The role of trace metals in wine 'reduction'

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Copper salts have traditionally been added to wines to remove unpleasant volatile sulfur aromas. However, investigations of interactions between metals and volatile sulfur compounds are now revealing that metals can also promote the formation and release of these unwanted aroma compounds, particularly in low oxygen storage environments. Winemakers can minimise the risk of 'reductive' aromas by managing the timing of any copper additions and taking steps to minimise metal concentrations.

AT A GLANCE

- 'reductive' aromas in wine are caused by volatile sulfur compounds including hydrogen sulfide (H_2S), methanethiol (MeSH) and dimethyl sulfide (DMS)
- H_2S is described as rotten egg, MeSH as rubber or natural gas, and DMS in high concentration as canned corn or vegetal
- metal ions have been shown to affect the formation and release of these unpleasant aroma compounds in wine
- some reactions of metal ions with volatile sulfur compounds are reversible – with metal ions initially decreasing their concentration but later resulting in high concentrations
- to reduce the risk of 'reductive' aromas, grapegrowers and winemakers should aim to minimise the metal concentrations in grapes and wine
- copper additions are most effective if made around the end of fermentation, when yeast cells are still available to remove residual copper ions.

Winemakers are familiar with adding copper sulfate to wines that show rotten egg or other 'reductive' characters when in tank. Many winemakers have also seen these 'reductive' characters disappear from their wines in the short term, only to see them return at a later date, sometimes after bottling. By exploring the chemistry of volatile sulfur compound formation and the important role played by metals, these common winemaking observations can be better understood, potentially leading to recommendations on ways to reduce the risk of unwanted 'reductive' aromas.

WHERE DO 'REDUCTIVE' AROMA COMPOUNDS COME FROM?

The volatile sulfur compounds responsible for 'reductive' aromas in wine are mainly derived from yeast metabolism. They can also form via the degradation of sulfur-containing amino acids and sulfur-containing pesticides. One of the important factors that influence their production is the amount of oxygen a wine is exposed to post-bottling, with wines exposed to very low levels of oxygen more likely to develop 'reductive' aromas (Ugliano 2013). Recent reports have shown that H_2S, MeSH and DMS concentrations can increase in wine post-bottling and that lower post-bottling oxygen exposure results in greater increases (Ugliano *et al.* 2012, Ugliano *et al.* 2011, Lopes *et al.* 2009).

Metal ions are naturally present in grapes and wine. In trace amounts, metals are important in fermentation. They can also be introduced into wine by human activity, both through direct addition and as a by-product of other winery processes. Metals such as tungsten (W), zinc (Zn), copper (Cu), cobalt (Co), iron (Fe), nickel (Ni) and manganese (Mn) all have the ability to catalyse oxidation and reduction reactions, but of these only Fe, Zn, Cu and Mn are likely to be present in wine at concentrations high enough to have a significant effect (Lachner and Nicolini 2008). Aluminium (Al) has also been shown to be important in limiting oxygen consumption in wine (Vivas 2002). Several of these metals have been associated with undesirable effects in wine.

A MULTI-METAL EXPERIMENT

To investigate the effects of metals on the formation of the 'reduced' aroma compounds MeSH, H_2S and DMS during bottle ageing, a large experiment was designed where five metals (Cu, Fe, Mn, Zn, Al) were added to Chardonnay and Shiraz wine samples singly and in all possible combinations (31 metal treatments, one control) (Viviers *et al.* 2013). The metals were present at two levels: a low level equivalent to the concentration of the metals already present in the base wine, and a high level that was spiked to approximately 10 times the concentration of the metals measured in the base wine. The concentrations of volatile sulfur compounds in the wines were analysed over a 12-month period. At bottling, the wines contained oxygen at around the recommended level of 1mg/L (Chardonnay 1.11 ± 0.34mg/L; Shiraz 1.43 ± 0.35mg/L) and after four months of anaerobic storage the dissolved oxygen (DO) of both Chardonnay and Shiraz samples decreased to 0µg/L. Significant changes in volatile sulfur compounds were observed over the 12-month period, with the Chardonnay samples showing increases in H_2S and DMS, and the Shiraz samples showing increases in H_2S and MeSH.

IT'S NOT ONLY COPPER

The most remarkable results of this current study were the effects observed

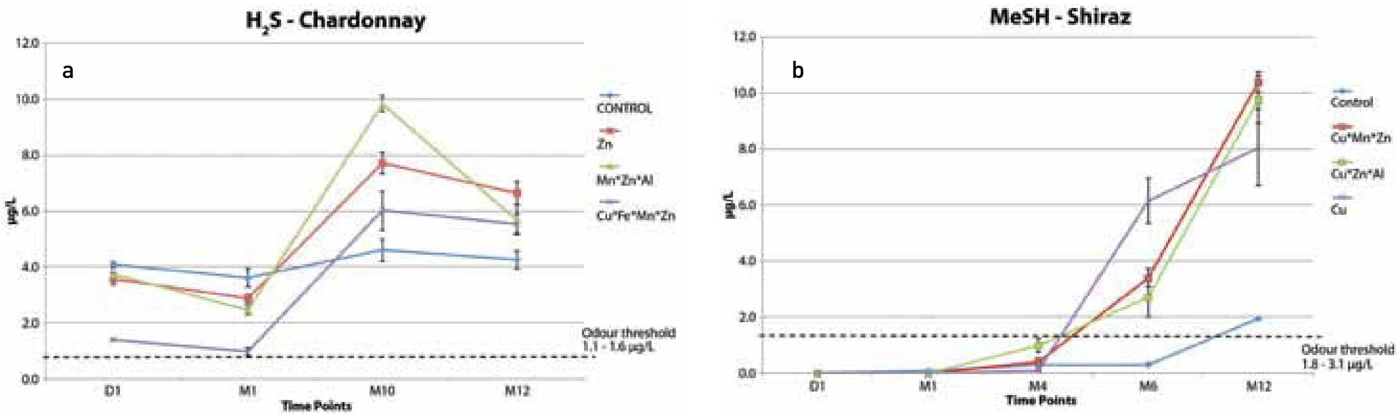

Figure 1. Line graphs showing three of the metal additions that were associated with the largest increases in H_2S concentrations at the twelfth month for Chardonnay samples (a) and three of the metal additions associated with the largest increases in MeSH concentrations at the twelfth month for Shiraz samples (b). Odour threshold values are indicated by the dashed black line parallel to the x-axis at 1.1-1.6µg/L for H_2S and 1.8-3.1µg/L for MeSH.

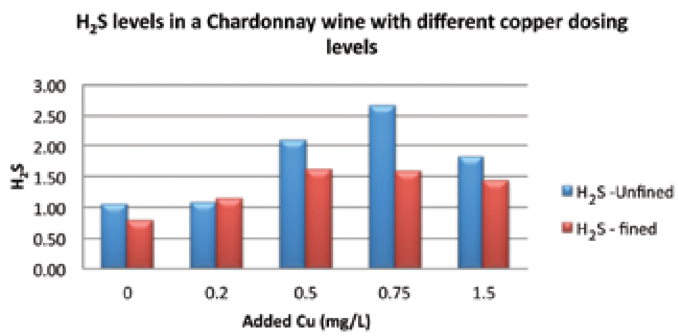

Figure 2. The relationship between Cu dose and H_2S formation after six months for a bentonite-fined and unfined Chardonnay wine bottled under commercial conditions.

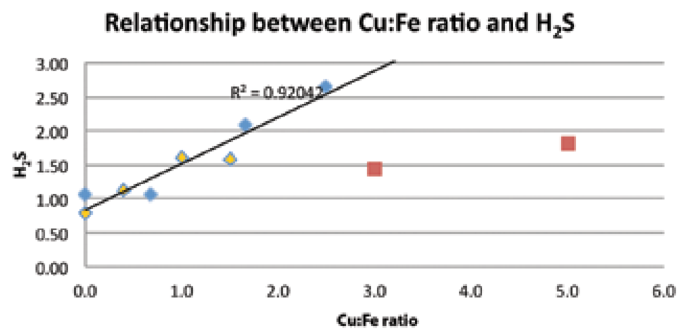

Figure 3. The relationship between Cu:Fe ratio and H_2S formation after six months for bentonite-fined and unfined Chardonnay wine. The blue diamonds represent the unfined wines (Fe 0.2mg/L), the yellow diamonds the fined wines (Fe 0.5mg/L) and the two red squares the wines with the extreme Cu dose (1.5mg/L).

due to metals that have not previously been considered in the context of volatile sulfur compounds in wine (Mn, Zn and Al), as well as the interactions between the five metals. If the Chardonnay and Shiraz samples are considered together, only seven of the 31 metal treatments significantly affected the evolution of H_2S in both wines: Cu, Fe, Zn, Al, Cu*Fe[1], Cu*Mn*Al and Cu*Zn*Al.

Three of the metal treatments - Zn, Mn*Zn*Al and Cu*Fe*Mn*Zn - associated with the largest increases in H_2S concentrations in the Chardonnay samples at the tenth month are shown in Figure 1a. Using multivariate statistics, we found that the increases in H_2S concentrations shown in the figure were due to the specific metal combinations: Zn, Al, Zn*Al or Mn*Zn*Al and were not influenced by Cu or Fe. Similarly, three examples of metal treatments associated with some of the largest increases in MeSH concentration in the Shiraz samples are shown in Figure 1b. The increased MeSH concentrations in samples with added Cu*Mn*Zn, Cu*Zn*Al and Cu were found to be driven by the significant effect of Cu, and not through the interaction with the other metals.

Overall, fewer metals produced significant effects on DMS evolution, and the effect of the metal treatments was mostly associated with an overall decrease in DMS concentration. The only metal treatments associated with significant effects on DMS concentration in both Chardonnay and Shiraz samples were Al and Zn*Al. The effects of these metals in decreasing the DMS concentration could possibly be due to the metals inhibiting the formation of DMS from its precursor molecules already present in the wine, or due to the catalytic degradation of DMS.

BUT COPPER IS STILL IMPORTANT

The influence of the concentration of Cu and other metals in wine on H_2S production was reinforced in another recent AWRI trial where different levels of Cu (0, 0.2, 0.5, 0.75 and 1.5mg/L) were added to a Chardonnay (both bentonite-fined and unfined) which was then bottled under commercial conditions. After six months, the wines with a 0.5mg/L or greater Cu addition had significantly higher H_2S concentrations than the lower dose wines (Figure 2). The dosing relationship was especially apparent for the wine that had not been bentonite-fined for protein stability.

The difference in results for the fined and unfined wines led to further investigations of these wines, which revealed that they had significantly different iron (Fe) levels (0.2mg/L for the unfined wine and 0.5mg/L for the bentonite-fined wine). The extra Fe was added through the bentonite fining process. When the levels of H_2S formed after six months were plotted against the Cu:Fe ratio for each dose rate, a significant linear trend was apparent for Cu additions below 1.5mg/L (Figure 3). This clearly shows the importance of the Cu:Fe ratio in the formation of H_2S. The non-linear results seen at the highest dose rate suggest that once this high level of Cu was reached, the chemistry followed a different pathway.

IT'S NOT JUST 'ACADEMIC'

These effects are not just limited to 'academic' trials. The metal concentrations in 144 wines rejected from a 2011 international

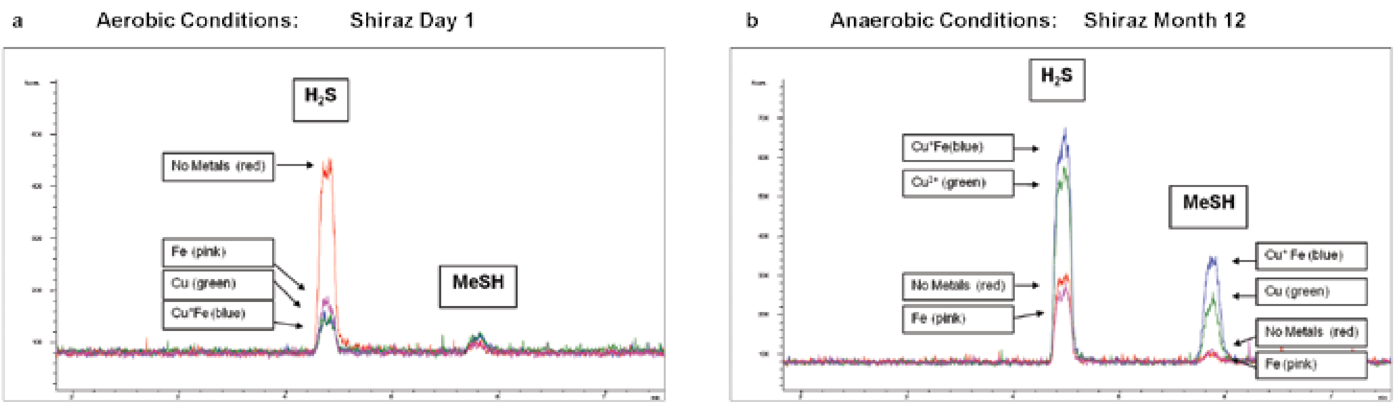

Figure 4. Typical chromatograms for the analysis of H_2S and MeSH in Shiraz wine samples with added Cu, Fe and the metal combination Cu*Fe shown here at (a) Day 1 and at (b) the twelfth month. The metals Cu, Fe and Cu*Fe were associated with significant decreases in H_2S concentration at Day 1, but after 12 months of anaerobic storage Cu and Cu*Fe were associated with significant increases in H_2S and MeSH concentrations.

wine show because of 'reduced' characters were analysed and compared with the metal concentrations of another 514 wines rejected for other faults unlikely to be influenced by metal content. Comparing the concentrations of metals for wines that were shown to have above-threshold levels for MeSH (>1µg/L) to those that did not, it was apparent that higher levels of Fe and Mg and lower levels of Al were associated with the 'reduced' wines compared with the non-'reduced' wines. Interestingly this study did not show any effect of copper, probably because the majority of wines tested in this study had a relatively low copper concentration (median <0.1mg/L for both 'reduced' and non-'reduced' groups).

METAL EFFECTS CAN BE REVERSIBLE

In the large multi-metals study, some metal treatments were initially associated with decreases in volatile sulfur compound concentrations, but these effects were shown to reverse after four months of anaerobic storage (Figure 4). At Day 1, when samples were analysed directly after metal spiking, when DO concentrations were high (0.150–1.50mg/L), the three metal treatments (Cu, Fe and Cu*Fe) decreased the H_2S concentration compared with the control, but after 12 months of anaerobic storage, the samples treated with Cu and with Cu*Fe displayed significant increases in H_2S concentration.

In the Chardonnay and Shiraz samples the same reversible effect was observed for MeSH as was seen for H_2S. At Day 1 no MeSH was measurable in Shiraz samples with or without added Cu, but after one month of anaerobic storage the samples not treated with Cu showed increases in MeSH compared with the Cu-treated samples. However, as the wine consumed all available oxygen, the MeSH concentration in the Cu-treated wines slowly increased. After 12 months of anaerobic storage, the MeSH concentration in all samples with added Cu had reached an average of 6.39µg/L, substantially higher than its odour threshold value of 1.8-3.1µg/L (Siebert *et al.* 2010). These results show that the formation of MeSH is not only influenced by the presence of metals, but that the oxygen concentration in wine also significantly affects its evolution.

BE CONSCIOUS OF WHAT YOU'RE ADDING TO YOUR WINE

Winemakers should pay attention to this observation of reactions reversing over time, particularly when considering routine additions of copper to remove unwanted sulfur aromas from wine. Copper additions are effective if made early in a wine's life, preferably around the end of fermentation, when yeast cells are still available to help 'mop up' residual metals. If, however, copper is added later, significant amounts can remain in the final wine, greatly increasing the risk of developing 'reductive' aroma compounds in bottle. This study has demonstrated the importance of keeping metal concentrations as low as possible in wine, as the metals can act singly or in combination to greatly influence evolution of unwelcome 'reductive' aromas.

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FOOTNOTE

[1] The notation 'Cu*Fe' indicates a treatment of Cu and Fe in combination.

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