

Review Article

## Interaction of silicon with cell wall components in plants: A review

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### Abstract

Silicon (Si) is the utmost element of the earth's crust involved in various plant processes. Despite being a non-essential element of the plant, its role in plant tolerance is appreciable. The interaction of Si with the plant cell wall provides structural and mechanical strength to the plants. This review article discusses the different forms of silica (simple to complex), the nature of Si, and its interaction with plant cell wall components after being taken up by plants. Ligands of plant cell wall like hemicellulose, pectin, lignin, cellulose, callose, and mixed-linked glucans (MLG) are the possible linker, which helps the Si in crosslinking with the plant cell wall. This review also incorporates the interrelation of Si with different cell wall components, the role of Si-cell wall complexes in different stress alleviation, and enhancing stress resistance in plants. Accumulation of Si after crosslinking with the cell wall provides rigidity and stability to the plant wall and enhances mechanical strength. Many studies have been conducted on the Si role in different stress alleviation, but little knowledge is available on how plants react when Si is taken up, how Si interacts with the plant cells, how Si accumulation is enhanced by the plant itself, how the possible ligands help Si in bonding with the cell wall. This study helps to understand the relationship of cell wall components with Si and to think about the precise bonding patterns between them.

**Keywords:** Cell wall, Components, Interaction, Ligands, Silicon, Stress

### INTRODUCTION

Silicon (Si) is abundant in complex forms in the earth's crust, mostly reported in silicon dioxide (SiO<sub>2</sub>) form in the soil environment, and can vary greatly depending on the dry matter, from less than 1 to more than 40%. Si is found in mostly all terrestrial plant parts and is usually precipitated as amorphous silica or polymerized silica in specific cells or cell walls. Many studies have shown that Si forms covalent bonds with different components of cell walls like pectin, hemicellulose, lignin, and cellulose, and non-covalent bonds via polymerized silica (Sheng and Chen, 2020). Si in its mono silicic acid form (Si(OH)<sub>4</sub>) is taken up by plants, as it is the plant-available form of Si (Sommer *et al.*, 2006; Singh *et al.*, 2022). Si in the soil is mainly present in concentrations of 0.1 to 0.6 mM, far greater than that of various macronutrients. However, no proof is known of the Si formation reaction in soil (Epstein, 1994; Soury *et al.*, 2021). Applying Si in stressed conditions helps the

plants tolerate the stresses and improve their growth by maintaining their structural and mechanical strength. Moreover, Si is found as an essential nutrient for many agricultural crops under various stress conditions at different stages of their lifecycle and enhances their production and yield (Bhardwaj and Kapoor, 2021). However, Si is not always easily available in the form that plants can absorb. Many factors, such as severe rainfall and leaching of Si from the soil due to high water logging, are responsible for the low Si content within soil. As a result, plants cannot absorb substantial Si from the soil and become susceptible to many stressful situations (Schaller *et al.*, 2021; Pooja *et al.*, 2022). In many studies, Si was found to be a good fertilizer in agricultural production, as it increases plant growth and yield and provides stress tolerance to the plants against any stressed conditions. It was suggested that Si could improve different biochemical and physiological functions in stressed plants (Kovács *et al.*, 2022). The Si in plants can affect the structure and arrange-

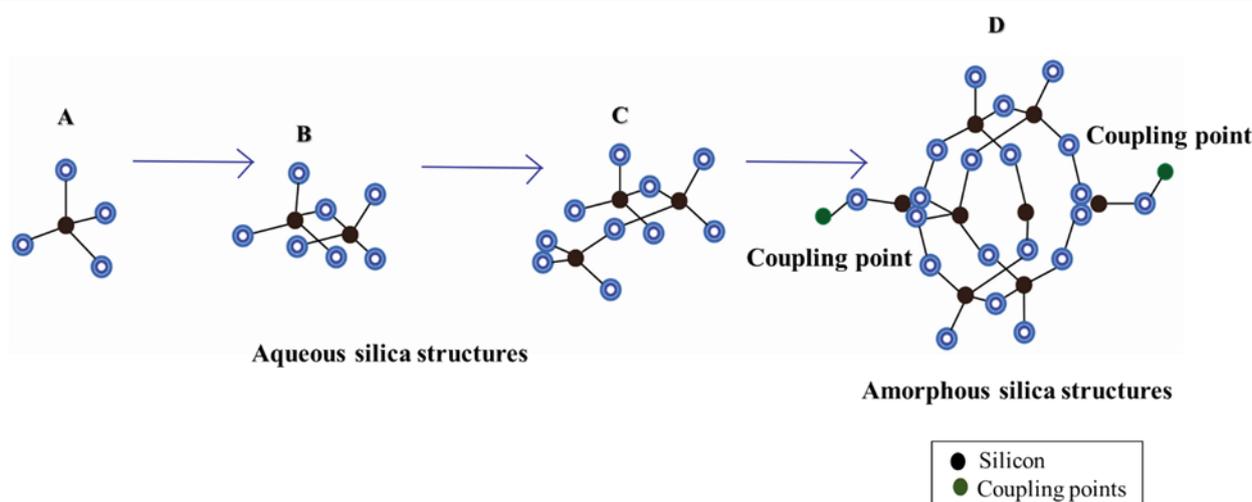
ment of plant cell walls by crosslinking to different cell wall components and making alterations in linking patterns with carbohydrate, lignin, cellulose, and phenolic compounds during the polymerization process (Dragišić Maksimović *et al.*, 2007; Głazowska *et al.*, 2018; Radotić *et al.*, 2022). In addition, Si increases the rigidity and strength of the plant shoot by increasing the lignin formation (Zhao *et al.*, 2021). According to Radotić *et al.* (2022), the crosslinking of Si with lignin components can be fascinating for the emerging uses of Si-lignin complexes as hydrogels in biomedicine or biosensors.

### Chemical Nature of Si

Si as silicic acid ( $\text{Si}(\text{OH})_4$ ) is the simplest form of silica, also recognized as orthosilicic acid or monosilicic acid. It is also known as monomers of silica, which is the fundamental unit of polymeric silica, i.e., amorphous silica, a polymerized form of silicic acid (Currie and Perry, 2007). Si is the richest electropositive element present in the earth's crust. It contains tetrapositive ions and is generally tetravalent in chemical behavior. By the nature of tetravalency, it forms different covalent compounds. Si forms a number of compounds with oxygen and shows different covalent characteristics. Besides tetravalent, Si is also found in its bivalent, pentavalent, and hexavalent compounds. Si is present in its three stable natural isotopes, i.e., isotope 28 (92.2%), isotope 29 (4.7%), and isotope 30 (3.1%) in the earth's crust. Moreover, many radioactive artificial isotopes of Si have also been found. Si behaves like metals in their chemical nature. This could be the probable reason for Si in alleviating metal stress in plants by competing with them and increasing the uptake of Si via roots. Most forms of Si and its compounds are nontoxic in nature even after they are abundant in the soil (Britannica, 2021). Si exists in three phases in soil environments: solid, liquid, and adsorbed phase (Matichenkov and Bocharnikova, 2001; Pooja *et al.*, 2022). The solid phase of Si consists of microcrystalline, poorly crystalline, crystalline, and amorphous forms. The primary and secondary silicates, which make up a significant portion of Si in the solid phase, are the main sources of crystalline forms (Pooja *et al.*, 2022). Both the liquid and adsorbed phases of Si contain similar forms of Si, however, in the liquid phase, Si is found dissolved in the soil environment, and in adsorbed phase, they are merged into soil particles and oxides and hydroxides of iron and aluminum. The major type of Si in the liquid phase are monomeric ( $\text{H}_4\text{SiO}_4$ ), oligomeric, or polysilicic acid (Iler 1979; Shivaraj *et al.*, 2022). The polymerized form of silica or polysilicic acid in the soil stimulates soil aggregation and increases the soil's ability to store water (Matichenkov and Bocharnikova, 2001). The quantity of Si in the soil environment is affected by a) adsorption/desorption of Si with nutrients or minerals, b) polymeri-

zation and depolymerization reaction, and c) crosslinking and bonding between Si and different ligands (Schaller *et al.*, 2021; Shivaraj *et al.*, 2022). The concentration of Si in the liquid phase depends on how easily Si dissolves in the solid phase. In the soil solution, the dissolvability of both crystalline and amorphous forms of Si lies between pH 2 and 8. However, this dissolvability increases quickly at pH around 9. At this pH, the Si forms of  $\text{H}_4\text{SiO}_4$  quickly split into  $\text{H}_3\text{SiO}_4^- + \text{H}^+$ , which lowers the level of  $\text{H}_4\text{SiO}_4$  in soil environment and causes both forms of silica to dissolve in order to restore the  $\text{H}_4\text{SiO}_4$  concentration (Dove, 1995; Tubaña and Heckman, 2015; Shivaraj *et al.*, 2022). Si is absorbed by the plant in monosilicic acid or orthosilicic acid form, a plant-available form of Si from the soil, and transported through the root xylem to its final destination. After the accumulation of Si in the plant part, it forms amorphous silica or phytoliths through the polymerization of Si. These phytoliths or polymerized silica are accumulated in the cell walls and in between the intercellular space of particular plant cells (Prychid *et al.*, 2003). Plant cell walls are comprised of different components and proteins, such as polysaccharides, cellulose, cellulose microfibrils, hemicellulose, lignin, pectins, mixed-linked glucans, and callose. According to Perry and Keeling-Tucker (1998), the different biochemical environment of a plant's cell wall is helpful in enhancing the solubility of Si in different plant cells and binding capacity of silica to different cell wall components. But the interconnection of Si with different cell wall components in plants is not completely understood.

The amount of Si is low in absorbed parts of plants, such as roots, and high in those plant parts where transpiration occurs at a higher rate, such as leaves, showing that the upward movement of the evapotranspiration stream regulates the accumulation rate of Si. After being absorbed by the plant roots, Si is translocated to the stem through the xylem. There are two primary routes by which Si is transferred within plants via absorption through roots. Si is first absorbed from soil environment by various Si-transporters and passive diffusion into various plant cells. Then it is discharged into the transpiration stream through the xylem after uptake. The deposition of Si in various plant tissues majorly relies on these processes (Mandlik *et al.*, 2020). Fascinatingly, the quick discharge of Si into the xylem is found against a concentration gradient. After being discharged from the xylem, Si is transported to the periphery of the leaves and inflorescences in the aerial plant parts. Moreover, Si has been detected in many parts of *Cannabis sativa*, although accumulation occurs exclusively in the anterior part of the cell wall in bast fiber cells (Guerriero *et al.*, 2019). These Si-impregnated walls are believed to reinforce the plant



**Fig. 1.** Polymerization of dissolved silica structures (monomeric silica to polymerized silica) to amorphous silica in plants (Iler, 1979). This figure illustrates the simplest form of silica as a monomeric to dimeric, trimeric, and polymeric form. Si is taken up by plants in the simple monomeric form i.e., monosilicic acid, and in plants, this silicic acid is converted into polymerized silica or amorphous silica through polycondensation reaction.

and offer lodging resistance.

### Biological processes of silica structures: Simple to complex forms

Naturally, Si has been found in three oxidation states comprised  $-4$ ,  $+2$ , and  $+4$ , in which the  $+4$  oxidation state is most common (Tubaña and Heckman, 2015; Souri *et al.*, 2021). Si was reported in over 370 rock-forming elements, which comprise a large percentage of most soils (Richmond and Sussman, 2003; Souri *et al.*, 2021). Si is found in soil as silica (silicon dioxide:  $\text{SiO}_2$ ), silica gel (a kind of silica with an extremely porous structure that can absorb 40% of its weight in saturated vapour), and silicate (a silicic acid,  $\text{H}_2\text{SiO}_3$ , that occurs in abundance in rocks, and earth masses). However, Si also occurs in nature in other forms of minerals, such as calcium silicate, aluminum silicate, magnesium silicate, and many more (Farooq and Dietz, 2015; Souri *et al.*, 2021). Different life forms like diatoms, sponges, and plants can accumulate, store, and process Si to form biogenic silicas. On the industrial scale, silica is produced by living organisms from low-saturated solutions of silicic acid in aquatic environments. Temperature ranges from  $4$  to  $40$  °C and atmospheric pressure are the two main requirements for silica production. Every year, this production of silica far exceeds industrial production in the measure of gigatonnes (Currie and Perry, 2007). The different ways by which silica can be attained from living organisms is a matter of controversy and debate. But it is clear that the biological environment, including carbohydrates, proteins, lipids, polysaccharides, and a wide range of phenolic components, play a major role in silica production in plants (Perry and Lu, 1992; Harrison, 1996).

Orthosilicic acid as a monomer is the simplest form of silica which is formed of Si linked to four hydroxyl

groups in a tetrahedral shape (Fig 1). This monomer of silica is weakly acidic in nature and present in soil at a very low level (a few  $\text{mg kg}^{-1}$ ) (Iler, 1979). This form of Si is used by plants through different processes. In the place where Si concentration is present in high amounts (around  $100\text{-}200 \text{ mg kg}^{-1}$ ), silica monomers begin to polymerize through a polycondensation reaction. The monomers of silica are converted into polymerized silica or amorphous silica after polymerization, which further forms well-developed spherical particles containing stable nuclei (Fig. 1). These spherical particles aggregate to form complex structural motifs (Perry and Keeling-Tucker, 2003). The formed Si particles carry a negative charge and acquire around 2 nm size. These Si particles interact with the cell wall molecules of plants. It was found that Si forms covalent bonds with the molecules of cell walls in plants (He *et al.*, 2015). According to Law and Exley (2011), lignin and cell wall polysaccharides act as a template to form biosilicification in plants. The composition of silica formation and the state of their deposition in cells differ in different plant species. Silica structure was found in different plants like dumbbell-shaped cells of silica, bulliform cells of silica, silica bodies, and silica cells. They are mostly found in the Poaceae family as a silica coating below the cuticle and as a double deposit in rice leaf blades (Currie and Perry, 2007). Though the deposition of silica is not limited to leaf cells and silicate cells, it was also observed in the epidermal cells of the root, shoot, and vascular tissue of leaves (Prychid *et al.*, 2003). According to research by Kumar *et al.* (2017), the Si formation in silica cells is an active process that does not rely on the evapotranspiration of water, even if transpiration is necessary to draw Si up and into the leaves. In another study, it was found that a particular substance in the apoplast that promotes Si

accumulation is involved in the mechanism of silicification in silica cells. This substance could contain proteins, peptides, or carbohydrates that can polymerize liquid silicic acid to solid amorphous silica. The polymerization and precipitation of Si at the cell wall may create a concentration gradient within the leaf, attracting Si to the silica cell (Gallagher *et al.*, 2015).

#### Possible ligands of plant cell wall involved in interaction with Si

Plants develop various mechanisms to interact with Si in the plant cell wall, and this results in a physiological or structural alteration to cope with various stress conditions (Sheng and Chen, 2020). Plants have different possible ligands for interaction of Si with cell wall components. By these ligands, Si can crosslink the wall components and form a covalent bond with them. The wall complex with Si improves cell wall formation, increases the plants' mechanical strength, forms a mechanical barrier for stress resistance, provides stability and rigidity to the cell wall for mechanical supports, and many more. Different cell wall components acted as a ligand in crosslinking the Si with cell walls in different

plants.

Si in plants interacts with the cell wall components and conjoint with them by a covalent bond. In hemicellulose, pectin, cellulose, and lignin, Si has a great binding with lignin component of the plant cell wall (Sheng and Chen, 2020). As the stem matured, the secondary cells multiplied continually, the secondary cell walls thickened even more, and the supplementation of Si greatly enhanced the thickness of both the secondary cell walls and sheets of thickened secondary cells (Zhao *et al.*, 2021). But there is no clear knowledge of the interaction between Si and cell wall components, how Si provides mechanical strength to plants, and how its silicification in plant cell walls makes the plant resistant to biotic stresses.

#### SI WITH PLANT CELL WALL COMPONENTS

##### Organosilicon in cell wall

The role of Si is found beneficial in many studies, mostly in providing mechanical strength to the plants by depositing a silica layer on the cell wall. Organosilicon present cell wall conjoint the silica with cell wall compo-

**Table 1.** Different plants showing Si-cell wall complexes with different ligands of bonding Si with cell wall.

Sr. No.	Plants	Method of Detection	Ligands of Plant cell wall	Function	References
1.	<i>Oryza sativa</i>	X-ray Photoelectron spectroscopy	Hemicellulose	Provide mechanical strength; Membrane stability, Limit ammonium uptake	Sheng <i>et al.</i> (2018)
2.	<i>Poales</i>	Chromatography	Hemicellulose (Mixed-linked-glucans)	Strengthening of cell wall	Sorensen <i>et al.</i> (2008)
3.	<i>Oryza sativa</i>	Fourier transform infrared spectroscopy (FTIR)	Lignin	Enhance the formation of lignin in the cell wall	Inanaga and Okasaka (1995); Radotić <i>et al.</i> (2022)
4.	Rutaceae		Pectin	Biological conjoiner	Schwarz (1973)
5.	<i>Equisetum arvense</i>	Anion-exchange Chromatography	Mixed-linked-glucans, callose	Firming of cell wall	Law and Exley (2011)
6.	<i>Oryza sativa</i>	X-ray Photoelectron spectroscopy	Mixed-linked-glucans	Building and firming of cell wall	Kido <i>et al.</i> (2015)
7.	<i>Oryza sativa</i>		Hemicellulose matrix	Alleviation of cadmium stress	Ma <i>et al.</i> (2017)
8.	<i>Oryza sativa</i>	Proteomic analysis	Hemicellulose	Increases cadmium tolerance	Ma <i>et al.</i> (2016)
9.	<i>Equisetum, Poales</i>	Hydroxyl complexation	Hemicellulose, pectin, lignin, callose	Mitigation in biotic and abiotic stresses	Sheng and Chen (2020)
10.	<i>Fagus</i>	Transmission electron microscopy (TEM)	Lignin	Provide rigidity and firmness, promote lignification	Watteau and Villemin (2001)
11.	<i>Paeonia lactiflora</i> Pall.	Transcriptome analysis, Environmental scanning electron microscopy (ESEM), and Transmission electron microscopy (TEM)	Lignin	Increased lignin biosynthetic enzyme activities and gene expression, enhanced stem strength by promoting lignin accumulation	Zhao <i>et al.</i> (2021)

nents by forming a bond of C-O-Si, their bonding makes the cell wall more stable and firmer under any stress conditions (Schwarz, 1973; Sheng and Chen, 2020). Also, by forming complexes with plant sugar, Si helps improve cell wall elasticity or inflexibility (Currie and Perry, 2009). Moreover, a complete set of cellulose microfibrils were observed in Si-cell wall complexes while the nonappearance of Si broke the cell wall and cellulose microfibrils, this signifying the role of organosilicon in the formation of cellulose and cell wall stability (Sheng *et al.*, 2018). A study discovered that inorganic silica and organosilicon might form a twofold defensive shield that decreases nanoplastics (NPs) stresses by electrostatic adsorption and modification of cell wall porosity, as well as lower oxidative damage to promote cell activity (Pu *et al.*, 2021; Pu *et al.*, 2023).

### Si and cellulose

Cellulose is the major primary component of the plant cell wall that provides firmness and strength to the cell wall. It was hypothesized that cellulose is made up of cellulosic microfibrils which are confined in very little space. This reduces the ability of Si to bind with cellulose (He *et al.*, 2015). Cellulose microfibrils in the cell wall, are present at the cell surface and help in strengthening of cell wall (Zhang *et al.*, 2019). In research by Sheng *et al.* (2018), on the basis of atomic force microscopy (AFM), it was found that the microfibrils in the cellulose are fragmented and small present on the cell layer unequally in the absence of Si and have lighter peak force. In contrast, the cellulose microfibrils in the plant cell wall were improved in diameter and height and had denser peak force through AFM in presence of Si. Plant cell wall components with cellulose microfibrils may develop properly after the application of Si. In an experiment, it was found that the diameter of cellulose microfibril of Si-treated cells is more than the non-treated cells in plants (Sheng *et al.*, 2018). In a study, a defective protoplast membrane was found in the absence of Si in plants (He *et al.*, 2015). In addition, no direct role has been reported of Si in bonding with cellulose microfibrils and their accumulation in plants till now. It was suggested that Si might only enhance the formation of cell walls, but the role of cellulose as a possible ligand for bonding Si with the cell wall is not clearly reported. Si may mediate the overexpression of enzymes responsible for the cellulose formation in cell walls (He *et al.*, 2015). The proper function of Si interaction with wall components is not yet known, but it improves plant cell wall formation.

### Cell wall protein

Apart from being interactive with cell walls, Si is also involved in the formation of amino acids and enzymes related to protein synthesis (Lavinsky *et al.*,

2016; Sanglard *et al.*, 2016). Proteomic studies also show the role of Si in different biochemical or metabolic processes in rice plants (Nwugo and Huerta, 2011). In addition, any particular amino acid conformation of cell wall proteins may affect the Si deposition in plants. Amino acids carry a positive charge on their side chains and can crosslink with Si by the negative charge of silica through electrostatic connections, thus promoting Si accumulation in plants (Currie and Perry, 2007). For instance, in *Triticum durum*, the silica composition of the lumen of silica cells was observed to be continually interspersed with organic materials, with higher N/C ratios showing amino acids or peptides as a template for silicification in silica cells. (Alexandre *et al.*, 2015; Wani *et al.*, 2022). Similarly, a proline-rich protein (PRP1) with a greater proportion of arginine and lysine residues was found to be involved in Si polymerization, primarily near the region of infection in cucumber plants (Kauss *et al.*, 2003; Wani *et al.*, 2022). Kumar *et al.* (2020) discovered the sole known protein (Siliplant1), a basic protein with seven repeat units rich in proline, lysine, and glutamic acid, that crystallizes silica in vivo in sorghum silica cells, which is responsible for silicification in plants and offers fascinating information for biological control of silica in plants. In *Rhizophora apiculata*, a serine-rich protein that was not likely to be confined in the cell wall showed great influence on Si deposition (Sahebi *et al.*, 2015). It was observed that Si up-regulates the gene expression of this protein in mangrove leaves and roots (Sahebi *et al.*, 2014). In research, supplementation of Si enhanced the nitrogen uptake, stimulated amino acids, and assembled them by changing the primary metabolites in plants (Detmann *et al.*, 2012). The conserved NPA domains in plant cell walls have 108 amino acids that control the absorbency of silica in plant cells (Deshmukh *et al.*, 2015).

### Si and callose

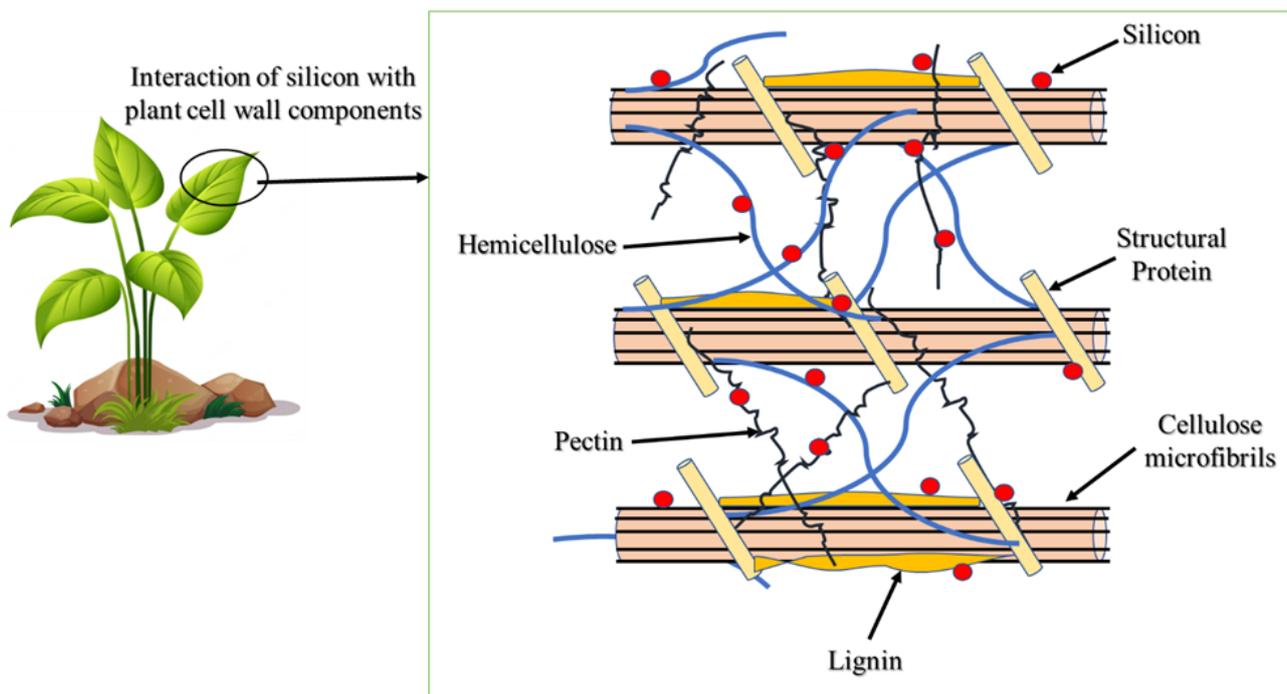
Callose is present in the cell wall of the plant in a special condition like stress response. It is similar to cellulose in structural type. It is a polysaccharide that comprises repeating units of glucose connected with  $\beta$ -1,3 glycosidic bonds (Galatis and Apostolakos, 2010). Its functional role is mainly found in stressed conditions in plants. The formation of silica cells and callose and their linkage in plant development is first found in *Equisetum* plants. A study on *Equisetum* found that this is the first vascular plant that accumulates a high amount of Si in its plant parts (Law and Exley, 2011). Moreover, it is found that Si deposits in plants followed the deposition of callose layer in plant cell walls. Induction of Si accumulation in plant cells is also a fascinating role of callose layer. It was suggested that the hydroxyl groups of repeating glucose in callose polymer interact with Si

and contributes to forming a mechanical barrier in stressed conditions (Guerriero *et al.*, 2016). Callose in plants acts as a ligand for bonding Si to the plant cell wall components and this bonding provides mechanical strength to plants in stressed conditions (Law and Exley, 2011). In addition, the callose polymer of plant cell walls catalyzes the production of silica *in vitro* and also plays a significant role in biological silicification in *Equisetum* and *Arabidopsis* plants *in vivo*. Callose is an excellent silicification companion because its amorphous nature and transient behavior create appropriate growth conditions for silicic acid precipitation into silica (Guerriero *et al.*, 2018).

### Si and hemicellulose

Hemicellulose is the most important component of the cell wall that is present between cellulose and lignin. Hemicellulose also acts as a conjoiner of Si to plant cell walls in many plants. Most of the Si accumulates in the hemicellulose component and thereby allows Si to interact with hemicellulose polysaccharides and covalently bind with them (He *et al.*, 2015). Bonding of Si with cell walls via hemicellulose helps the plant in alleviating stress and providing tolerance (Sheng and Chen, 2020; Ma *et al.*, 2017). According to He *et al.* (2015), on the basis of examination through XPS spectroscopy, Si present in cell wall connects with the wall components especially with hemicellulose through Si-O-C bonding in rice plants. Moreover, Si recovers the cell wall damage by strongly linking with wall components and aids the reformation of cell walls. Enhancement in mechanical properties has been seen in rice plants with application of Si. The crosslinks of Si-hemicellulose may en-

hance the cell wall properties of the plants (He *et al.*, 2015). Hemicellulose in the cell wall is the best possible ligand for bonding Si to the cell wall. This linkage of Si with hemicellulose is found very beneficial in alleviating metal toxicity, improving stress tolerance, and forming mechanical barriers in rice plants (Ma *et al.*, 2015). According to Ma *et al.* (2015), 64% of Si can be covalently bonded with hemicellulose on the cell wall of rice suspension, and the hemicellulose-bound form of Si suppresses the cadmium (Cd) ions in the rice suspension cells. The cell wall was altered by the Si hemicellulose complexes to produce an unequal distribution of negative charge, which was then balanced by Cd to produce the co-complex of [Si-hemicellulose] and Cd (Riaz *et al.*, 2021). Głazowska *et al.* (2018) suggested the role of hemicellulose-bound Si in the restoration of cell wall building and associations with other cell wall components. Xyloglucan, which is a hemicellulose polysaccharide, provides resistance to pathogen infection and degradation of cell walls by pathogens enzymes and enhances the structural characteristics of cell walls. The xyloglucan-Si complex inhibits the activity of cellulase enzymes which destroy the cell wall and help in improving resistance. Moreover, organosilicon can covalently cross-link with xyloglucan in the hemicellulose of the rice cell wall (Pu *et al.*, 2021), affecting the pore size and controlling the elasticity of the cell wall (Bidhendi and Geitmann, 2015; Pu *et al.*, 2023). Pu *et al.* (2021) discovered that Si linked to xyloglucan improves wall nanomechanical characteristics in the deformation at the single-cell level and increases resistance to hydrolysis by cellulase. The results demonstrate a clear relationship between an inorganic Si com-



**Fig. 2.** Interaction of Si with different cell wall components in plants.

ponent and the nanoscale design of plant cell wall components for long-term usage. Enhancement in the mechanical strength by xyloglucan-Si complex creates a direct relation between Si and a hemicellulose polysaccharide (Pu *et al.*, 2021).

### Si and mixed-linked glucans

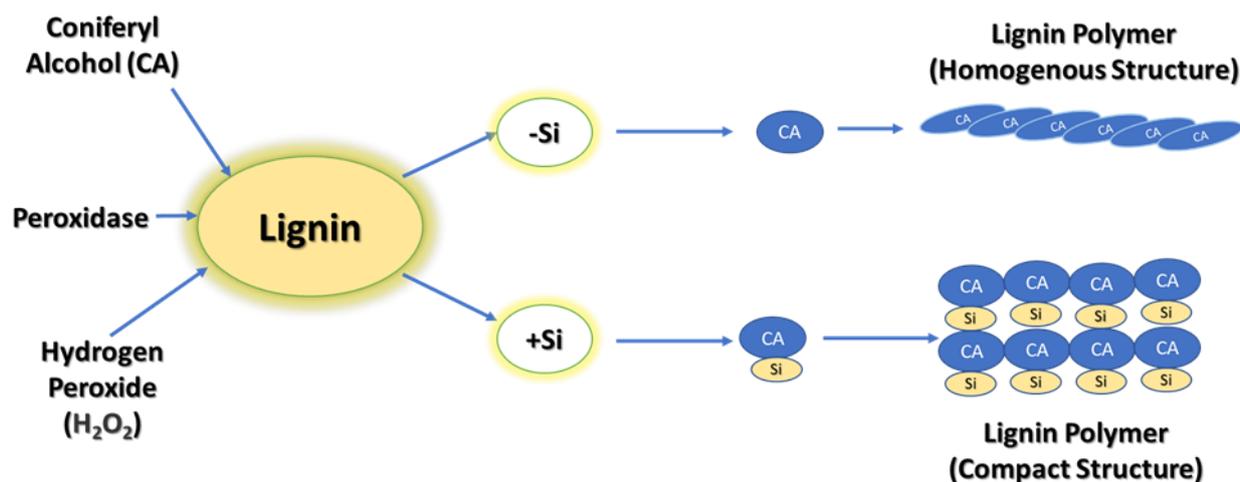
Mixed-linked glucan (MLG) is mainly found in the Poaceae family and monocotyledonous plants. MLG is also an essential component of the plant cell wall which comprises  $\beta$ -1,4-linked polymers of glucose dissipated with  $\beta$ -1,3-linkages (Kim and Brandizzi, 2021). Along with hemicellulose, MLG also functions as a ligand of cell wall for binding of Si. Crosslinking of Si with MLG has a significant role in firming the cell wall and incrementing mechanical strength in *Equisetum arvense* (Kido *et al.*, 2015). According to Sørensen *et al.* (2008), MLG has a significant contribution to building cell walls in Horsetail plants. It was reported that MLGs act as a template for biosilicification in plants (Fry *et al.*, 2008). This research is supported by Kido *et al.* (2015) in rice plants. A positive correlation has been seen between Si and MLG in rice plants. The MLG, with other cell wall components, can regulate the deposition and distribution of Si in rice plants (Kido *et al.*, 2015). Consequently, it was believed that these plants would deposit more silica as a result of this high MLG concentration (Fry *et al.*, 2008; Wani *et al.*, 2022). As a result, this type of organic matrix-bound Si can play an important role in membrane function and cell wall formation, giving insight into Si's structural and biochemical involvement in retaining cellular structure and mechanical characteristics, and also in the protection from different types of stresses (Gaur *et al.*, 2020; Wani *et al.*, 2022).

### Si and lignin

Lignin is a complex polymer that provides structural support to plants. It can be considered in forming cell walls specifically in woody plants as it provides rigidity and hardness to the plants. Si is a helpful component for plants because it accumulates mostly in cell walls, where the structure and composition of lignin determine its distribution and amount. However, it is still unknown how Si connects with the lignin production process in plant cell walls (Radotić *et al.*, 2022). Lignin as a cell wall component supports the Si deposition in the cell wall and its distribution in the plant parts. It was suggested that the organic hydroxyl groups could also form bonds with Si and it was found that the cell wall components of plants have hydroxyl groups and they can conjoin with the silicic acid or Si in the plant cell wall. Lignin, as a cell wall component also contains a hydroxyl group and can interact with Si easily in plants (Williams, 2007). The structure of lignin also acts as a ligand in crosslinking with Si and promotes the bonding of Si-cell wall complex (Radotić *et al.*, 2022). It was proposed that Si in the cell wall forms a linkage with the phenolic

acid of a ligno-carbohydrate complex in rice plants. Si-lignin complex in plant cell wall promotes the synthesis of lignin in cell walls and also offers stress tolerance to the plants by making the cell wall rigid and firm (Inanaga *et al.*, 1995). In an *in vitro* study, that mimicked the conditions of the last stage of lignin synthesis, the involvement of Si was found with the peroxidase-catalyzed polymer chains of a lignin monomer into the lignin model compound. Based on various techniques, including FTIR, spectroscopy, and microscopy, it was discovered that Si is linked to last lignin polymer and that Si-dehydrogenative polymer (DHP) varies in composition from pure DHP (Radotić *et al.*, 2022). In plants, the accumulation of Si changes their physical characteristics and enhances their ability to withstand various biotic and abiotic forms of stress. Studies from the past suggest connections between the accumulation of lignin and silica (Klotzbücher *et al.*, 2018). Si can crosslink with lignin during the synthesis of lignin in plant cell walls or can be directly linked to lignin in plants (Zexer and Elbaum, 2020; Soukup *et al.*, 2020). The final stage in the synthesis of lignin, that is the conversion of monomer-and short oligomer-radicals into lignin polymer chains in the cavity of the cell wall, is enzymatically regulated and hence represents one successful site of involvement with Si (Radotić *et al.*, 2022).

Fang and Ma (2006), confirmed the crosslinking of Si and lignin by showing a study by which lignin is responsible for Si precipitation in the cell and the presence or absence of lignin affects the deposition of Si. This research is supported by Zhang *et al.* (2013), by study on rice plants. It was found that lignin formation in the cell wall promotes the deposition of Si in lumen of the cells. The accumulation of Si and lignin formation in *Cucurbita* plants is driven by the same gene, *Hr* (hard rind), this shows the linkage of Si and lignin and connects the deposition of Si to its mechanical role in plants (Piperno *et al.*, 2002). A fascinating role of Si-lignin complex has been seen as hydrogels for drug release in pharmaceuticals industries (Culebras *et al.*, 2021). Many studies show the crosslink between Si and lignin. In *Paeonia lactiflora*, the application of Si has been found to regulate factors that affect stem strength. Si increases stem strength by interacting with lignin. The outcomes demonstrated that adding Si improved stem strength by thickening secondary cell walls and layering secondary cells. Furthermore, after Si treatment, more lignin was deposited, notably G-lignin and S-lignin, and the activity of lignin biosynthesis enzymes were also increased. Also, according to a transcriptomic study, Si treatment increased the gene expression involved in the lignin production process. Amongst them, the hydroxycinnamoyl-CoA: shikimate hydroxycinnamoyl transferase gene (*HCT1*) was identified from *P. lactiflora* and shown to be primarily located in the cell cytoplasm (Zhao *et al.*, 2021). Lignin deposit was then no-



**Fig. 3.** A conceptual framework for lignin production with and without Si. CA - coniferyl alcohol,  $H_2O_2$  - hydrogen peroxide, and POD - peroxidase. Using the information provided, it is possible to describe how Si affects the polymerization of CA into lignin, as indicated in Fig. 3: In the presence of  $H_2O_2$ , peroxidase catalyzes the synthesis of CA dimers from CA monomers. The dimers must be polymerized to produce a lignin polymer with a homogeneous structure. The interaction between peroxidase,  $H_2O_2$ , and CA monomers takes place efficiently and produces CA dimers if Si is present in the reaction mixture. Electrostatic interactions enable Si to attach to dimers. Due to steric and electrostatic forces, CA-

ticed in the stems of *P. lactiflora*, and Si treatment dramatically boosted the amount of lignin deposit. Lignin deposition was also seen to rise progressively as the stem matured. This finding was supported by the measurement of lignin content after the addition of Si (Li et al., 2016; Zhao et al., 2021).

### Si and pectin

Pectin is a heteropolysaccharide component of plant cell walls that functioned as adhering cells, hydrating the cell wall and providing permeability to the cell wall after bonding with the cell wall (Xiao and Anderson, 2013). The cell wall in which Si was accumulated, in those regions, pectin homogalacturonan epitopes were also found in fern plants. Pectin is covalently bonded with polysaccharides and contains a high number of galacturonic acid and homogalacturonan, rhamnogalacturonan I, and II polysaccharides in plants (Mohnen, 2008). Rhamnogalacturonan II polysaccharides of pectin can conjoin with boron by a linkage of borate diol ester. This borate diol ester is formed between the apiosyl deposits in two monomers of rhamnogalacturonan II side chain (O'Neill et al., 1996). It was observed that Si, like boron, can also interact with the pectin component of cell wall via borate diol ester linkage (Miwa et al., 2009). The interaction of Si with pectin increased the stability and integrity of the plant cell walls during heavy metal stress conditions. The complexes formed by Si enhance the ability of cation exchange in rice suspension cells and boost the pectin formation in the cell walls under metal stress. It was noticed that the exposure of Si nanoparticles dramati-

cally increased the pectin content in the plant walls and provided mechanical strength, which further reduced the uptake of metal stress into plant cells (Cui et al., 2020). According to earlier research, the degree of demethylation of pectin, which is regulated by the activation of pectin methyltransferase (PME) enzymes, determines the concentration of the negative charges on pectin (Yang et al., 2013; Cui et al., 2020). The cross-linking of Si with cell wall pectin components boosted the wall reinforcement and mechanical strength in plants. It has been observed that the use of Si-nanoparticles in plants stimulates the activity of PME enzymes and increases pectin concentration, indicating that pectin is the primary site for cation binding (Peaucelle et al., 2012; Cui et al., 2020). Additionally, the porosity of cell walls may be regulated by the adherence and cross-linking of cations to the pectin matrix. Also, it has been proposed that pectin levels in cell walls may modify their properties and functions. The application of Si-nanoparticles can promote the formation of pectin, strengthen the cell walls, and thus prevent the entry of arsenic (As) into cells by enhancing the mechanical force of the cell wall (Cui et al., 2020). According to research, it was found that Si crosslinks with the pectin component and is deposited in the external region of cell walls, making the cells expand before the development of a secondary wall (Leroux et al., 2013). Another study on *Equisetum hyemale* showed similar results after the bonding of Si with the pectin component. Simultaneous occurrence of Si accumulation with pectin in the plant cell walls was observed (Gierlinger et al., 2008). In rice, it was reported

that application of Si decreases the deposits of aluminium (Al) in the plant cell wall by enhancing the process of pectin methyl-esterification and mitigating the metal toxicity (Xiao *et al.*, 2021).

According to Mera and Beveridge (1993), Si can cross-link with different cell wall components in three possible ways, including phosphoryl, carboxyl, and hydroxyl complexation. Si was found to be interactive with different cell wall components in these three ways. In certain conditions, Si forms hexa-coordinated complexes in plants while boron forms only three-coordinated complexes. It has been observed that when Si reacts with aliphatic polyols (cell wall molecules), it forms a large number of five- or six-coordinate Si complexes under *in vitro* conditions (Kinrade *et al.*, 1999). The mechanical characteristics of the cell walls were also enhanced after the Si crosslinking of the wall elements. Individual cells then benefit from stable cell membranes and the restoration of intracellular ion homeostasis as a result. When compared to -Si cells, the  $K^+$  outflow was considerably reduced in +Si cells (Sheng *et al.*, 2018). Si can interact with various cell wall components on the basis of structural similarity with other elements or compounds in plants. For instance, Si is structurally and chemically similar to boron, so their properties are similar in plants in many processes.

Moreover, Si forms Si-O-C bonds which are comparable to borate-diol ester bonds in plants. It was suggested that the interaction of Si via linkage pattern by ligands of the cell wall comprises hydroxyl complexation between Si and *cis*-diols structures of hemicellulose, cellulose, and lignin (Sheng and Chen, 2020).

#### Alleviation of different stresses by Si-cell wall complexes

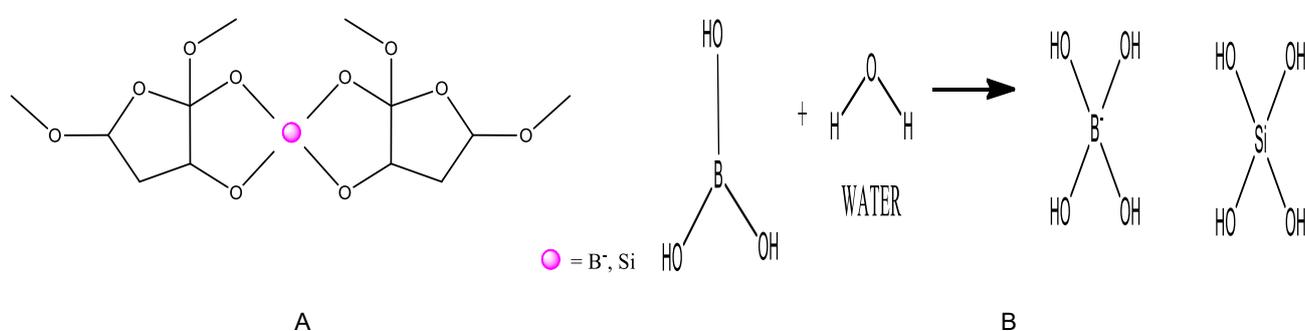
In plants, the cell wall is composed of structural proteins, lignin, pectin, hemicellulose, and carbohydrate polymer as it is discussed earlier. These all components contribute to the cell wall stability, inflexibility, and elasticity, which helps in providing stress resistance

and strength. Plant cell walls play a protective role against both biotic and abiotic stresses. For pathogens or insects, this is the first barrier that inhibits their entry up to an extent. But beyond this extent, it starts gaining susceptibility to those pathogens. Alteration in the cell wall composition due to any kind of environmental stress reduces the plants' stability and mechanical strength (Charrier *et al.*, 2019). In plants, Si, after crosslinking with cell wall components, forms Si-cell wall complexes and mitigate the different type of biotic and abiotic stresses.

#### Si-cell wall complexes in heavy metal stress conditions

Plant cell walls contain pectin and hemicellulose components that can bind 71-85% of the heavy metal Cd (Yu *et al.*, 2020; Riaz *et al.*, 2021). The cell wall of higher plants can absorb 80% of the total amount of aluminium (Al) and acts as a protection against other metals like Al in addition to Cd. (Riaz *et al.*, 2018). The cell wall, which is comprised of negatively charged functional groups like cellulose, hemicellulose, pectin, and lignin, contributes a significant role in providing a mechanical or physical barrier and inhibiting heavy metal uptake. These metal elements interact and bind with negative charge components of cell walls (Ren *et al.*, 2020). The cell wall comprises a variety of polysaccharides that not only provide stability and compact structures but also act as a structural barrier to prevent Cd ions from entering the cell. The number of negative charges and, eventually, the cell wall's ability to adsorb Cd ion, are influenced by the modification in the components of cell wall and the degree of methyl esterification of the cell wall (Zhu *et al.*, 2012; Riaz *et al.*, 2021).

As stated, Si is deposited in plant cell walls by crosslinking with cell wall components. The Si accumulation in cell wall-bound Si with the wall prevents the entry of heavy metals like Cd into the rice plants. This inhibition may be due to the co-deposition of Si and heavy metals



**Fig. 4.** Structural similarity of boron with Si (A); Crosslinking of boron and Si with pectin polysaccharides (Rhamnogalacturonan II) via borate diol ester linkage (B). This figure illustrates that Si is structurally and chemically similar to Boron. And this similarity of boron with Si helps Si in crosslinking with pectin polysaccharides via the formation of a borate diol ester bond.

**Table 2.** Interaction of Si with cell wall components based on the similarity with other compounds in plants.

Sr. No.	Cell Wall Component	Similarity	Structure	Mode of Interaction of Si	References
1.	Pectin	Structural similarity to borate-diols ester formation		Covalent bond with pectic rhamnogalacturonan II (RG-II)	Kobayashi <i>et al.</i> (1996); Sheng and Chen (2020)
2.	Lignin	Pyrocatechol structurally similar to lignin		Covalent bond with lignin	Sheng and Chen (2020)
3.	Hemicellulose	Hydroxyl group structurally similar to cis-diol structure		Crosslinking with cis-diol structure	Cosgrove (2005)
4.	Cellulose	Hydroxyl group structurally similar to cis-diol structure		Crosslinking with cis-diol structure	Cosgrove (2005)
5.	Carbohydrate	Similarity with borate-mediated Formose reaction		Silicate-sugar complexes by Formose reaction	Lambert <i>et al.</i> (2010); Ricardo <i>et al.</i> (2004)

in the cell wall and co-complexes with cell wall components (Liu *et al.*, 2013). The plant cell wall comprises different polysaccharides that carry negative charges on their surface and have a chance to bind with different metal ions (Duval and van Leeuwen, 2011). The negative charge on cell wall surface helps in crosslinking of Si to the wall and this linking of Si enhances the negative charge on the surface which increases Cd deposition into the cell wall. The co-deposition of Si and Cd forms co-complexes with the cell wall. The Si-cell wall complexes have not only increased the accumulation of Cd in the cell wall but also down-regulate the gene expression of Cd transporter (Ma *et al.*, 2015).

Furthermore, Si also promotes the sequestration of metal ions from the cell wall to vacuoles of the plant cells and stresses out the plants from being affected (Fig 3).

It was found that Si-treated cells had low Cd content in the cell cytoplasm than Si-deprived cells. The possible reason for that is Si helps in sequestration of Cd into the vacuoles and reduces the concentration of Cd in cell cytoplasm (Ma *et al.*, 2016). In another study, it was reported that Si accumulation in plants forms phytoliths, and these phytoliths retain metal ions into them and reduce the movement of metal ions in the plants. By this, the high concentration of metal ions in a plant

cannot affect plant growth (Liu *et al.*, 2022). The majority of Si in higher plants is accumulated in the plant cell walls or in the inter or extracellular matrix and is subsequently transformed into phytolith forms (Puppe and Sommer, 2018; Liu *et al.*, 2022). Numerous elements, both major (like C, Al, and Fe) and trace (like Pb, As, Zn, and Cu) are incorporated into phytoliths during the phase of Si accumulation and phytolith production, highlighting the critical function of phytoliths in controlling the nutrient cycling of these elements. (Tran *et al.*, 2019; Delplace *et al.*, 2020). Much research conducted in the last ten years has revealed that Si plays a significant part in long-term carbon storage through the formation of phytolith-occluded carbon (PhytOC), that further influences the global carbon cycle and, consequently, global warming (Qi *et al.*, 2017; Zhang *et al.*, 2020). In a polluted soil system, toxic trace metals (TTMs) like Pb, Cu, As, and Zn may also be stored inside phytoliths, creating an unrecognized pool of TTMs. (Nguyen *et al.*, 2019, 2021; Tran *et al.*, 2019; Delplace *et al.*, 2020).

#### **Si-cell wall complexes in inhibiting polystyrene nanoplastics (PS-NPs) uptake in plants**

Polystyrene nanoplastics (PS-NPs) in rice plants have gained a lot of attention due to their toxicity, which is a rising major environmental issue. However, there isn't much research that has looked specifically at Si-induced connections between PS-NPs and rice (Pu *et al.*, 2023). Si is primarily accumulated as inorganic silica in the special cells or on the cell walls of rice plants (Epstein, 2009; Mandlik *et al.*, 2020), and minute quantities of Si can interact with hemicelluloses in the cell wall to generate organosilicon (He *et al.*, 2015; Pu *et al.*, 2021). These two types of Si (inorganic silica and organosilicon) can mitigate the different types of abiotic stresses (Ma *et al.*, 2016; Ma *et al.*, 2017). Findings from earlier studies indicated that the presence of inorganic silica or organosilicon in plants bears a higher negative charge, which can bind cations ( $\text{Na}^+$  and  $\text{Cd}^{2+}$ ) on the cell wall to restrict them from entering the cells and lower the intake of  $\text{Na}^+$  and  $\text{Cd}^{2+}$  by plant cells (Fleck *et al.*, 2015; Greger *et al.*, 2016; Ma *et al.*, 2016; Pu *et al.*, 2023). As a result, these two types of Si in rice may have a high potential for resistance to nanoplastics (NPs) stress, particularly for positively charged NPs like PS-NH<sub>2</sub>. But, due to high heterogeneity of plant parts and a shortage of appropriate assessment instruments, it is unclear if the abundant Si can relieve the toxicity of NPs for rice and its putative detoxification pathways (Pu *et al.*, 2023).

#### **Si-cell wall complexes in nutrient uptake in plants**

This Si-cell wall complex also mitigates the deficiency of micronutrients like manganese (Mn), iron (Fe), zinc

(Zn), and copper (Cu) in plants. The positive charge of micronutrients helps in binding with Si-cell wall complexes which carry negative charges on the surface (Bityutskii *et al.*, 2014). In this way, Si can improve nutrient uptake in plants by enhancing the negative charge on the cell wall surface and helping them to attach to it. Long-term experiments on different crops have shown that Si supplementation improves the nitrogen usage efficiency and crop agronomic indices (yield and nutritive quality) in rice (Cuong *et al.*, 2017), maize (Mabagala *et al.*, 2020), rapeseed (Laïné *et al.*, 2019), and wheat (Neu *et al.*, 2017). It has been established that Si-mediated production of amino acids and remobilization of nitrogen can partially explain this behavior, even if the exact mechanisms have not been thoroughly investigated (Detmann *et al.*, 2012). One of the key mechanisms influencing high seed yields is thought to be the remobilization of nitrogen (mostly in the form of amino acids) from storage pools in leaves and stems to the grains (Tegeder and Masclaux-Daubresse, 2017). Modification of the C:N:P stoichiometry is yet another potential consequence of Si (Schaller *et al.*, 2012; Neu *et al.*, 2017; Deus *et al.*, 2020). These investigations are supported by the theory that Si may partially replace C in shoot parts of Si accumulator plants, such as sugarcane, grasses, and rice, in order to maintain function and improve photosynthesis, modifying the ratio of C:N:P. In a pot experiment using soil-implemented Si to sugarcane, the highly advantageous benefits of partial replacement of a C by Si were demonstrated very unambiguously (Frazão *et al.*, 2020). Si substitution for C resulted in reduced plant C concentration and was linked to better biomass output due to higher rates of N and P uptake and accumulation as well as increased rates of photosynthesis. Plants may profit from changed C:N stoichiometry, especially when there is a restricted supply of nitrogen since Si absorption into roots and leaves is bioenergetically cheaper than the production of structural C compounds (Neu *et al.*, 2017; Pavlovic *et al.*, 2021).

#### **Si-cell wall complexes in pathogen stress conditions**

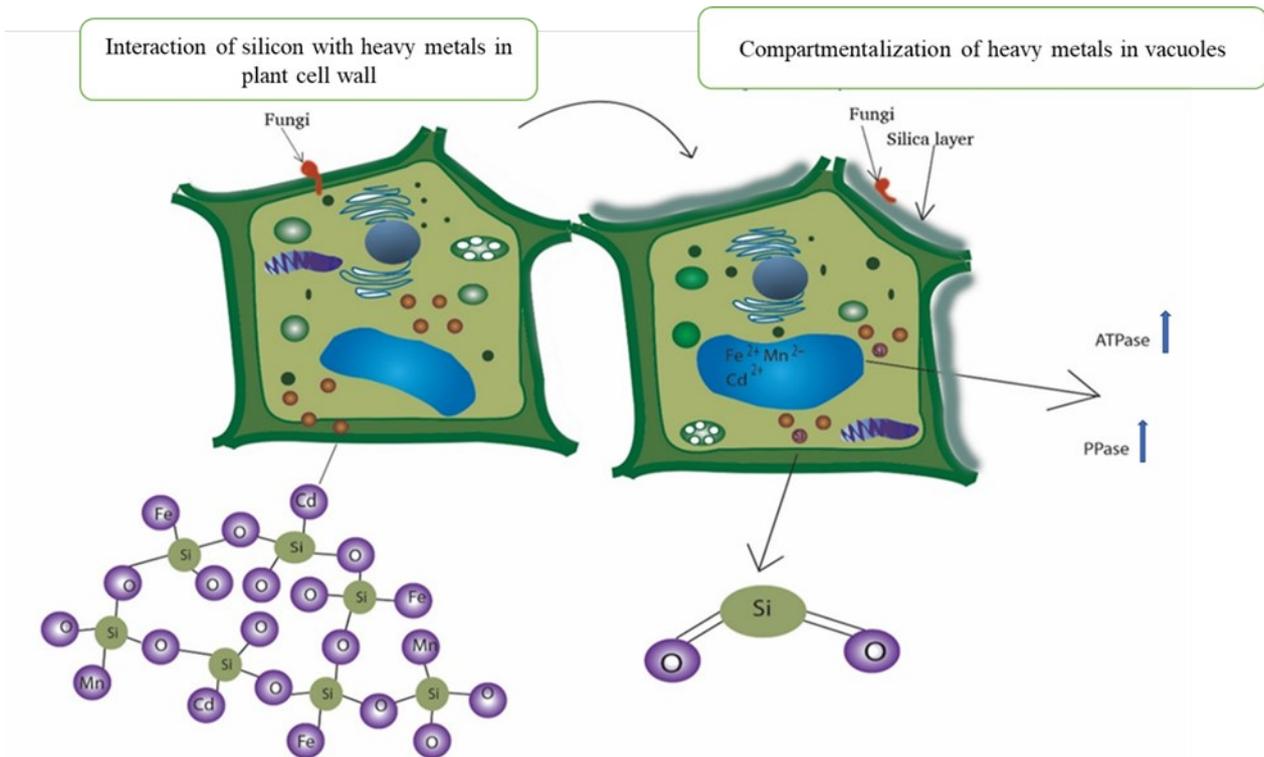
Si has great importance in providing mechanical support to plants by accumulating in the plant cell wall. This deposition of Si in cell wall forms a structural layer in plant's wall and this inhibits the penetration of pathogens into the plant cells. According to apoplast obstruction theory, Si accumulation affects the host-pathogen specificity by creating barriers that obstruct the effector's mobility inside the plant (Coskun *et al.*, 2019). Moreover, Si induces biochemical resistance in plants against pathogen infection and activates the defense mechanisms in the plants (Cai *et al.*, 2009). Overall, plants defend themselves against fungi by reinforcing

and altering their cell walls. This included papilla development, the fusion of cell walls with phenolic compounds, and the lignification and suberization of cell walls (Fortunato *et al.*, 2014; Bathoova *et al.*, 2018). Plant cell walls form complexes with different polymeric constituents which further results in partial or complete inhibition of pathogen invasion. These polymers are often very resistant to fungal digestion because they contain various crosslinks, polyaromatic domains, and biologically stable connections. And the deposition of these compounds disrupts the open channel network of the plant cell walls and helps to more effectively control the flow of water, dissolved salts, and pathogens between intracellular and apoplastic routes (Ranathunge *et al.*, 2011; Bathoova *et al.*, 2018). Si is one of those polymeric compounds in plants that form complexes with plant cell walls and enhance their reinforcement and strength (Najihah *et al.*, 2015; Pooja *et al.*, 2022). The mechanical and biochemical resistance is induced by bonding of Si to the cell wall components after its deposition in the plant cells. Deposition of Si forms a double cuticle layer on the plant wall, providing mechanical support and stress re-

sistance to plants. The bounded form of Si with plant cell walls regulates the gene expression associated with stress resistance (Zargar *et al.*, 2019). Formation of a double cuticle layer of Si on plant cell wall blocks the site of the pathogen's entry into rice plants (Fig 5). This inhibits the invasion of pathogens into plants and enhances mechanical strength by reducing pathogen-associated diseases (Wang *et al.*, 2022). Si activates various defense mechanisms associated with phytohormone biosynthesis and osmolytes in response to different abiotic stresses (Majeed Zargar *et al.*, 2012; Mir *et al.*, 2020).

**Conclusion and future approach**

Si has been identified as Si-cell wall complex after the application of Si in many plants. Previously, it was known as a stress mitigator, but the exact mechanism behind how Si confers stress resistance and mechanical strength in plants is not yet known. Si is bonded with the cell wall components with a covalent bond of Si-O-C. Ligands of plant cell wall like pectin, hemicellulose, lignin, cellulose, callose, and MLG plays a great



**Fig. 5.** Interaction of Si with metal ions and its localization in vacuoles of plants (Sahebi *et al.*, 2015a); Inhibition of pathogen penetration by a dense layer of Si on the cell wall. This figure illustrated that Si forms complexes with metal ions and other micronutrients and increases the uptake of metal ions within itself in plant cell walls. Co-deposition of Si with metal ions form co-complexes of Si-Cd with cell wall and then sequesters the metal ions into the vacuoles. This figure also shows the inhibition of pathogen entry into plant cell walls because of accumulation of Si as a double layer of silica on the cell wall. Si forms covalent bonds of Si-O-C with the components of the cell wall. The pathogen's enzymes cannot easily break this bond, thus rendering the cell wall non-degradable from pathogens and conferring mechanical resistance (Schwarz, 1973).

role in crosslinking the Si with the cell wall. After crosslinking with the cell wall, Si enhances the negative charge on the cell wall surface and helps the nutrient ions uptake as well as metal ions. The Si-cell wall complex is most prominent in providing cell wall firming, reformation, stability, elasticity, and rigidity and enhancing mechanical strength, structural stability, and stress resistance. The wall-bound form of Si increases the pectin polysaccharides in the cell wall resulting in non-degradation of cell wall from pathogen's enzymes and improving mechanical resistance. Its role in the formation of cell walls is also appreciable. Regulation of cellulose formation in the plant cell wall and the growth of dense long cellulose microfibrils to strengthen plants also occurs after crosslinking of Si with the cell wall. There is a great need to study the possible ligands of cell walls with Si interaction and the role of Si-cell wall complexes in providing stress resistance against any stress in the near future. A thorough study on ligands of plant cell walls involved in crosslinking Si with cell walls needs to be required.

### Conflict of interest

The authors declare that they have no conflict of interest.

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