

SERB decreased after storage with increasing prestorage treatment concn between 0 and 40% CO<sub>2</sub>. Those of 20 and 40% CO<sub>2</sub> resulted in significantly less SERB than did 10% CO<sub>2</sub> (Table 1).

No significant differences in SERB were found in fruit stored in air at a continuous temp of 4.5° (8.6%), and that exposed to air at 21° for 3 days, (10.0%), or 7 days (8.2%), prior to being stored at 4.5° in air. Fruit treated with CO<sub>2</sub> averaged 3.9% SERB after storage, and untreated fruit averaged 8.7%.

A gradual increase occurred in each group in the percentage of fruit developing SERB when fruit were held for 7 and 14 days at 21° after storage. However, the percentages affected continued to be significantly less in the fruit treated with CO<sub>2</sub> than in that not treated with CO<sub>2</sub> in all but the 10%

CO<sub>2</sub> group after 14 days.

Rind pitting, a type of chilling injury, was reported in 1975 in fruit from the same groves involved in these experiments (3). All prestorage CO<sub>2</sub> treatments significantly reduced rind pitting in stored fruit. Fruit stored without CO<sub>2</sub> treatments had excessive pitting. Treatments resulted in no significant differences in decay.

If high CO<sub>2</sub> treatments are to be used to minimize the risk of pitting due to chilling injury, treatment at 21° thus avoids the hazard of increased SERB previously found when the initial high CO<sub>2</sub> was used at storage (4.5°) temp.

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## Ash, Silicon, Calcium, and Copper in 'Concord' Grape Leaves<sup>1</sup>

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**Abstract.** The concentration of Cu in 'Concord' grape (*Vitis labrusca* L.) leaves remained nearly constant throughout the growing season; ash, Si, and Ca percentages increased continually. The Si concentration increased 9 fold, Ca increased 3 fold and ash increased almost 2 fold over the growing season. The percentage of Ca was about three times that of Si at the end of the season. SiO<sub>2</sub> was deposited in the form of opal in the cell walls. Calcium was deposited in the leaf veins and in small oval particles throughout the leaf.

The concentrations of ash, silicon and calcium deposited vary considerably by species as well as by plant parts in the same species (7, 8, 9, 10, 11). Silica in a number of plants has been found to increase steadily over the growing season (8, 10, 13). In this study, growing season concentration changes of Ca, Si, and Cu in 'Concord' grape leaves and their localization within the leaf were determined.

The Ca concn of 'Concord' grape leaves picked May 1 has been reported as 0.57% (14). Ca concn increases following bloom in *vinifera* (6) and muscadine (4) grapes. Boynton (2) reported that Ca content of 'Portland' grape leaves affected with K deficiency (scorch) and picked in Sept. was 2.71% and in 'Delaware' grapes with K deficiency was 2.29%.

Copper concn in grape leaves usually

varies from 12-15 ppm (1, 3) but Teakle et al. (17) report normal healthy leaves of 'Sultana' (*V. vinifera* L.) contain 7.5-10 ppm, while copper-deficient leaves contained only 1-4 ppm. Gil Salaya et al. (5) report slight fluctuations in *V. vinifera* leaf blades but nearly constant petiole values in the growing season.

In this study 'Concord' grape leaves were collected from vines in Manhattan, Kansas on May 28, July 11, August 27, and Oct. 9, 1975. The plants grew in a silty clay loam soil with a pH of 7.2; 127 g of NH<sub>4</sub>NO<sub>3</sub> fertilizer per vine was applied once in the spring. No copper sprays were used. Healthy mature, green, sun leaves were sampled to follow the change in mineral concn in leaves during their growth. Vines were healthy and had bloomed before the first leaves were picked and all leaves used had formed on the vines before the first collection date. Leaf blades were washed with distilled water, dried at 110°C to constant weight, and ground to a powder for analysis.

Silica and ash levels in the leaves

were determined by traditional gravimetric techniques. About 2 g samples of leaves were ashed at 490°C to constant weight. After being weighed, the ash was treated with 6N HCl and washed to remove other minerals. The resulting residue was filtered out, ignited, and weighed in a platinum crucible. SiO<sub>2</sub> level was determined by difference in weights before and after treatment with 49% HF. These and all other determinations were run in duplicate or triplicate.

The filtrate was made up to 25 ml in a volumetric flask with 0.1 N HCl and used to determine the other minerals. Aliquots of solutions were treated with NH<sub>4</sub>Cl and made slightly basic with NH<sub>4</sub>OH to precipitate Al<sub>2</sub>O<sub>3</sub> and Fe<sub>2</sub>O<sub>3</sub>.

Ca was determined on the filtrate by the gravimetric method of precipitating calcium as the oxalate, igniting and weighing. The first oxalate precipitate was dissolved in 3N hydrochloric acid and reprecipitated.

Cu was determined by absorption flame photometry. The instrument was adjusted as follows: Wavelength = 3248 Å; Hollow cathode current = 10 ma, Photomultiplier tube = 0.6 kv; Fuel flow rate = 1.4 liters/min; Oxidant flow rate = 10.0 liters/min; Sample uptake = 4.0 ml/min; Height, burner-to-light path = 0.4 cm. The burner was flushed with a solution of 0.1 N HCl between each sample. To prepare the calibration curve, standards including the concn range for the plant material were used.

The apparatus used consisted of a Jarrell-Ash model 82-360 Ebert-mounted 0.5 m grating monochromator with Jarrell-Ash electronics, including a mechanical chopper (90 cycles/sec), ac amplifier, and 1P28 photomultiplier detector. The entrance and exit slits on

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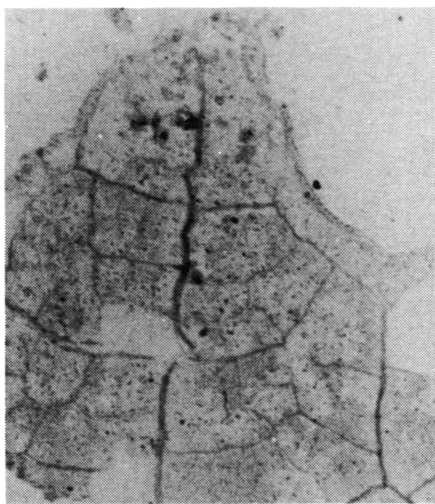


Fig. 1. Spodogram of tip of a 'Concord' grape leaf showing deposition of calcium in leaf veins and small oval particles (40X).

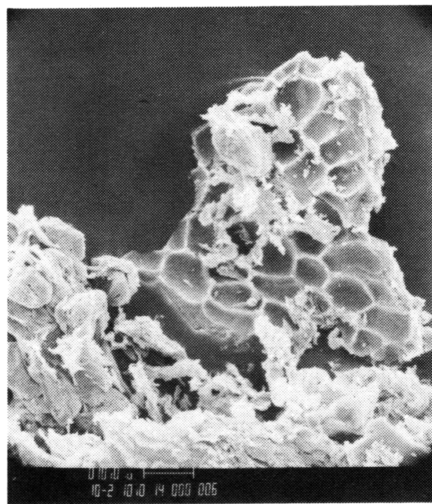


Fig. 2. Electron micrograph of silicified cell walls in the tip of 'Concord' grape leaf (1000X).

the monochromator were fixed at 50  $\mu$ m. The readout device was a Sargent Model S-72150 recorder. The spectral source was Westinghouse hollow cathode copper tube operated by a Jarrell-Ash power supply.

The sampling system consisted of a Jarrell-Ash tri-flame premix laminar flow burner (5 cm slot). Fuel and oxidant flow rates to the burner were controlled by Jarrell-Ash regulators and monitored with model F-1300 (Roger Gilmont Instruments) flow meters. The tri-flame burner was operated with an air-acetylene flame.

The pattern of silica and Ca deposits in leaves was studied by Uber's spodogram techniques (18), described by Ponnaiya, (16), and used by Lanning, et al. (12). Tips of leaves were ashed between glass plates at 490°C.

The silica for petrographic studies was obtained in the same manner as the silica determination except that, after acid treatment and washing, the silica was dried at 110°C to constant weight. An ETEC Autoscan E-1 Electron Microscope was used to determine the depositional pattern of the silica.

The pattern of Ca deposited in a grape leaf picked in Oct. is shown by the spodogram (Fig. 1). Ca is deposited in the leaf veins and as small oval particles throughout the leaf. Petrographic microscope studies show that Ca in the ash takes the form of calcite, but it may have assumed a different form in the original leaf.

Careful examination of residues with a petrographic microscope shows that silica deposits in the cell walls. Petrographic microscope studies of the silica, from which other minerals had

been removed, showed that it was clear, colorless, and isotropic with a 1.43 index of refraction — all characteristics typical of the mineral opal. No  $\alpha$ -quartz was observed. Heating at 490°C has no effect on opaline silica (12).

Deposition of SiO<sub>2</sub> in cell walls at the tip of a mature grape leaf collected in Oct. is shown by the scanning electron micrograph (Fig. 2). Results for ash, Si, and Ca analyses are given in Table 1. All increased in percentage during the growing season. The rate of increase was greatest between May 28 and July 11; and thereafter relatively constant. The 'Concord' grape leaf is a Ca and silica accumulator and the leaves contain nearly 3 times as much Ca as Si at the end of the season.

The percentage of copper in the leaves remained nearly constant during the season (Table 1) and did not fluctuate as reported by Gil Salaya et al. (5) for *V. vinifera* cv. Semillon leaves. The copper level was considerably above the deficiency level reported by Teakle et al. (17) for *V. vinifera* cv. Sultana leaves and lower than that reported for 'Concord' grape leaves by Myers et al. (15). It was somewhat below the average reported by Beattie

Table 1. Ash, silicon, calcium and copper in Concord grape leaves, 1975.

Date	Leaf concn (dry wt)			
	Ash (%)	Si (%)	Ca (%)	Cu (ppm)
May 28	6.45	0.098	0.865	143
July 11	8.52	0.457	2.12	142
Aug. 27	9.45	0.681	2.25	142
Oct. 9	10.67	0.896	2.62	145

and Forshey (1) for 'Concord' grape leaves in Ohio.

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