Cork as a Closure -

Post-bottling reduction, and 'Permeability' performance

Prepared for 'A closer look at cork closures'
Napa, June 2006
By Dr Alan Limmer

Cork as a Closure

- Post bottling reduction;
- *What is it?*
- *How is it caused*
- *What role does the closure play?*

- Cork 'Permeability' (OTR)
- *How variable is cork as a closure?*
- *The things that determine its performance*

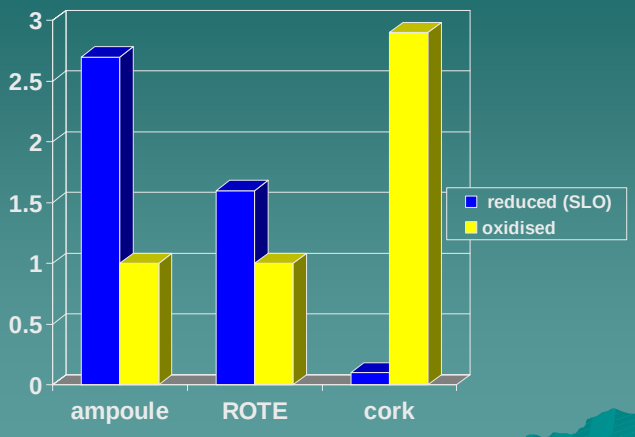
- Closure trials have demonstrated that different closures produce different wines over time, after bottling the same wine.
- The style and development of the wine is strongly influenced by the choice of closure.

Do Corks Breathe?

- General assumption by winemakers that corks provide anaerobic environment for the development of wine.
- "..the quantities of oxygen that normally penetrate into the bottles are negligible if not zero. Oxygen is not the agent of normal bottle maturation."
  - **J Ribéreau-Gayon *et al* (1976),** "Traité d'Oneologie - Sciences et Techniques du Vin" Vol. 3
  - "...it is the opposite of oxidation, a process of reduction or asphyxia, by which wine develops in the bottle."
  - **E. Peynaud (1981),** "Knowing and Making Wine"

- A common observation of all closure trials is that the wine under the most anaerobic closure exhibits ‘reduced’ character after a period of time.
- The AWRI trials have referred to this note as SLO – sulfur like odours.
- A typical profile of this character with respect to the closure is like this;

AWRI Closure trial wine after 48 months in bottle



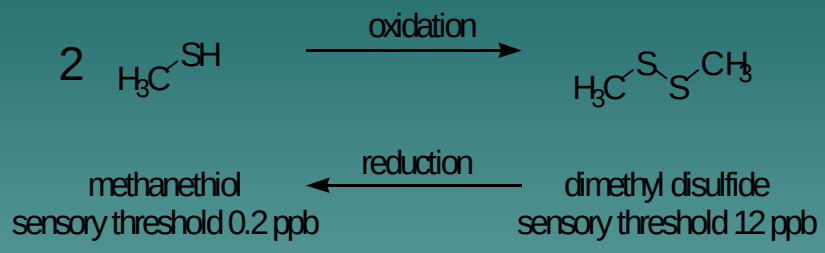
Origin of SLO

- Most wine chemistry is determined by REDOX reactions – REDuction/OXidation
- The term 'reduced' is a misnomer when we refer to sulfides. They will exist in the wine whether the wine is 'reduced' or 'oxidized'. But the form of the sulfides will change with the different Redox state of the wine.
- Sulfides consist of a range of components from simple H2S to Thiols *or Mercaptans* (R-S-H), Disulfides (R-S-S-R) and Thioesters (R-S-CO-R)
- *For a more detailed discussion of this topic see Limmer, PWV Mar/Apr ,May/Jun, 2006*

Thiol – Disulfide reactions

- The sensory properties of these compounds vary markedly, with Thiols generally having much lower thresholds than Disulfides – ie Thiols 'smell' a lot more than Disulfides (20-40 X more).
- Thiols are easily oxidised to Disulfides – eg by racking, or any introduction of air.
- The smell appears to disappear or diminish.
- But the sulfides are still present in the wine – they just smell less as Disulfides.

- Most redox reactions are reversible – so our 'innocuous' Disulfide is able to be reduced – back to Thiol – with an increased smell.
- We need a reducing agent to reduce the Disulfide ; SO2 (SO3=) is the culprit. (Bobet,Noble and Boulton. 1990. Kinetics of ethanethiol and diethyl disulfide interconversion in wine-like solutions. *J. Agric. Food Chem*. 38:229-452)



- H2S and Thiols (Mercaptans) are easily removed with Copper fining pre-bottling.
- Disulfides and Thioesters are not. Any Disulfide and Thioester present in the wine will be bottled.
- It is impossible to make wine without a large range of these sulfide compounds – blame the yeast – not the winemaker. (see ref below)
- Thioesters have also been demonstrated to degrade to Thiols (and esters). (Rauhut D, Kurbel H, Die Entstehung von H2S aus Netzschwefel – Rückständen während der gärung und dessen Einfluß auf die Bildung von böckserverursachenden schwefelhaltigen Metaboliten in Wein. Wein –Wissenschaft 49; 1, 27-36. 1994)

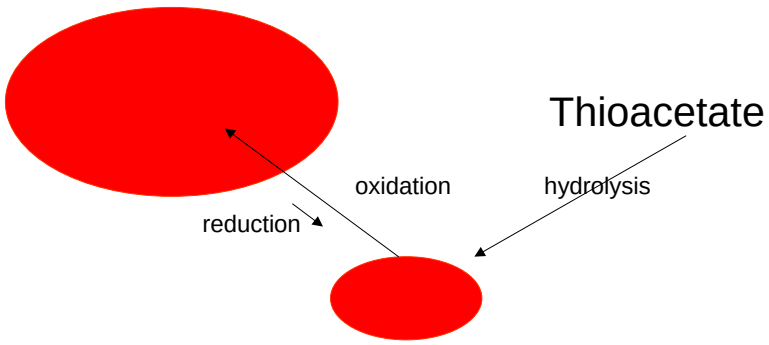
Post –bottling problems

- We now have two sources for Thiol production, post bottling, from an otherwise 'clean'wine -
- Disulfide reduction
- Thioester degradation (hydrolysis)

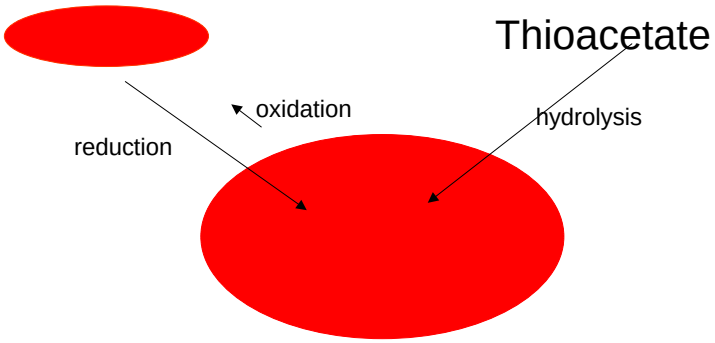
How much SLO?

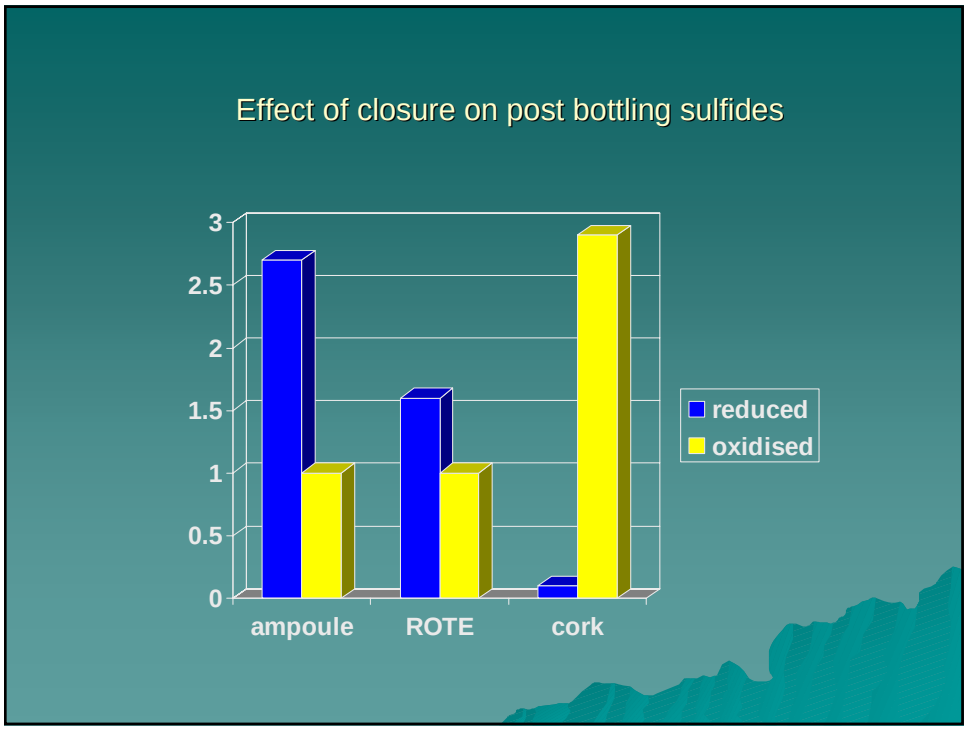
- How much Thiol we accumulate, post –bottling depends on;
- The quantities of the precursors present (Di-S, ThioAc)
- The amount of reducing agent (Free SO2)
- The amount of oxygen ingress post bottling – for oxidation of the Thiol back to Disulfide

Delicate balance – Disulfide accumulation vs....



Thiol accumulation





Misinterpretation

- … to avoid ‘reduction’ under screw caps, the wine must first be in the right state of oxidation pre – bottling..’
  - Para phrase – Taming the screw – a manual for winemaking with screw caps. Winepress 2005. T Stelzer

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- It is about rates of oxygen ingress through the closure vs rates of thiol production/accumulation *post – bottling, irrespective of the ‘oxidative’ state of the wine pre-bottling.*

How prevalent is SLO ?

- Too many wines showing sulfides under screw cap. *Chief judge's report , Air NZ Wine Awards 2004*
- This is the article I never wanted to write – about screw caps. It's a negative article. It's a major concern.

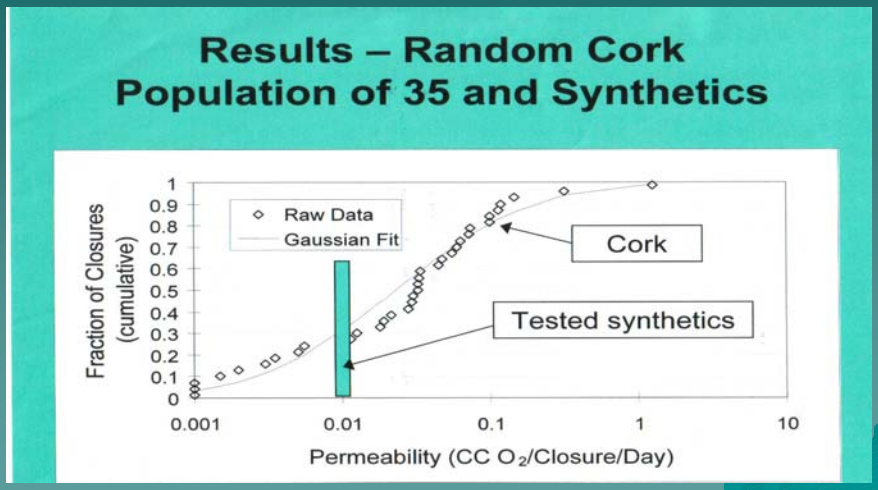
  I have never seen widespread reduction issues in a clutch of wines like I did in the NZ wines presented on the opposite page at any tasting where cork is the predominant seal….

  Do we need to introduce a Screwcap License system?
- *Campbell Mattinson. Winefront Monthly. Mar/Apr 2006 www.winefront.com.au*

The cork permeability/1000fold variation myth.

- Corks have frequently been cited as the cause of serious bottle variation, which has been attributed to variable rates of oxygen ingress.
- The 'permeability' data for corks has exacerbated this belief, in that oxygen transmission rates (OTR) measured for cork show large (1000 fold) variability.

Southcorp MOCON OTR data
Australian Closure Fund report Feb 2005



MOCON OTR data

	ccO2/day	
	Mean	Range
ROTE	0.0005	0.0002 - 0.0008
Cork	0.0179	0.0001- 0.122

(ref 2)

AWRI data, Screw Cap Symp, NZ 2004

Actual performance of cork as a closure

- **Is far more complex than simple MOCON data and is governed by the following chemistry and interaction with the wine;**
- **Henry's Law – which tells us that the distribution of a gas is approximately 1000 fold less in the solution compared to atmosphere.**
- **Ficks law - which tells us that the diffusion of a gas is approx 10,000 times slower in a liquid than a gas.**
- **Poiseuilles Law – which tells us it is about 100 times harder to push a liquid through a porous medium than a gas.**
- For a more complete description of the important interaction between the cork and wine see "The permeability of closures." *A Limmer. The Australian and NZ Grapegrower and Winemaker. Annual Technical issue 2006*

63 months data from AWRI closure study

	Free SO2 (mg/L)		Total SO2 (mg/L)		OD420 au	
	mean	Std Dev	mean	Std Dev	mean	Std Dev
Altec	12	1.0	75	1.6	0.17	0.004
1+1	8	1.6	68	1.2	0.20	0.006
Ref 2	7	2.3	65	6.7	0.20	0.014
Ref 3	3	1.7	52	9.1	0.23	0.013
ROTE	14	1.9	80	3.5	0.17	0.005

Variability of cork closures

- The SD values of SO2 and OD420 for cork are approximately 0.3 -3 times that of ROTE, depending on the type of cork and the parameter measured.
- The worst variance measured is 3 times that of ROTE, and the best is 3 times better than ROTE.
- This is ***not*** the performance of a closure with 1000 fold variation in OTR.

Conclusions

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- The variability of the OTR of cork as a wine closure is slightly higher than ROTE, but bears little resemblance to the MOCON OTR data, unlike other closures.
- This is due to some chemistry and an interaction between the cork and wine, which is unique to cork as a closure.