

EXPANDING ON REDUCTION

By sealing the bottle tightly, metal-lined screwcaps create a low redox potential environment that can turn clean wines into smelly ones, explains Dr Jamie Goode. But this doesn't seem to be an issue for consumers - so should those selling wines worry?

Reduction is one of the most complex and interesting of all wine science topics, at the heart of some of the most lively exchanges in the wine bottle closures debate. Yet despite its importance to the wine trade, it's rarely had the sort of clear, accurate coverage that's needed to make it understandable to those who lack a strong scientific grounding.

Explaining reduction

So let's start at the beginning, with the term 'reduction' itself, which is a misnomer. It refers to a suite of sulfur-containing compounds, alternatively referred to as VSCs (volatile sulfur compounds) and SLOs (sulfur-like odours), commonly found as off-odours in wine. These chemicals are important in wine-making, not only because they cause faultiness, but also because they can contribute positively to wine quality. Almost everyone who has done basic science will be familiar with hydrogen sulfide, which smells of rotten eggs. Clearly, hydrogen sulfide at any level above threshold in a wine is not desirable.

Then there is an important group known as the mercaptans, or thiols. These are sometimes good in wine, at certain levels, and sometimes bad. There are also disulfides, which, again, can be good or bad depending on the context. Also in the mix are thioesters, and then finally other sulfur-containing amino acid metabolites. Some of the descriptors used to describe these chemicals include rubber, burnt match, struck flint and onion. The reason the term 'reduction' is used to describe the presence of these sulfur compounds stems from their frequent appearance in winemaking situations where oxygen is excluded. A chemical term, 'redox potential', is used

as a measure of where a particular chemical system, such as a bottle of wine, is along the spectrum of oxidation and reduction, which themselves describe two different events in chemical reactions: the loss and gain of electrons.

If a bottle of wine is left open, or a cask isn't topped up, the presence of atmospheric oxygen will cause the redox potential to shift towards the oxidation end of the spectrum, and the wine will oxidise. If the wine is sealed tightly from air ingress, then it will shift the other way and reduction reactions will occur. The reason 'reduction' is a misnomer when used to describe this sort of wine fault is that in some circumstances it is possible for a wine that has been han-

dled in an oxidative fashion to show above-threshold levels of these sulfur compounds and thus appear reduced: in this case, introducing more oxygen to the wine to try to deal with the 'reduction' could be a big mistake.

The problem's origin

These sulfur compounds are produced by yeasts, which all wines have. They only become problematic when they reach levels above which most people can detect them in wine. Why they are such a worry for winemakers is because we are able to detect them at low levels - as low as one part per billion. Why is this? I have a theory that has to do with the evolution of human olfaction. If we are exquisitely sensitive to particular compounds, it is likely there was strong evolutionary pressure for us to have that sensitivity: in humans, olfaction is used primarily to keep us away from dangerous situations (e.g. a forest fire) or unsuitable food (e.g. rotten meat).

When olfaction was being shaped by selective pressure, toilets didn't exist. It was therefore important that we should find faecal material extremely unpleasant, because being in close proximity to it could be dangerous. Inside our guts, there is rich microbial life, living in a largely anaerobic environment, poor in oxygen. In such conditions, microbes will often make use of a metabolic pathway that uses the sulfur-containing amino acids methionine and cysteine as a nitrogen source, thus liberating sulfur to produce the sorts of sulfur-containing compounds we are talking about here. It could be that the reason we find such compounds smelly and aversive is because they are such a good marker for hazardous faecal material.



Sulfur compounds are also reactive, and can change their form in wine. The chemistry is poorly understood, and sulfur taints are difficult to remove. But perhaps even less would have been known about them were it not for the widespread use of tin-lined screwcaps which began in earnest in 2000 in Australia and New Zealand. At the time the view in the industry was that the ideal wine bottle closure was one that provided as tight a seal as possible, with no or very little oxygen transmission. This is what screwcaps delivered. Today, more than 95% of New Zealand and around 70% of Australian wine bottles are sealed this way.

But by sealing the bottle so tightly, the metal-lined screwcap was creating a low redox potential environment in the wine that encouraged some of the sulfur compounds to change form. This made it possible for wines that were clean at bottling to develop sulfur off-odours later. This 'screwcap reduction', as it has become known, became a hot topic in 2001, with the first publication from the Australian Wine Research Institute's closure study. The screwcap performed best across measures like fruit retention and freshness, but tasters picked up a hint of struck flint and rubber in the wines – reduction. Other closure trials reported similar findings, creating a controversy. Advocates of screwcaps argued that such reduction was entirely avoidable if good winemaking practices were carried out. Others countered that it seemed perverse to get winemakers to change their wines to fit the closure, particularly when other taint-free alternatives to cork existed. The cork lobby had a field day. All this controversy focused attention on the as-yet poorly understood topic of wine sulfur chemistry.

A vocal contributor to the debate was New Zealand winemaker Dr Alan Limmer, of Stonecroft in Hawkes Bay. Limmer first noted problems with screwcapped wines in a newsletter he published in 2002, and since then has been a regular contributor to the debate on closure-related reduction. This has not made him popular with many of his colleagues, who are heavily committed to

the use of screwcaps, but Limmer has a scientific background and as a chemist has been able to explain many of the complex post-bottling sulfur compound changes that have left others dazed and confused. Limmer thinks the issue may be much bigger than just the relatively few obviously reduced screwcapped bottles that are spotted by most tasters. His view is that a high proportion of screwcapped sealed wines are suffering from some low level reductive effects that are only apparent by means of comparison. "Screwcapped wines harden up," says Limmer. "They go into a tight ball." Limmer is currently using Diam for his wines (a taint-free technical cork), but says "if I could be sure of get-



➤➤ Screwcapped wines harden up. They go into a tight ball.

Most people don't get a chance to see the comparisons. ◀◀

Dr Alan Limmer, chemist and winemaker at Stonecroft

ting clean corks, I'd use them." He also says the choice by some winemakers to use screwcaps for their whites, but corks for their reds, is not logical.

If there are all these problems with screwcaps, how come the wine industries that have relied on them – chiefly New Zealand and Australia – been so successful in recent years? Screwcap-sealed wines sell well, and do well in competitions. While the faults clinic

results from the International Wine Challenge in 2006 caused a media storm when it was announced that 2.2% of screwcapped wines were rejected because of reduction (a figure not far off the 2.8% of cork-sealed wines that were kicked out because of cork taint), it is hard to imagine that these reduction defects would be spotted by consumers in the absence of a side-by-side comparison. Perhaps this is the answer: screwcap reduction, as it exists, is a non-issue for consumers, and by extension, also for those in the business of selling wines. But perhaps a similar statement could be made about cork taint and random oxidation; while this is a cause of concern to winemakers, consumers happily keep buying cork-sealed bottles.

But winemakers are anxious to see their product reach the consumer the way they intended it to taste. If Limmer is correct that the problem is more pervasive than thought, then consideration needs to be given about whether a liner with little oxygen transmission is suitable for wine. Both Guala closures and Alcan, the two largest manufacturers of wine screwcaps, are working to produce new liners that allow a little more oxygen transmission, similar to the best corks.

Avoiding the problem

Many winemakers believe strongly that most screwcap reduction can be avoided by putting in place a set of practices to minimise the build up of sulphur compounds. But Limmer disagrees. "In essence we are talking about thiol accumulation, post-bottling, from complex sulfides which do not respond to pre-bottling copper treatment," he claims in response to the assertion that fining with copper removes reduction defects. "This reaction occurs to all wines containing the appropriate precursors, irrespective of closure type. But the varying levels of oxygen ingress between closures leads to significantly different outcomes from a sensory point of view." Because yeasts are responsible for the production of these compounds during fermentation, they are the focus of a lot of the attention.

Bernard Hickin, winemaker with Jacobs Creek in Australia, explains how

he ensures clean wines. “We use low-sulfide-producing strains of yeast, and check the nitrogen levels in the must,” he explains. “We monitor FAN [free available nitrogen] and never stress the yeasts. We also don’t want too high a cell count of yeasts, which can strip the fruit – if you have twice as many soldiers in an army, they all start smelling.” Hickin avoids adding diammonium phosphate (known simply as DAP; a nitrogen source) until the yeasts are hungry. “We wait until the nitrogen source has almost run out, we don’t add too much, and the timing of additions is important.”

This minimises the need for copper additions at the end of fermentation. Copper is commonly used as a fining agent to remove unwanted mercaptans, but its increasing use has come under

fire, first because of the health implications of putting a heavy metal in wine, and secondly because it can strip out some of the ‘good’ reduction.

Yeasts differ markedly in the levels of sulfides that they produce. Angela Lee Linderholm recently completed her PhD studies working in Linda Bisson’s laboratory at University of California Davis, and identified some of the key genes involved in pathways of sulfide production by yeasts. This work is promising and efforts are underway to produce low sulfide yeast strains by conventional crossing, as GM yeasts are not currently acceptable to most wine markets.

While the development of sulfur compounds is normally best avoided, there are some circumstances where their development can contribute something

positive. Bready, brioche characters in Champagne from long lees ageing, nuttiness in some Chardonnays, subtle cabbage and matchstick in high-end white Burgundies and cat’s pee in Sauvignon Blanc are all related to sulfur compounds. Some winemakers even deliberately flirt with reduction because they feel it can add complexity at the right level, and also that it sets up some wine styles for long development.

So while there has been a lot of progress, there are still unanswered questions that should keep wine scientists busy for some time. A broad understanding of these closure and post-bottling wine chemistry issues could be more than just an intellectual luxury, because even a small gain in wine quality could confer a competitive advantage. ■

1 Volatile sulfur compounds in wine

COMPOUND	SENSORY IMPACT	NOTES
Hydrogen sulfide	Rotten eggs, sewage.	Made by yeasts when they use one of the sulfur-containing amino acids as a nitrogen source.
Mercaptans (also known as thiols)	This is a large group of very smelly sulfur compounds: cabbagey, rubbery, struck flint or burnt rubber are used as descriptors.	If hydrogen sulfide isn’t removed quickly, it can result in mercaptan production.
Ethyl mercaptan	Burnt match, sulfidy, earthy.	Often negative, but can be positive at certain levels.
Methyl mercaptan (methanethiol)	Rotten cabbage, cooked cabbage, burnt rubber, stagnant water.	One of the compounds implicated in screwcap reduction.
Dimethyl sulfide	Cooked vegetables, cooked corn, canned tomato at high levels; blackcurrant drink concentrate at lower levels. Quince, truffle.	Produced by the breakdown of amino acids in wine; can be positive at low levels.
Diethyl sulfide	Rubbery.	Usually below threshold in wine.
Dimethyl disulfide	Vegetal, cabbage, onion-like at high levels.	Disulfides are a big problem: while they are usually below threshold levels, they can revert to the more smelly mercaptans and cause problems.
Diethyl disulfide	Garlic, burnt rubber.	Usually below threshold in wine.
Carbon disulfide	Sweet, ethereal, slightly green, sulfidy.	Not much known about this; rarely a problem in wine and can be positive.
4-mercapto-4-methylpentan-2-one (4MMP), 3-mercaptohexan-1-ol (3MH), 3-mercaptohexyl acetate (3MHA)	Tropical fruit/passion fruit at low levels; cat’s urine at higher levels.	Common in Sauvignon Blanc but also found in red wines where they can contribute to the blackcurrant fruit aroma. An example of sulfur flavours that can be positive in the right environment.
Benzenemethanethiol	Smoky, gunflint aromas.	Can be positive in the right context and at the right levels.