OXYGEN BRINGS NEW LIFE TO CLOSURE DEBATE

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As closure research and development projects increasingly focus on the role of the closure in the development of wine in the bottle, it is timely to consider some recent results in the context of the overall importance of oxygen at all stages of winemaking.

Oxygen makes the wine

As school children, we learn the simple fact that we cannot live without oxygen. But for those of us with an interest in the superb combination of art and science that constitutes modern winemaking, some of the roles played by oxygen during the various stages of fermentation and wine development are still surprisingly unclear.

Most living organisms need oxygen, including many that we value for their ability to transform relatively simple materials into some of our most enjoyable foodstuffs, such as bread, cheese, wine and beer.

For example, the fermentation process that transforms grape juice into wine is essentially a micro-aerobic process, i.e. one that requires small amounts of oxygen. As the Australian Wine Research Institute (AWRI) noted in 2004, "oxygen is an essential component of modern red wine production, particularly in the control of yeast activity, sulphur off-odour management, and fermentation-derived volatile composition" (Jones et al. 2004). The traditional source of this oxygen has been air contact during storage and multiple racking of the new wine in barrels.

Louis Pasteur, the eminent 19th century French microbiologist and chemist famous for his contributions to pasteurisation, immunisation and medical hygiene, spent some time considering the factors that influence the success or otherwise of winemaking processes.

A few years ago, French researcher Véronique Cheynier and her colleagues reminded us of Pasteur's views on oxygen and wine (Cheynier et al. 2002).
"As long ago as 1873, Pasteur stated: "l'Oxygène est le pire ennemi du vin,' (oxygen is the greatest enemy of wine) but also, 'C'est l'oxygène qui fait le vin, c'est par son influence qu'il vieillit' (oxygen makes the wine, which ages under its influence)."
Cheynier (2002) went on to say that: "It is commonly admitted that extensive oxidation is unfavourable to wine quality, but slow and continuous oxygen dissolution may play a positive role in wine ageing. To promote the beneficial effects of oxygen exposure while avoiding spoilage risks, it is essential to understand the mechanisms governing oxygen dissolution and consumption in wine."

There is ongoing debate about the extent to which micro-oxygenation, adding controlled amounts of oxygen to a wine, usually after the alcoholic fermentation process is finished, can bring about desirable changes in wine texture and aroma (Paul 2002, Jones et al. 2004). Its proponents say the process is simply a more effective way to introduce oxygen into wine, simulating barrel maturation, while avoiding the disastrous effects of too much oxygen at any one time.

The micro-oxygenation process is said to improve the apparent weight and mouth-feel of white wines, provide better colour stability in red wines, diminish excessive herbaceous characters, and remove unpleasant reductive characters (Paul 2002). Some of these changes appear to be associated with various polymeric phenol compounds. For example, changes in astringency appear to be due at least in part to changes in tannin (proanthocyanidin) composition (Jones et al. 2004).

Achieving closure

But what happens after the wine is made and bottled? What role, if any, does oxygen play in the development of wine in the bottle? And how important is the closure?

Several recent studies have shown that different closure types differ in their ability to exclude atmospheric oxygen. In general, synthetic stoppers allow oxygen to pass into the bottle at a relatively high rate compared to other closure types, while screwcaps (ROTE closures) let in relatively little oxygen. Natural cork closures occupy the middle ground.

Although it appears possible for a wine to develop in the bottle in the total absence of oxygen, recent studies by the AWRI suggest that undesirable reductive characteristics can develop if the wine's redox potential is too low as a result of too little oxygen at bottling or as a result of the closure's oxygen barrier properties.

For example, a five-year study by George Skouroumounis and his colleagues (Skouroumounis et al. 2005a) in conjunction with an Australian winemaker found that Riesling and wooded chardonnay sealed in ampoules or under screwcap (ROTE) closures developed a "struck flint/rubber (reduced) aroma".

On the other hand, too much oxygen leads to the development of browning and the loss of beneficial flavour compounds. Under synthetic closures, the wines in the Skouroumounis study were "relatively oxidised in aroma, brown in colour, and low in sulphur dioxide". The synthetic-closed wines were also generally low in fruity attributes and high in "oxidised, wet wool, toasty and plastic" aromas.

The Skouroumounis study found that the same wines sealed under cork showed "relatively high perceived fruit intensity" and "negligible reduced characters". This reflects that fact that over many years of using natural cork closures, consumers have come to appreciate the qualities of wines that have developed under cork.

Many factors at play

The factors that can affect the impact of oxygen on the development of wine stored in bottles are not yet fully understood. Although the closure is "perhaps the most obvious variable that might influence wine development in the bottle, it is only one factor" (P. Godden et al. 2005). Others include headspace volume and gas composition, levels of free and total SO_2, bottling line conditions, storage temperature—and the particular composition of the wine itself. While empirical studies are helping to improve our understanding of the impact of these different factors, we are still a long way from achieving "a full understanding of wine development in bottle", if in fact we can ever attain this ultimate goal.

Enough but not too much

In terms of the closure itself, the main factor appears to be the oxygen barrier properties, i.e. the ability of the closure to exclude atmospheric oxygen from the bottled wine. Too much oxygen leads to premature oxidation; too little may lead to undesirable ‘reduced’ characters. Between these two extremes lies an area where the use of different closures associated with even relatively minor differences in the availability of oxygen can lead to the creation of different wines.

However, it is also possible for closures with different oxygen barrier properties (or oxygen transmission rates, OTRs) to influence the levels of particular wine components without affecting sensory perceptions of the wine.

Studies have shown that synthetic closures have relatively high OTRs. For example, most of the nine synthetic closures in the AWRI closure trial had transmitted significantly more oxygen than corks and screwcaps by the 24-month mark and the wine under the synthetic closures was showing undesirably high oxidised aroma scores (P. Godden 2002, L. Francis et al. 2003). The University of Bordeaux 2 tested a range of natural cork and synthetic closures and found that the synthetics allowed substantially higher OTRs than the cork (Lopes et al. 2005). The Bordeaux research was supported by Amorim as part of its ongoing program of sponsoring research and development projects that will expand our knowledge of the behaviour of natural cork and cork-based closures and lead to the development of even better cork closures.

The University of Bordeaux found that first-grade natural cork stoppers had an OTR equivalent to between 0.002 and 0.004 millilitres of oxygen per day. Over the same period, Twin Top® closures had an OTR of 0.0002 millilitres of oxygen per day. Lopes and his colleagues used a non-destructive method that measured the colour of an indicator solution in bottles stored lying down, i.e. they inferred the rate of oxygen ingress from the changing colour of the indicator solution rather than trying to directly measure the OTR.

The full range of natural cork closures (three first-grade and one third-grade colmated cork) tested by the University of Bordeaux researchers varied in permeability by a factor of less than three. This level of variability in cork’s ability to exclude oxygen is similar to the variability found for screwcaps, as supported by the results of the AWRI closure trials.

Other investigations of the oxygen transmission rate of natural cork have relied on the Mocon method, which is an established method for directly measuring oxygen permeability in packaging materials (‘dry packages’) but does not give reliable results for wetted natural corks.

Using the Mocon method, the AWRI found an OTR for reference 2 corks of 0.0001 to 0.1227 millilitres of oxygen per day and an OTR for screwcaps of 0.0002-0.0008 millilitres of oxygen per day (Godden et al. 2005). Research conducted at Southcorp Wines in 1999 yielded OTRs for natural cork ranging from less than 0.001 to more than 1.0 millilitres of oxygen per day and an OTR for screwcaps of less than 0.001 millilitres of oxygen per day (Gibson 2005).

Independent wine industry consultant Richard Gibson was manager of the team that carried out the Mocon measurements at Southcorp in 1999. He believes the Mocon method is a good indicator of oxygen transmission in synthetic closures, dry corks in upright bottles and screwcaps, but says that "there appears to be little relationship between the Mocon figures for cork and what actually happens in the bottle when the wine is in contact with the cork" (Mills 2005).

Former wine chemist John Casey argues that the Mocon method cannot measure the oxygen barrier properties of cork because the conditions required for taking Mocon measurements effectively destroy these properties by reducing the gas content of the cork cells and the moisture content of the cork (Casey, pers. comm. April 2006).

According to New Zealand winemaker and chemistry PhD Alan Limmer, “it is reasonable to assume that the OTR of corks in reality is in the order of 1000 times less than their highest Mocon results” (Limmer, pers. comm. April 2006). Limmer argues that this is because a cork in a wine bottle absorbs some of the wine, effectively creating a “liquid plug” that dramatically slows the movement of oxygen into the wine.

A two-year study by the University of Auckland in conjunction with New Zealand winemaker Michael Brajkovich concluded that natural cork and screwcap closures “presented a similar effective barrier to gas movement” (Brajkovich et al. 2005). The study found that a trained sensory panel could not distinguish between a sauvignon blanc wine sealed under natural cork and the same wine sealed under screwcap. After two years, both closures retained good levels of two volatile thiols considered to be essential for the distinctive box tree/passionfruit and grapefruit varietal aromas of sauvignon blanc.

Through the closure or around it?

There is an apparent contradiction between cork’s proven ability to act as an effective long-term seal for bottled wine and its ability to allow minute amounts of oxygen to enter the bottle. Cork is a remarkable natural material consisting of a honeycomb of tiny cells made from suberin, a complex fatty acid, and filled with an air-like gas. There are on average about 40 million cells per cubic centimetre of cork or around 800 million cells in a single wine cork.

So how does oxygen get into a cork-sealed bottle?

In one of its closure trials, the AWRI investigated the different routes by which oxygen might travel through or around the closure in the neck of a wine bottle. They concluded that the main route for oxygen permeation in natural cork closures was “probably through the cork-glass interface” (Skouroumounis et al. 2004). The AWRI researchers used araldite to cover part or all of the top of the closure and then looked at the extent of browning as an indicator of oxygen entry. The closure-glass interface is also believed likely to be the route by which oxygen enters a screwcap-sealed bottle, as the tin-foil layer in a screwcap wad should be impermeable to oxygen (Casey, pers. comm. April 2006).

However, the preliminary results of a more recent study by the University of Porto’s Department of Chemical Engineering suggest, for natural cork closures, that most of the oxygen diffuses through the closure, although some permeation through the cork-glass interface was also found (Cristiana Pedrosa, University of Porto, pers. comm.). The Porto researchers used the Wicke-Kallenbach method, a Mocon-like test that uses different concentrations of oxygen on either side of the cork to drive the movement of oxygen, but maintains the same total gas pressure on both sides of the cork. The study was partly funded by Amorim.

A better understanding of the mechanism of oxygen entry will enable Amorim to determine whether its products might require modification or whether it should recommend modified bottling practices in order to afford winemakers greater control over the entry of oxygen into the wine bottle.

Other factors

Variable levels of dissolved oxygen in wine can result from contact with air and the formation of oxidants prior to bottling, contact with air in the filling bowl and on entry into the bottle during bottling, and variations in headspace volume, pressure and gas composition. Other contributing factors include the chemical composition of the particular wine, including the presence of key metal ions, and the extent of any chemical additions such as SO_2 and ascorbic acid.

On the bottling line

Possible bottling line sources include vacuum corkers, small leaks in feed lines and turbulent flow during filling. Vacuum corkers are used to remove air from the headspace between the cork and the wine. They help to reduce the risk of high internal pressures, but if not working consistently well can lead to some bottles being sealed with significant amounts of oxygen. Some wineries have modified their filling procedures to guard against oxygen pick-up resulting from turbulent flow.

Although often attributed solely to the closure, the phenomenon known as ‘random oxidation’ or ‘sporadic post-bottling oxidation’ is more likely to be the result of one or a combination of bottling line factors acting to increase the oxygen level in a small proportion of bottles. John Casey, a former chief chemist with McWilliam’s Wines, lists the main factors behind sporadic post-bottling oxidation (Casey 1998) as the presence of exogenous auto-oxidisable substances (including ellagitannins from oak, and ascorbic acid), low carbon dioxide levels, air contact, changes in brimful capacity of the bottles, variations in bottle bore profiles, inconsistent performance of corking machines, inadequate or marginally adequate levels of SO_2, difficulties in achieving target levels for free SO_2, and the entry of atmospheric oxygen associated with the closure.

In relation to screwcaps, Tyson Stelzer lists potential risk factors that can lead to variable levels of dissolved oxygen in wine as including contact with air prior to bottling, contact with air during bottling, bottling line stoppages, turbulent flow during filling—and variation in headspace volume, pressure and gas composition (Stelzer 2005).

The delayed onset of sporadic post-bottling oxidation (typically six to 18 months after bottling) may be explained in part by data from recent AWRI experiments that suggest “oxygenation events before or at bottling may not generate detectable changes in wine colour until some months later” (Skouroumounis 2005b).

The two faces of ascorbic acid

Ascorbic acid is sometimes added to wine as an anti-oxidant, but may also play other less desirable roles. For example, it has been observed to promote oxidative activity and use up SO_2, further increasing the potential for premature oxidation and browning reactions (Bradshaw et al. 2004). On the other hand, a recent AWRI study found that SO_2 levels in a Riesling and a wooded Chardonnay wine after five years storage were either “little different or slightly but statistically significantly higher” in wines to which ascorbic acid had been added at bottling (Skouroumounis et al. 2005b). However, other findings from the AWRI study are consistent with the hypothesis that the pro-oxidative effect of ascorbic acid is only observed after most of the ascorbic acid has been consumed. This delayed effect may also contribute to the delayed onset of sporadic post-bottling oxidation.

The importance of sulphur dioxide

Sulphur dioxide is added to wine for its antimicrobial and anti-oxidant properties and its ability to inhibit the activity of enzymes that catalyse oxidation. Some of the added SO_2 becomes bound to other wine components, while the rest remains ‘free’. The bound SO_2 plays a crucial role in tying up acetaldehyde and other carbonyl compounds that, if released, would lead to adverse colour and odour development.

The free SO_2 helps to inhibit bacterial growth, ensures the complete suppression of free carbonyls and counteracts the effects of any oxidants or oxygen (Casey 1996). If the free SO_2 drops below a certain level, some of the bound SO_2 is converted back into free SO_2, releasing some of the carbonyl compounds. There is a close correlation between SO_2 consumption and oxygen entry, although the situation is by no means straightforward, with some of the other chemical components of the wine also playing significant roles.

Position, position, position

In terms of storage position, Skouroumounis and his AWRI colleagues (Skouroumounis et al. 2005a) found that, for cork closures, upright bottle storage "generally resulted in wines with higher scores for brown, orange and overall colour intensity". Bottle storage position did not appear to affect the performance of the other closures tested by AWRI. The cork-sealed bottles tested by the University of Auckland were stored lying down (Brajkovich et al. 2005), providing further evidence of the importance of correct storage position.

Conclusion

The chemistry of winemaking and wine development is complex and not fully understood. However, it is clear that oxygen exerts a significant influence during most if not all stages of the process. In particular, the availability of small but controlled amounts of oxygen appears to have a beneficial impact on the long-term ageing of fine wines.

Some good progress is being made in determining the reasons for the importance of oxygen and identifying the many factors that can enhance or dilute its impact—including the closure.

Claims of 1000-fold variability in the oxygen transmission rates of natural cork-based closures have been shown to be in error by more recent OTR studies and careful analysis of the results of various closure trials.

The phenomenon of 'random oxidation' is increasingly acknowledged as being the result of a range of bottling line factors rather than solely due to the properties of cork closures.

However, more research is required to improve our ability to control these factors in the way that modern winemaking demands. A key priority will be to investigate the oxidation states of wines under a range of cork and non-cork closures. This should provide useful information to complement the findings of studies showing that corks and screwcaps, for example, have similar oxygen barrier properties.

References

M.P. Bradshaw, G.R. Scollary & P.D. Prenzler, 2004, 'Examination of the sulfur dioxide-ascorbic acid anti-oxidant system in a model white wine matrix', *J Sci Food Agric*, **84**, pp318-324.

M. Brajkovich, N. Tibbits, G. Peron, C.M. Lund, S.I. Dykes, P.A. Kilmartin, & L. Nicolau, 2005, Effect of Screwcap and Cork Closures on SO_2 Levels and Aromas in a Sauvignon Blanc Wine, *J. Agric. Food Chem.*, Vol. 53, pp 10 006-10 011.

J. Casey, 1996, 'Oxidation, serendipity and sulphur dioxide', *The Australian Grapegrower and Winemaker*, Annual Technical Issue 1996, pp42-52.

J. Casey, 1998, ‘Sporadic oxidation of packaged wine’, *The Australian Grapegrower and Winemaker*, August 1998, pp37-39.

V. Cheynier, V. Atanasova, H. Fulcrand, J-P. Mazauric & M. Moutounet, 2002, ‘Oxygen in wine and its role in phenolic reactions during ageing’, Proceedings of Australian Society of Viticulture and Oenology Seminar on ‘Use of gases in winemaking’, October 2002, ed. M. Allen et al., ASVO, Adelaide, p23.

L. Francis, J. Field, M. Gishen, A. Coulter, P. Valente, K. Lattey, P. Høj, E. Robinson & P. Godden, ‘The AWRI closure trial: sensory evaluation data 36 months after bottling’, *Aust. & NZ Grapegrower and Winemaker,* August 2003, 59-64.

R. Gibson, 2005, ‘Variability in permeability of corks and closures’, Presentation to American Society of Enology and Viticulture Science of Closures Seminar, June 2005. Available from www.scorpex.net/ASEVClosures2005RGibson.pdf.38-39

P. Godden, 'Update on the AWRI trial of the technical performance of various types of wine bottle closures', *Technical Review* 137, April 2002.

P. Godden, K. Lattey, L. Francis, M. Gishen, G. Cowey, M. Holdstock, E. Robinson, E. Waters, G. Skouroumounis, M. Sefton, D. Capone, M. Kwiatkowski, J. Field, A. Coulter, N. D’Costa & B. Bramley, 2005, ‘Towards offering wine to the consumer in optimal condition – the wine, the closures and other packaging variables: A review of AWRI research examining the changes that occur in wine after bottling’, *Aust. & NZ Wine Industry Journal*, July-August 2005, Vol. 20 No. 4, 20-30, p28.

P.R. Jones, M.J. Kwiatkowski, G.K. Skouroumounis, I.L. Francis, K.A. Lattey, E.J. Waters, I.S. Pretorius & P.B. Hoj, 2004, Exposure of red wine to oxygen post-fermentation – if you can’t avoid it, why not control it?, *Aust. & NZ Wine Industry Journal*, May-June 2004, Vol. 19 No. 3, pp17-24.

P. Lopes, C. Saucier & Y. Glories, ‘Nondestructive Colorimetric Method To Determine the Oxygen Diffusion Rate through Closures Used in Winemaking’, *J. Agric. Food Chem*. 2005, *53*, 6967-6973.

N. Mills, 2005, Sealing themes and variations, *Aust. & NZ Wine Industry Journal*, September-October 2005, Vol. 20 No. 5, p52.

R. Paul, 2002, ‘Micro-oxygenation – where now?’, Proceedings of Australian Society of Viticulture and Oenology Seminar on ‘Use of gases in winemaking’, October 2002, ed. M. Allen et al., ASVO, Adelaide, pp18-22.

G. Skouroumounis, M. Kwiatkowski, Z. Peng, R.G. Dambergs, A. Kleinig, B. Duncan, H. Oakey, D. Cozzolino, D.L. Capone, L. Francis, M. Sefton, E. Waters, 2004, The effect of ascorbic acid, closure type and storage conditions on the composition, colour and flavour properties of a Riesling and a wooded Chardonnay wine, presentation to 12 AWITC (Australian Wine Industry Technical Conference) workshop on ‘Modelling random oxidation in white wine’, Melbourne, 2004.

G.K. Skouroumounis, M.J. Kwiatkowski, I.L. Francis, H. Oakey, D.L. Capone, B. Duncan, M.A. Sefton & E.J. Waters, 2005a, ‘The impact of the closure type and storage conditions on the composition, colour and flavour properties of a Riesling and a wooded Chardonnay wine during five years’ storage’, AJGWR **11.3**, pp369-384.

G.K. Skouroumounis, M.J. Kwiatkowski, I.L. Francis, H. Oakey, D.L. Capone, Z. Peng, B. Duncan, M.A. Sefton & E.J. Waters, 2005b, ‘The influence of ascorbic acid on the composition, colour and flavour properties of a Riesling and a wooded Chardonnay wine during five years’ storage’, AJGWR, **11.3**, pp355-368.

T. Stelzer, *Taming the Screw: a manual for winemaking with screw caps*, Wine Press, Adelaide, 2005.