Chapter 9
Review: The Functions of Phytoliths in Land Plants

**Inga C. Keutmann, Björn Melzer, Robin Seidel,
Ralf Thomann and Thomas Speck**

9.1 Introduction

Phytoliths have interested scientists for more than one hundred years (Fig. 9.1; Struve 1835; Ehrenberg 1846, 1854; Gregory 1855; Sachs 1862; Kohl 1889). Not only botanists were drawn to these fascinating, multifunctional structures, but also chemists, agronomists, geologists, palaeontologists and archaeologists (Cooke et al. 2011). Though the expression phytolith is most commonly associated with silica inclusions in plants, there are many different definitions of the term. Calcite inclusions, whether calcium carbonate or calcium oxalate, also known as cystholiths, and inclusions with combined silicate and calcite are described as phytoliths as well. In 2006 Sommer et al. proposed a definition for phytoliths *sensu stricto* as defined silicon precipitates of plant origin with a diameter >5 µm to separate them from 'undefined phytogenic silicon <5 µm'. This criterion is used in several recent publications as well as in this review.

Phytoliths are widely found in plants (Hodson et al. 2005), so it is not surprising that they have been the subject of much research. Especially in agronomy the influence of higher silicon uptake and therefore increased inclusion of silica as phytoliths and its importance as a nutrient in economic plants, like rice, sugar cane or wheat were studied (Takahashi 1968; Savant et al. 1999). In palaeontology, phytoliths were used for the determination of floral composition in fossil ecosystems and in

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I. C. Keutmann (✉) · T. Speck · B. Melzer · R. Seidel
Plant Biomechanics Group, Botanic Garden of the Albert-Ludwig University, Faculty of Biology,
Schänzlestraße 1, 79104 Freiburg im Breisgau, Germany
e-mail: thomas.speck@biologie.uni-freiburg.de

R. Thomann
Freiburg Materials Research Center (FMF) and Institute of Macromolecular Chemistry of the
Albert-Ludwig University, Stefan-Meier-Str. 21–31, 79104 Freiburg im Breisgau, Germany

T. Speck
Freiburg Materials Research Center (FMF), Stefan-Meier-Str. 21–31, 79104 Freiburg im
Breisgau, Germany

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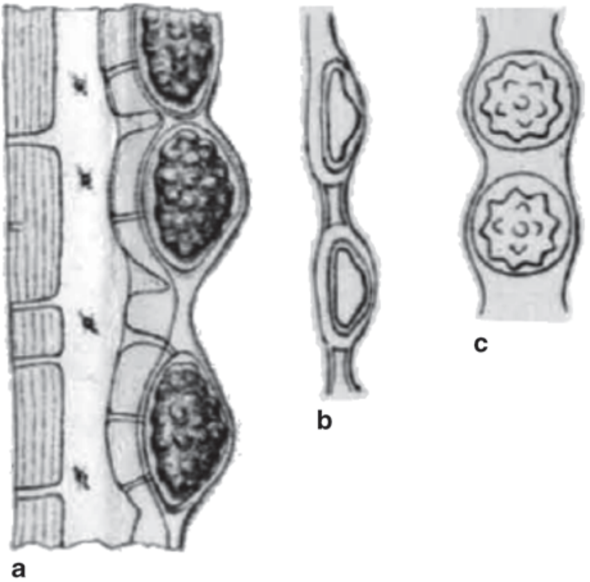


Fig. 9.1 Historical images of phytoliths from Kohl 1889. **a** *Masdevallia* spec., phytoliths with elliptic base and 'von Brod'—shape. **b** *Epidendrum nocturneum*, phytoliths as smooth caps. **c** *Phalaenopsis grandiflora*, phytoliths as warty balls

ethno-botany the composition of agricultural systems was analysed with the help of phytoliths (Tubb et al. 1993; Sangster et al. 2001). Interestingly, there is a striking chronological relationship between the evolution of angiosperms, especially grasses, and the radiation of diatoms found in the fossil record. This synchroneity seems to be linked to continental orogeny and hence enhanced erosion occurring at this time, which increased the supply of nutrients, and especially silica fluxes to the oceans. Probably, the silica fluxes intensified the production and diversification of diatoms. Later on, the expansion of grasslands pushed the diversification and massive increase of large herbivore abundances, especially ungulates (see Chap. 1c) with their teeth designed to process silica rich plant material. The concomitant marked rise of grasslands and large herbivore numbers biologically catalysed the availability of silica fluxes to the oceans, resulting in a concordant evolution of diatoms (Falkowski et al. 2004).

9.2 Amount and Appearance of Phytoliths in Land Plants and Soil

Silicon, after oxygen, is the second most abundant element in the Earth's crust. The amount of silicon in soil varies between <1% and 45% (Epstein 1999, 2001; da Cunha et al. 2008; da Cunha and do Nascimento 2009). Plants are an essential part of the silicon cycle (Fig. 9.2). They accumulate silicon as silicic acid [$Si(OH)_4$], with concentrations in soil ranging commonly between 0.1 and 0.6 mmol L^{-1} (Epstein

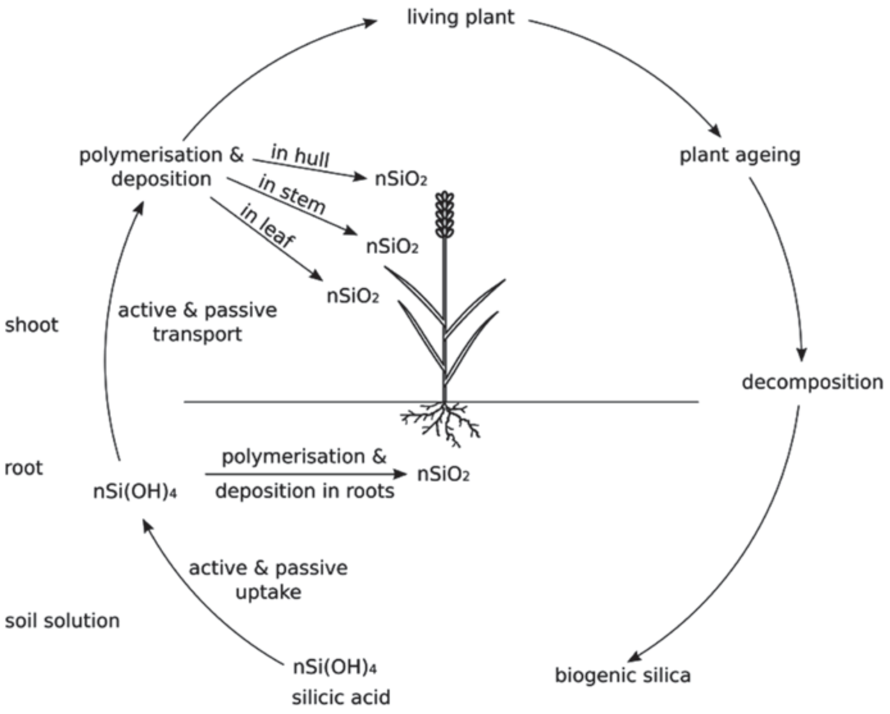


Fig. 9.2 Schematic illustration of the silicon cycle. Plants absorb silicic acid through the roots and transport it. Besides silica deposition in roots, it is also found in the shoot, where it is deposited in different plant organs. Due to plant ageing and following decomposition, biogenic silica becomes part of the soil again

1994, 1999), varying with soil types (Jones and Handreck 1965). Silicic acid occurs in soil due to rock weathering and the slow dissolution of biologically deposited SiO_2. The transport takes place in both a passive way through the transpiration stream and actively due to energy-dependent transporters (Ma et al. 2006; Ma and Yamaji 2006; Mitani and Ma 2005; Currie and Perry 2007). Furthermore, transpiration has been proven to be significantly correlated with silica content in plants (Euliss et al. 2005). The silicic acid is absorbed by roots, transported to the shoots and finally stored in different parts of the plant: in cell lumen, cell wall or outside of plant cells (Sangster et al. 2001; da Cunha et al. 2008; da Cunha and do Nascimento 2009). The accumulated silicon is stored as solid, amorphous, hydrated silica ($SiO_2{*}nH_2O$) forming phytoliths (Currie and Perry 2007) which is much more reactive than crystalline silica (Epstein 1999, 2001). The amount of silica in land plants varies from 0.1 to 10% of dry plant weight strongly depending on plant species and silicon content in the soil (Epstein 1999, 2001; Hodson et al. 2005; Ma et al. 2006; Currie and Perry 2007). This amount is comparable to or even exceeds the amount of various macronutrients in plants (Epstein 1999). The plant groups best known for their silica inclusions are Poales, Equisetales and Arecales, due to the fact that these orders have the highest and most frequent silica concentrations and accumulation (>4 % Si dry matter; Hodson et al. 2005; da Cunha et al. 2008; da Cunha and do Nascimento 2009).

Detailed analysis showed that not only the amount but also the form of phytoliths in plants is species dependent (Piperno 1988; Epstein 1994; 1999; Hodson et al. 2005). Variations in form are very pronounced, including e.g. conical, spherical, druse-like and dumbbell-shaped bodies to name just a few (Prychid et al. 2004). The uniqueness of phytoliths in a taxon is used especially in archaeology and palaeontology, e.g. for the determination of farming behaviour of earlier cultures or feeding behaviour of extinct animals.

Besides the variation in form, there is also great variation in size from 100 nm (Watteau and Villemin 2001) to over 1000 µm in diameter (Piperno 1988; Sommer et al. 2006) which partly defines the name of the specific phytolith structures, e.g. silica sand for many tiny particles in a cell (Prychid et al. 2004). Phytoliths are deposited in many different places and at all hierarchical levels in plants. However, their most common location is in the epidermis.

9.3 Functions of Silicon in Plants

Silicon is said to have many different functions in plants, including mechanical stability, growth promotion or defence against various biotic and abiotic stresses (Epstein 1994, 1999; Ma et al. 2001; Ma 2004). Up until now, some functions are proven and some are mere assumptions. Mostly, studies on the influence of silica were carried out with agronomically relevant plants like rice, soybean, maize, grains or sugar cane. Studies on plants without agronomic interest are scarce.

9.3.1 Mechanic Stability/Lodging

The term mechanical stability is used in many different contexts for plants. Some aspects of silica-influence on mechanical plant stability have not yet been analysed, such as the influence of silica inclusions on bending or torsion stiffness and on the respective moduli. Influence of silica on mechanical properties was mostly studied in relation to stem lodging of crop plants in agronomy. Different studies showed the reduction of lodging through fertilizing with silicon (Welton 1928; Tisdale et al. 1985; Hong et al. 2009), due to increased culm wall thickness and increased size of vascular bundles (Shimoyama 1958; da Cunha et al. 2008).

Leaf erectness which has pronounced influence on light interception is also increased by elevating the amount of silica in the plant (Yoshida et al. 1969, Ma 2004) and decreases the sensitivity to stem lodging amongst other causes due to an improved assimilation system (Takahashi 1968; Savant et al. 1999). Additionally, a high amount of silica in the cuticula, which can be increased by silicon fertilizing, gives enhanced mechanical stability against penetrators, such as stalk borers (Keeping et al. 2009) or pathogenic fungi (Haysaka et al. 2008).

9.3.2 Reduction of Climatic Stress

Climatic stresses are common for plants. They include water deficiency, cold temperatures and freezing (Savant et al. 1999; Liang et al. 2008) as well as mechanical (wind) loads and radiation.

Silicon in plants is able to reduce the extent of stress due to water deficiency. This is caused by the reduction of transpiration which is accomplished by the formation of a silica double layer in the cuticle leading to a reduced cuticular transpiration (Savant et al. 1999; Ma et al. 2001; Ma 2004). Additionally, silicon is proved to enhance water uptake in some plants due to an improvement in hydraulic conductance (Sonobe et al. 2009). However, there are many different factors involved and the different effects are still not completely analysed and understood (Sonobe et al. 2009). Another mechanism which needs additional investigation is the reduction of freezing stress in plant tissues due to increased silica content. Although it has been proven that additional silicon enhances water content of leaf tissues and reduces the amount of freezing injuries, the mechanism can only be guessed. Liang et al. (2008) assume that reductions of freezing injuries probably depend on higher antioxidant defence activity, lower lipid peroxidation, and membrane permeability.

9.3.3 Defence Against Chemical Stress

Lack or excess of nutrients and other elements might cause profound problems in plants. Silicon may mitigate effects of nutrition problems or chemical stress, as shown in many different studies. For example, silicon reduces excess toxicity of different elements, including manganese, iron, aluminium, cadmium, zinc (da Cunha et al. 2008; da Cunha and do Nascimento 2009) and phosphate (Ma and Takahashi 1990a, b; Ma et al. 2001).

In case of manganese the mechanism of preventing toxicity seems to be different depending on the plant species and has not been completely solved. Assumptions for this mechanism are a decreased uptake of manganese, but also binding of manganese by silicon, as well as increased enzyme activities (Shi et al. 2005; Shi et al. 2010) and two opposing assumptions: (a) a more distinct concentration of manganese (Iwasaki and Matsamura 1999), or (b) a more homogenous distribution of manganese in the leaves (Williams and Vlamis 1957; Horst and Marschner 1978; Savant et al. 1999). Even though the exact mechanism of how silicon interacts with manganese remains unclear, there is no doubt about the influence silicon has in alleviating excess toxicity of manganese.

Toxic Al^{3+} is probably bound by silicon in the plant (Cocker et al. 1998) as well as in the soil solution (Ma et al. 1997). The limiting effects of aluminium excess like reduced root growth and nutrition uptake are neutralized.

Cadmium and zinc are both found to build metal-silicate complexes in soil and in the plant, which decreases the availability of these two elements for the plant and supports detoxification of cells (da Cunha et al. 2008; da Cunha and do Nascimento 2009).

In case of phosphate, silicon has a great influence on both, phosphate deficiency and excess. With a sufficient phosphate supply there is no effect of silicon on the phosphate balance. However, with a lack of phosphate in soil, silicon has indirect beneficial effects on plant growth, due to a silicon-induced decreased manganese and iron uptake of the plants. Since phosphate binds manganese and iron, a decreased Mn and Fe uptake results in a higher availability of essential phosphate in the plant (Ma and Takahashi 1990; Ma et al. 2001). If the content of phosphate in soil is exceedingly high, silicon reduces the uptake of inorganic phosphate, which otherwise would affect growth negatively due to an inhibition of enzyme activity or inactivation of necessary metals like zinc (Ma and Takahashi 1990; Miyake and Takahashi 1978, 1982, 1985, 1986).

9.3.4 *Defence Against Herbivores*

Increased resistance against herbivores due to a higher amount of phytoliths in plants is the best known benefit of their occurrence in plants. Plants with high silica content have a rough surface, causing an increased abrasion of the teeth of herbivores and hence a reduced feeding on plants with higher silica content (Massey et al. 2007; Hunt et al. 2008). Comparing studies of pastures with different grazing intensity show that plants on heavily grazed land store much more silica than plants on lesser grazed land (McNaughton et al. 1985). The result can also be generated artificially by defoliation of the plants (McNaughton and Tarrants 1983), indicating higher silicon accumulation and therefore higher silica content in plants, as a defence against herbivores. However, not only plants adapted their silica content to grazing but also herbivores such as horses seem to have adapted their teeth to higher silica content in grass. It is thought that co-evolution took place in which, for example, North American Equidae evolved high-crowned molars due to the spread of grasslands (Falkowski et al. 2004; Mihlbachler et al. 2011).

9.3.5 *Resistance Against Pathogenic Fungi and Germ Infections*

Plants are highly endangered by pathogenic fungi, bacteria, and insects. It is proven that silica inclusions enhance the defence against the above mentioned organisms. Especially in the field of agriculture, the influence of fertilizing with silicon and hence the influence of a higher amount of silicates in plants is studied since the exact mechanisms of the protective effects are not yet understood (Cai et al. 2009). There are three different possible types of defence. Firstly, through a physical barrier due to the higher amount of silica in outer plant tissues and the resulting stronger defence against pathogenic penetration (Zhang et al. 2006; Hayasaka et al. 2008). Secondly, bio-chemically by inducing higher production rates of protective enzymes under stress (Yang et al. 2003; Fauteaux et al. 2006; Cai et al. 2009; Reynolds et al. 2009). Thirdly on the molecular level by up-regulation of genes known for their defence and pathogenic function under stress conditions (Watanabe et al. 2004; Fauteaux et al. 2006). Nevertheless, the exact defence mechanisms remain an interesting field of research.

9.3.6 *Growth Promotion*

Silica inclusions have great influence on plant growth. In addition to the reduction of negative stress effects, which would lead to growth reduction, silicon promotes several physiological processes in plants (Korndörfer et al. 2001). One example is an up to 50 % higher activity of Rubisco in silica-rich plant leaves (Epstein 1999). Additionally, silicon acts as a growth stimulant, e.g. for larger leaves (McNaughton 1985) with a bigger biomass (Epstein 1999), and increases the yield of crop plants like sugar cane or rice (Savant et al. 1999; Korndörfer et al. 2001).

Because of multifunctional benefits in plants, the role of silicon in plant physiology is much discussed. In classic understanding, silicon does not belong to the necessary elements for most plants and as such is not considered to be one of the essential nutrients (Epstein 1999, 2009; Cooke and Leishman 2011). However, several researchers disagree with this position since the benefits of silicon for plants can easily be seen in phenotype and have definitely been proven by comparing the results of experiments on plants grown in soil with high and low silicon amounts (Epstein 1999, 2009; Korndörfer et al. 2001; Euliss et al. 2005; Currie and Perry 2007; Cooke and Leishman 2011). Despite this conflict, silicon is dealt with like every other nutrient element in plants with regards to the uptake mechanism (Epstein 2009).

9.3.7 *Window Hypothesis*

For a long time it had been speculated that silica bodies located in the leaf epidermis work as ‘windows’ to increase the transmission of light in the photosynthetic tissue. Agarie et al. (1996) however, could not support this hypothesis in their study. Even though only plants supplied with extra silicon built ‘windows’ in their leaves, the optical properties of leaf transmittance, reflectance, and absorbance spectrum were nearly the same which led Agarie et al. (1996) to reject the ‘window hypothesis’.

9.4 Qualitative and Quantitative Detection of Phytoliths in Land Plants

9.4.1 *Qualitative Analysis*

There are different methods to detect phytoliths in plants and a comparison of the most commonly used methods is given in Blecher et al. (2012). The detection with the secondary electron microscope (SEM) by electron-dispersive X-ray detection (EDX; Fu et al. 2002; Sapei et al. 2007; Keeping et al. 2009) is most common, sometimes in combination with backscattered electron imaging (BSE; Dietrich et al. 2003; Laue et al. 2006). EDX is the classical method which is also element specific. BSE provides a higher special resolution than EDX, but is not specific to silicon. Other possibilities are stains in light microscopy like methyl red and counterstaining with fast green (FG-MR) or crystal violet lactone and counterstaining with safranin (S-CVL) as proposed by Dayanandan (1983). These stains are not yet silica specific, and in case of some other colorants difficult in terms of security regulations. Raman analysis (Sapei et al. 2007; Gierlinger et al. 2008) is another silica specific method which not only determines the positions of phytoliths in the plant, but can also analyse the exact chemical composition of the phytoliths. Despite these advantages Raman is very complex in handling and interpretation and several possibilities of interference exist (Blecher et al. 2012). A short comparison of the listed methods is shown in Figs. 9.3 and 9.4.

In the end, the choice of method is tied to available equipment, even though only EDX and Raman provide reliable results.

9.4.2 Quantitative Analysis

The methodologies for quantitative analysis of silica in plants are manifold. The most frequent first step of quantitative silica analysis is isolation of the phytoliths, if the plant material is not measured directly by EDX (Keeping et al. 2009) or chromatographic methods (Fu et al. 2002). The isolation of phytoliths can generally be achieved in two different ways, wet ashing and dry ashing. Wet ashing means

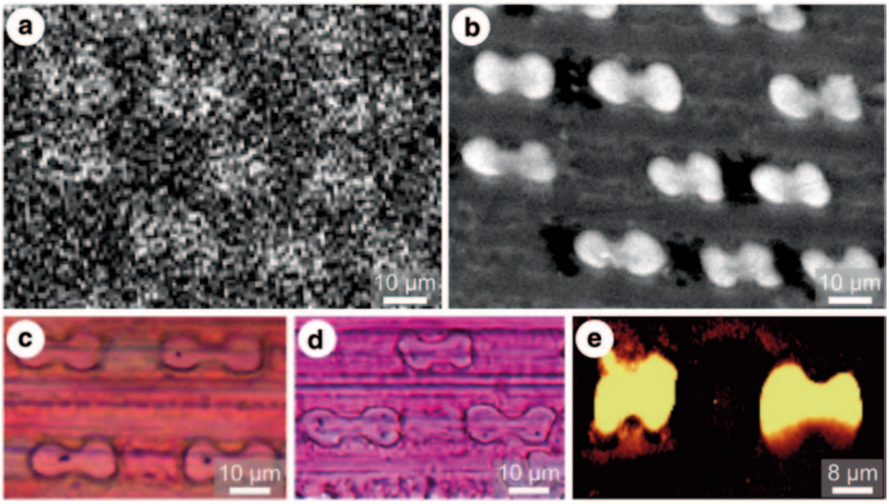
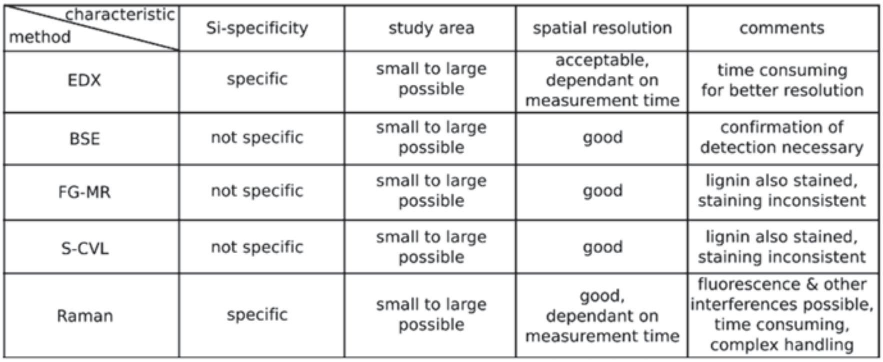


Fig. 9.3 Comparison of different silica-detecting methods using the dumbbell-shaped silica inclusions of *Miscanthus sinensis* (Poaceae) as an example. **a** EDX, dumbbells visible in average resolution. **b** BSE, dumbbells clearly visible. **c** light microscopic staining FG-MR, dumbbells visible, but surrounding tissue also stained (both *red*). **d** light microscopic staining S-CVL, dumbbells visible, but surrounding tissue also stained (both *violet*). **e** Raman imaging at wavelength 254–570 cm^{-1}, dumbbells clearly visible (*orange*)



characteristic method	Si-specificity	study area	spatial resolution	comments
EDX	specific	small to large possible	acceptable, dependant on measurement time	time consuming for better resolution
BSE	not specific	small to large possible	good	confirmation of detection necessary
FG-MR	not specific	small to large possible	good	lignin also stained, staining inconsistent
S-CVL	not specific	small to large possible	good	lignin also stained, staining inconsistent
Raman	specific	small to large possible	good, dependant on measurement time	fluorescence & other interferences possible, time consuming, complex handling

Fig. 9.4 Comparison of different silica detecting methods with essential characteristics

isolation by chemical treatment, dissolving organic material, using chemicals like hydrogen peroxide, hydrochloric acid or nitric acid (Blackman and Parry 1968; Saccone et al. 2006; Saccone et al. 2007; Sapei et al. 2007; Mali and Aery 2008). Dry ashing means burning the plant material at high temperatures from 400 up to 600 °C (Jones and Milne 1963; Sapei et al. 2007; Keeping et al. 2009). A combination of both ashing procedures can also be done by applying the chemical treatment to the sample either before or after the heat treatment. A common procedure during the combination of both types of ashing is cooking the sample or the ash in hydrochloric acid (Euliss et al. 2005; Sapei et al. 2007). The ash, whether it is obtained by wet or dry ashing, can be analysed in different ways. Often the ash is weighed and compared to the dry weight of the used plant material or the ash content before the combined chemical treatment methods. Other possibilities include different spectroscopic methods (Fu et al. 2002) and colorimetric estimation where the ash is diluted, e.g. in sodium hydroxide solution. Then a reducing mix including a colorant is added and finally the colouration of the solution is measured at a specific wavelength (Blecker et al. 2007; Nwugo and Huerta 2008). A sole standard method cannot be found.

9.5 Conclusion

Although research on phytoliths has considerably increased over the last ten to fifteen years, several functions, especially their influence on the mechanical properties of plants, are still poorly understood. Conversely, it is expected that the role of silicon as an essential nutrient for plants will be revealed soon due to its manifold functions.

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