

# **Silicic acid water extraction and plant available-silicon from the mineral Wollastonite**

Report prepared by:

Professor Richard Bélanger  
Canada Research Chair in Plant Protection  
Département de phytologie, Université Laval

Submitted to :

Mr. Bob Vasily  
President  
Canadian Wollastonite

May 15, 2019

## Introduction

Nearly 25 years ago, the seminal review by E. Epstein (1994), “The anomaly of silicon in plant biology”, became a turning point of accelerated interest in silicon’s properties and benefits to plants. Prior to that, the bulk of research efforts and discoveries had been pioneered by Japanese scientists whose reports, originally published in Japanese, were summarized by Ma *et al.* (2001). Apart from these major works, there is a dearth of solid research data in the peer-reviewed literature prior to 1994, with a total of 250 papers dealing with silicon (Si) effects in plants, as opposed to the more than 1,000 articles focusing on various aspects of silicon’s potential in plants that have been published since. As a result, many important discoveries, such as the identification of Si transporters, have impacted our understanding of Si in plants, and mounting evidence supporting the advantages of Si fertilization has finally, in 2015, led the International Plant Nutrition Institute (IPNI) to upgrade Si from complete omission to the status of “beneficial substance” ([www.ipni.net/nutrifacts](http://www.ipni.net/nutrifacts)).

The chemistry of Si is complex and difficult to master even in simple laboratory practice (Iler, 1979; Evered & O’Connor, 1986; Voogt & Sonneveld, 2001), and many features intrinsic to Si have hampered its widespread application in agriculture. For one, the silicate salts typically used to supply Si in growth media (*e.g.*, potassium silicate and sodium silicate) are highly alkaline and can cause precipitation issues if not carefully handled (Voogt & Sonneveld, 2001). Moreover, orthosilicic acid ( $\text{Si(OH)}_4$ ;  $\text{pK}_{\text{a}1} = 9.84$ ,  $\text{pK}_{\text{a}2} = 13.2$ , at 25 °C), the form of Si accessible to plants (Casey *et al.*, 2004), is soluble in water only up to 1.7 mM at 25 °C, above which polymerization into silica ( $\text{SiO}_2$ ) gel begins to occur (Ma *et al.*, 2001). From a biochemical perspective,  $\text{Si(OH)}_4$  is largely uncharged and unreactive at physiological pH. As Pace (2001) notes, unlike carbon (C), Si cannot engage in as many chemical bonds with as many other atoms, and is thus largely “monotonous” (forming mostly silicates and silica polymers), compared to the vast combinations of organic macromolecules. As a result, in spite of the impressive body of Si research now in the literature, the precise role of Si in plants remains largely unknown, and in particular the potential for its practical application largely unexploited.

Plants will absorb Si in the form of  $\text{Si}(\text{OH})_4$  from soil or nutrient solutions. As mentioned, the maximum solubility of  $\text{Si}(\text{OH})_4$  in solution is 1.7 mM, often reported as 100 ppm Si, and its concentration in soils usually varies between 0.1 and 0.6 mM (Raven, 1983; Epstein, 1994). Under similar conditions, plant species have different abilities to accumulate Si, a notion that has been known, if poorly understood, for a long time.

Silicon is the second most abundant element after oxygen in the earth's crust and in soil. The averaged content of elemental Si in the lithosphere is approximately 28%. Total Si content in soil ranges normally from 25% to 35% with an average of 30%, depending greatly upon soil types. However, in some highly weathered soils such as latosols or latosolic red soils in the tropics where desilification and fersialitization processes are extremely active, Si content can be as low as less than 1%. Silicon content and its availability in soil depend greatly upon soil forming processes and consequently soil types. Silicon is mainly present in soils including various categories of aluminosilicates and quartz ( $\text{SiO}_2$ ), which may account for up to 75-95% of soil inorganic constituents. Except organic soils (Histosols), most mineral soils are composed of sands (largely  $\text{SiO}_2$ ), various crystalline forms of primary (e.g. olivine, augite, hornblende, quartz, feldspars-orthoclase, plagioclase, albite, and mica) and secondary silicate minerals (clay minerals like illite, vermiculite, montmorillonite, chlorite and kaolinite); and amorphous (non-crystalline) Si-containing minerals such as allophone and opal. These forms of silicate compounds are only sparingly soluble and usually biogeochemically inert.

Because the concentration of plant available silicon is usually too low, it is often necessary to use silicon fertilizers for the purpose of increasing the concentration of silicic acid,  $\text{Si}(\text{OH})_4$ , the only form available to a plant. For this purpose, calcium and magnesium silicate ( $\text{CaMgSiO}_3$ ) is commonly used. This product comes from iron steel slag heavy metal recuperation. However, this product often contains contaminants that can be hazardous. On the other hand, Wollastonite is a naturally occurring mineral rich in Si, and mined for production of ceramics, friction products, metallurgy, paints, and plastics (Virta, 2004) It has an ideal composition of 34.3% calcium (Ca), 24.3% Si, and some minor amounts of aluminum (Al), iron (Fe), manganese (Mn), magnesium (Mg), potassium (K), sodium (Na), and minerals such as calcite, diopside, garnet, idocrase, and quartz (Virta, 2004, Maxim et al., 2008). Ca and Mg silicates, with high residual effect, should be applied at least 3 months before planting. The residual effect (carryover) can last up to 4 to 5 years after application.

Fine-grained silicates tend to react faster with the soil, while larger one may have a longer residual effect.

### **Plant available silicon in Wollastonite and plant uptake**

At Laval University in the Biocontrol Laboratory, Wollastonite samples provided by Mr. Bob Vasily of Canadian Wollastonite were tested for the purpose of evaluating the concentration of plant-available silicon in two formulations; 1) a coarse Wollastonite sand, and 2) a finer preparation.

#### *Experimental protocol*

One g of Wollastonite sand, coarse or fine, was mixed in 40 ml H<sub>2</sub>O. The experiment was repeated in four separate suspensions. The suspension was agitated and left to rest for 96 hours. It was then centrifuged at 3200G for 15 min and soluble Si was extracted using the CaCl<sub>2</sub> method.

#### *Results*

Table 1. Soluble silicon (Si(OH)<sub>4</sub>) concentrations in Wollastonite extracts of fine and coarse sand following water extraction over 4 days.

<b>Formulation</b>	<b>Si (mg/L)</b>	<b>Si (mM)</b>
Fine	9,8	0,35
Fine	10,0	0,36
Fine	9,8	0,35
Fine	9,7	0,35
Fine	9,7	0,35
Coarse	2,4	0,08
Coarse	2,7	0,09

Coarse	2,2	0,08
Coarse	2,2	0,08
Coarse	2,2	0,08

### **Plant silicon content**

In 2016, soybean plants cv. Hikmok were used to determine plant silicon content following addition of two formulations and two concentrations of Wollastonite in 8-inch pots filled with Pro-Mix.

#### *Experimental protocol*

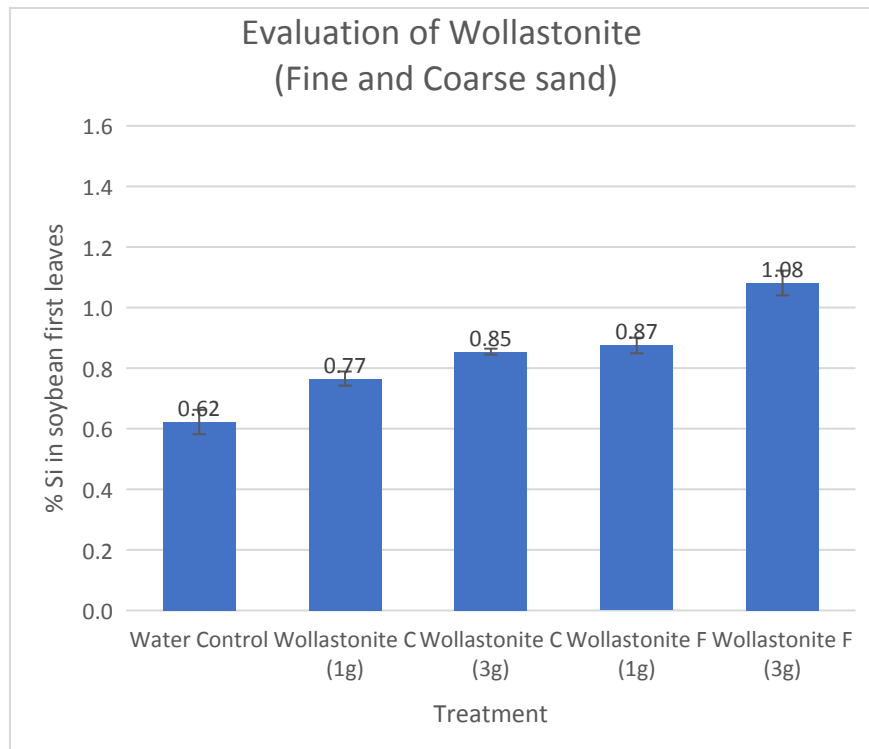
The experiment was carried out over a period of four weeks and for each treatment, 10 plants were treated. The treatments were as follows:

1. Control i.e plants grown in Pro-Mix without supplement
2. Wollastonite coarse, 1 g per pot
3. Wollastonite coarse, 3 g per pot
4. Wollastonite fine, 1 g per pot
5. Wollastonite fine, 3 g per pot

Plants were watered with tap water every other day.

At the end of the experiments, plants were harvested, dried ground to a powder and measured for silicon content using the XRF methodology as described by Deshmukh et al (2015).

#### *Results*



**Figure 1.** Percent silicon in soybean leaves of plants fertilized with two formulations of Wollastonite (C = coarse and F = fine) over a period of four weeks.

## Conclusions

Silicon is well known to provide a multitude of benefits to plants, namely in the context of alleviating biotic and abiotic stresses (Coskun et al., 2019). For these benefits to be manifest, plants must be able to extract silicon in the form of silicic acid,  $\text{Si}(\text{OH})_4$ , from the substrate in which they are growing. Plant-available silicon is usually naturally present in low quantities (0.1-0.6 mM) in soils and can never exceed 1.7 mM, the maximum solubility of silicic acid in solution. Consequently, silicon fertilizers can be used to increase the quantity of plant-available-silicon in the soil, although the solubility of silicon can vary greatly from one fertilizer to the next.

In this study, we evaluated the water solubility of Wollastonite, the only naturally occurring mineral rich in silicon, in terms of silicic acid, also known as plant-available silicon, and how plants responded to silicon fertilization in terms of silicon accumulation. For this purpose, two formulations of Wollastonite, coarse and fine, were tested, as previous results indicate that fine formulations should release more silicic acid because of the greater surface area being exposed to solvents.

In the first experiment aimed at assessing the water solubility of Wollastonite, the results showed first that Wollastonite did indeed release silicic acid in water after a brief

extraction (4 h). Interestingly, it was shown that a fine formulation released on average 4 times more silicic acid than a coarse one. We found on average 0.39 mM Si in the solution, which, in the limited period of time tested, corresponds to ¼ of the maximum solubility. However, the coarse formulation still released nearly 0.1 mM in this short period of extraction. Considering the high residual expected effect, this indicates that Wollastonite, both in coarse and fine formulation can significantly increase the amount of plant-available Si when applied as a fertilizer.

In order to verify if indeed Wollastonite increased the amount of silicon absorbed by plants, we tested the percent silicon found in plants grown four weeks in a substrate amended with Wollastonite. Our results confirmed that, regardless of the formulation or concentration, addition of Wollastonite to the substrate significantly increased percent silicon in plants. The results also corroborated the findings of silicic acid in solution whereby the fine formulation at the highest concentration yielded the highest percent silicon, exceeding by nearly 75% the concentration found in plants grown in a control substrate.

In conclusion, our results confirm that Wollastonite is a *bona fide* source of plant-available silicon, and can be expected to have a long residual effect. When used as a fertilizer, Wollastonite significantly increases the percent silicon absorbed by plants, and as a consequence should help plants better tolerate different stresses owing to the intrinsic properties of silicon.

## References

- Casey WH, Kinrade SD, Knight CTG, Rains DW, Epstein E. 2004. Aqueous silicate complexes in wheat, *Triticum aestivum* L. *Plant Cell & Environment* 27: 51-54.
- Coskun, D., Deshmukh, R., Sonah, H., Menzies, J.G., Reynolds, O., Ma, J.F., Kronzucker, H.J., Bélanger, R.R. 2019. The controversies of silicon's role in plant biology. *New Phytologist*, 221:67-85.
- Deshmukh, R.K., Vivancos, J., Ramakrishnan, G., Guérin, V., Carpentier, G., Sonah, H., Labbé, C., Isenring, P., Belzile, F., Bélanger, R.R. 2015. A precise spacing between NPA domains of aquaporins is essential for silicon permeability in plants. *The Plant Journal* 83: 489-500.
- Epstein E. 1994. The anomaly of silicon in plant biology. *Proceedings of the National Academy of Sciences of the United States of America* 91: 11-17.



- Ma JF, Miyake Y, Takahashi E. 2001. Silicon as a beneficial element for crop plants. In: Datnoff LE, Snyder GH, Korndörfer GH, eds. *Silicon in agriculture*. New York, USA: Elsevier Science, 17-39.
- Evered D, O'Connor M. 1986. *Silicon biochemistry*. New York, USA: John Wiley & Sons.
- Iler RK. 1979. *The chemistry of silica: solubility, polymerization, colloid and surface proteins, and biochemistry*. New York, USA: Wiley Interscience.
- Maxim L. D., Niebo R., LaRosa S., Johnston B., Allison K., McConnell E. E.. 2008. Product stewardship in wollastonite production. *Inhal. Toxicol.* 20:1199–1214.
- Pace NR. 2001. The universal nature of biochemistry. *Proceedings of the National Academy of Sciences of the United States of America* 98: 805-808.
- Raven JA. 1983. The transport and function of silicon in plants. *Biological Reviews of the Cambridge Philosophical Society* 58: 179-207.
- Virta R. L. 2004. Wollastonite—U.S. Geological Survey Minerals Yearbook 82:1–3.
- Voogt W, Sonneveld C. 2001. Silicon in horticultural crops grown in soilless culture. In: Datnoff LE, Snyder GH, Korndörfer GH, eds. *Silicon in agriculture*. New York, USA: Elsevier Science, 115-131.