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Understanding calcium tartrate precipitation in wines: A comprehensive study from soil and grapevine to stabilisation strategies before bottling

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ABSTRACT

Calcium (Ca^{2+}) plays a pivotal dual role in grapevine physiology, acting both as a structural element essential for cell wall integrity and membrane stability, and as a secondary messenger regulating plant growth and stress responses. Calcium accumulation in grape berries significantly affects composition and wine chemistry, influencing one of the most complex forms of wine instability: calcium tartrate (CaT) precipitation. CaT instability remains difficult to predict due to its slow crystallisation kinetics, delayed precipitation onset, and the complex interactions among calcium, tartaric acid, and the various components of the wine matrix.

This review integrates past and current findings from soil science, plant physiology, berry development, and wine chemistry (integrated "vineyard → winery" approach) to provide a comprehensive overview of Ca^{2+} dynamics from vineyard to bottle. Key agronomic factors, including soil composition, active limestone content, rootstock selection, irrigation strategies, and climate change, are explored for their influence on calcium uptake and distribution within grape tissues.

At the oenological level, this review analyses the main biochemical and physicochemical factors influencing CaT precipitation, including pH, ethanol, organic acids, phenolic compounds, and macromolecules such as grape-derived polysaccharides and mannoproteins. It further evaluates both traditional and innovative stabilisation strategies, such as cold treatment, electrodialysis, ion-exchange resins, and protective colloids, assessing their effectiveness and impact on wine quality. Finally, it highlights existing knowledge gaps and emphasises the need for an integrated vineyard-to-winery approach to develop predictive models (*e.g.*, Calcium Tartrate Risk Index) and optimise stabilisation techniques, ensuring wine stability and preserving sensory quality under changing climatic conditions.

KEYWORDS: calcium tartrate, precipitation, wine stability, calcium dynamics, vineyard-oenology interaction, stabilisation techniques

INTRODUCTION

Beyond water availability, the capacity of plants to acquire and regulate mineral nutrients from the soil is a critical determinant of both ecosystem sustainability and crop quality. Among these nutrients, calcium (Ca^{2+}) occupies a unique position as a key element in plant physiology and fruit composition. Unlike other cations, calcium plays a dual role: it functions as an essential structural nutrient, contributing to cell wall integrity, membrane stability, and berry development; simultaneously, it acts as a secondary messenger in numerous signalling pathways that regulate plant growth and responses to environmental stress (Cabanne *et al*., 2003; Shao *et al*., 2008). Furthermore, calcium availability is strongly influenced by numerous factors, which will be discussed in detail below. This complexity explains why Ca^{2+} nutritional studies often produce different results and why its role in grapevine metabolism and berry ripening remains partially unresolved.

Understanding these dynamics is particularly relevant in viticulture, as calcium accumulation in berries directly affects the chemical composition of wine and the risk of calcium tartrate (CaT) precipitation. Calcium tartrate precipitation is among the most complex and least predictable forms of wine instability, posing significant challenges to both vineyard management and winemaking practices. Calcium concentrations in wine typically range from 7 to 310 mg/L (Waterhouse *et al*., 2024); however, several studies report increasingly frequent cases exceeding 300 mg/L, especially in wines from regions affected by water stress and rising temperatures (Kallithraka *et al*., 2001). Unlike potassium bitartrate (KHT), whose precipitation kinetics, saturation thresholds, and stabilisation methods are well established, CaT instability remains difficult to control due to its slower crystallisation rates, delayed onset of precipitation, and the multifactorial interactions among calcium ions, tartaric acid, and the various components of the wine matrix (AWRI, 2024).

This review integrates current knowledge from soil science, plant physiology, berry development, and wine chemistry to provide a comprehensive understanding of the mechanisms underlying calcium tartrate precipitation. Specifically, it examines the following key themes:

– The impact of soil composition, rootstock, physiology, and vineyard practices on Ca^{2+} uptake and distribution in grape berries;
– The role of the main agronomic practices in the vineyard and post-harvest interventions in promoting calcium accumulation in the berry;
– The biochemical and physical factors within the grape and wine matrix that regulate Ca^{2+} solubility and CaT crystal formation;
– The strengths and limitations of current stabilisation methods, and their impact on wine quality and sensory attributes;
– The potential of an integrated approach, linking vineyard management with oenological techniques to predict and mitigate CaT instability.

To this end, the review is organised into six main sections, which can be summarised as follows: (i) Agronomic aspects, examining the sources and dynamics of Ca^{2+} from soil to grape berry. (ii) Calcium physiology in grapevine, focusing on uptake, transport mechanisms, and compartmentalisation in berry tissues. (iii) Wine chemistry and CaT precipitation, discussing the molecular and physicochemical factors influencing CaT formation and solubility. (iv) Predictive testing, highlighting the pros and cons of the tests currently used. (v) Stabilisation strategies, evaluating both traditional and innovative techniques to manage CaT instability, including electrodialysis, ion-exchange resins, and protective colloids. (vi) Future perspectives, highlighting knowledge gaps and potential multidisciplinary approaches to integrate agronomic and oenological solutions.

Previous reviews and studies have extensively addressed tartaric instability and calcium tartrate precipitation mainly from an oenological perspective, focusing on wine chemistry and stabilisation techniques (McKinnon *et al*., 1995; Ribéreau-Gayon *et al*., 2006). The present review integrates oenological aspects with agronomic, physiological, and environmental factors influencing calcium accumulation in grape berries, adopting a vineyard-to-winery perspective that has been only marginally explored so far. Through this structure, the review not only summarises existing findings but also identifies critical control points and research priorities, aiming to support winemakers and viticulturists in adopting evidence-based strategies for preventing CaT instability while preserving wine quality.

1. UNDERSTANDING CALCIUM AND ITS ROLES

Calcium is a silvery chemical element similar to lead, but its lustre disappears when oxidised in air. It has an atomic number of 20 and its symbol is Ca. It is the third element in group II (alkaline earth metals) of the periodic table, placed between magnesium and strontium, found in the fourth period, and its outer electron configuration is $4s^2$ (Figure 1). It reacts with water and is obtained by electrolysing calcium chloride, a process that enabled Humphrey Davy to isolate it for the first time in 1808 (Ambudkar, 2020). This metallic element owes its name to the Latin word “calx”, meaning lime, obtained by heating limestone. Among the elements, it is the 5th most abundant in Earth’s crust (3.5 % of the lithosphere), the 3rd most abundant metal after Al and Fe, and the 4th most abundant by relative abundance in the lunar highlands (Jaiswal, 2001).

It is present in many minerals in the form of calcite ($CaCO_3$), dolomite ($CaMg(CO_3)_2$), fluorite (CaF_2), gypsum ($CaSO_4\cdot 2H_2O$), anhydrite ($CaSO_4$), and apatite ($Ca_5(PO_4)_3(F,Cl,OH)$). Due to its high chemical reactivity with water, pure calcium is not found in nature, except within living organisms where it performs vital physiological functions (Al Sabti *et al*., 2023). Calcium carbonate ($CaCO_3$) in soils occurs naturally in three different anhydrous crystalline forms: vaterite, calcite, and aragonite. It is the main constituent

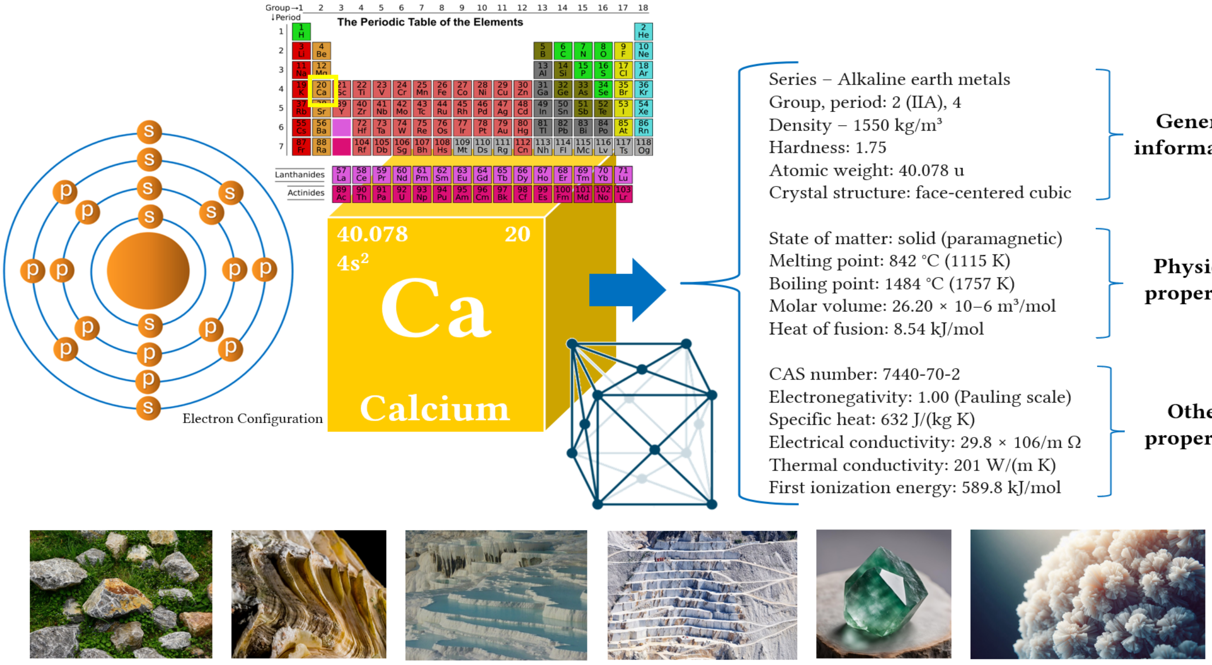

FIGURE 1. General information, physical and other properties of calcium.

of limestone, the most abundant calcium mineral in soils. Another salt present in soils is calcium sulphate ($CaSO_4$), a fundamental component of gypsum. In small concentrations, we also find Ca^{2+} ions in rocks such as fluorite and apatite (Al Sabti *et al*., 2023).

Calcium serves a dual function in agroecosystems: it is an essential plant nutrient and an effective conditioner of the soil matrix. By moderating acidity and promoting the aggregation of humus and clay colloids (*i.e.*, "flocculant" action), Ca improves soil structure, much like liming with $CaCO_3$, thereby creating conditions more favourable for root growth and resource uptake (Bronick & Lal, 2005). At the tissue level, Ca is incorporated as calcium pectate within the protopectin network of the middle lamella, where it cross-links pectins to confer firmness and maintain cell turgor; this supports ripening control, slows senescence, and helps preserve the integrity of cell walls and membranes (Jaiswal, 2001).

Calcium has been found to stabilise cell membrane surfaces, affect cell pH, reduce lipid peroxidation, and prevent solute loss from the cytoplasm. External calcium interferes with intracellular calcium and affects the osmotic adjustment of cells under stress conditions. It also acts as an intracellular courier, harmonising responses to several environmental challenges (Al-Whaibi *et al*., 2012). During a plant-pathogen interaction, calcium contributes to activating defence responses by inducing the production of salicylic acid through calmodulin (*i.e.*, a Ca^{2+}-modulated protein) (Ren *et al*., 2021). Overall, the importance of Ca^{2+} can be summarised as follows: it is difficult to find a physiological process within cells that does not depend on calcium (Jaiswal, 2001).

2. CALCAREOUS SOIL: THE PRIMARY SOURCE OF CALCIUM IN PLANTS

Calcium is a soluble cation widely present in many soils on Earth; this statement holds whether calcareous or non-calcareous soils are considered. However, deficiencies of exchangeable calcium can be found in saline soils in which sodium and magnesium are dominant, acid sulfate soils, and other strongly acidic mineral soils where aluminium can be dominant as well as very acidic peats with a high content of hydrogen ions (Bache, 1984). Calcareous soil ($CaCO_3$Soil), land widely used for growing vines, is characterised by more than 15 % calcium carbonate (pH > 7), including limestone, shells, and calcareous glacial tills. $CaCO_3$ soils have a wide worldwide distribution, covering more than 30 % of the Earth's ice-free land surface. A substantial proportion of these calcareous soils is in the Americas and Oceania. Alkaline (*i.e.*, calcareous, sodic, saline-sodic) and saline soils fall into the broader classification of aridisols (Bolan *et al*., 2023).

In calcisols soils, calcium, magnesium, potassium, and sodium cations occupy the exchange sites. Even if not directly, free calcium carbonate gives the soil a high buffer capacity. In the soil system, we refer to carbonic acid (H_2CO_3) and its conjugate base (CO_3^{2-}), which can absorb the H^+ contribution from the addition of a strong acid. In fact, calcareous soils have a very high buffer capacity, with a dAB/dpH ≃ value of approximately 1000 $Eq.m^{-3}$ (Bache, 1984). Some physical and chemical characteristics of $CaCO_3$ soils are shown in Table 1.

A distinction must be made between total limestone and active limestone. Total limestone is defined as the mineral soil fraction mainly composed of calcium carbonate ($CaCO_3$), and in some cases magnesium carbonate ($MgCO_3$, dolomite),

TABLE 1. Morphological, physical, and chemical characteristics of calcareous soils, and possible critical issues (Mengel & Kirkby, 2012; Havlin *et al.*, 2016; Bolan *et al.*, 2023).

Morphological characteristics	– They have a shallow horizon (< 100 mm), pale to medium brown, overlies a slightly darker or yellow-brown layer peppered with whitish calcite specks. Below this, the profile shifts to a blocky structure with larger peds, often taking on a reddish hue or merging into the underlying parent material. – They are created from limestone and/or in arid surroundings (scarce rainfall avoids carbonates leaching).
Physical characteristics	– Fine/medium texture. – Advantageous water holding capacity and good drainage. – Higher bulk density: $CaCO_3$ Soils > non-$CaCO_3$ Soils. – Carbonate-rich horizons. – Sporadic vegetation coverage in dry habitats.
Chemical characteristics	– Ca^{2+} represents the prevailing cation on the exchange complex. – Poor leaching of plant nutrients. – High CEC (10–25 cmol (+)/kg). – Alkaline, $7.0 < pH < 8.5$. – SOM shortage is common ($0.5 < SOM < 1.0$ %). – Intense buffering and an elevated capacity of metal ions retention with possible PO_3^{-4} deficiency. – Poor soil phosphorus content. – EC (dS/m; 1:1 *w/w*) = 0.5–7.5. – Good development of nitrifying bacteria.
Possible critical issues	– Ca-induced K or Mg deficiency (absorption antagonism). – Possible deficiency of other nutrients (Fe, Mn, Cu, Zn, and B) (decreased solubility). – Iron chlorosis as lime-induced Ferrum-lack (Fe insolubilisation). – Phosphorus bioavailability is reduced by high levels of calcium and magnesium (*i.e.*, P immobilisation). – N losses due to NH_3 volatilisation.

characterised by low solubility and long-term persistence in soils. The second term, active limestone, represents the fraction of limestone present in more finely divided forms and consequently more hydrolysable and soluble; it is, in fact, the fraction that reacts most easily with the other components of the soil, replenishing it with exchangeable Ca, and that plays an important role in grapevine rootstock choice (Cambrollé *et al*., 2014). Active limestone in soil can be estimated by titrating with ammonium oxalate ($(NH_4)_2C_2O_4$), which forms calcium oxalate; higher calcium oxalate levels indicate finer particles and thus greater active limestone content. In fact, according to the Regional Agency for Environmental Prevention & Protection of Veneto (Italy) interpretative scheme, as a percentage of $CaCO_3$, soils can be distinguished as: non-calcareous < 1.0 %, slightly calcareous 1–10 %, medium calcareous 11–25 %, calcareous 26–50 %, very calcareous > 50 %. The useful classification of the soil based on the active limestone content is as follows: low < 1 %, medium 1–3.5 %, high 3.6–10 %, and very high > 10 % (ARPAV, 2007).

This last fraction is also important for defining the CPI index (*i.e.*, (% active $CaCO_3$) × 10^4 / Fe^{2+}; Fe is calculated via $(NH_4)_2C_2O_4$ extraction) and, consequently, the crop's susceptibility to possible iron chlorosis (Pavloušek, 2010).

The tolerance or susceptibility of a species to limestone is linked to a different capacity of the roots in the absorption of nutrients, particularly iron, Fe^{2+} ion, which remains insoluble in the soil. Briefly, for Fe root uptake, crops typically fall into two groups: Strategy I (eudicot plants; grapevine is included here) and Strategy II (grass plants) (Stangoulis & Knez, 2022). The first employs iron from the soil as Fe^{+2}, which, in calcareous soil, is oxidised to Fe^{+3}, reducing the Fe available for plant uptake. Nevertheless, in this situation, iron-deficiency-tolerant species lower rhizosphere pH by extruding protons through the activity of the root plasma membrane H^+-ATPase, or they increase root ferric chelate reductase activity, directly reducing rhizosphere Fe^{3+} to Fe^{2+}. Whilst in graminaceous crops, an efflux of phytosiderophores and mugineic acids is generated, transporting Fe^{3+}complexes towards the cytoplasm (Covarrubias & Rombolà, 2013).

It was found that *Vitis vinifera* and *V. berlandieri* hybrids are more reactive to iron deficiency owing to their enhanced physiological responses, including rhizosphere acidification and increased production of root organic acids such as citrate, malate, 2-oxoglutarate, and ascorbate. In 140 Ruggeri rootstocks, iron deficiency triggers increased phosphoenolpyruvate carboxylase activity (Covarrubias & Rombolà, 2013). Considering the above-mentioned species, *Vitis berlandieri* has the best tolerance to limestone, followed by *Vitis rupestris*, while *Vitis riparia* is very susceptible even to low concentrations. A useful rootstock classification based on active lime content and/or CPI was given (Pavloušek, 2010). The most lime-tolerant rootstocks are the following: Fercal (120 CPI), 333 EM (70 CPI), 31B (60 CPI), 140Ru (90 CPI), 161-49 (50 CPI), and 5BB, 420A, 34 EM group (40 CPI). Using iron-chlorosis-tolerant genotypes is an effective agronomic approach to attenuate the incidence of chlorosis.

This "nutritional disorder" negatively affects vine longevity, root and shoot growth, and berry quality. The associated oxidative stress increases reactive oxygen species, causing lipid peroxidation and malondialdehyde accumulation (Karimi & Salimi, 2021). Additionally, iron chlorosis can alter dry matter distribution at the end of the vegetative development. The plant would tend to accumulate most of the dry matter in the roots to compensate for the great difficulty in absorbing nutrients, drastically limiting the growth of bunches and shoots (Bavaresco *et al*., 2003).

A word of caution is needed regarding the heterogeneity of soils. Due to this natural variability, vineyard soils cannot be accurately described by a single physico-chemical model, making precision agriculture and on-site mapping essential. In fact, localised fragments of chalky rock or limestone residues can create areas of higher pH, while the surrounding soil may exhibit lower values.

3. ABSORPTION AND TRANSPORT OF CALCIUM IONS

Calcium uptake is influenced by several factors, including its concentration in solution, the proportion of cation-saturated exchange sites, leaf transpiration rates, colloid type, aluminium presence, and the cation exchange capacity, which modulates ionic balance via the Donnan equilibrium (Yu *et al*., 2022). Additionally, nitrate availability, through CNGC15-mediated Ca^{2+} channel activity triggering NO_3^--induced calcium spikes (Wang *et al*., 2021), and the presence of antagonistic minerals can either enhance or limit Ca^{2+} absorption (Bolan *et al*., 2023). Roots absorb calcium as a divalent cation (Ca^{2+}) through voltage-dependent and voltage-independent plasma membrane channels (Jaime-Guerrero *et al*., 2024). Higher-plant tissues commonly hold ~ 0.5–3.0 % Ca (*i.e.*, 5–30 mg g^{-1} DM). Ca in good health tissue is estimated to be higher than 0.1–1.0 % DM (White, 2001).

In the cortex epidermis, calcium exhibits apoplastic flux (Jaime-Guerrero *et al*., 2024). The first important obstacle encountered by the calcium ion is represented by the Casparian band, a continuous layer of hydrophobic material (lignin and suberin) that develops at the level of the transverse and longitudinal cell walls in the endoderm portion of the roots.

Due to apoplastic movement restriction, Ca^{2+} enters the cytosol via plasmalemma Ca^{2+} channels, following a symplastic pathway. Subsequently, calcium is transported into the vacuole through Ca^{2+}/H^+ antiporters and Ca^{2+}-ATPases at the tonoplast and later released back to the apoplast, from where it is loaded into the xylem and transported through the stem (Thor, 2019). The transfer from the apoplast to the symplast follows a concentration gradient, whereas the symplast-to-xylem transport requires active mechanisms against the gradient. With water mass flow and ion exchange, calcium is conducted in the trunk. Within the xylem, Ca^{2+} is mainly translocated as chelated complexes, primarily Ca-citrate and Ca-malate (Xing *et al*., 2024). Calcium mobilisation and translocation can be accelerated when pH decreases due to increased malic acid (complex formation), which up-regulates glutamate receptor channel genes (Zhang *et al*., 2024). Transpiration (E) represents the major coefficient of calcium moving. E low rate can carry out calcium-scarce rate accumulation in the canopy. Xylem sap flow alteration, for example, after a wound or laceration, can also modify calcium accumulation in leaves. It has been proven, on *Lycopersicon esculentum*, that the compromised cells will release their vacuolar lymph into the apoplast, generating a greater solute flow (Malone *et al*., 2002).

In leaf, the vacuole is largely treated to be the greatest calcium repository in plant tissues, but, unlike cytoplasm, the $[Ca^{2+}]$vacuole changes significantly among cell types. $[Ca^{2+}]$vacuole in root is under 10.0 mM (except it precipitates with oxalate), while in leaves can achieve values higher than 150.0 mM. Besides, in barley leaf tissue, $[Ca^{2+}]$vacuole is remarkably higher in the epidermis with respect to mesophyll (150.0 mM vs 10.0 mM), whilst in several eudicots the ratios are reversed (*i.e.*, in mesophyll the values are higher than 60.0 mM and lower in the epidermis and bundle sheath cells). Once accumulated in the vacuole, calcium is rarely redistributed, resulting in higher Ca^{2+} levels in organs with elevated transpiration rates (Gilliham *et al*., 2011). The types of calcium in plant tissue are depicted in Figure 2 (Yu *et al*., 2022; Morales *et al*., 2023).

Once it reaches the xylem, Ca^{2+} is channelled to different shoots; here, it must be unloaded into and redistributed within the apoplastic zone of leaves and stored in the inner part of the cell by cyclic nucleotides (Thor, 2019). A little while back, in *Arabidopsis thaliana*, Wang *et al*. (2017) detected CNGC 2 (Cyclic nucleotide-gated channel 2) as a calcium channel liable for its influx into the leaf cell after dumping from the vascular system. Because Ca^{2+} macronutrient is largely immobile in the phloem, it cannot readily move from older, fully developed tissues to actively growing ones (Jaime-Guerrero *et al*., 2024). It is worth remembering that both cell wall cation exchange capacity and extracellular matrix structure (intended as cross-linked pectin network and not only) can influence how $[Ca^{2+}]$ apoplastic is transferred inside crop tissues (Gilliham *et al*., 2011).

It is important to remember that temperature rise and water stress, through abscisic acid (ABA) signalling, increase cytosolic free calcium levels even in guard cells, assigning Ca^{2+} the role of a gatekeeper in stomatal closure. However, prolonged elevation of cytoplasmic $[Ca^{2+}]$ can disrupt normal cellular metabolism, making its removal via ATP-driven Ca^{2+}-ATPases and Ca^{2+}/H^+ exchangers essential. As mentioned before, they also cooperate in calcium accumulation in the vacuole (the primary pool) (Huda *et al*., 2013). The water balance of the grape berry changes from the herbaceous phase to the veraison phase. Before colour change, when the berries are still in transpiration mode, the xylem contributes up to 50 mm^3 per day per berry (driven by water potential gradients) and the phloem only 20 mm^3 per day per berry. From veraison to harvest, the roles change significantly. In fact, the phloem is the main contributor (driven by a hydrostatic pressure gradient) (Figure 3) (Hocking *et al*., 2016). It follows that

Ca^{2+} is mainly imported during the first growth phase (in flesh and skin).

However, it has been shown that xylem vessels remain intact in the berry pedicel, indicating that from veraison onward, peripheral xylem flow becomes blocked (xylem sap blockage in the pericarp), while axial xylem flow continues toward the seeds. An increase in Ca concentration was shown from anthesis to ripeness, with a transfer from the flesh to the skin and an increase in seeds (Cabanne & Doneche, 2003). Grape seeds were found rich in calcium in amyloplast stroma and around granule starch (*i.e.*, embryonic cells: 5.62 g per kg; intact grape seeds: 6.32 g per kg) (Lü & Zhao, 2015). Calcium content was found to be 54 % in grape seeds and 53 % in defatted grape seeds, making it the predominant mineral element in the percentage composition (Mironeasa *et al.*, 2017).

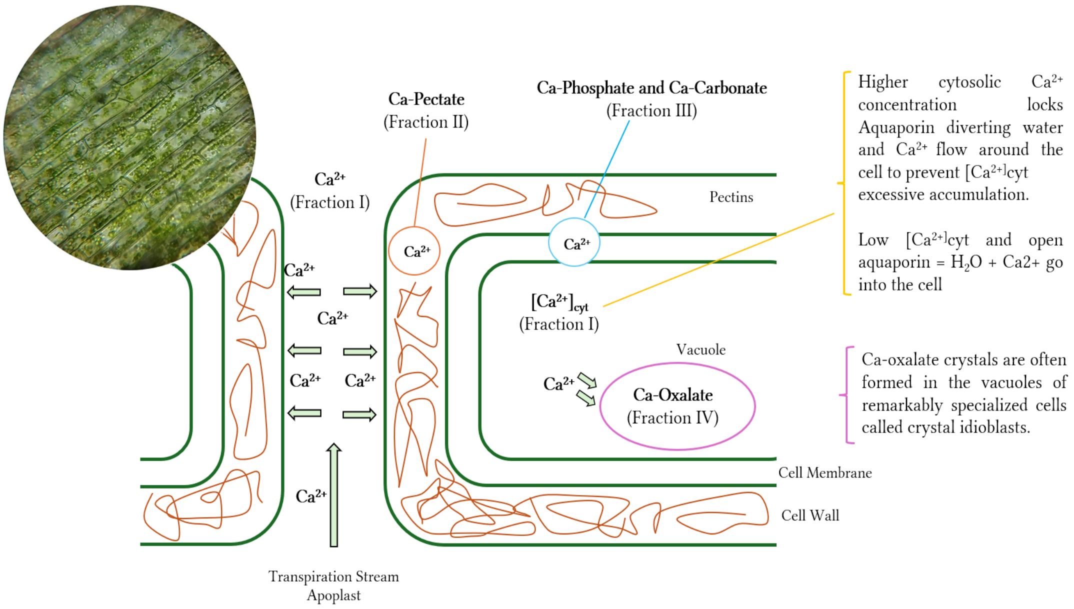

FIGURE 2. Calcium in plant cells. Schematic showing the principal Ca^{2+} reservoirs and intracellular compartments in a plant cell.

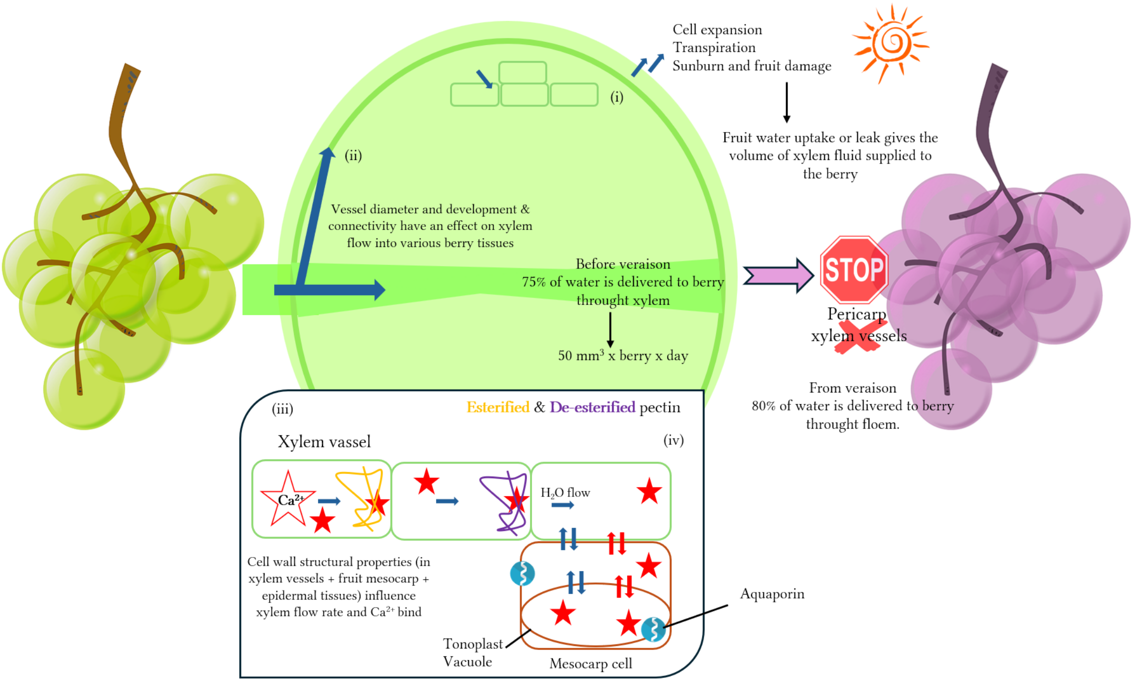

FIGURE 3. Calcium in grapevine berries. Several primary drivers shape calcium availability and partitioning in fruit.

(i) Growth- and transpiration-driven water fluxes set the volume of xylem sap delivered. (ii) Xylem anatomy (development, vessel diameter, connectivity) steers flow between tissues. (iii) Cell-wall/pectin status, de-esterified pectin forming Ca-cross-linked gels, modulates pit-membrane porosity, sap movement, and Ca binding. (iv) Membrane transport (aquaporins, Ca^{2+}-ATPases, CAX on plasma membrane/tonoplast) buffers cytosolic Ca^{2+} and promotes tissue-specific accumulation.

4. CALCIUM ACCUMULATION IN BERRIES: CAUSES AND IMPLICATIONS

The dual function of calcium in plants makes it involved in multiple physiological and biochemical processes. It is, first, a nutritional element, therefore fundamental for the balance of macronutrients of the vine, but it is also a secondary messenger and amplifies the alert systems in the plant, acting as a counter-ion for trans-tonoplast carriage of inorganic or organic anions and triggering replies to biotic/abiotic stress. It can therefore be sequestered by the wall in the middle lamella or resolubilised and removed from cellular storage in response to numerous events passing from apoplast, where it is bound to the wall pectins (Ca-pectate), to symplast (Hocking *et al*., 2016).

In table grapes, calcium levels are highly controlled to compensate for any defects during storage. Here, Ca advantages are accepted as true, arising from its important structural role in the cell walls and membranes, crosslinking with heteropolysaccharide pectins to form an egg-box-like framework that strengthens the cell wall and, ergo, maintains the textural grade of berries (Martins *et al*., 2020). In fact, when calcium supply is limited or its transport is disrupted, localised calcium deficiencies may develop. This condition may result in membrane rupture or cell wall weakening, triggering blossom-end rot disorder in many fruits. This scenario would be catastrophic in table grapes, which is why research has turned towards applications of different forms of calcium such as $CaCO_3$, $[Ca_3(C_6H_5O_7)_2]$, $C_6H_{10}CaO_6$, $[Ca_3(PO_4)_2]$, and $CaCl_2$ to increase its content in the berry and thus to slim postharvest disfigurement on clusters by boosting enzymatic antioxidant activity (upregulation of CAT1, GLPX1, ASPX1, ASPX3, CSD3, and CSD6 genes) and pathogen safeguarding genes (upregulation of PME, PGIP, PIN, and PR1 genes) (Martins *et al*., 2021).

While increases in calcium in table grapes are desirable for the preservation of the bunches, this scenario is opposite for grapes suitable for winemaking. The reason why an increase in calcium content in the wine grape would be counterproductive to winemaking will be discussed in detail later. Here, it is necessary to focus on questions at the root of the problem, namely, why calcium levels can increase in vines, which factors trigger this increase, which of these are due to external circumstances and therefore not directly attributable to agronomic practices, and which are instead linked to anthropogenic changes in the vineyard ecosystem. The discussion below aims to provide a comprehensive response to these issues.

4.1. Soil calcium

A key factor that is at the basis of the increase of calcium is certainly given by the presence of calcareous soils, which has been widely discussed previously. Most of the soils on which vines are grown are characterised by alkaline qualities (it's "elective soil"). Soils with high carbonate content (up to 40.0 % CaO) can lead to bicarbonate accumulation, negatively affecting nutrient uptake, decreasing magnesium (Mg) availability, and increasing calcium levels in vines (Herak Ćustić *et al*., 2008). It was found that crops grown with high levels of $CaCO_3$ had higher Ca^{2+} concentrations in shoots and roots. The presence of bicarbonate and carbonate (*i.e.*, HCO_3^- and CO_3^{2-}) alkalises the soil, imparting buffer capacity and causing the precipitation and adsorption of some plant macro- and micro-nutrients (Ca, Mg, and Zn) (Sagervanshi *et al*., 2022). However, soil calcium availability alone does not necessarily translate into an increase in wine Ca concentration, unless coupled with physiological or technological factors that provoke grape Ca accumulation and its release during vinification. The work by Hao *et al*. (2021) provides clear data on calcium accumulation in berries, even in Ca-rich soils. It highlights the fact that soil calcium is not a good predictor of berry calcium. Soils show wide variations in Ca across the different regions analysed, but berry Ca does not show significant correlations with soil Ca. In the soil-berry correlation, only K and Cd are positively correlated, while Ca is not among the correlated elements. This may mean that high soil Ca availability (typical of calcareous soils) does not automatically translate into greater berry Ca accumulation.

4.2. Exogenous calcium applications

Exogenous applications of calcium, sprayed on leaves or fruits (*e.g.*, $CaCl_2$, $Ca(C_2H_5COO)_2$, or $Ca(NO_3)_2$) or applied to the soil as a fertiliser (*e.g.*, $CaNO_3$ or CAN), are agronomic practices that certainly increase the calcium levels within foliar and fruit tissues. Tests showed that the calcium accumulation rate in tissues grew with augmenting Ca supply levels (Madani *et al*., 2015). It follows that calcium-formulate treatments, for example, used against *Phaeomoniella chlamydospora* and *Phaeoacremonium mini* (Calzarano *et al*., 2017) or applied to augment p-cymene, geraniol, malvidin-3-cis-cmglc, nonanal, and neral, in grapes (Garde-Cerdán *et al*., 2023), could lead to unintended increases in calcium during winemaking. It should be noted that calcium levels in leaves and fruits are correlated, and that as leaves progress through senescence, they accumulate more calcium (Jaime-Guerrero *et al*., 2024). Calcium supplements, in fact, are gradually more applied for decay prevention or sanitations as "environmentally friendly substitutes" to fungicides. However, their effects during storage are very little discussed. Preharvest calcium application increased berry Ca content and reduced postharvest fruit damage by about 60 % after cold storage, showing lower phenolic and anthocyanin levels (*i.e.*, reduced PAL1 and STS expression), while exhibiting enhanced antioxidant enzyme activity (upregulated CAT1) and less 36 % H_2O_2 accumulation. The upregulation of defence and cell wall-related genes, such as PME, PGIP, and PR1, probably contributed to reduced fruit rot (Martins *et al*., 2021). While high Ca levels inhibit pectin degradation, they can also induce a strong repression of anthocyanin biosynthetic pathways at the transcriptional level (Martins *et al*., 2018). This post-harvest agronomic practice is clearly useful only in a physiological/protective sense for the berry as a biological organ. In fact, reduction in colour, chromatic stability, and phenolic potential, especially in red wines, along with the inhibition of pectin degradation, can limit phenolic extraction during maceration and alter clarification and filtration kinetics (Claus & Mojsov, 2018).

4.3. Nitrate and calcium uptake

Nitrate, originating from atmospheric N_2 and converted into inorganic forms (NH_4^+, NO_2^-, and NO_3^-) or supplied through fertilisation, is used by crops for the synthesis of proteins and nucleic acids. Soil nitrate concentration typically ranges from a few hundred micromolar to 70.0 mM. Hence, the root, aided by nitrate transporters (NRT1 and NRT2), is exposed to a wide concentration range (Dechorgnat *et al*., 2011). Classic work on *Solanum lycopersicum* prompted that raising NO_3^- supply, the dominant anion in xylem sap, boosts the uptake and translocation of NO_3^- and co-transported cations (K^+, Ca^{2+}, Mg^{2+}), with examples ranging from 0.5 meq L^{-1} NO_3^- & 92 meq L^{-1} Ca to 8 meq L^{-1} NO_3^- & 134 meq L^{-1} Ca (Kirkby & Knight, 1977). Consistent with this view, xylem delivery reflects the balance between NO_3^- loading and retrieval in root pericycle cells (Rossdeutsch *et al*., 2021).

The nitrate anion promotes, by synergistic action, the absorption of the calcium cation. On the contrary, fertilisation with excess ammonium can reduce calcium absorption in crops by acidifying the soil and reducing water uptake, leading to slower transpiration (Da Silva *et al*., 2016). Recent findings revealed that CNGC15 acts as a molecular switch with the nitrate transporter NRT1.1, regulating nitrate-dependent Ca^{2+} influx. With restricted nitrate availability, NRT1.1 suppresses CNGC15 activity, restoring cytosolic Ca^{2+} to basal levels, whereas high nitrate availability weakens this interaction, allowing CNGC15 to reactivate and trigger a cytosolic Ca^{2+} increase (Ren *et al*., 2021). This dynamic regulation demonstrates how plants integrate environmental cues, nutrient sensing, and hormonal pathways through Ca^{2+}-dependent signalling networks.

Numerous studies show that increasing nitrate nutrition and the NO_3^-:NH_4^+ ratio can be associated with increased uptake or translocation of cations (including Ca^{2+}) in tomato, and in some cases, increased Ca in tissues. In a study by Gholamnejad *et al*. (2023) on the NO_3^-:NH_4^+ ratio and Ca in nutrient solution, the authors report that a 75:25 ratio, combined with 320 mg L^{-1} Ca supply, improves the movement of Ca toward the distal end of the fruit and reduces the risk of blossom-end rot (therefore functional evidence of improved Ca delivery to the fruit). However, this evidence derives from controlled systems and highly transpiring fruits. There are currently no direct studies demonstrating that nitrate fertilisation consistently increases the calcium content of grapevine berries, nor that this translates into a reliable effect on calcium concentration in wine. Generally speaking, for both mycorrhized and non-mycorrhized plants, it was seen that the concentration of Ca in grapevine leaves does not differ significantly among urea, ammonium sulfate, calcium nitrate, and ammonium nitrate (Karagiannidis *et al*., 2007). In grapevines, berry calcium accumulation is constrained by transpiration and by strong xylem discontinuity after veraison (Hocking *et al.*, 2016), which markedly reduces the predictability of nitrate-based fertilisation strategies for increasing fruit and wine calcium concentrations. Therefore, nitrate supply should be regarded as an indirect, context-dependent driver of calcium dynamics rather than a selective agronomic tool to control calcium levels in grapes and wine.

4.4. Irrigation, light, and transpiration

The proven climate change directly and indirectly affects the vine. Increasingly hot summers and unpredictable rainfall require agronomists to make choices that can compensate for prolonged water shortages. The use of irrigation is one of these (Cataldo *et al*., 2024). It was observed that, in the days after irrigation or rainfall, transpiration exceeded that measured during non-irrigated periods (Montoro *et al*., 2016). Briefly, calcium transport upward depends on transpiration-driven xylem flow and is facilitated by divalent cations and calcium chelation. Therefore, high leaf and before-veraison bunch transpiration may contribute to calcium accumulations in the vine fruit, as indicated by the positive correlation between Ca content and transpiration rate.

An interesting study on *Actinidia* also revealed that calcium accumulation is influenced not only by transpiration but also by light. Considering that auxin can spur calcium uptake and light promotes the synthesis of phenolic compounds that protect auxin (*e.g.*, hydroxycinnamic acids), it has been hypothesised that light, by stimulating this biosynthesis, may indirectly reduce auxin breakdown and consequently increase Ca^{2+} storage (Montanaro *et al*., 2006).

Based on these observations, canopy light management (*i.e.*, pruning systems or "safety tools") may be an agronomic lever for indirectly modulating calcium accumulation in grape tissues. In this context, the use of shading nets, increasingly adopted in viticulture to mitigate heat and radiation stress, could influence calcium dynamics by altering light exposure and, consequently, the synthesis of phenolic compounds that protect auxins. By partially reducing the excess of solar irradiance, shading nets create a more balanced phenolic and aromatic profile, potentially limiting auxin degradation and indirectly supporting Ca^{2+} storage at the tissue level.

Moreover, shading strategies are known to affect transpiration rates, berry temperature, and metabolic activity, all of which may interact with calcium uptake and partitioning. However, it must be emphasised that, to date, no specific studies have directly investigated the effects of shading nets on Ca accumulation in grape berries or their subsequent impact on calcium tartrate precipitation risk in wine. Therefore, this hypothesis needs experimental validation under controlled vineyard conditions.

4.5. Abiotic stress and calcium signalling

An enhancement in cytoplasmic Ca^{2+}, mediated by Ca^{2+} channels in the plasma membrane and endomembrane systems, is essential for abscisic acid (ABA) signal transduction in guard cells. Drought is an abiotic stress that triggers this type of response. Under drought stress, vines enhance ABA biosynthesis, activating a signalling cascade that culminates in stomatal closure. However, it was discovered that abscisic acid promotes a marked rise in cytosolic Ca^{2+} concentration within guard cells, tightly coupled with membrane hyperpolarisation, which regulates ion fluxes and modulates downstream stress responses (Shao *et al*., 2008). Additionally, drought and salinity reduce proton extrusion into the apoplast, causing apoplastic alkalinisation and further stimulating ABA accumulation (Sagervanshi *et al*., 2022). High Ca levels in berries in water-stressed vines were registered (Porro *et al*., 2008).

Another transient rise in free cytosolic Ca^{2+} concentration could be induced by heat shock (a factor associated with lipid peroxidation risk) through the direct participation of calmodulin (an intracellular Ca^{2+} sensor) as a calcium signal transduction mediator. Briefly, heat stress initiates $[Ca^{2+}]$ cytosol accumulation, which is transported to the nuclei via protein kinase or the Ca^{2+}/CaM complex to enhance thermotolerance (Goswami *et al*., 2015). Recent studies have revealed that the specificity of calcium signalling in plants is largely determined by molecular switches (= cyclic nucleotide-gated channels (CNGCs) + their regulatory proteins, such as calmodulins (CaMs)). CNGCs are non-selective cation channels located on the plasma membrane and endomembrane systems, finely modulating Ca^{2+} influx in response to distinct stimuli. By interacting with CaMs, these channel complexes generate highly specific Ca^{2+} signatures that orchestrate plant responses to environmental cues. In particular, CNGCs critically mediate the integration of hormonal cues with adaptive mechanisms under abiotic stresses, ensuring precise regulation of growth, development, and stress tolerance (Ren *et al*., 2021). Overall, plants exploit these highly dynamic Ca^{2+} signatures to decode and coordinate adaptations to diverse abiotic stresses and developmental processes.

Considering climate change, characterised by an increase in the frequency and intensity of water and heat stress, it remains unclear how these conditions influence calcium accumulation and partitioning in grape berries. Available evidence is fragmentary, making it difficult to distinguish between apparent concentration effects and actual increases in structural or extractable calcium. Targeted studies are therefore needed to clarify the role of abiotic stresses in modulating berry calcium content and its oenological implications. This knowledge is essential for developing vineyard management strategies consistent with future climate scenarios.

4.6. Calcium and anthocyanins interactions

Even the buildup of anthocyanins, which are central to grape quality but which the vine accumulates as a defence against stress, could lead to resolubilisation of calcium, removing it from cellular storage points. In their recent work, Yu *et al.* (2020) have raised many questions by postulating multiple theories. (i) Ca markedly upregulated total soluble sugar amount in berries and affected 23MYB, 11bHLH, 7NAC, and 2bZIP transcription factors correlated to anthocyanin setting, contributing to anthocyanin accumulation. (ii) Ca could enhance anthocyanin accumulation by spurring the Camodulin/UDP-glucose: flavonoid 3-O-glucosyltransferase interaction. UFGT, encoding an enzyme catalysing anthocyanin glycosylation, was discovered to be regulated by Ca^{2+}/CaM. (iii) Ca^{2+}/CaM or directly Ca^{2+} could regulate transcription factors related to anthocyanin (*e.g.*, VvMYBA1 and VvMYBA2), stimulating genes in a biosynthetic pathway. (iv) Ca could ameliorate berry colour by up-regulating genes involved in jasmonic acid and ethylene synthesis, which are known to increase endogenous sugar levels.

Hu *et al.* (2021) showed that calcium supplementation not only increases the total anthocyanin content but also modifies their qualitative profile. In particular, Ca^{2+} significantly enhanced the accumulation of cyanidin-3-O-glucoside and peonidin-3-O-glucoside. This selective enhancement of anthocyanins was associated with the upregulation of structural genes in the flavonoid biosynthetic pathway, including CHS (chalcone synthase, initiating flavonoid biosynthesis), ANS (anthocyanidin synthase, responsible for anthocyanidin formation), and UFGT (UDP-glucose: flavonoid 3-O-glucosyltransferase, catalysing anthocyanin stabilisation via glycosylation). These findings suggest that Ca^{2+} promotes both the synthesis and stabilisation of anthocyanins through a Ca^{2+}/CaM-mediated signalling pathway. However, the role of Ca in anthocyanin biosynthesis remains widely unexplored.

From this perspective, exploring non-invasive agronomic strategies compatible with organic and biodynamic practices, such as biochar, biostimulants, and zeolites, may offer sustainable ways to maintain grape quality while mitigating stress.

4.7. Wound-induced calcium dynamics

Crops have developed capable mechanisms to recognise wounds and the skill to produce a defence reply by transducing signals to their neighbouring cells (*i.e.*, hydraulic, electrical, and calcium signals), involving also jasmonic acid and abscisic acid. ROS, Ca^{2+}, and electrical signalling are integrated into a network that supports rapid signal transmission. Calcium message is transmitted by calmodulin, Ca^{2+}-dependent protein kinases, and annexins. Both insects that feed on the canopy and any wounds caused by telluric organisms can generate $[Ca^{2+}]$ cytosolic promotion, depolarising plasma membrane potential (Parmagnani & Maffei, 2022). However, although wound-induced calcium signalling is well established at the cellular and physiological level, its potential contribution to net calcium accumulation in grape berries, and consequently to Ca concentration in wine and Ca-tartrate precipitation, remains hypothetical and has not yet been experimentally demonstrated.

4.8. Calcium-related berry disorders

Two physiopathies are noteworthy in this discussion: berry shrivel and late bunch stem necrosis. Grapevine berries shrivel, a “matureness jumble”, is described as an early ripening interruption disorder leading to berry puckering, reducing K^+ and sugar accumulation, and increasing hydroxyproline and titratable acidity. It was seen that, unlike potassium, the soluble calcium content (mg per berry) declined during the beginning of ripening, but this drop was less pronounced in berry shrivelled berries than in healthy ones, probably due to insoluble Ca-oxalate crystals (Keller *et al.*, 2016). Similarly, in the late-season bunch stem necrosis, berries held higher Ca^{2+} amounts than non-affected berries (Bondada & Keller, 2012). The causes of these disorders are still uncertain to this day (Griesser *et al.*, 2024). Nevertheless, the rising incidence of these phenomena, potentially driven by climate change or by an increased scientific awareness and understanding of the underlying mechanisms, has prompted the formulation of multiple hypotheses regarding their origin; however, comprehensive and targeted studies are still required to fully elucidate the processes involved. In summary (Figure 4), all these phenomena that can contribute to the increase in calcium content can be grouped into two macroscopic categories: the first phenomena inherent to transpiration flows and the others inherent to the remobilisation of Ca^{2+} tightly bound in the cell walls (Ca-pectate) or the vacuoles (Ca-oxalate) following stress responses (signalling role).

The vineyard must be considered a complex system in which abiotic stresses, transport dynamics, agronomic practices, and metabolic responses act synergistically. In this context, increases in calcium could more often result from indirect effects or stress-related remobilisation mechanisms, rather than from controlled nutrient accumulation. This complexity makes it difficult to predict and manage calcium in wine grapes with unidirectional approaches. This necessitates an integrated approach that considers the full range of plant-environment-management interactions.

Given this complexity, close and ongoing collaboration between agronomists and oenologists is essential to analyse the dynamics that lead to increased calcium levels throughout the entire supply chain, from the vineyard to the winery. In particular, wine analyses must be complemented by direct grape investigations to progressively and causally identify the factors responsible for calcium accumulation and partitioning prior to winemaking.

5. CALCIUM TARTRATE INSTABILITY IN WINES: A RENEWED CHALLENGE FOR WINEMAKERS

Precipitation of tartaric acid salts, chiefly potassium bitartrate (KHT) and calcium tartrate (CaT), is a natural phenomenon that can arise during alcoholic fermentation and subsequent wine storage. Although the presence of tartrate crystals in bottled wines does not pose any health risk to consumers, their occurrence negatively affects wine clarity and visual quality, often leading to consumer rejection. For this reason, tartrate stabilisation before bottling is a critical step in winemaking. Despite both being tartrate salts, KHT and CaT exhibit markedly different crystallisation behaviours, forming under distinct conditions and at different rates (Cui *et al.*, 2024). In particular, calcium tartrate precipitation represents a more insidious challenge, as its crystallisation kinetics are significantly slower, and crystals can appear several months after bottling (AWRI, 2024). To date, unlike potassium tartrate instability, calcium tartrate precipitation has received comparatively less attention from winemakers, which is reflected in the relatively limited number of scientific studies dedicated to this topic.

5.1 Calcium content in wine: key factors affecting its solubility and stability

Calcium levels in wine have been documented to range from 7 to 310 mg L^{-1} (Waterhouse *et al.*, 2024). These variations and potential increases are influenced by the natural calcium content of grapes, as extensively described

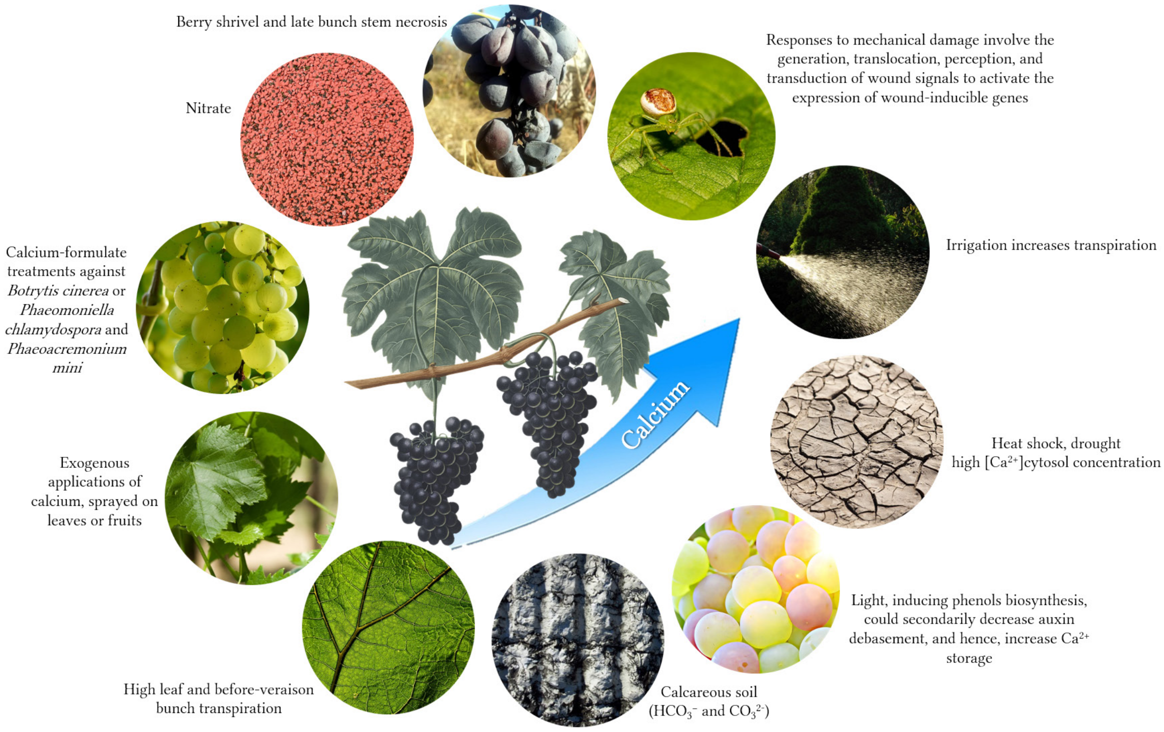

FIGURE 4. Graphic representation of the phenomena that can contribute to the increase in calcium content in grapes.

above, and by several winemaking practices. These include: (i) deacidification using calcium salts, particularly calcium carbonate ($CaCO_3$), (ii) fining with casein or other milk-derived products, and (iii) the use of cement tanks, especially when they are not properly passivated.

However, in recent years, in response to climate change, wines have shown not only higher calcium ion concentrations (see Paragraph 4), as found in six Greek red and white wines (320–539 mg/L Ca^{2+}) (Kallithraka *et al*., 2001), but also elevated pH levels and increased ethanol content (van Leeuwen *et al*., 2019). This contributes to the higher risk of calcium tartrate instability in bottled wines (see Table 2).

Indeed, at the customary wine pH, HT^- is the prevailing species (~ 60 %), whereas as the pH of the wine increases, the bivalent tartrate required to form CaT [T^{2-}] increases (Figure 5).

Therefore, at elevated pH levels, more T^{2-} ions are present, which enhances their interaction with calcium ions (Ca^{2+}) to produce CaT. This reaction has been shown to increase the likelihood of CaT precipitating from solution, thereby reducing its overall solubility. (Mckinnon *et al*., 1995; Cisterna-Castillo *et al*., 2024; Cui *et al*., 2024). In this context, McKinnon *et al*. (1995) observed that with a starting pH of 3.5, the induction period (time until precipitation begins) can be 4 minutes, while at pH 3.1, precipitation might not occur even after 96 hours. This also suggests that the wines may become more unstable after malolactic fermentation, since this process tends to increase the pH value. It is worth noting that the traditional "Concentration Product" (CP) method (see Paragraph 5.2) for evaluating CaT instability estimates the precipitation risk based on the product of free calcium ions and tartrate anions, according to the formula: $CP = [Ca^{2+}] \times [T^{2-}]$. In this context, [$T^{2-}$, tartrate anion] is calculated from the pH-based distribution of tartaric acid species. Wines exhibiting CP values above a critical threshold are considered supersaturated, thus showing a higher propensity for CaT precipitation.

Ethanol, on the other hand, contributes to the reduced CaT solubility by lowering the dielectric constant of the medium,

TABLE 2. CaT instability risk thresholds.

Thresholds*	References
> 70/80 mg/L	AWRI (2024)
> 90 mg/L at pH 3.5 > 40 mg/L (with compromised fruit)	Zoecklein, B. W. (2000)
> 60 mg/L (red) & > 80 mg/L (white)	Ribéreau-Gayon *et al*. (2006)
> 60–70 mg/L	Bimont, A. (2023)

*The values represent the calcium thresholds contained in wines, beyond which there is a risk of precipitation.

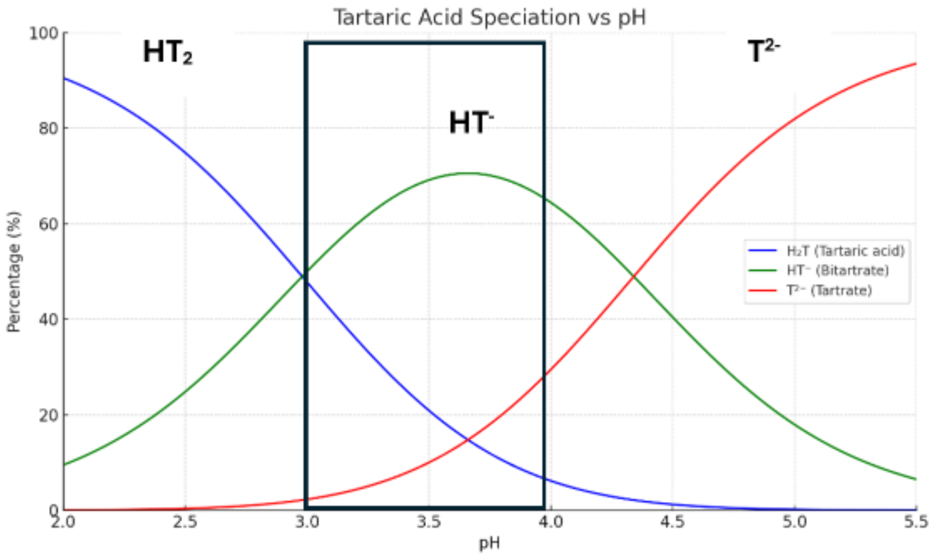

FIGURE 5. Relative concentrations vs pH for tartaric acid (H_2T) and its anions (bitartrate: HT^-, tartrate: T^{2-}) in aqueous medium.

thereby decreasing the solvent's capacity to stabilise calcium and tartrate ions in solution. This promotes ionic association and, consequently, CaT precipitation. McKinnon *et al*. (1995) found that at a pH of 3.2, the solubility product was estimated at 1.97×10^{-7} with 11 % ethanol, but this dropped substantially to 3.13×10^{-8} when the ethanol content was increased to 20 %. In the same study, the authors found that increasing ethanol from 11 % to 20 % decreased the induction time 12-fold and increased the crystallisation rate 11-fold in model wine solutions. These findings provide a mechanistic explanation for the increasing incidence of CaT instability in wines, a trend further exacerbated by the higher alcohol levels commonly associated with climate change.

Nonetheless, because wine contains crystallisation inhibitors and other matrix effects, CaT often remains in a metastable, supersaturated state, with the CP exceeding Ksp by roughly 2–5 × (Berg & Keefer, 1959). Indeed, many components in wine can significantly increase the ability of a wine to hold calcium tartrate, including some natural acids and macromolecules. This is also the reason why different wines, although having a similar concentration of Ca, will undergo a different time to the formation of crystals. For instance, organic acids can interact with potassium (K^+) and calcium (Ca^{2+}) ions, competing with tartaric acid and thus hindering the formation of crystalline nuclei. McKinnon *et al*. (1995), using a model solution with 2 g/L of added acid, revealed the following inhibition order: (greatest → least) citric → malic → lactic → succinic. Notably, malic acid increased the induction time for CaT crystallisation by a factor of 16, whereas lactic acid only achieved a 4-fold increase. These results suggest that the malolactic fermentation (MLF) process promotes CaT precipitation not only by raising the pH but also by converting malic acid into lactic acid, which, due to its single carboxylic group compared to the two in malic acid, exhibits a significantly weaker calcium-binding capacity.

In addition to pH and organic acid composition, the macromolecules naturally present in wine, such as polygalacturonic acid, rhamnogalacturonan-I (RG-I), rhamnogalacturonan-II (RG-II), arabinogalactan protein (AGP), and mannoproteins (MPs), play a crucial role in modulating CaT stability. All these macromolecules can inhibit CaT precipitation by maintaining CaT in a dissolved supersaturated state for longer periods. Polysaccharides, including AGPs, RG-I, RG-II, and MPs, can adsorb onto the surfaces of nascent CaT crystals, physically hindering their growth and preventing them from reaching a detectable size, even in wines with elevated calcium concentrations (Pellerin *et al*., 2013). Furthermore, certain grape polysaccharides and MPs can chelate Ca^{2+} ions, reducing the pool of free Ca^{2+} available for crystal nucleation and growth. This dual mechanism of surface adsorption and ionic sequestration lowers overall supersaturation, delays nucleation, and extends the induction period before CaT precipitation occurs (Cui *et al*., 2024).

Pellerin *et al*. (2013), evaluating the impact of AGP, RG-I, RG-II, and MPs as tartaric acid stabilising, identified RG-I as the most effective inhibitor of spontaneous CaT precipitation. It significantly extended the induction period for CaT crystallisation from 7 minutes in a standard model to 180 minutes. RG-I's strong inhibitory effect was attributed to its high uronic acid content and its structure, composed of two aligned polymer strands, which allows it to form an "egg-box" model capable of sequestering and chelating Ca^{2+}, thereby preventing its participation in CaT formation. On the contrary, AGP and MPs showed minimal to no significant effect on the induction time of CaT precipitation. Calcium binding to phosphate groups, which MPs contain, is less likely at typical wine pH values, meaning mannoproteins generally do not effectively chelate Ca^{2+} under these conditions (McKinnon *et al.*, 1996). In model conditions, polygalacturonic acid (grape pectin) acted as a calcium L-(+)-tartrate inhibitor (McKinnon *et al*., 1996); at 0.5 g L^{-1} it extended the crystallisation time from 7 to 510 min (~ 73 ×). Moreover, calcium binding to polygalacturonic acid reached its highest level at pH 4, showing strong complexation across pH 3.0–3.5.

While proteins can contain sequences of amino acids capable of binding calcium, according to McKinnon *et al.* (1995), typical residual-protein concentrations in finished wines are inadequate to alter CaT precipitation through calcium binding. For instance, calculations showed that even with maximal protein content and multiple calcium-binding sites per protein molecule, the amount of bound calcium was very small, often less than 0.1 mg Ca/L.

The available literature provides limited insight into another major group of macromolecules present in wine, the phenolic compounds. Microscopic observations of calcium tartrate crystals reveal that they remain colourless, unlike potassium bitartrate (KHT) crystals. This suggests that wine's phenolic complexes may not act as protective colloids during the formation of the CaT crystal (Ribéreau-Gayon *et al*., 2006).

In addition to the intrinsic components of the wine matrix, external conditions can influence wine stability. For example, while temperature has a significant impact on the stability of potassium bitartrate, it exerts minimal influence on the rate and amount of CaT precipitation from wine. Indeed, the solubility of calcium tartrate is significantly less influenced by temperature changes compared to that of potassium bitartrate, even if low temperatures can reduce its solubility, promoting crystallisation. Therefore, although lower temperatures can theoretically increase the level of supersaturation, which drives precipitation, they do not sufficiently promote CaT nucleation in wine in the same way as KHT. Even at low temperatures, the activation energy required for insoluble CaT formation remains high (Clark *et al*., 1988).

5.2 Methods for predicting the stability of calcium tartrate in wine

A major ongoing challenge for winemakers is the prediction of CaT stability, given that this compound frequently crystallises in bottled wine, often occurring months after the product has reached the market. Compared to KHT, CaT precipitation is considerably more complex and difficult to predict.

The concentration of calcium in wine is often used to estimate the stability of calcium tartrate.

In this context, the limit at which wine is deemed unstable is 80 mg/L for white and *rosé* wines, and 60 mg/L for red wines (Ribéreau-Gayon *et al.*, 2006). However, these reference values may not reliably indicate calcium tartrate instability due to the varying impacts of pH and crystallisation inhibitors on the crystallisation process, along with their differing values and concentrations present in various wines.

The calculation of the wine concentration product (CP = $[Ca^{2+}][T^{2-}]$) and its comparison with the solubility product can be used to assess calcium tartrate stability. However, this approach not only requires the determination of calcium concentration in a specialised laboratory, but the results may also be overestimated if measured using atomic absorption spectrophotometry (McKinnon *et al.*, 1996).

Additionally, although the cold test and conductivity analysis are commonly used to assess the stability of potassium hydrogen tartrate (KHT) in wine, both methods present criticisms for evaluating the stability of CaT. This is because temperature has little effect on CaT precipitation and because conductivity analysis using CaT seed crystals can induce KHT crystallisation, leading to misleading results (Berg & Keefer, 1959).

Abguéguen and Boulton (1993) proposed a CaT stability test based on monitoring calcium concentration after the addition of micronised CaT crystals (5 g/L). The wine is equilibrated at the test temperature, seeded with CaT, mixed for two hours, and then filtered. A decrease in calcium concentration indicates instability due to crystal growth, whereas an increase reflects stability from seed crystals dissolution; an unchanged concentration signifies full stability under the test conditions. More recently, Quinterno *et al.* (2021) proposed a precipitation test to assess the CaT stability of wine. The test involves adding micronised CaT (4 g/L) to the wine, followed by cooling to encourage crystal formation and precipitation. Stability is assessed by measuring the change in Ca^{2+} concentration (ΔCa) after treatment: wines with $\Delta Ca < 15$ ppm are considered stable, those with $15 \leq \Delta Ca \leq 25$ ppm are slightly unstable, and those with $\Delta Ca > 25$ ppm are classified as unstable. The authors also proposed a multifactor statistical model combining wine parameters, such as pH, tartaric acid, and Ca^{2+} concentration, to predict the likelihood of CaT precipitation.

5.3 Treatments for preventing CaT precipitation in the bottle

Subtractive and additive methods are commonly used in the wine industry to obtain a stable product that is suitable for the post-bottling period.

Subtractive methods are based on the removal of the tartrate crystals themselves or the cations necessary for the precipitation of tartaric acid in the form of calcium and potassium tartrate crystals. These methods can be carried out through cold treatment (with or without seeding the wine with tartrate crystals), electrodialysis, or ion exchange. The cold treatment, which consists of cooling the wine for several days at a temperature close to the freezing point, is widely used to induce the precipitation of KHT before bottling, but it is not a suitable strategy for the stabilisation of CaT, since its precipitation is slightly affected by the temperature (Berg & Keefer, 1959). On the contrary, the seeding of the wine with calcium tartrate crystals, at cellar temperature, eliminating the need for cooling, has been proposed as an effective subtractive method for the reduction of the Ca concentration (Minguez & Hernandez, 1998). According to Abgueguen and Boulton (1993), to achieve CaT precipitation from supersaturated wines, it is necessary to have a high seeding rate of micronised CaT to overcome the nucleation limitation, rather than relying on temperature reduction alone. However, McKinnon *et al.* (1995) found this treatment to be ineffective. This was attributed to an inappropriate size and purity of the CaT crystals. Recently, the use of commercially available micronised calcium tartare crystals, at a dose of 50 g/hL with a contact time ranging from 7 to 15 days and at cellar temperature, has been reported to aid in CaT stabilisation (Quiterno *et al.*, 2021). Although this approach has little effect on wine acidity and does not alter its sensory characteristics significantly (Quiterno *et al.*, 2021), it can be costly and time-consuming (Fioschi *et al.*, 2024).

Electrodialysis (ED) and cation-exchange resins (IERs) are additional subtractive techniques that can be used to stabilise calcium tartrate in wine (Figure 6).

In the case of ED, ion migration occurs through selective membranes under an external electric field, enabling the removal of calcium, tartrate, bitartrate, and other ions (Gonçalves *et al.*, 2003).

The removal of tartrate anions (T^{2-}) in addition to bitartrate (HT^{-}) can lead to a slight decrease in pH (around 0.2 pH units) (Waterhouse *et al.*, 2024). ED effectively removes Ca^{2+} and other metals (*i.e.*, Fe^{3+} and Cu^{2+}), which can contribute to other forms of wine instability, making it potentially effective at preventing calcium tartrate instability (Martínez-Pérez *et al.*, 2020). In certain instances, ED has been observed to reduce colour intensity and total phenol index in red wines, potentially due to the adsorption of high-molecular-weight compounds like polysaccharide polymers on the membranes (Martínez-Pérez *et al.*, 2020). However, other studies report that ED does not significantly affect wine colour or organoleptic properties (Gonçalves *et al.*, 2003; El Rayess & Mietton-Peuchot, 2016). Recent studies have investigated the performance of various ion-exchange membranes in ED for wine tartrate stabilisation. Pasechnaya *et al.* (2024) compared homogeneous and heterogeneous membranes, highlighting that homogeneous types achieved more efficient tartaric acid removal, while heterogeneous ones showed steric limitations in transporting bulky, highly hydrated tartaric anions, favouring smaller ions such as chloride. Membranes made of polystyrene cross-linked with divinylbenzene were also more prone to fouling, reducing transport efficiency. Additionally, the application of pulsed electric fields (PEF) instead of continuous fields lowered energy consumption by 10–30 % by enhancing electroconvection and limiting foulant layer formation.

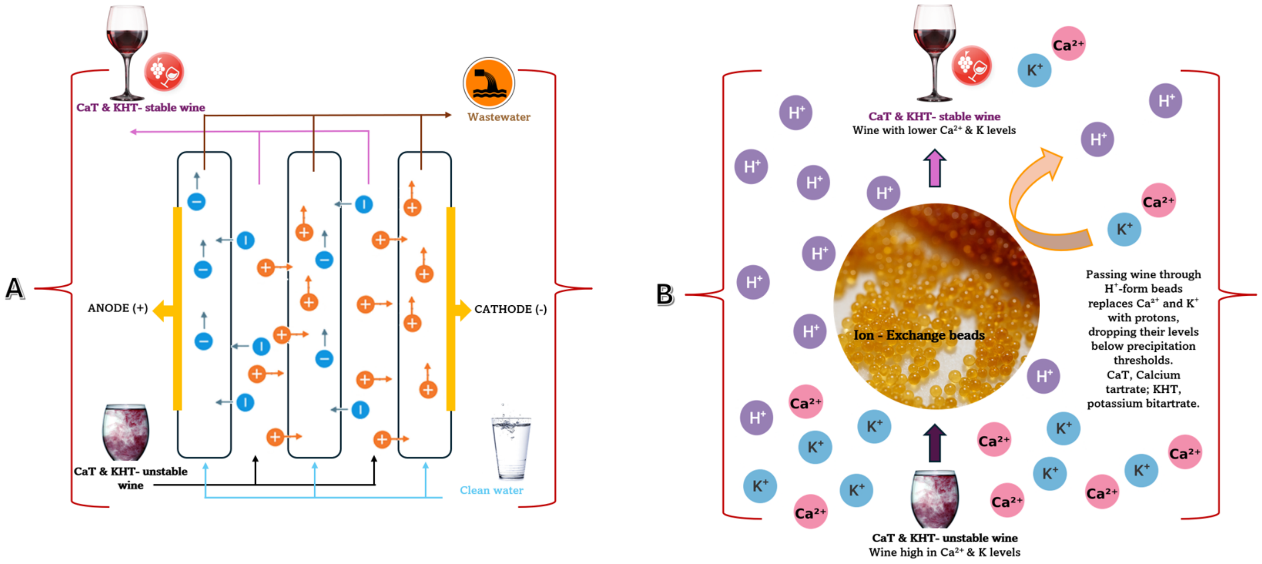

FIGURE 6. Subtractive stabilisation methods. (A) Electrodialysis: this process removes calcium, potassium, tartrate, and bitartrate ions from wine by applying an electric field. This field drives their migration through ion-selective membranes, where the ions are separated and discarded. (B) Ion-exchange resins: in this process, calcium and potassium ions present in wine are exchanged with hydrogen ions bound to synthetic resin beads.

It is important to note that the high initial cost of the ED equipment can be a disadvantage for small-scale electrodialysis applications. Yet, the initial use of electrodialysis revealed a higher water consumption rate. However, incorporating reverse osmosis to recycle the waste stream could reduce water usage (Bories *et al*., 2011).

Instead, IERs improve CaT stability by directly eliminating calcium ions and indirectly lowering the pH level (Walker *et al*., 2002). They are polymeric substances, such as styrene-divinylbenzene copolymer, which contain ionised functional groups that can exchange ions with the wine (Lasanta & Gómez, 2012). Prior to use, IERs are generally activated by washing them with a strong acid solution, typically sulfuric acid (H_2SO_4) or hydrochloric acid (HCl), to load them with hydrogen ions (H^+). This process ensures that the resin is in its protonated form. As wine passes through a column containing the activated resin, the hydrogen ions (H^+) are exchanged for the cations present in the wine. The resins display selective affinity, generally favouring cations with higher charge states over those with lower ones (*e.g.*, $Al^{3+} > Ca^{2+} > K^+$). Among cations of the same charge states, those with a higher atomic number are preferred. However, weak exchangers prefer higher charge states ($Ca^{2+} > K^+$), while strong exchangers prefer lower charge states ($K^+ > Ca^{2+}$) (Waterhouse *et al*., 2024). The substitution of K^+ ions with H^+ ions leads to a reduction in the wine's pH, accompanied by a corresponding rise in its total acidity. Research on IERs' impact remains contradictory. Some studies report a significant effect, showing reduced aromatic compounds (Lasanta *et al*., 2013), sensory scores, and lower consumer preference, particularly for red wines, due to compositional changes such as increased acidity and decreased pH (Ibeas *et al*., 2015; Martínez-Pérez *et al*., 2020). However, other findings suggest minimal influence on red wine colour and no substantial impact on overall sensory perception (Lasanta & Gómez, 2012). On the other hand, other findings have shown that IER may be beneficial for certain aromatic compounds during ageing due to the lowered pH (Cui *et al*., 2024). Like ED, this method is time and energy-efficient (Lasanta & Gómez, 2012). However, a specific drawback of IERs in terms of sustainability is the need for regeneration with strong acids. This produces an acidic waste stream that must be carefully managed and treated, thus posing a potential environmental hazard.

Compared to subtractive methods, using protective colloids is more cost-effective (Geveke *et al*., 2020). This approach requires minimal energy and does not depend on specialised, high-cost equipment, like ED.

Additive techniques aim to stabilise wine by introducing substances that, while not inhibiting nucleation, stop the growth of crystals before they reach a visible size (Lankhorst *et al*., 2017).

To date, various protective hydrocolloids have been approved as stabilisers. Among them are metatartaric acid (MTA), carboxymethylcellulose (CMC), potassium polyaspartate (KPA), and yeast mannoproteins (MP). While their effectiveness in preventing potassium hydrogen tartrate (KHT) precipitation is well documented (Lasanta & Gomez, 2012; Guise *et al*., 2014), there is limited data on their ability to inhibit CaT crystallisation.

Cisterna-Castillo *et al*. (2024) used five different commercially available protective colloids, MTA, KPA, CMC, MP, and Arabic gum (AG), at the supplier's recommended standard dosage. Among them, only CMC demonstrated a true protective effect against CaT crystallisation. This effectiveness is likely linked to CMC's ability to chelate calcium ions (Ca^{2+}), reducing their availability for crystal formation (McKinnon *et al*., 1996). Nonetheless, it is worth noting that the OIV typically restricts its utilisation to white and sparkling wines. This is due to concerns regarding the potential for colour degradation and haze development in red wines. In order to address these challenges in red wines, a combination of CMC + GA has been suggested as a viable alternative (Martínez-Pérez *et al*., 2020).

Moreover, carrageenans, another product currently being studied for wine protein stabilisation (Marangon *et al*., 2013), have also been tested to assess their effectiveness in counteracting the instability of calcium tartrate in wines (Fioschi *et al*., 2024). Although the addition of 0.25 g L^{-1} carrageenan led to a notable reduction in saturation temperatures, it did not result in complete stabilisation. In contrast, a dosage of 0.75 g L^{-1} carrageenan enabled two white wines to reach CaT stability (Tsat CaT ≤ 18 °C). According to the authors, carrageenans are sulfur-rich polysaccharides that create ionic interactions with monovalent and divalent ions, such as K^+ and Ca^{2+}, via their sulfated groups. In the case of Ca^{2+}, they can also establish Van der Waals interactions, which contribute to the stabilisation of the helical structure of the hydrocolloid. This, in turn, reduces Ca^{2+} activity, thereby enhancing stability. Additionally, when used in combination with bentonite, carrageenan notably reduced the calcium tartrate saturation temperature (Tsat CaT), effectively promoting wine stability.

The use of carrageenan is not yet authorised in winemaking practices. Nonetheless, based on the authors' findings, it presents a promising alternative due to its mechanism of colloidal stabilisation.

Alginic acid, a linear heteropolysaccharide constituted by β-D-mannuronic and α-L-guluronic acid units, derived from brown algae, has also recently been proposed as a stabiliser for CaT (Cosme *et al*., 2024). Alginic acid is already authorised by the OIV for use in winemaking for the clarification of wines. In particular, Cosme *et al*. (2024) conducted a study specifically investigating the efficiency of alginic acid as a calcium tartrate (CaT) stabiliser in wines, comparing it to carboxymethylcellulose (CMC) and potassium polyaspartate (KPA). Alginic acid was found to be more efficacious than both CMC and KPA in reducing calcium tartrate instability in wine. According to the authors, the increased charge density, attributable to a higher concentration of carboxylic acid groups relative to CMC, and its capacity to bind calcium ions, are considered the key factors behind its more effective role in preventing CaT precipitation. While these results are very promising, it should be noted that they represent only temporary stabilisation effects. The authors themselves recommend conducting long-term studies using various dosage levels to determine the optimal concentration and to evaluate the impact of alginic acid on the sensory characteristics of wine, even though no negative effects are expected. In addition to colloid-based inhibition, algae-derived polysaccharides can also be used more proactively to lower the calcium load before bottling. A recent contribution (Laurie *et al*., 2025) proposed sodium alginate (the salt form of alginic acid) as a fining aid to partially remove Ca^{2+}. The authors observed ~ 5–25 % decreases in dissolved calcium, accompanied by improved Ca-tartrate stability. Although these are preliminary conference data, the findings are consistent with the mechanistic rationale proposed for alginic acid, namely the higher density of carboxylate groups and consequent calcium-binding capacity compared with CMC. These results suggest that alginate fining could complement temporary stabilisers and help manage high-Ca wines. As with Cosme *et al*. (2024), broader dose-response work and long-term/sensory assessments are still needed to confirm durability and practical limits.

It is important to highlight that, regarding the aforementioned hydrocolloids (whether naturally present or added during winemaking) that may play a protective role in preventing CaT precipitation, it has been shown that the use of sterilising membrane filtration systems immediately prior to bottling could retain these compounds, thereby reducing or nullifying their effectiveness (Cabrita *et al*., 2016; Geveke & Runnebaum, 2020). However, Puškaš *et al.* (2021), evaluating the impact of various oenological products (including MTA, CMC, mannoproteins, and gum Arabic) on wine filterability, found that they generally did not worsen the filterability of white and *rosé* wines.

CONCLUSIONS

Calcium dynamics, from vineyard soils to the final stages of winemaking, play a pivotal role in determining the stability of calcium tartrate (CaT) in wines. Agronomic factors, including soil composition, active limestone content, and rootstock-specific calcium uptake strategies, directly influence calcium accumulation in grape berries, thereby shaping the potential risk of CaT precipitation during vinification and storage. However, the vineyard represents a complex system in which environmental stress, transport processes, agronomic practices, and metabolic responses interact synergistically, making increases in calcium often the result of indirect effects or stress-related remobilisation mechanisms rather than controlled nutritional intake. This complexity limits the effectiveness of unidirectional approaches and requires an integrated view of plant + environment + management interactions. In this context, ongoing collaboration between agronomists and winemakers, supported by analyses conducted directly on grapes as well as on wine, is essential to progressively identify the causes of calcium accumulation and partitioning before winemaking.

On the oenological side, the complexity of calcium interactions with tartrate ions, polysaccharides, proteins, and other wine matrix components highlights the multifactorial nature of this phenomenon. Advances in stabilisation techniques, such as electrodialysis, ion-exchange resins, carboxymethylcellulose (CMC), potassium polyaspartate (KPA), and alginic acid, have significantly improved winemakers' ability to manage CaT instability, yet no single method ensures complete control under all conditions. Emerging evidence suggests that a holistic approach integrating vineyard management, through optimised calcium fertilisation, rootstock selection, and irrigation strategies, with targeted oenological interventions, could provide a more effective and sustainable solution.

Future research should focus on unravelling the molecular mechanisms underlying Ca^{2+} transport within the plant, exploring its redistribution among grape tissues, and linking these findings with the wine matrix behaviour. Additionally, novel predictive models combining vineyard parameters (*e.g.*, soil Ca^{2+} availability, berry composition) and winemaking variables (*e.g.*, pH, alcohol content, colloid concentration) could enhance risk assessment of CaT precipitation. For example, it would be worthwhile to develop a simple Calcium Tartrate Risk Index (CaTRI) that integrates measured Ca with pH/EtOH and key vineyard drivers (active limestone/CPI, irrigation-transpiration status, N form, Ca sprays) to predict instability risk and guide stabilisation decisions. Lastly, further studies are required to evaluate the long-term impact of emerging stabilisers, not only on the chemical stability of wines but also on their sensory integrity, ensuring that technological innovation aligns with quality preservation.

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