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Calcium Source Affects Calcium Content, Firmness, and Degree of Injury of Apples during Storage

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Abstract. **Fruit from five apple (*Malus domestica* Borkh.) cultivars were pressure-infiltrated at 103 kPa for 6 min with a 0%, 0.73%, 1.46%, 2.91%, or 5.82% (w/v) Ca-equivalent solution of $CaCl_2$, Ca EDTA chelate, or buffered $CaCl_2$ solution (Stopit). The fruit were stored at 0 ±1C for 18 weeks and then evaluated for Ca content, firmness, and injury. Fruit treated with Ca chelate had no increase in fruit Ca content and were injured at all treatment levels. No significant differences occurred in fruit Ca levels between $CaCl_2$ and Stopit treatments across all cultivars tested. Apples treated with Stopit were firmer than apples treated with $CaCl_2$, when averaged across cultivars. Fruit Ca levels, firmness, and incidence of injury were positively correlated with concentrations of $CaCl_2$ and Stopit for all cultivars.**

A close correlation has been documented between fruit Ca concentrations and physiological and pathological deterioration in apples. Disorders such as internal breakdown (Bangerth et al., 1972) and bitter pit (Reid and Padfield, 1975) are alleviated by postharvest Ca treatments. In addition, the rate of fruit softening is decreased by Ca treatment (Mason et al., 1975; Sams and Conway, 1984). Increasing the Ca concentration of apples through postharvest treatments has also resulted in a reduction of decay caused by several postharvest pathogens (Conway et al., 1991).

A major disadvantage of postharvest Ca treatments has been the inability to predict potential injury to the fruit. Bangerth et al. (1972), Klein et al. (1990), and Johnson (1979) reported varying degrees of Ca-induced injury in their respective treatments. Scott and Wills (1979) reported no serious skin injury with infiltration of a 4% solution of $CaCl_2$ into 'Granny Smith' apples, provided the fruit were immediately rinsed after treatment. Conway and Sams (1982, 1983) also reported no serious skin injury when pressure-infiltrating a 4% $CaCl_2$ solution into 'Golden Delicious' fruit or an 8% solution into 'Delicious' fruit when the fruit was rinsed immediately.

In a study to determine the effects of postharvest infiltration of chloride formulations of Ca, Mg, or Sr on various postharvest maladies, Ca was found to be the optimum cation for alleviating postharvest physiological and pathological problems (Conway and Sams, 1987). Scott and Wills (1979) tried eight Ca compounds, of which only $CaCl_2$ and Ca lactate were effective in reducing bitter pit, with Ca lactate being ≈50% as effective as $CaCl_2$.

Since postharvest Ca treatments have a potential to improve commercial fruit storage, various sources of Ca must be tested to determine the best one for ensuring optimum storage benefits while keeping fruit injury to a minimum. The objectives of this experiment were to 1) study the relative performance of three Ca sources for postharvest infiltration of apples and 2) expand the range of cultivars treated to determine if the same beneficial firmness effects that occur with 'Delicious' and 'Golden Delicious' fruit also benefit other cultivars similarly pressure-infiltrated with Ca.

Materials and Methods

This study was conducted over 2 years with five apple cultivars: 'Golden Delicious', 'McIntosh', 'Mutsu', 'Red Rome', and 'Winesap'. The three sources of Ca were prilled food-grade $CaCl_2$ (Mallinckrodt Specialty Chemical Co., St. Louis); a Ca EDTA chelate (Miller Chemical Corp., Hanover, Pa.); and Stopit, a proprietary $CaCl_2$ solution (Shield Brite Corp., Kirkland, Wash.) formulated as a buffered liquid. All Ca sources were tested on two cultivars in the first year. 'Golden Delicious' was infiltrated with 0%, 0.73%, 1.46%, or 2.91% Ca-equivalent solutions (w/v), and 'Red Rome' was treated with 0%, 1.46%,

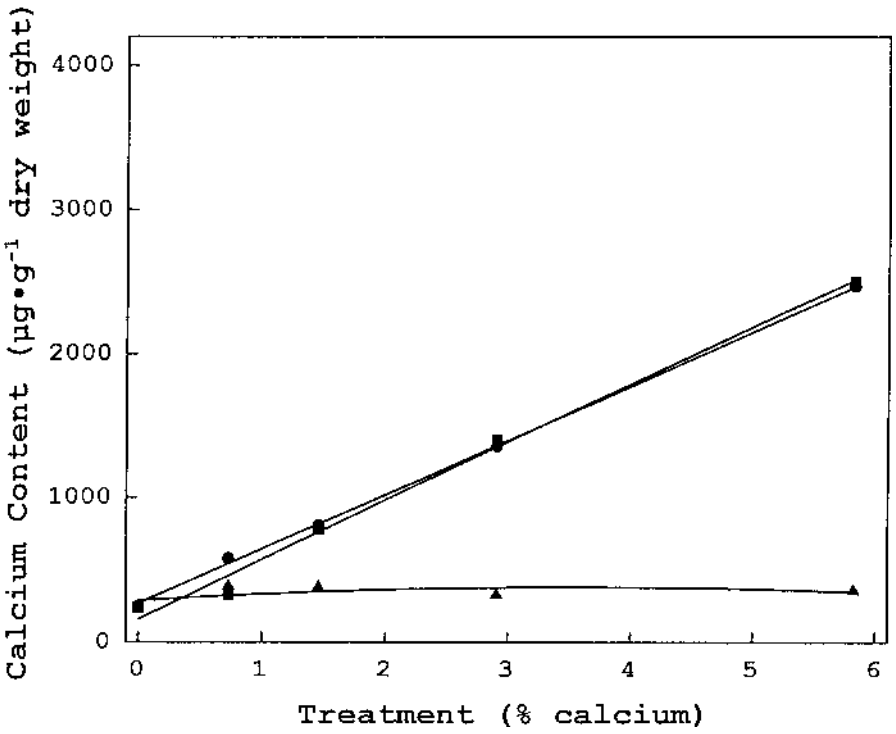

Fig. 1. Relationship between treatment solution concentration and tissue Ca concentration across apple cultivars ['Golden Delicious' (both years), 'McIntosh' (second year), 'Mutsu' (second year), 'Red Rome' (first year), and 'Winesap' (second year)] averaged across years following pressure infiltration (103 kPa) of either $CaCl_2$ [(●) $r^2 = 0.99$, $y = 273.40 + 372.87x + 0.69x^2$, both years], Stopit [(■) $r^2 = 0.99$, $y = 159.89 + 417.67x - 2.23x^2$, both years], or Ca chelate [(▲) $r^2 = 0.30$, $y = 291.69 + 52.57x - 7.28x^2$, first year]. Data points indicate the mean fruit Ca concentration at each treatment solution concentration of (**left to right**) 0%, 0.73%, 1.46%, 2.91%, or 5.82%.

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2.91%, or 5.82% Ca-equivalent solutions (w/v). A nontreated control was used with each cultivar. We used a higher Ca concentration with 'Red Rome' because previous experience indicated that this cultivar was more resistant to Ca infiltration. In the second year, 'Golden Delicious', 'Mutsu', 'McIntosh', and 'Winesap' were treated with 0%, 1.46%, 2.91%, or 5.82% Ca-equivalent solutions of $CaCl_2$ or Stopit. In both years, three 20-fruit replications were used in each treatment. Infiltration was conducted 1 or 2 days after harvest in a 12-liter container that was pressurized to 103 kPa for 6 min. The fruit were not rinsed after treatment to allow for maximum peel exposure to the compounds during storage. The fruit were allowed to drain for 1 h, placed in traypac boxes with ventilated polyethylene bag liners, and stored at 0 ± 1C for 18 weeks.

In the first year, we used a mechanical peeler to remove a 2-mm slice of tissue from five fruit per treatment; then we combined these tissue samples to determine the degree of solution penetration into the fruit. The fruit were washed, the peel removed, and the layer immediately beneath (2 to 4 mm depth) was analyzed for Ca content. In the second year, a combined tissue sample was taken from 20 fruit per treatment by using a 10-mm-diameter cork borer to extract an equatorial cross section of each washed fruit; then we cut out a 2-mm-thick layer under the peel from the cross section. The number of fruit sampled was increased the second year due to the reduced amount of tissue obtained per fruit. Three replications per treatment were analyzed both years.

About 50 g fresh fruit per sample was wrapped in cheesecloth and frozen in liquid N. The samples were freeze-dried to constant weight and then ground. For each sample, 0.5 g of dried material was dry-ashed 12 h at 500C and then dissolved in 8 ml of 2 N HCl. The tissue Ca content was determined by atomic absorption spectrophotometry the first year and by inductively coupled plasma atomic emission spectrometry the second year. All Ca values are reported on a dry-weight basis.

Firmness measurements were taken after the fruit had been held overnight at 20C, from three replications of 10 fruit in the first year, and from 20 fruit in the second year. Firmness was determined at two freshly pared sites on opposite sides of the equator of each fruit with an Effegi (Effegi, Alfonsine, Italy) penetrometer (11.1-mm tip) mounted on a stationary frame.

The fruit were visually rated for Ca injury (surface discoloration and lenticel pitting) by a five-person panel before firmness measurements were taken. Three replications of 20 fruit per treatment were inspected. The percentage of fruit showing any Ca-related injury was statistically analyzed after arcsin transformation. The design was a factorial arrangement within a randomized complete block. Statistical analysis was performed using the GLM procedure of SAS statistical software (SAS Institute, 1989). Differences are reported as significant at $P = 0.05$.

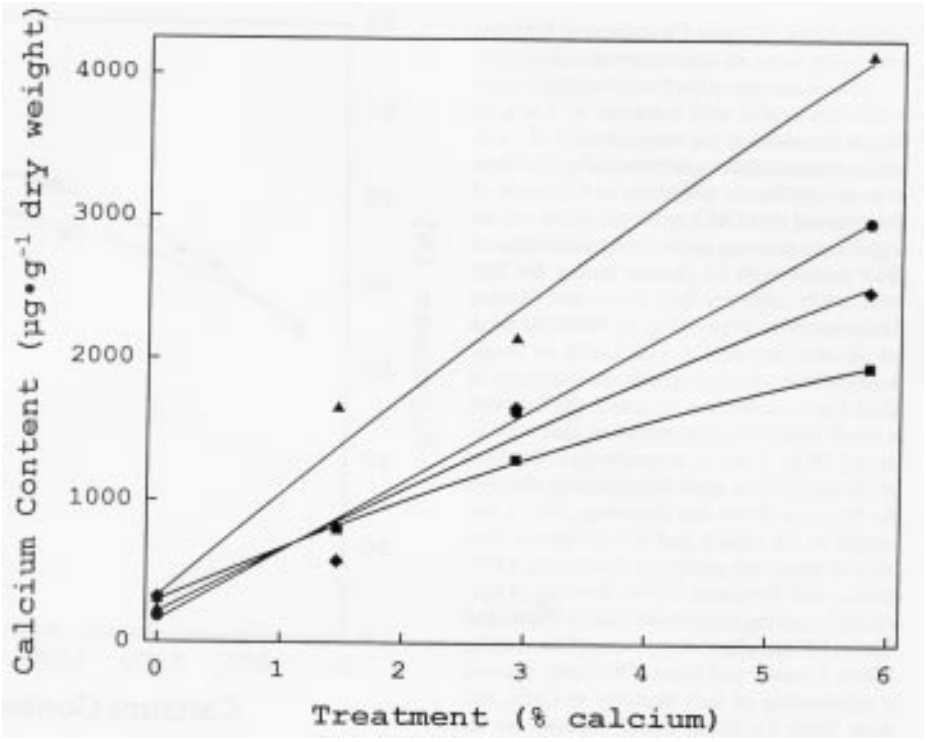

Fig. 2. Tissue Ca concentration of 'Golden Delicious' [(●) $r^2 = 0.99$, $y = 156.71 + 490.80x - 1.32x^2$), 'McIntosh' [(■) $r^2 = 0.99$, $y = 296.39 + 386.28x - 17.53x^2$], 'Mutsu' [(▲) $r^2 = 0.98$, $y = 328.59 + 737.38x - 15.66x^2$], or 'Winesap' [(◆) $r^2 = 0.96$, $y = 213.29 + 452.60x - 9.77x^2$] apples (second year) following pressure infiltration (103 kPa) of $CaCl_2$ and Stopit. Data points indicate the mean tissue Ca concentration pooled across $CaCl_2$ and Stopit at each solution concentration of (**left to right**) 0%, 1.46%, 2.91%, or 5.82%.

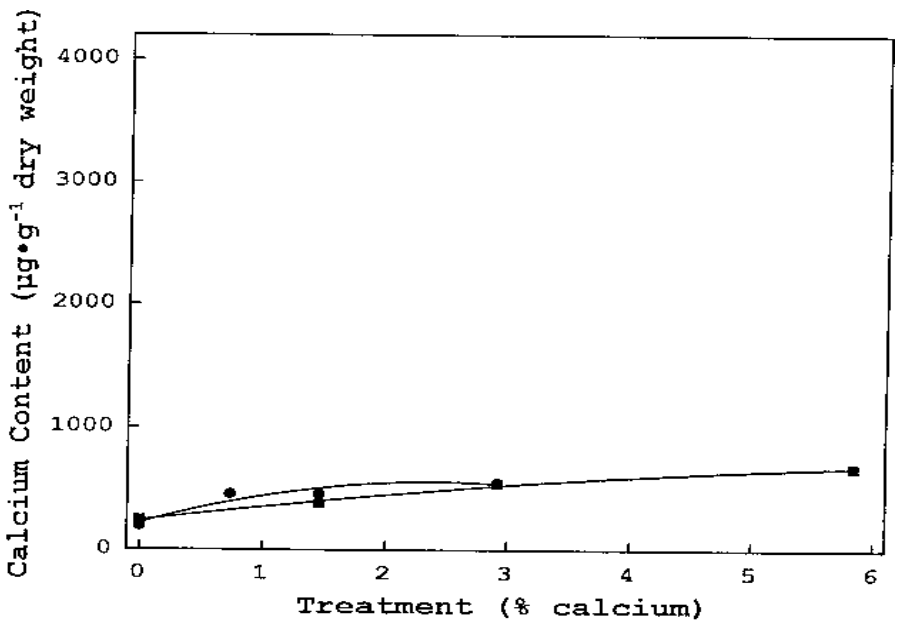

Fig. 3. Tissue Ca concentration of 'Golden Delicious' [(●) $r^2 = 0.81$, $y = 217.05 + 285.31x - 59.35x^2$] or 'Rome' [(■) $r^2 = 0.99$, $y = 238.10 + 122.29x - 8.09x^2$] apples (first year) following pressure infiltration (103 kPa) of Ca solutions ($CaCl_2$ and Stopit). Data points indicate the mean tissue Ca concentration pooled across $CaCl_2$ and Stopit at each solution concentration of (**left to right**) 0%, 0.73%, 1.46%, 2.91%, or 5.82%.

Results and Discussion

In both years, a significant interaction occurred between cultivar and Ca source; therefore, preplanned mean comparisons were used to determine treatment differences. For $CaCl_2$ and Stopit, the relationship between solution concentration and tissue Ca content and the

relationships of tissue Ca content to firmness and injury were all significant and quadratic.

The Ca content of the fruit (averaged across cultivars) treated with solutions of $CaCl_2$ or Stopit increased as the concentration of Ca in the treatment solutions increased (Fig. 1). There was no significant difference in Ca levels of fruit treated with $CaCl_2$ or Stopit. There was no significant increase in the Ca concentration of fruit treated with Ca chelate during the first year when cultivars Red Rome and Golden Delicious were treated (Fig. 1). While the flesh of all cultivars treated with $CaCl_2$ or Stopit formulations showed significant increases in flesh Ca concentration, in year 2, the fruit had a much higher Ca concentration than fruit in year 1 (Figs. 2 and 3, respectively). Calcium solutions infiltrate apple fruit primarily through the lenticels (Betts and Bramlage, 1977), but cracks in the cuticle and the epidermis may also be important pathways (Clements, 1935; Harker and Ferguson, 1988). Severity of epidermal cracking varies with variety (Faust and Shear, 1972) and growing season (Glenn et al., 1985). Conway and Sams (1985) also showed a relationship of fruit maturity to $CaCl_2$ uptake. Such variations could account for an annual difference in solution uptake by 'Golden Delicious' apples and differences in solution uptake between cultivars within the same year.

Excessive fruit injury prevented accurate firmness measurements for the fruit treated with Ca chelate; therefore, no correlation can be established between fruit Ca levels and fruit firmness. Fruit firmness was positively correlated to tissue Ca levels for all $CaCl_2$ and Stopit treatments across all cultivars (Fig. 4). Apples treated with Stopit showed a slight but significant increase in firmness over fruit treated with $CaCl_2$ when analyzed across cultivars, even though there was no significant difference in tissue Ca concentration based on the treatments. When the data were analyzed by cultivar, 'Rome', 'McIntosh', and 'Winesap' were significantly firmer when treated with Stopit than with $CaCl_2$, while 'Golden Delicious' and 'Mutsu' were not (data not shown). Moreover, 'Rome' and 'Golden Delicious' from the first year of the study had a significantly higher tissue Ca content when treated with $CaCl_2$ than with Stopit (data not shown). Tissue Ca content and firmness were positively correlated in all cultivars (Fig. 5).

The percentage of fruit injury resulting from treatment with $CaCl_2$ or Stopit solutions was directly proportional to solution Ca concentration and the fruit flesh Ca concentration (Fig. 6). There were no statistical differences in fruit injury between $CaCl_2$ and Stopit across all treatment levels. The injury in the treated fruit would limit their fresh-market sale, but since the discoloration and pitting did not extend into the cortex, all apples treated with $CaCl_2$ or Stopit would have been acceptable for processing.

Excessive fruit injury occurred at all treatment concentrations of Ca chelate. Fruit injury caused by $CaCl_2$ or Stopit was mainly superficial, but injury caused by Ca chelate extended well into the cortex, often resulting in tissue necrosis. Because of this severe injury, and the lack of significant treatment differences in tissue Ca uptake, the Ca chelate formulation was discontinued after the first year.

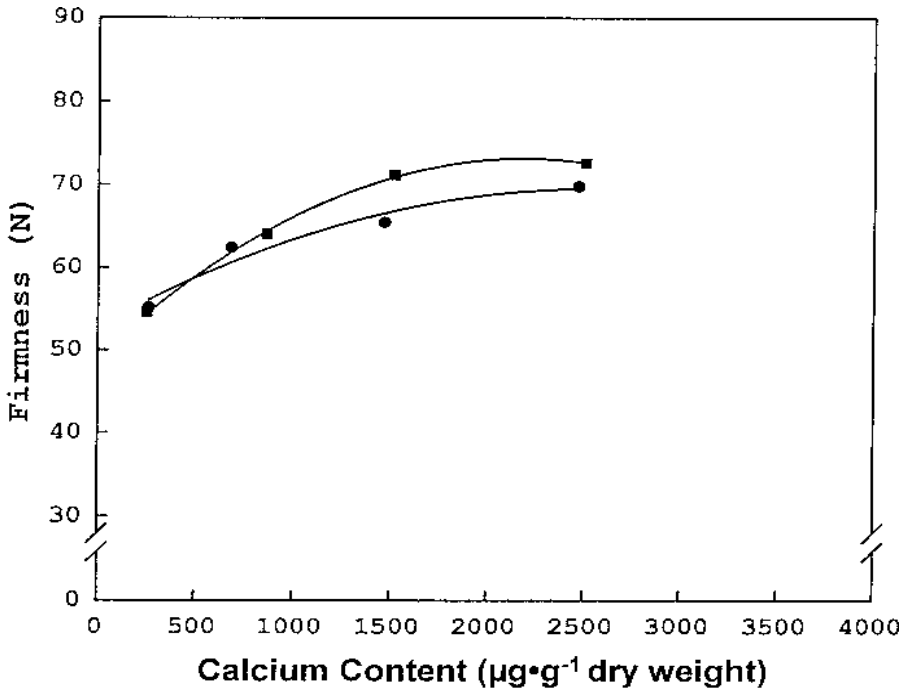

Fig. 4. Relationship between tissue Ca concentration and fruit firmness analyzed across cultivars ('Golden Delicious', 'McIntosh', 'Mutsu', 'Red Rome', and 'Winesap') following pressure infiltration (103 kPa) of either $CaCl_2$ [(●) $r^2 = 0.95$, $y = 52.83 + 0.01x - 2.59x^2$] or Stopit [(■) $r^2 = 0.99$, $y = 49.19 + 0.02x - 5.04x^2$]. Data points indicate the mean fruit firmness at solution concentrations of (**left to right**) 0%, 0.73%, 1.46%, 2.91%, or 5.82%.

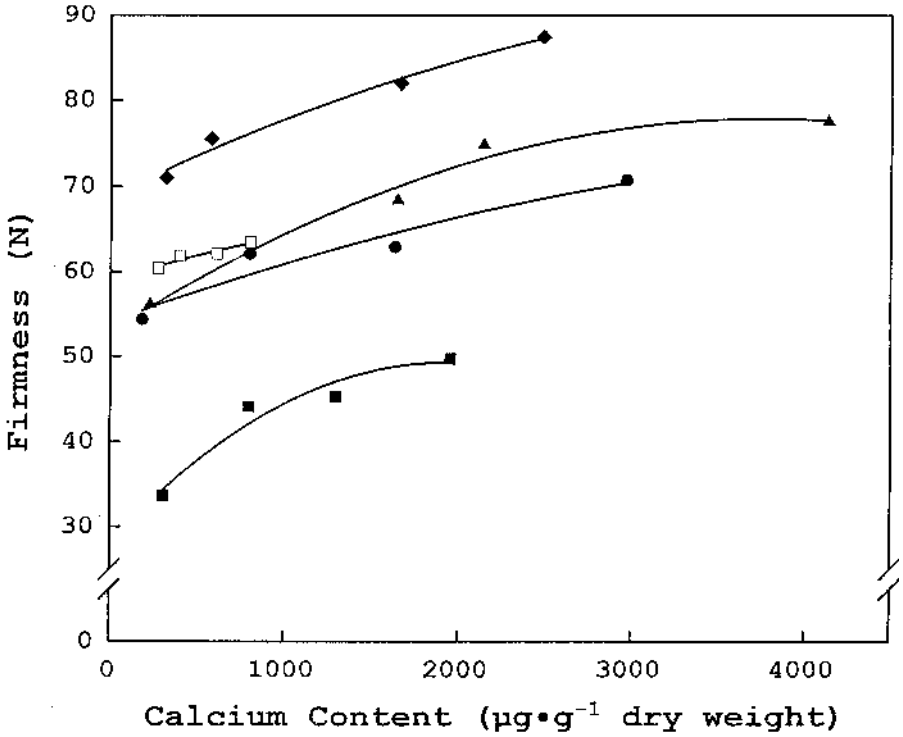

Fig. 5. Firmness of cultivars Golden Delicious [(●) $r^2 = 0.93$, $y = 54.08 + 7.59x - 7.01x^2$], McIntosh [(■) $r^2 = 0.94$, $y = 28.19 + 0.02x - 5.74x^2$], Mutsu [(▲) $r^2 = 0.98$, $y = 52.93 + 0.01x - 1.77x^2$], Rome [(❑) $r^2 = 0.91$, $y = 58.86 + 7.73x - 1.94x^2$], Winesap [(◆) $r^2 = 0.98$, $y = 68.52 + 0.01x - 1.04x^2$] following pressure infiltration (103 kPa) of $CaCl_2$ and Stopit. Data points indicate the mean fruit firmness across both $CaCl_2$ and Stopit at concentrations of (**left to right**) 0%, 1.46%, 2.91%, or 5.82%.

Calcium injury to fruit is usually associated with high flesh Ca concentration (>1000 $\mu g \cdot g^{-1}$ dry weight). Since extreme injury in the Ca chelate-treated fruit is not a result of an increase in tissue Ca content, other factor(s)

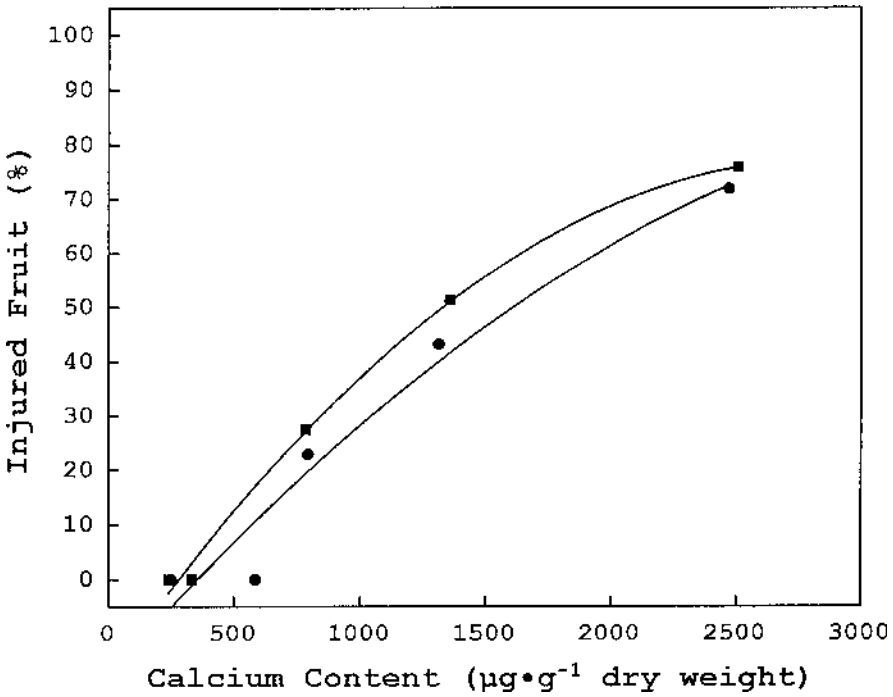

Fig. 6. Relationship between tissue Ca concentration and fruit injury analyzed across cultivars ('Golden Delicious', 'McIntosh', 'Mutsu', 'Red Rome', and 'Winesap') following pressure infiltration (103 kPa) of either $CaCl_2$ [(●) $r^2 = 0.96$, $y = -17.83 + 0.05x - 6.52x^2$] or Stopit [(■) $r^2 = 0.99$, $y = -17.83 + 0.07x - 1.16x^2$). Data points indicate the mean fruit firmness across both $CaCl_2$ and Stopit at concentrations of (**left to right**) 0%, 1.46%, 2.91%, or 5.82%.

must be involved. The chelate injury resembled low-O_2 injury encountered under some controlled atmospheres. The Ca chelate formula may have blocked the openings in the fruit surface to such a degree that gaseous exchange was restricted. Infiltration of solutions into fruit can impede gas exchange (Hewitt and Thompson, 1992). Since the excessive tissue injury appears to have been caused by factors other than high Ca levels, no correlation can be assumed between injury and fruit Ca concentrations for the Ca chelate treatments.

Conclusions

Postharvest pressure infiltration of $CaCl_2$ and Stopit solutions resulted in significant increases in tissue Ca concentration in an amount directly correlated with the concentration of the Ca in the treatment solution for all five cultivars. There were annual differences in Ca uptake by 'Golden Delicious', and there were also differences among cultivars within the same growing season. 'Mutsu' took up the most Ca in the second treatment year, followed by 'Golden Delicious', 'Winesap', and 'McIntosh', respectively. Before postharvest Ca infiltration can become commercially viable, the differential uptake between cultivars as well as the annual variations within cultivars will have to be studied further to optimize treatment solution concentrations. Both formulations also maintained fruit firmness of all five cultivars during storage, with Stopit being slightly more effective at equivalent Ca treatment concentrations. Fruit injury due to the Ca treatments was similar for both formulations. Thus, the decision to use either $CaCl_2$ or Stopit should be based on economics and ease of use because the two compounds react essentially the same. Although fruit injury occurred at higher solution concentrations, this injury would not preclude these fruit being used for processing. If fruit are intended exclusively for processing, Ca treatment and standard cold storage could provide an economical alternative to controlled-atmosphere storage. Any injury would limit the sale of fruit on the fresh market.

The Ca chelate formulation was obviously not suitable as a substitute for $CaCl_2$, since its infiltration resulted in no increase of fruit tissue Ca concentration and severely injured the fruit at all treatment concentrations.

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