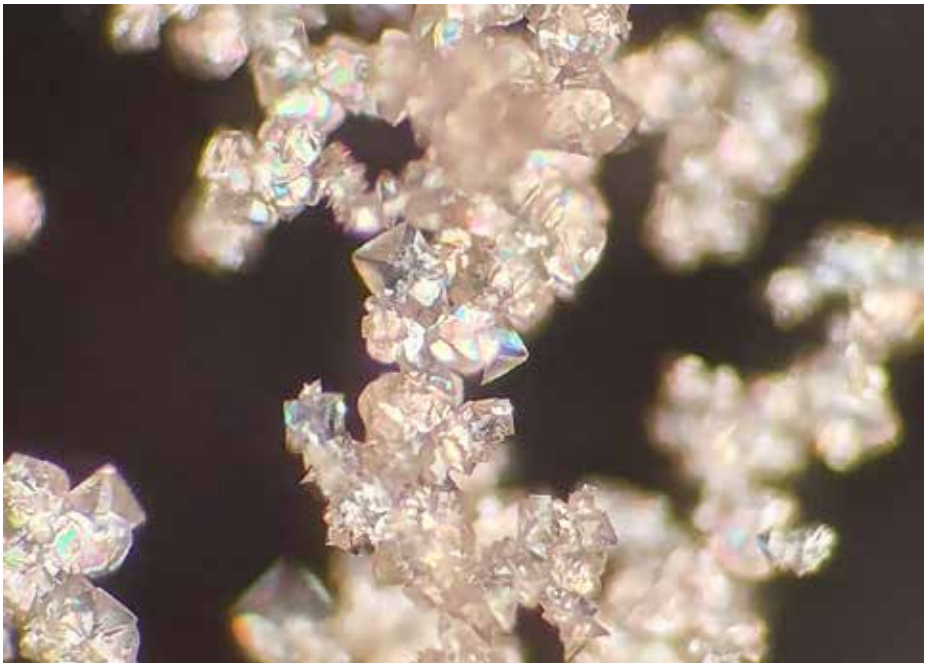
ask the AWRI

Calcium oxalate deposits – kidney stones in wine?

While calcium tartrate instability in wine is well known and was discussed in a previous 'Ask the AWRI' column (Holdstock 2016), winemakers may be less familiar with a more peculiar calcium instability: calcium oxalate. In humans, calcium oxalate crystals are the most common type of kidney stone. However, in wine, these crystals only seem to occur in Botrytis wines. In this column, AWRI Senior Oenologist, Adrian Coulter, responds to questions about this enigmatic, crystalline deposit.



Why do calcium oxalate deposits only seem to occur in Botrytis wines?

Calcium oxalate deposits occur in wine when oxalic acid levels are high enough to precipitate out with the calcium ions present. However, generally, oxalic acid levels in wine are very low, making such deposits rare. For example, Siener et al. (2017) found the oxalate concentration ranged from 3.0 to 12.7 mg/L in wine, with the higher values observed in red wines. These results are consistent with results obtained by the AWRI during the 1990s, when helpdesk investigations showed the oxalate level in wines ranged from 'none detected' to 15 mg/L. However, Botrytis wines may contain elevated levels of oxalic acid compared to other wine types. For example, recent helpdesk investigations revealed an oxalate concentration of approximately 700 mg/L in one Botrytis wine containing a calcium oxalate deposit, and approximately 1,100 mg/L in another, younger, deposit-free Botrytis wine.

Yin *et al.* (2018) indicated that *Botrytis cinerea* synthesises and secretes oxalic acid to acidify host tissues, which subsequently enhances the activity of enzymes that degrade cell walls. It is therefore assumed that the oxalate-excreting property of *Botrytis cinerea*, combined with the concentrating effect resulting from the infection, ultimately result in elevated levels of oxalic acid in Botrytis wines. The amount of oxalic acid produced by *Botrytis cinerea* appears to be strain-dependent, as Sun *et al.* (2019) found that one strain (B05.10) of *Botrytis cinerea* produced approximately twice as much oxalic acid as another strain (T4).

Why do the crystals take so long to form?

It is well known that calcium tartrate crystals are slow to form, often dropping out of solution several months after bottling. However, calcium oxalate deposits take even longer to form, typically two to three years after bottling.

Amerine *et al.* (1980) indicate that oxalic acid can form stable complexes with iron which prevent its precipitation as the calcium salt. Over time, an increase in the redox potential causes the transformation of the stable ferrous oxalate to the unstable ferric oxalate. The ferric oxalate salt can then release oxalic acid into solution, which can combine with calcium and precipitate as calcium oxalate. However, the situation is likely more complex than this, as the concentrations of oxalic acid in the two Botrytis wines recently investigated by helpdesk mentioned above were approximately 500 and 1,000 times higher than their respective iron concentrations. That is, it is not feasible that low levels of iron could complex with such high levels of oxalate anions. It might be possible that iron is involved in redox cycling with other wine components (e.g. polysaccharides, proteins and organic acids other than oxalic acid) that might inhibit calcium oxalate crystal growth, such that calcium oxalate crystallisation inhibitors become degraded over time, resulting in eventual calcium oxalate deposition. However, this is speculation and research would be required to elucidate the true mechanism involved in calcium oxalate deposition in Botrytis wines.

Are calcium oxalate crystals harmful to health if accidentally ingested?

Given oxalate in the diet can contribute to formation of kidney stones, calcium oxalate crystals in wine might represent a concentrated source of oxalate if ingested. However, Noonan and Savage (1999) indicate that calcium oxalate crystals remain largely undissolved within the digestive tract, are not absorbed into the blood stream and therefore are not toxic to humans. These authors also report that 10–15 g of oxalate is the usual amount required to cause death in an adult. For a Botrytis wine containing

1,000 mg/L of oxalate, a person would need to consume 10 L of the wine on one occasion in order to ingest 10 g of oxalate. It is unlikely an adult person could consume 10 L of this wine, as they would likely die from ethanol poisoning after consuming 5 L!

While calcium oxalate crystals are mainly an aesthetic issue, people who may be limiting their oxalate intake due to a family history of kidney stones, or because they have previously experienced calcium oxalate kidney stones, should be aware that Botrytis wines might contain elevated levels of oxalate compared to other wine types.

Is there a predictive test for calcium oxalate?

Unfortunately, the AWRI is not aware of a predictive test for calcium oxalate stability. It is difficult to devise a predictive test when so little is known about the mechanism of calcium oxalate crystallisation in Botrytis wines and the particular conditions or compositional factors that lead to calcium oxalate deposition.

AWRI helpdesk

The AWRI helpdesk provides a free-of-charge technical advisory service to Australia's grapegrowers and winemakers. For further information about calcium oxalate or any other technical matter, contact the helpdesk on (08) 8313 6600 or helpdesk@awri.com.au.

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