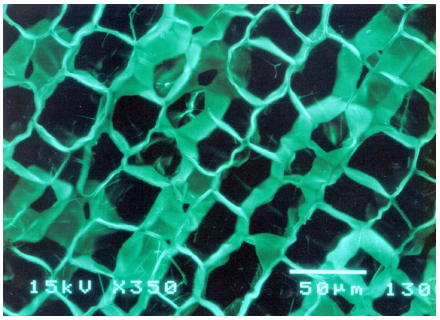
Oxygen Ingress by Closure Type

Oxygen Pathway — Diffusion or Permeation

Natural Cork – Diffusion

Oxygen ingress with natural corks is primarily a result of diffusion. A typical 44mm cork contains an estimated at 3.5ml of oxygen. When the cork is compressed the internal air pressure increases to between 6 and 9 atmospheres. This establishes a pressure imbalance that is solved by the gradual equalization of gasses between cork and headspace.

The exchange of gasses explains why studies of oxygen ingress show that bottles with natural cork "pick up" a small amount of oxygen over the first 6-9 months of aging. After that, oxygen ingress is no longer significant (the referenced study ran for 36 months).



Natural cork consists of millions of tiny "cells" – 40 million cells fit in one cubic centimeter. Each cell is filled with air, and that air provides a small dose of oxygen for each bottle.

Variations in oxygen diffusion between corks appear in the first six months of storage and likely reflect differences in cellular structures. After the initial diffusion period, additional variation was not observed.

Alternative Closures – Permeation

Artificial closures provide oxygen ingress primarily through permeation. Oxygen passes directly through the closure from the outside air. This can happen at a controlled rate, but unlike diffusion, the permeation does not stop. Oxygen continues to enter the bottle at whatever rate is determined by the closure.

The majority of synthetic closures will exhibit significant oxygen permeation within 18 months. Some manufacturers now advertise optional products with reduced permeation rates. Recent developments with screwcap manufacturers show an interest in fitting screwcaps with a permeable seal, so that more oxygen can be introduced into the wine.

In both instances, the mechanism for oxygen ingress is by permeation of outside air. This will occur for the duration of wine storage, and creates a discrete time frame for optimum oxygen effect.

A Natural Balance

Natural cork has been the standard closure used in wine bottles since the science of winemaking was established in the 18th Century. Its sealing performance has been incorporated into our compiled assumptions of wine development and oxygen management.

With the relatively new introduction of alternative closures, the industry has shown great interest in questions that were previously considered academic. The use of alternative closures has brought unintended consequences to the wine industry regarding oxygen permeability, extraction forces, aging performance and consumer acceptance.

In particular, the role of oxygen in wine development has experienced increasing importance as the performance of alternatives are compared to cork closures.

Natural cork normally allows a variable but limited amount of oxygen to contact the wine. The process is primarily due to diffusion of air contained and pressurized in the cork when it is compressed during bottling. Alternative closures normally introduce oxygen due to permeability from the outside.

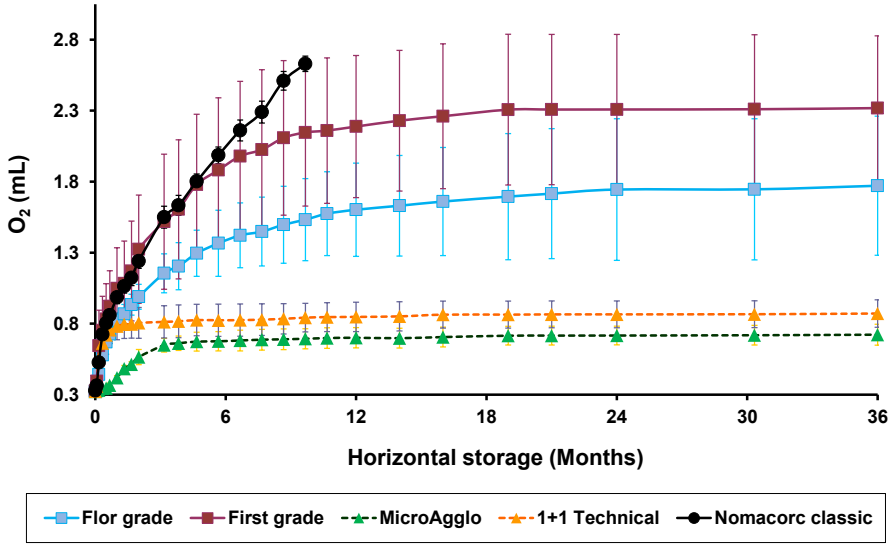
In the case of synthetics, Oxygen permeability has usually been too high, and has been implicated in a significant limitation on bottle aging. Some screwcaps have allowed too little oxygen contact and their use is sometimes associated with reduced wine aromas.

OTR Variation by Closure Type

Oxygen is an important factor in any wine's development – sometimes for better and sometimes for worse. Total package oxygen (TPO) includes the total oxygen dissolved in the wine and available in the headspace. It is the most critical measurement used to determine SO_2 additions and handling during winemaking and bottling. TPO can be significantly modified after bottling based on the oxygen transfer rate (OTR) of the selected closure.

Different wine closures present a range of OTR behaviors. The table titled "OTR by Closure Type" shows observations of oxygen ingress over 36 months for a variety of inserted closures. Ingress measurements were determined using a nondestructive colorimetric method. Technical corks had low OTR measurements – below 0.8 ml over 36 months. Two grades of natural corks produced a similar pattern of OTR increasing in the first twelve months followed by a two year period with minimal ingress. The synthetic closure had the highest OTR. It measured 2.6ml at 10 months and was no longer in range of the analytical matrix.

OTR by Closure Type



These examples are based on closures available in 2014 and many alternative closure marketers have introduced new products that will adjust the OTR performance so that it might more closely resemble the range of 1.5ml to 2.5ml that is seen with natural cork.

OTR Variance for Cork Closures

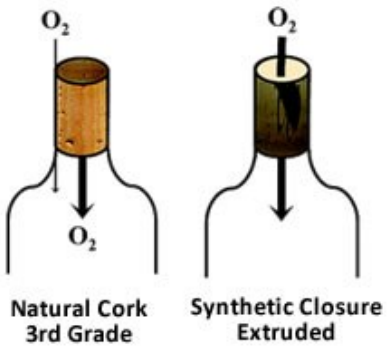
The vertical bars on the graph indicate the standard deviation between samples. They are significantly higher for natural cork than reported for technical corks or the synthetic example. They are, however, relatively consistent and range between 21% and 28% of the average OTR from months 12 through 36. This is consistent with the process of oxygen diffusion and the variance between corks reflects different matrices of cellular density, gas content and possibly the corking mechanism.

Lopes, et.al. Impact of Storage Position on Oxygen Ingress through Different Closures into Wine Bottles. . *J. Agric. Food Chem.* ***2006,*** *54, 6741–6746*

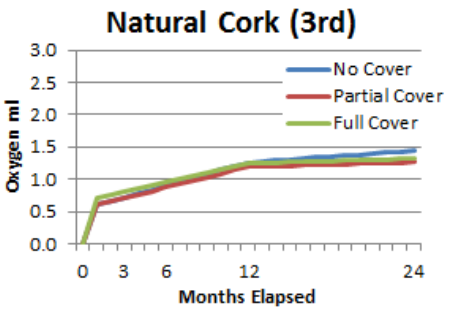
Pathway for Oxygen Ingress

In a 2007 study by Paulo Lopes et al. (University of Bordeaux), a comparison of closures was made between those with closures completely covered with a polyurethane impermeable varnish, and those with only the closure–glass interface covered.

The oxygen pathway would be observed by comparing ingress into the bottles using a nondestructive colorimetric method. If the pathway was down the side of the closure, the samples with partial interface seal would display a lower OTR than the control. If the pathway was through the center, the samples with a full seal would display lower OTR .

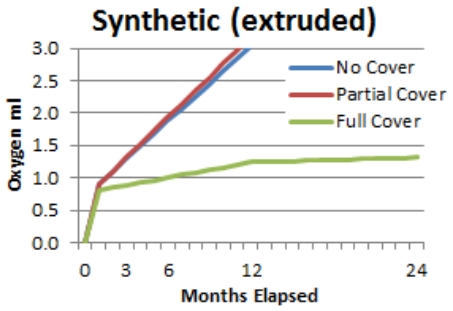


Results for the natural cork showed diffusion of oxygen at a slow but continuous rate over the first 12 months of storage and in very tiny amounts through the cork–glass interface in the 12 months thereafter. Results for were similar under all test packages indicating that oxygen originated inside the cork and was transmitted by diffusion.



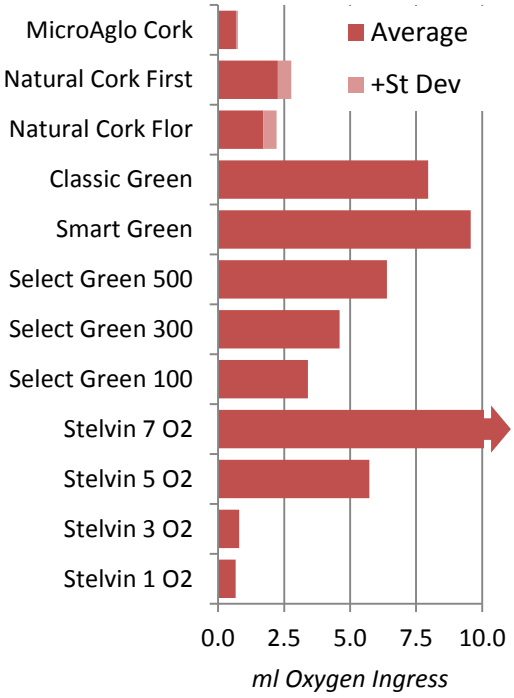
Pathway for Oxygen Ingress

Results for the synthetic closure showed no significant difference between the control sample and the sample with a partial cover of the closure interface. This demonstrates that the OTR path for synthetic closures lies directly through the body. and is consistent with the behavior of an oxygen permeable membrane.



Lopes, et.al. Main Routes of Oxygen Ingress through Different Closures into Wine Bottles *Bordeaux, Universite´ Victor Segalen Bordeaux 2, UMR 1219 INRA, 351 Cours de la libe´ration, 33405 Talence Cedex, France*

Comparison of OTR by Closure Through 36 Months



Lifetime OTR Variation by Closure

Wine is a four dimensional product, and the producer seldom knows how long each bottle will be in distribution before it is purchased and consumed. The real OTR variation is not a snapshot in time, but must consider the expected shelf life of the product. These two samples of natural cork display variation in OTR at any particular time, but over a three year period they remain in a range that is roughly 1.5 to 3.3 ml. These are observed values with Oxygen pickup at bottling calculated at .25ml. That number can vary based on bottling conditions.

	Bottling	12 Mos	24 Mos	36 Mos
Natural Cork Flor	0.25	1.55	1.94	1.97
Flor + St Dev	0.25	1.88	2.44	2.46
Natural Cork First	0.25	2.14	2.51	2.52
First + St. Dev	0.25	2.64	3.04	3.03

Nomacorc has released a line of closures offering a range of OTR levels. Because the transfer is based on permeation, they have calculated a predicted level of O_2 per year. The lowest permeation level is higher than the highest natural cork+ one standard deviation. The highest OTR is more than triple that level.

	ccO^2/Yr	Bottling	12 Mos	24 Mos	36 Mos
Select Green 100	1.10	na	1.20	2.30	3.40
Select Green 300	1.10	na	2.40	3.50	4.60
Select Green 500	1.70	na	3.00	4.70	6.40
Classic Green	2.25	na	3.46	5.71	7.96
Smart Green	2.73	na	4.11	6.84	9.57

Stelvin has released a series of liners that also offer a range of OTR expectations. Because the liners are permeable to Oxygen, the rate of ingress can be estimated—here as O_2 per day. According to the spec sheets, two of the liners allow considerably less oxygen than either natural cork. The Stelvin 5 has an OTR similar to a synthetic cork. The Stevin 7 has an OTR rate more than 5 times the most permeable synthetic closure.

	ccO^2/day	1 Year	Bottling	12 Mos	24 Mos	36 Mos
Stelvin 1 O_2 <	0.0005	0.14	0.25	0.39	0.52	0.66
Stelvin 3 O_2 ≈	0.0005	0.18	0.25	0.43	0.62	0.80
Stelvin 5 O_2 ≈	0.005	1.83	0.25	2.08	3.90	5.73
Stelvin 7 O_2 ≈	0.05	18.25	0.25	18.50	36.75	55.00

The comparison of natural cork, including its observed OTR variations, to alternative closures with permeable OTR characters shows that cork provides a more reliable range of OTR over time. The overall ranking shows that among closures allowing more than 1ml of oxygen over 36 months, natural cork has the lowest lifetime variation in OTR.

Do Cork Closures Protect Wines from Dimethyl sulfide Aromas?

Dimethyl Sulfide

Discussions of specific sulfide compounds are usually focused on the redox reaction between disulfides and mercaptans. While mercaptans are generally considered to be a serious but relatively infrequent wine fault.

The most commonly observed sulfide compound found in California wines is dimethyl sulfide (DMS). This sulfide compound is associated with aromas of canned corn, cooked cabbage and asparagus. It has a reported sensory threshold of 25 ppb.

In addition to grape origins, literature shows that DMS concentration can increase in wines after bottling. The concentration of DMS in bottled wines has been demonstrated to be subject to storage temperature and time in the bottle.

Influence of Closure Type on DMS Formation

A study of DMS formation in sparkling wines during secondary fermentation has shown that the concentration of DMS accumulated more rapidly with bottle caps having low oxygen permeability. This is consistent with the view that post bottling DMS formation is associated with reduction of DMSO.

Survey of Sauvignon Blanc by Closure Type

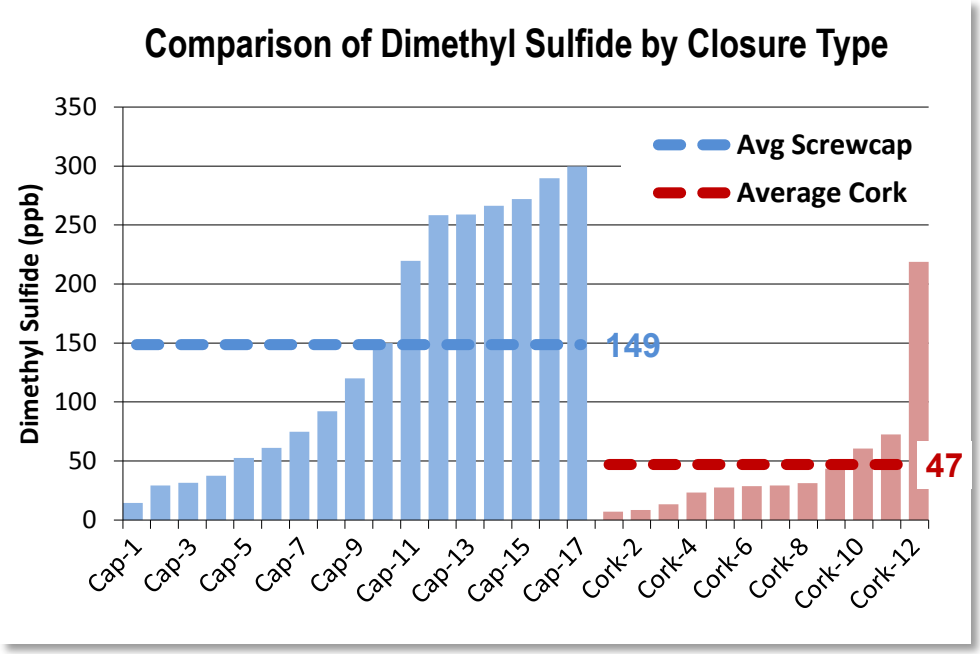
The Cork Quality Council conducted two market surveys of Sauvignon Blanc to measure DMS concentration. Wines in each survey were from comparable vintages, and samples were obtained from the same retail stores.

A total of 29 wines were Six wines finished in screwcap closures and six wines with cork closures were selected. Results showed that DMS ranged from less than 10µg/L to over 70 µg/L. Only two of twelve wines had DMS above 40 µg/L.

There was a noticeable difference between closure types. Wines with screwcaps had an average DMS concentration of 40µg/L compared to 18µg/L for wines under cork.

This ratio is comparable to an earlier CQC survey of Sauvignon Blancs from Australia and New Zealand. This study revealed much higher levels of DMS than seen in the recent California survey, but presented a similar ratio of DMS in wines under screwcap.

The large difference in DMS concentrations between the two surveys is likely due to differences in fruit characteristics and the fact that the southern hemisphere wines (made up of the '04 and '05 vintages) had more bottle aging at the time of analysis than seen in the California samples.



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