An examination of the role of calcium in wine instability

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FINAL REPORT to
GRAPE & WINE RESEARCH & DEVELOPMENT CORPORATION
PROJECT NO. UM 1GW

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Organisation : The University of Melbourne
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Grape and Wine Research and Development Corporation

Final report

Project Title An examination of the role of calcium in wine instability

Project Code UM1 GW

Organization The University of Melbourne

Location Melbourne

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Objectives

1. To develop a set of criteria which will allow wine makers to predict the possible occurrence of calcium tartrate instability in wines.
2. To examine the role of calcium in protein instability of wines.
3. To examine the role of calcium in the physical instability of Botrytis-affected wines.

Final Report

The major objective of this project was to investigate factors which influence the spontaneous precipitation of calcium tartrate and to establish criteria which would assist wine makers in producing sparkling wines which are stable with respect to calcium tartrate.

Experiments with model solutions showed that any form of solution agitation increases the rate and extent of calcium tartrate precipitation. This can be directly related to sparkling wine production, where it has been observed that calcium tartrate precipitation frequently occurs within two weeks of disgorgement. This sudden onset of precipitation is probably a consequence of the agitation which takes place during the disgorgement process. Filtration of wine at this stage will increase the likelihood of calcium tartrate precipitation due to the agitation involved and possibly also as a result of removing pectic substances, which may be potential inhibitors[1]. As agitation is a natural consequence of disgorgement, and therefore cannot be avoided, it is advantageous to ensure that calcium tartrate precipitation occurs during tirage (see below).

A major factor influencing the precipitation of calcium tartrate is the pH of the wine. Figure 1 demonstrates that the time taken for precipitation to occur, and in fact, whether precipitation occurs at all, is highly pH dependent. At higher pH values, a shorter time is required for precipitation to start and the rate and extent of precipitation is also increased. If precipitation is to be prevented, it is important to maintain as low a pH as possible, taking into account the style of the wine. Further, increases in pH which may occur during the lifetime of a wine should be avoided to minimize the likelihood of precipitation occurring post-disgorgement. While the

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incidence of calcium tartrate precipitation is increasing in Australian sparkling wines, it is interesting to note that American sparkling wines rarely have calcium instability problems[2,3]. This may be due, in part, to the difference in pH between American and Australian sparkling wines. The pH of American sparkling wines is normally at or below a pH of 3.0, whereas the pH of Australian sparkling wines is frequently 3.2 or higher. Crystallization experiments undertaken with the model demonstrate that precipitation does not occur at pH 3.0, but does at pH 3.2. Thus, the higher pH of Australian wines ensures favourable conditions for calcium tartrate precipitation. If Australian wine makers can produce and market wines with pH values similar to those produced in the USA, calcium tartrate instability problems should decrease.

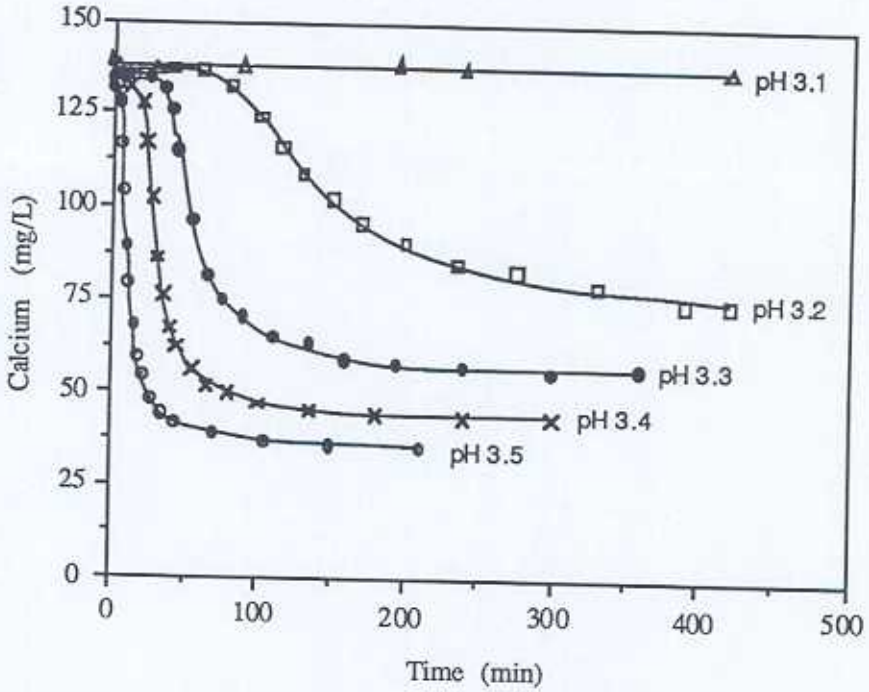


Figure 1 Crystallization curves for the spontaneous precipitation of calcium tartrate in the model solution at various initial pH values.

The presence of malic acid requires considerable precautions to be taken during wine production as, of the organic acids in wine, it is the most susceptible to microbiological degradation[4]. Sulfur dioxide may be used to minimize the onset of bacterial breakdown of malic acid. Alternatively, the wine maker can induce the degradation of malic acid through the use of appropriate bacterial starter cultures. This induced degradation of malic acid is becoming a more common practice in sparkling wine production and it also has the advantage of reducing the excessive acidity of some (particularly cool climate) wines. The bacterial degradation of malic acid is commonly known as "malolactic fermentation" (MLF)[5]. Wines with a high initial malic acid concentration can have this lowered to less than 0.5 g/L after MLF with a corresponding increase in pH by 0.2 units[6].

Figure 2 demonstrates that malic acid is a more effective inhibitor of nucleation and crystal growth than lactic acid. Therefore, if a wine undergoes MLF, an efficient precipitation inhibitor is removed from solution and replaced by a less effective one. This will increase the likelihood of calcium tartrate precipitation occurring. The resulting increase in pH that accompanies MLF will also encourage precipitation.

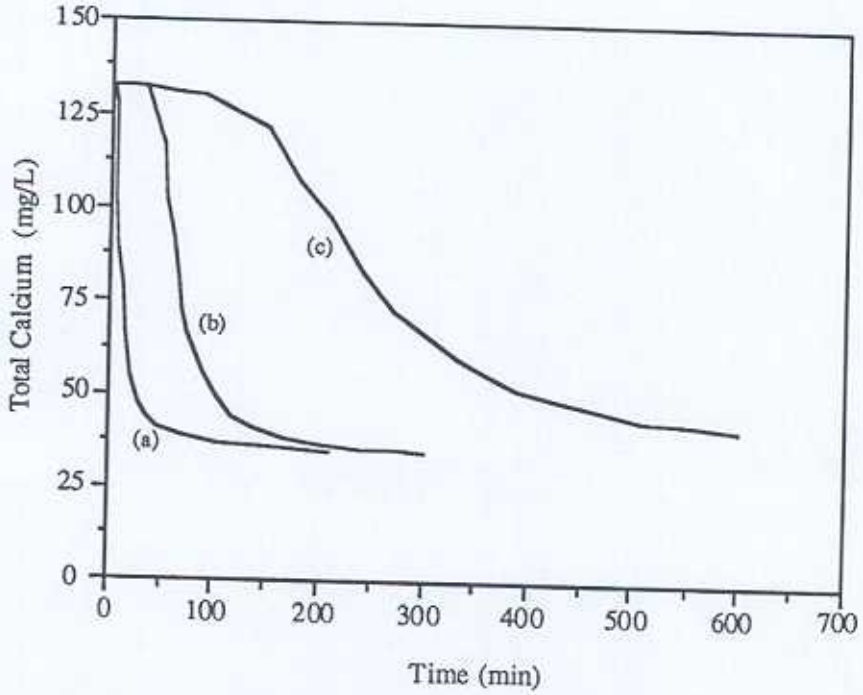


Figure 2 Crystallization curves for the standard model and the model containing various organic acids at pH 3.5 : (a) standard model, (b) 2 g/L lactic acid and (c) 2 g/L malic acid.

Thus, MLF creates conditions which favour the spontaneous precipitation of calcium tartrate by the removal of a strong inhibitor and by raising the pH of the solution. These experimental observations agree with the results found in Australian sparkling wines. A survey of Australian sparkling wines[7] with calcium instability problems showed that the only correlation between the wines and calcium tartrate precipitation was that 90 % of the samples containing calcium tartrate crystals had undergone an uncontrolled MLF during tirage. It has also been observed that, within a batch of wines where instability problems have occurred, only those wines that had undergone MLF precipitated calcium tartrate. To control the influence of MLF, either MLF has to be prevented from occurring during the lifetime of the wine or encouraged to occur early in processing. The prevention of MLF is difficult to achieve with certainty (particularly with wines made by the transfer method) and it is therefore preferable to ensure that base wines have been through MLF. This will help to stabilize the pH of the wine. An early MLF also encourages tartrate-unstable wines to precipitate during the tirage stage. This is an advantage because the crystals are removed along with the dead yeast cells at disgorgement, leaving the disgorged wine stable with respect to calcium tartrate. Australian wine producers should consider the American experience, where sparkling wines are put through MLF early in processing.

The inhibitory effect of pectic substances was also identified as having a major influence on the spontaneous precipitation of calcium tartrate. Commercial polyuronic acids were used and polygalacturonic acid was found to be an extremely effective inhibitor. Uronic acid monomers had no effect on calcium tartrate precipitation, confirming other reports that the complexation capacity requires long chain (ie. : > 15 - 20 units) polymers[8,9].

A survey of some Australian wines showed that the polyuronic acid concentrations in still white table wines were approximately three times higher than in sparkling wines (Table 1). This observation offers a possible explanation as to why white wines are stable at similar calcium and tartrate concentrations to unstable sparkling wines. That is, white wines contain higher amounts of effective inhibitors and consequently, the rate of crystallization will be significantly reduced. Anecdotal evidence that older white table wines do contain crystal of calcium tartrate does support this contention.

Table 1 Polyuronic acid concentrations in Australian wines (mg/L)

Variety	No. of wines	Range	Mean
Still white	13	97 - 282	176
Sparkling	12	44 - 107	72

This project did not address the reasons for various wine styles having different concentrations of polyuronic acids. However, it is reasonable to suggest that the polyuronic acid concentration may be linked to grape processing. It is possible that, as the extent of grape processing is increased, the extraction of pectic substances from berries is also increased. Preliminary results from the polyuronic acid content survey suggest that premium sparkling wines have lower polyuronic acid levels than lower quality sparkling wines and that bag-in-box white wines have the highest polyuronic acid concentrations. Minimal skin contact is common practice in the preparation of base wines for sparkling wine production and whole bunch pressing is frequently used for juice extraction in the production of premium sparkling wines. Further, the juice used in base wine preparation is either "free run" or that obtained from pressing at low pressure. In table wine production, especially those made in large volumes (ie. bag-in-box style wines), extensive maceration may occur during grape processing and higher proportions of pressed juice may be used. Whilst little is known about the distribution of the polyuronic acids in the grape berry, there is some evidence[10] that the majority are located in the skin of the grape. Thus, it is possible that the type of grape processing may influence the polyuronic acid content of the wine.

The polyuronic acid concentration may also be influenced by the use of pectolytic enzymes. Pectolytic enzymes are added to juices to increase filtration speed and to improve clarity[4]. These enzymes function by decreasing the chain length of pectic substances and it is therefore possible that the addition of pectolytic enzymes to a juice will decrease the amount of polyuronic substances with chain lengths greater than 15 to 20. This will decrease the amount of those polyuronic acids which can bind calcium effectively, thereby decreasing the amount of inhibitors present.

Relevant References

(1) Lubbers, S.; Leger, B.; Charpentier, C.; Feuillat, M. *J. Int. Sci. Vigne Vin* **1993**, *27*, 13-22.
(2) Boulton, R. B., Personal Communication.
(3) Howe, P., Personal Communication.
(4) Ough, C. S.; Amerine, M. A. *Methods for Analysis of Musts and Wines;* Second ed.; Wiley-Interscience: New York, 1988, p 269.
(5) Schütz, M.; Radler, F. *Arch. Mikrobiol* **1973**, *91*, 183-202.
(6) Wilkinson, J., Personal Communication.
(7) Scollary, G. R., Unpublished Consulting Report, 1989.
(8) Yalpani, M. *Polysaccharides - Syntheses, Modifications and Structure/Property Relationships*; Elsevier: Amsterdam, 1988, p 110.
(9) Kohn, R.; Luknár, O. *Coll. Czech. Chem. Commun.* **1977**, *42*, 731-744.
(10) Baldwin, G., Personal Communication.

SUMMARY

This project has demonstrated that various wine making procedures influence the precipitation of calcium tartrate. Control of pH and malo-lactic fermentation are of particular importance. If these parameters are not controlled and if a wine is potentially unstable with respect to calcium tartrate crystallization, physical factors such as agitation will induce the precipitation. Identification of these factors is a significant advance in establishing criteria for predicting the occurrence of calcium tartrate instability (Objective 1). Polyuronic acids were also shown to be critical in determining the induction of calcium tartrate precipitation. The effect of wine making procedures on the extent and chemical composition of the polyuronic acids will be examined in detail in a subsequent project.

During this work, it was established that amino acids had no effect on the rate of calcium tartrate crystallization. Further, calculations based on the amount of protein in wine and of the number of potential calcium complexing sites associated with the protein molecules indicated that the residual protein would have little impact on calcium tartrate instability. On the basis on these observations, it was concluded that calcium is unlikely to be involved in protein instability (Objective 2).

Whilst Botrytis-affected wines were not examined as such, the results of the polyuronic acid study carried out in this project are relevant to Objective 3. That is, the observation that polyuronic acids are extremely effective binding agents for calcium at wine pH may well be related to the often observed physical instability of Botrytis-affected wines. This will also be examined in more detail in a subsequent project.

THESIS

Anthony McKinnon has successfully completed his PhD thesis at The University of Melbourne for his research work on this project.