# Further understanding of bentonite's impact on metals in wine

Bentonite is a naturally occurring clay used in wine production world-wide to remove grape-derived proteins that might otherwise lead to haze formation. It has a high surface area and negative charge which attracts positively charged proteins, binding them so they can be removed via settling and filtration. A range of bentonite products is available for winemaking, mined from different natural deposits around the world. These products differ in their composition as well as in the way they are processed. The natural deposits themselves are not uniform, and batches of the same product can vary. This means that just like vineyards, the performance of a given bentonite product may vary from one vintage to the next.

Bentonites are generally classified as sodium, calcium or sodium/calcium bentonites; however, they also contain many other trace metals that can be transferred to wine through ion exchange (Catarino et al. 2008). Given that there are regulatory limits for metals in different markets (AWRI 2018) and that metal ions play a significant role in oxidation and reduction reactions in wine (Viviers et al. 2013), it is important to understand any changes in metal concentrations that may result from using processing aids. Such changes may also have an impact on authenticity testing that relies on absolute concentrations of metal ions (Jaganathan et al. 2006).

## Previous results

A previous AWRI study (Loveridge et al. 2017) showed a significant influence of wine pH on metal transfer from bentonite, the direction of which differed for different metals. For example, calcium, lead and iron were extracted at higher rates at lower wine pH; whereas lithium and strontium were extracted at higher rates at higher pH. The study also looked at metal ion changes when bentonite was added to protein-stable wine compared to protein-unstable wine. This significantly affected the exchange of major ions in the wine. For example, calcium concentration increased when bentonite was added to stable wine but decreased when it was added to unstable wine. Potassium decreased significantly when bentonite was added to unstable wine but only slightly when it was added to stable wine, and sodium decreased significantly when bentonite was added to the stable wine but saw minimal change following addition of bentonite to unstable wine. These effects were only tested in a single wine.

## New study

In extending the previous work, the current study looked at 14 different bentonite products (five sodium, eight sodium/calcium and one calcium) and three unstable wines (Chardonnay, Sauvignon Blanc and Viognier) from the 2017 vintage. The wines were dosed at the rate required to achieve stability, determined by individual fining trials with each product. The wines were also overdosed by 50% above the required rate to assess the effect of overdosing. All metal ion concentrations were measured using inductively coupled plasma mass spectrometry (ICP-MS). The initial metal concentrations in the untreated wines are shown in Table 1, with the regulatory limits imposed in overseas markets shown for comparison purposes.

## Ranges of metal concentration changes

Figure 1 summarises the changes in metal concentrations observed in the wines treated with bentonite at the optimal dose rates, with data for the three wines and the fourteen bentonite products combined in a single plot.

Wide ranges of changes were seen for most metal ions, with bentonite treatment generally causing an increase in metal ion concentration, although decreases were seen in some outlier cases. The exceptions were copper and strontium, which both saw general decreases after bentonite treatment. Despite most bentonites being classified as sodium and/or

**Table 1.** Initial metal ion concentrations in untreated wines used in this trial (µg/L) and limits for metal concentrations in wine imposed in international markets.

| | Chardonnay | Sauvignon Blanc | Viognier | International limits |
|---|---|---|---|---|
| Aluminium | 303 | 40 | 241 | 8,000 |
| Arsenic | < 2 | < 2 | < 2 | 100-500 |
| Calcium | 85,000 | 63,000 | 58,000 | - |
| Chromium | 3.0 | 6.0 | 9.0 | - |
| Copper | 400 | < 100 | < 100 | 1,000-10,000 |
| Iron | < 300 | < 300 | < 300 | 8,000-20,000 |
| Lead | < 2 | 4.3 | < 2 | 150-2,500 |
| Lithium | 13.5 | < 5 | 17 | - |
| Magnesium | 104,000 | 66,000 | 151,000 | - |
| Manganese | 1,000 | 400 | 1,000 | * |
| Nickel | 7 | 7 | 12 | - |
| Potassium | 990,000 | 757,000 | 741,000 | - |
| Sodium | 37,000 | 29,000 | 32,000 | 60,000-500,000 |
| Strontium | 1,670 | 605 | 2,208 | - |
| Zinc | 727 | 432 | 823 | 5,000-40,000 |

*Note: Until recently, China was imposing a limit of 2,000 µg/L for manganese in wine, but that limit has now been removed. There are reports that this limit is still being imposed in China on some older vintage wines.

calcium bentonites, potassium seemed to be the metal most involved in the ion exchange, although changes in wine potassium concentration were still small compared to the initial concentrations in the wines. The median percentage increases were 2% for potassium, 10% for calcium, 7% for magnesium and 17% for sodium. The transfer of major ions was also not necessarily correlated with dose rate. For example, the Chardonnay wine required higher dose rates of all bentonites to achieve stability than the Sauvignon Blanc or Viognier wines; however, greater increases of potassium and calcium were seen in the Sauvignon Blanc and Viognier wines (data not shown).

Looking at the trace metals, median increases of aluminium and manganese were both around 0.4 mg/L, while zinc and iron increased by around 0.2 mg/L. Aluminium and iron are both involved in oxidation/reduction reactions which can influence the production of reductive aromas and affect shelf life. Percentage increases of manganese, zinc and iron were around 30–50%. Percentage increases of aluminium were much higher, 100%-700%, depending on the base levels in the wines. Copper is also involved in oxidation/reduction reactions, but bentonite treatment appeared to have a stripping effect on copper in most cases. The previous study also saw a reduction in copper, but only when the wine being treated was protein unstable, suggesting that there is a chance to remove copper with bentonite during protein fining, but that bentonite cannot be used to remove copper later in production once the wine is stable. Strontium concentration was also lowered in most cases (median 20% reduction).

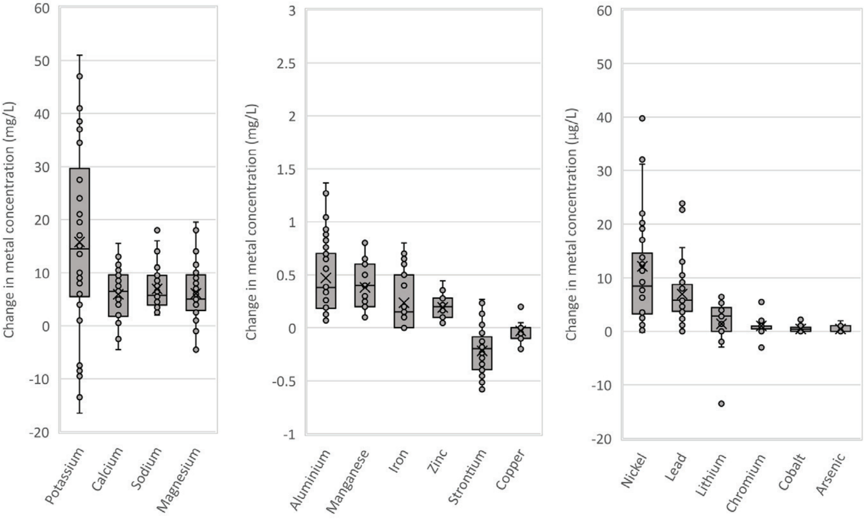

**Figure 1.** Summary of changes in metal concentration in three white wines treated with 14 bentonite products at the optimal treatment rate for each wine/bentonite combination (note different y-axis scales for the different metals). In this plot the box denotes the interquartile range, the line in the middle of the box denotes the median, the X denotes the mean, the circles show individual results, and results beyond the whiskers are considered outliers.

Strontium is often a key element in authenticity studies, so bentonite treatment may complicate authenticity determinations which use absolute concentrations of trace metals.

Of the elements tested, almost all of the lead in the wine came from bentonite treatment. Nickel concentrations were approximately doubled by bentonite treatment. Median increases of lithium, chromium, cobalt and arsenic were all around 20%. In some cases, arsenic increased by up to 100% (2 μg/L) but concentrations were still a long way below any regulatory limits or levels responsible for health concerns. Tin, vanadium, cadmium, selenium and silver were not found at quantifiable levels in any of the samples. None of the changes observed in the wines treated at the optimal fining rate resulted in concentrations higher than any of the international regulatory limits.

## Overdosing

The wines were also overdosed by 50% more than the optimal rates determined by fining trials, to assess the effect of over-fining on metal ion transfer. For each wine and bentonite variant where overdosing was performed, the ratio of the concentration change from the overdose to the concentration change from the optimal dose was calculated. A concentration change of 150% would be expected, in line with the 150% dose; however, this is not what was observed for many of the metals. The ranges of these values for each metal ion are shown in Figure 2. The results for many of the metals were variable and did not scale proportionally with dose rate. Concentrations of aluminium, arsenic, calcium, iron, nickel and sodium did appear to

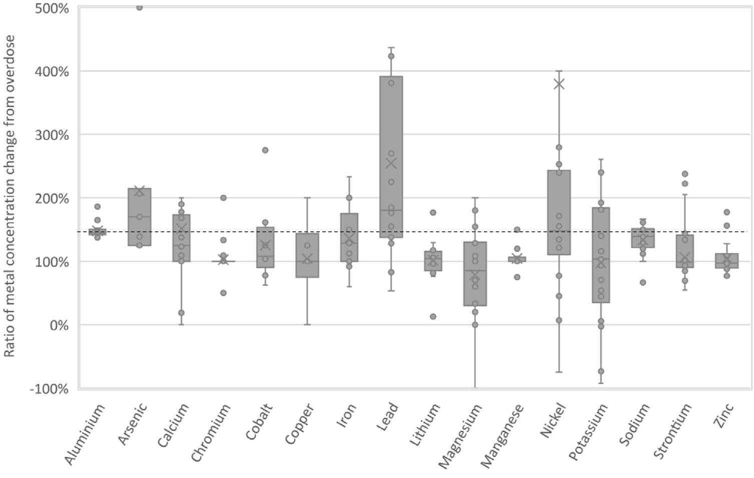

**Figure 2.** Ratio of metal concentration change from 1.5x overdose of bentonite to the concentration change from the optimal dose of bentonite, expressed as a percentage. Dotted line shows expected increase according to dose increase. Values around the dotted line imply a linear relationship between concentration and dose rate when overdosing. Values below the dotted line increased less than expected from overdosing. Values above the dotted line increased more than expected when overdosing.

scale with dose rate. Lead concentrations from overdosing were higher than expected from the higher dose rate. Chromium, cobalt, lithium, manganese, potassium, strontium and zinc did not seem to be influenced by overdosing. Magnesium concentrations were slightly lower after overdosing compared to the optimal doses. For some wine/bentonite combinations, overdosing with bentonite was enough to near or exceed regulatory limits for some metals in some markets; for example, one of the wines would have exceeded the limit for sodium in Switzerland. This highlights the need for wineries to be aware of metal content and the potential influence of bentonite treatment, particularly if a 'standard' dose is used across a winery, which raises the potential for overdosing of some wines.

## Conclusion

Metal concentrations in wine can be significantly influenced by bentonite treatment, and those influences can vary between products and batches. Many of the metals in wine affected by bentonite treatment have limits imposed in export markets and/or have potential for significant effects on wine shelf life and the production of reductive aromas. Winemakers around the world therefore need to be aware of the potential for changes in metal concentrations following bentonite use and the importance of metals analysis to ensure continuing compliance with regulatory requirements. Benchmarking of bentonite products can also help inform winemakers of differences in their performance, and identify changes in products over time as different parts of the natural deposits are mined.

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