.

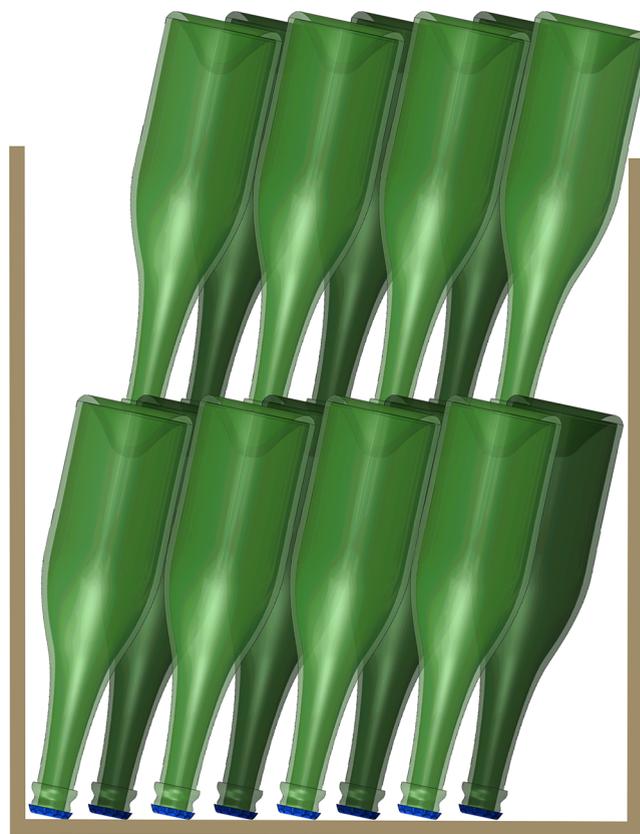


Figure 6. In the cellar of Champagne Castelneau (Reims, France), vintage bottles and magnums were stored for years in wooden racks in the upside-down position for prolonged aging with the yeasty sediment in their necks.

After the second in-bottle fermentation was achieved for this collection of bottles and magnums, the level of ethanol classically reached nearly 12.5% by volume. Moreover, before aging on lees, it is important to mention that the 13 successive vintages were all classically elaborated with 24 g L⁻¹ saccharose to launch the *prise de mousse* whether in bottles or magnums. The same amount of saccharose to launch the second in-bottle alcoholic fermentation, identical crown caps, and identical neck diameters for the bottles and magnums were indeed three crucial conditions to be met to correctly compare and discuss the influence of the bottle capacity on the losses of dissolved CO₂ experienced by the various vintages whether elaborated in bottles or magnums.

4.2. Pressure of Gas-Phase CO₂. The pressure of CO₂ in the sealed bottles and magnums was achieved with a non-destructive and non-invasive digital aphrometer (L.Sensor-

CO₂, L PRO SRL, Camisano Vicentino, Italy) at a temperature of 12 °C close to that of the cellar where they have aged for several decades. The pressure values expressed in bar were then normalized at 20 °C using Henry's law temperature correspondence. To enable a statistical treatment, measurements of CO₂ pressures were carried out on three bottles and three magnums per vintage.

4.3. Concentration of Dissolved CO₂. Concentrations of dissolved CO₂ found in bottles and magnums having experienced prolonged aging on lees were determined immediately after having uncapped the vessel (to prevent any leakage of dissolved CO₂ due to the slow but ineluctable diffusion of CO₂). Measurements of CO₂ concentrations in the various champagne vintages were classically done by chemical assay using carbonic anhydrase (labeled C2522 Carbonic Anhydrase Isozyme II from bovine erythrocytes and provided from Sigma-Aldrich, US). This method is still the official method recommended by the International Office of Vine and Wine (OIV).⁴⁰ The whole procedure was thoroughly described by Liger-Belair et al.⁴¹ CO₂ concentrations were commonly expressed in grams per liter. As for the pressure of gas-phase CO₂, measurements of dissolved CO₂ were done on three bottles and three magnums per vintage.

AUTHOR INFORMATION

Corresponding Author

Gérard Liger-Belair – *Equipe Effervescence & Champagne (GSMA), UMR CNRS 7331, Université de Reims Champagne-Ardenne, 51687 Reims, France*; orcid.org/0000-0002-4474-7283; Phone: +333 26 91 33 93; Email: gerard.liger-belair@univ-reims.fr

Authors

Chloé Khenniche – *Equipe Effervescence & Champagne (GSMA), UMR CNRS 7331, Université de Reims Champagne-Ardenne, 51687 Reims, France; Champagne Castelnau, 51100 Reims, France*
 Clara Poteau – *Champagne Castelnau, 51100 Reims, France*
 Carine Bailleul – *Champagne Castelnau, 51100 Reims, France*
 Virginie Thollin – *PE.DI France, 51530 Pierry, France*
 Clara Cilindre – *Equipe Effervescence & Champagne (GSMA), UMR CNRS 7331, Université de Reims Champagne-Ardenne, 51687 Reims, France*; orcid.org/0000-0003-0639-9078

Complete contact information is available at: <https://pubs.acs.org/10.1021/acsomega.3c01812>

Author Contributions

G.L.-B., C.B., V.T., and C.C. conceived and designed the research. G.L.-B., C.P., C.B., V.T., and C.C. supervised the project. C.K. and C.C. performed the experiments. G.L.-B. conceived and developed the multivariable model. G.L.-B. wrote the paper, and all authors reviewed the manuscript.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

The authors are indebted to Champagne Castelnau (Reims, France) for supplying us with an outstanding collection of old vintages aged in bottles and magnums. The authors also thank Florian Lecasse for some technical drawings.

ABBREVIATIONS

C_L	concentration of dissolved CO ₂ in the liquid phase (mol m ⁻³)
C_{CB}	concentration of dissolved CO ₂ recovered in the re-corked bottle after the disgorging step (mol m ⁻³)
C_{PDM}	concentration of dissolved CO ₂ after the prise de mousse was achieved (mol m ⁻³)
C_L^*	critical concentration of dissolved CO ₂ in the liquid phase required to enable bubble nucleation from a gas cavity (mol m ⁻³)
C_{SB}^*	critical concentration of dissolved CO ₂ below which the champagne in the bottle still sealed with a crown cap will no longer be able to produce bubbles in a glass (mol m ⁻³)
k_H	Henry's law constant of dissolved CO ₂ in the liquid phase (i.e., its solubility) in (mol m ⁻³ Pa ⁻¹)
K	mass transfer coefficient for gas-phase CO ₂ through the closure system used to seal the bottle during on lees (m ³ s ⁻¹)
n	CO ₂ mole number produced per liter of wine in the sealed bottle after the prise de mousse was achieved (mol L ⁻¹)
n_T	total CO ₂ mole number trapped in the sealed bottle (mol)
n_L	mole number of dissolved CO ₂ in the liquid phase (mol)
n_G	mole number of gas-phase CO ₂ in the bottle headspace (mol)
P_G	partial pressure of gas-phase CO ₂ (Pa)
P_{PDM}	partial pressure of gas-phase CO ₂ found in the headspace after the prise de mousse was achieved (Pa)
P_{CB}	partial pressure of gas-phase CO ₂ found recovered in the headspace in the re-corked bottles after the disgorging step (Pa)
$P_{ATM}^{CO_2}$	partial pressure of gas-phase CO ₂ in the atmosphere of the cellar where bottles and magnums have aged for several decades (Pa)
r	radius of curvature of the pre-existing air bubble immersed in the liquid phase and acting as a bubble nucleation site (m)
R	ideal gas constant; 8.31 J K ⁻¹ mol ⁻¹
t	time (s)
t_B^*	shelf-life beyond which bubbling would become thermodynamically impossible due to the lack of dissolved CO ₂ to trigger bubble nucleation in the glass (s)
T	temperature (K)
V_G	volume of the gas phase found in the headspace in the sealed bottles (m ³)
V_G^{AD}	headspace volume of the re-corked bottle after disgorging (m ³)
V_L	volume of the liquid phase in the sealed bottle (i.e., volume of champagne) (m ³)
x_V	dimensionless ratio of the wine volume to the gaseous headspace (i.e., $x_V = V_L/V_G$)
τ	timescale of the exponential decay-type model (s)
γ	surface tension of champagne or sparkling wine (with 12.5% v/v of ethanol); $\sim 5 \times 10^{-2}$ N m ⁻¹

REFERENCES

- (1) Cavaillon, J.-M.; Legout, S. Louis Pasteur: Between Myth and Reality. *Biomolecules* **2022**, *12*, 596.

- (2) Brissonnet, F.; Maujean, A. Characterization of foaming proteins in a Champagne base wine. *Am. J. Enol. Vitic.* **1993**, *44*, 397.
- (3) Liger-Belair, G. The physics and chemistry behind the bubbling properties of champagne and sparkling wines: A state-of-the-art review. *J. Agric. Food Chem.* **2005**, *53*, 2788.
- (4) Kemp, B.; Condé, B.; Jégou, S.; Howell, K.; Vasserot, Y.; Marchal, R. Chemical compounds and mechanisms involved in the formation and stabilization of foam in sparkling wines. *Crit. Rev. Food Sci. Nutr.* **2019**, *59*, 2072.
- (5) Liger-Belair, G. Effervescence in champagne and sparkling wines: From grape harvest to bubble rise. *Eur. Phys. J.: Spec. Top.* **2017**, *226*, 3.
- (6) Liger-Belair, G.; Cilindre, C. Recent progress in the analytical chemistry of champagne and sparkling wines. *Annu. Rev. Anal. Chem.* **2021**, *14*, 21.
- (7) Dessirier, J. M.; Simons, C.; Carstens, M.; O'Mahony, M.; Carstens, E. Psychophysical and neurobiological evidence that the oral sensation elicited by carbonated water is of chemogenic origin. *Chem. Senses* **2000**, *25*, 277.
- (8) Chandrashekar, J.; Yarmolinsky, D.; von Buchholtz, L.; Oka, Y.; Sly, W.; Ryba, N. J.; Zucker, C. S. The taste of carbonation. *Science* **2009**, *326*, 443.
- (9) Moriaux, A.-L.; Vallon, R.; Lecasse, F.; Chauvin, N.; Parvitte, B.; Zéninari, V.; Liger-Belair, G.; Cilindre, C. How does gas-phase CO₂ evolve in the headspace of champagne glasses? *J. Agric. Food Chem.* **2021**, *69*, 2262.
- (10) Lecasse, F.; Vallon, R.; Polak, F.; Cilindre, C.; Parvitte, B.; Liger-Belair, G.; Zéninari, V. An infrared laser sensor for monitoring gas-phase CO₂ in the headspace of champagne glasses under wine swirling conditions. *Sensors* **2022**, *22*, 5764.
- (11) Yeo, H.; Linforth, R.; Mac Naughtan, W.; Williams, H.; Hewson, L.; Fisk, I. D. Effect of sweeteners and carbonation on aroma partitioning and release in beverage systems. *Food Res. Int.* **2023**, *164*, No. 112373.
- (12) Leroy, M. J.; Charpentier, M.; Duteurtre, B.; Feuillat, M.; Charpentier, C. Yeast Autolysis during Champagne Aging. *Am. J. Enol. Vitic.* **1990**, *41*, 21.
- (13) Moreno-Arribas, M. V.; Pueyo, E.; Nieto, F. J.; Martín-Avarez, P. J.; Polo, M. C. Influence of the polysaccharides and the nitrogen compounds on foaming properties of sparkling wines. *Food Chem.* **2000**, *70*, 309.
- (14) Nunez, Y. P.; Carrascosa, A. V.; Gonzalez, R.; Polo, M. C.; Martinez-Rodriguez, A. J. Effect of accelerated autolysis of yeast on the composition and foaming properties of sparkling wines elaborated by a champenoise method. *J. Agric. Food Chem.* **2005**, *53*, 7232.
- (15) Liger-Belair, G.; Carvajal-Pérez, D.; Cilindre, C.; Facque, J.; Brevot, M.; Litoux-Desrués, F.; Chaperon, V.; Geoffroy, R. Evidence for moderate losses of dissolved CO₂ during aging on lees of a champagne prestige cuvee. *J. Food Eng.* **2018**, *233*, 40.
- (16) Gnoinski, G. B.; Schmidt, S. A.; Close, D. C.; Goemann, K.; Pinfeld, T. L.; Kerslake, F. L. Novel methods to manipulate autolysis in sparkling wines: Effects on yeast. *Molecules* **2021**, *26*, 387.
- (17) Todd, B. E. N.; Fleet, G. H.; Henschke, P. A. Promotion of autolysis through the interaction of killer and sensitive yeasts: Potential application in sparkling wine production. *Am. J. Enol. Vitic.* **2000**, *51*, 65.
- (18) Alexandre, H.; Guilloux-Benatier, M. Yeast autolysis in sparkling wines: A review. *Aust. J. Grape Wine Res.* **2006**, *12*, 119.
- (19) Babayan, T. L.; Bezrukov, M. G. Autolysis in Yeasts. *Acta Biotechnol.* **1985**, *5*, 129.
- (20) Marti-Raga, M.; Martin, V.; Gil, M.; Sancho, M.; Zamora, F.; Mas, A.; Beltran, G. Contribution of yeast and base wine supplementation to sparkling wine composition. *J. Sci. Food Agric.* **2016**, *96*, 4962.
- (21) Vasserot, Y.; Jacopin, C.; Jeandet, P. Effect of bottle capacity and bottle-cap permeability to oxygen on dimethylsulfide formation in Champagne wines during aging on the lees. *Am. J. Enol. Vitic.* **2001**, *52*, 54.
- (22) Bunner, D.; Landrieux, A.; Valade, M.; Langleron, E.; Tribaut-Sohier, I.; Moncomble, D.; Viaux, L.; Bourdelet Walter, L.; Chaperon, V.; Gouez, B. La mesure de l'oxygène dans les bouteilles par chimiluminescence. *Le Vigneron Champenois* **2010**, *131*, 84.
- (23) Karbowiak, T.; Gougeon, R. D.; Alinc, J.-B.; Brachais, L.; Debeaufort, F.; Voilley, A.; Chassagne, D. Wine oxydation and the role of cork. *Crit. Rev. Food Sci. Nutr.* **2010**, *50*, 20.
- (24) Faria, D. P.; Fonseca, A. L.; Pereira, H.; Teodoro, O. Permeability of cork to gases. *J. Agric. Food Chem.* **2011**, *59*, 3590.
- (25) Liger-Belair, G.; Villaume, S. Losses of dissolved CO₂ through the cork stopper during champagne aging: Toward a multiparameter modeling. *J. Agric. Food Chem.* **2011**, *59*, 4051.
- (26) Crouvisier Urion, K.; Bellat, J.-P.; Liger-Belair, G.; Gougeon, R. D.; Karbowiak, T. Unravelling CO₂ transfer through cork stoppers for Champagne and sparkling wines. *Food Packag. Shelf Life* **2021**, *27*, No. 100618.
- (27) Jolly, N.; Minnaar, P.; Booyse, M.; Gerber, P. Bottle fermented sparkling wine: Cork or crown closures during the second fermentation? *S. Afr. J. Enol. Vitic.* **2021**, *42*, 136.
- (28) Thollin, V.; Liger-Belair, G.; Cilindre, C.; Di Crescenzo, R. Champagne et vins effervescents: La première capsule de tirage dopée aux sulfites. *Revue des Œnologues de France* **2021**, *181*, 50.
- (29) Liger-Belair, G. How many bubbles in your glass of bubbly? *J. Phys. Chem. B* **2014**, *118*, 3156.
- (30) Wise, P. M.; Wolf, M.; Thom, S. R.; Bryant, B. The influence of bubbles on the perception carbonation bite. *PLoS One* **2013**, *8*, No. e71488.
- (31) Smith, F. L.; Harvey, A. H. Avoid common pitfalls when using Henry's law. *Chem. Eng. Prog.* **2007**, *103*, 33.
- (32) Sander, R.; Acree, W. E.; De Visscher, A.; Schwartz, S. E.; Wallington, T. J. Henry's law constants (IUPAC Recommendations 2021). *Pure Appl. Chem.* **2022**, *71*.
- (33) Lonvaud-Funel, A.; Matsumoto, N. The solubility coefficient of carbonic acid in wines. *Vitis* **1979**, *18*, 137.
- (34) Jeandet, P.; Heinzmann, S.; Roullier-Gall, C.; Cilindre, C.; Aron, A.; Deville, M.-A.; Moritz, F.; Karbowiak, T.; Demarville, D.; Brun, C.; Moreau, F.; Michalke, B.; Liger-Belair, G.; Witting, M.; Lucio, M.; Steyer, D.; Gougeon, R. D.; Schmitt-Kopplin, P. Chemical messages in 170-year-old champagne bottles from the Baltic Sea: Revealing tastes from the past. *Proc. Natl. Acad. Sci. U. S. A.* **2015**, *112*, 5893.
- (35) Liger-Belair, G.; Cordier, D.; Honvault, J.; Cilindre, C. Unveiling CO₂ heterogeneous freezing plumes during champagne cork popping. *Sci. Rep.* **2017**, *7*, 10938.
- (36) Liger-Belair, G.; Bourget, M.; Villaume, S.; Jeandet, P.; Pron, H.; Polidori, G. On the losses of dissolved CO₂ during champagne serving. *J. Agric. Food Chem.* **2010**, *58*, 8768.
- (37) Liger-Belair, G.; Parmentier, M.; Cilindre, C. More on the losses of dissolved CO₂ during champagne serving: Toward a multiparameter modeling. *J. Agric. Food Chem.* **2012**, *60*, 11777.
- (38) Liger-Belair, G.; Conreux, A.; Villaume, S.; Cilindre, C. Monitoring the losses of dissolved carbon dioxide from laser-etched champagne glasses. *Food Res. Int.* **2013**, *54*, 516.
- (39) La champagne, ses galeries souterraines et son milliard de bouteilles. https://www.lemonde.fr/le-monde-passe-a-table/article/2022/12/15/la-champagne-ses-galeries-souterraines-et-son-milliard-de-bouteilles_6154584_6082232.html (accessed April 12, 2023)
- (40) Caputi, A.; Ueda, M.; Walter, P.; Brown, T. Titrimetric determination of carbon dioxide in wine. *Am. J. Enol. Vitic.* **1970**, *21*, 140.
- (41) Liger-Belair, G.; Villaume, S.; Cilindre, C.; Jeandet, P. Kinetics of CO₂ fluxes outgassing from champagne glasses in tasting conditions: the role of temperature. *J. Agric. Food Chem.* **2009**, *57*, 1997.