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Tansley review

The controversies of silicon's role in plant biology

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Summary

Silicon (Si) is not classified as an essential plant nutrient, and yet numerous reports have shown its beneficial effects in a variety of species and environmental circumstances. This has created much confusion in the scientific community with respect to its biological roles. Here, we link molecular and phenotypic data to better classify Si transport, and critically summarize the current state of understanding of the roles of Si in higher plants. We argue that much of the empirical evidence, in particular that derived from recent functional genomics, is at odds with many of the mechanistic assertions surrounding Si's role. In essence, these data do not support reports that Si affects a wide range of molecular-genetic, biochemical and physiological processes. A major reinterpretation of Si's role is therefore needed, which is critical to guide future studies and inform agricultural practice. We propose a working model, which we term the 'apoplastic obstruction hypothesis', which attempts to unify the various observations on Si's beneficial influences on plant growth and yield. This model argues for a fundamental role of Si as an extracellular prophylactic agent against biotic and abiotic stresses (as opposed to an active cellular agent), with important cascading effects on plant form and function.

I. Introduction

Nearly 25 years ago, the seminal review by Epstein (1994), 'The anomaly of silicon in plant biology', became a turning point of accelerated interest in silicon's (Si's) properties and benefits to plants. Before this, 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 research in the peerreviewed literature before 1994, with c. 200 papers dealing with the effects of Si in plants, as opposed to the c. 800 articles focusing on various aspects of Si's potential in plants that have been published since (Fig. 1). 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 led, finally, in 2015, the International Plant Nutrition Institute (IPNI) to upgrade Si from complete omission to the status of 'beneficial substance' (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 (Si(OH)₄; $pK_{a1} = 9.84$, $pK_{a2} = 13.2$, at 25°C), the form of Si accessible to plants (Casey *et al.*, 2004), is soluble in water only up to *c*. 2 mM at 25°C, above which polymerization into silica (SiO₂) gel begins to occur (Ma *et al.*, 2001). From a biochemical perspective, Si(OH)₄ is largely uncharged and unreactive at physiological pH. As noted by Pace (2001), 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 SiO_2 polymers), compared with 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 remains largely unexploited.

In essence, there are four main areas of contention surrounding Si in higher plants: (1) its absorption (or lack thereof), (2) its essentiality, (3) its nutritional role (i.e. as a fertilizer) and (4) the mechanism(s) by which it confers protection against biotic and abiotic stresses.

One of the most puzzling properties of Si is its differential absorption by plants. Depending on the plant species, soil properties, Si source and Si amount, in planta Si contents can vary from 0.1% (near the detection limit) to 10% (on a dry weight basis; Epstein, 1994). This gives rise to additional confusion, as the beneficial properties of Si are generally linked to the amount absorbed by the plant (Ma, 2004). Consequently, some plant species benefit minimally from Si fertilization compared with others, a distinction that is often overlooked in experiments, which can lead to faulty conclusions and unrealistic expectations. Previous studies have attempted to phenotype and classify plants according to their ability to absorb Si (Hodson et al., 2005; Trembath-Reichert et al., 2015), a difficult endeavor considering the numerous factors that can influence the data. With novel experimental techniques, the advancement of genomics and developments such as the discovery of Si transporters, new opportunities are available to characterize accumulator and non-accumulator plants on the basis of specific molecular features (Section II).

The essentiality of Si for plants has been the subject of much debate and many reviews (Epstein, 1994, 1999, 2009; Datnoff *et al.*, 2001; Liang Y *et al.*, 2015), and will not be revisited in detail here. Since the pioneering works of Sprengel and von Liebig in the



Fig. 1 Number of silicon (Si)-related publications in the plant sciences from 1934 to 2017 (based on *Web of Science* search with the words 'silicon' or 'silicate' or 'silicic' in the title, and refined to the 'Plant Sciences' category).

early to mid-1800s (van der Ploeg *et al.*, 1999), and the refinements by Arnon & Stout (1939), plant nutritionists have maintained the exclusion of Si from the list of essential mineral elements for higher plants (i.e. with the exception of horsetail (*Equisetum arvense*); Gregoire *et al.*, 2012; Vivancos *et al.*, 2016). Epstein (1994) argued that the essentiality of Si is experimentally challenging to assess as Si is one of the most abundant elements in the Earth's crust and a ubiquitous contaminant, and thus difficult to exclude from plant growth media entirely. Cognizant of this reality, our review specifically focuses on the tangible, measurable benefits associated with Si amendment in excess of the background contamination found in various growth media, both natural and artificial.

Considering that plants cannot grow in an environment completely devoid of Si, the more realistically important question is whether plants will benefit from Si through addition to experimental growth solutions or soil fertilization. A few reports have claimed that Si fertilization can enhance plant growth and yield, whereas others have refuted such claims. This review casts a critical eye on the wide-ranging results in the literature on the effects of Si in an effort to bring consensus to the debate (Section III).

One area of Si biology that is settled involves the alleviation of stress (e.g. the decreases in growth rate; Grime, 2001), both biotic and abiotic (Sections IV and V, respectively), and numerous studies over the years have attempted to decipher the mechanisms by which Si confers such protection. These efforts have proven challenging on many levels, however, perhaps most fundamentally because of the discrepancy between the view of Si(OH)₄ as a biochemically inert substance and the numerous and wide-ranging mechanistic assertions (e.g. genetic, biochemical and physiological) put forth in the literature. It is our opinion that it is highly improbable that Si is biologically versatile and, consequently, its protective role, regardless of the stress, more likely stems from a common mechanism. Through comparative analysis of the literature describing Si's alleviation of different stresses, both biotic (e.g. microbial pathogens, herbivorous arthropods) and abiotic (e.g. salinity, heavy metals, nutrient deficiency), we propose a working model of Si's role in higher plants, termed the 'apoplastic obstruction hypothesis' (Section VI).

II. Silicon transport in plants: to absorb or not to absorb

Plants will absorb Si in the form of Si(OH)₄ from soil or nutrient solutions. The maximum solubility of Si(OH)₄ in solution is *c*. 2 mM, and its concentration in soil solutions 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 reality that has been known, if poorly understood, for a long time.

Handreck & Jones (1967) proposed a classification of plant species on the basis of their Si content, and identified three groups: low, intermediate and high accumulators. At the time, however, this classification could not take into account the fact that specific biological mechanisms could explain the inter-species variation. Years later, Takahashi *et al.* (1990) refined the classification system by categorizing plants on the basis of the basic mechanistic understandings of Si uptake. The authors described three mechanisms, active, passive and rejective, that associate, quite closely, with the high-, intermediate- and low-accumulator plants, respectively. Active accumulators have a shoot Si content ranging from 1.5% to 10%, and include monocots such as rice (*Oryza sativa*), wheat (*Triticum aestivum*) and sorghum (*Sorghum bicolor*). The passive accumulators encompass mostly dryland Gramineae with a shoot Si content of 0.5–1.5%. Finally, the rejective classification applies to plants with an Si content of < 0.2% and, at the time, was associated with most dicots.

With more data available on Si content in plants, Hodson *et al.* (2005) conducted an exhaustive analysis of 735 plant species from 125 studies and normalized the data on the basis of measurements from at least two independent studies for each species, in order to classify plants with regard to their ability to accumulate Si. At a time at which Si transporters had not been identified, this dataset provided a valuable resource on the phylogenetic distribution of Si content in the plant kingdom.

Classifications aside, the mechanisms by which plants absorb Si had long been elusive. Transpiration was believed to be one of the main factors determining Si uptake in plants. Although translocation of Si(OH)₄ from the xylem to the aerial part of the plant is certainly facilitated by transpiration, the idea that this process alone dictates the amount of Si found in a plant has been shown to be erroneous. Ma et al. (2001) first showed that transpiration had little influence on the Si content in rice plants. In addition, transpiration alone could not explain the wide variation in Si content observed among plants by Bélanger et al. (2016), who offered evidence that much of the variation in Si content could be explained by Si transport in roots. By using soybean (Glycine max) cultivars that differed markedly in their ability to absorb Si, the authors grafted interchangeably the rootstock of one cultivar with the scion of another, and supplied the plants with Si. Their results showed that the Si content found in leaves was directly associated with the rootstock, whereas the measures of evapotranspiration between the plants remained unchanged (Fig. 2). This provided strong evidence that the mechanisms influencing Si uptake were inherent to the roots.

The seminal discoveries of Si transporters in rice roots by Ma *et al.* (2006, 2007) have laid the foundation for our understanding of how plants can accumulate the element, and which plants do so. At the same time, these findings offer the opportunity to classify plants on the basis of precisely defined molecular mechanisms rather than solely on empirical observations. In essence, Si enters the plant from the external environment in the form of Si(OH)₄ through specific influx channels (termed Lsi1), and efflux transporters (termed Lsi2) mediate the loading of Si into the xylem and thus facilitate root-to-shoot translocation, which, in turn, moves Si to the aerial parts of the plant, where it deposits as amorphous SiO₂ (for a review, see Ma & Yamaji, 2015).

Lsi1, providing primary entry of Si(OH)₄ into plant root cells (and, to a lesser extent, arsenious acid (As(OH)₃) and boric acid (B (OH)₃); Mitani-Ueno *et al.*, 2011), belongs to the superfamily of major intrinsic proteins (MIPs, also known as aquaporins (AQPs); Ma *et al.*, 2006). AQPs are a class of channel-forming proteins that facilitate the transport of water and many other small solutes across cell membranes. They have a characteristic hourglass-like structure



Fig. 2 Leaf silicon (Si) content is dependent on rootstock genotype. (a) Schematic representation of grafting method. (b) The effect of rootstock genotype on Si accumulation in leaves of four separate soybean scions (taken from Bélanger *et al.*, 2016). DW, dry weight. Error bars denote \pm SEM.

made up of six transmembrane (TM) domains, and two half TM helices protruding from opposite sides towards the center of the pore (Murata et al., 2000). The two half TM helices form a constriction hosting two NPA (asparagine-proline-alanine) domains. The pore forms another constriction, often referred to as the selectivity filter, and is composed of four amino acids (AAs). The AAs at the selectivity filter are usually highly conserved and involved in the solute specificity of a given AQP (Hove & Bhave, 2011). Interestingly, the phylogenetic distribution of all known Si influx transporters identified in crops, including monocots and dicots, showed a specific clustering within the Nodulin 26-like intrinsic protein III (NIP-III) subgroup of AQPs. Moreover, these transporters have a selectivity filter composed of a conserved GSGR (glycine-serine-glycine-arginine) motif. In a recent study, Deshmukh et al. (2015) were able to further establish that the distance between the NPA domains was another selective feature for Si transport. They showed that, among other plants, tomato was a poor Si accumulator because it contained 109 AAs between the NPA domains, instead of the conserved 108 AAs among high accumulators. Therefore, plant AQPs belonging to the NIP-III subgroup with a GSGR selectivity filter and two NPA domains separated by 108 AAs can be categorized as being permeable to Si (OH)₄ (Fig. 3).

On the basis of the precise molecular characteristics conferring Si permeability to certain AQPs (Mitani & Ma, 2005; Ma *et al.*, 2006; Deshmukh *et al.*, 2015), and of the direct association established between a plant's ability to absorb Si and the presence of these AQPs, we suggest that molecular criteria should be adopted to classify plants for Si uptake. As such, plants could be categorized as accumulators or non-accumulators according to the presence of NIP-III channels possessing the necessary features for Si permeability (Fig. 3). With the availability of genomic data increasing

daily, one could, in essence, predict whether or not a plant can absorb Si by simply aligning sequences indicative of functional NIP-IIIs. Among accumulators, quantitative differences remain a fascinating subject and might be explained by agronomic traits, such as root architecture, presence of leaf silica cells (Kumar *et al.*, 2017b), leaf size and development (e.g. as is the case with strawberry (*Fragaria* × *ananassa*); Ouellette *et al.*, 2017), growth conditions, particularly with respect to the rooting media (e.g. soil properties, hydroponics, pH, plant-available Si), or the functionality of downstream Si transporters, such as Lsi2 (Mitani *et al.*, 2009) or shoot (node)-localized Lsi3 and Lsi6 (Ma & Yamaji, 2015; Yamaji *et al.*, 2015).

Although the understanding of Si transport has come a long way, there remains much to investigate. With regard to Lsi2, the fundamental issue of the mechanism of transport remains obscure. It is held that Lsi2 belongs to a class of putative anion transporters, showing similarity with the arsenite efflux transporter ArsB from bacteria and Archaea, and functions as an Si(OH)₄/H⁺ antiporter (Ma et al., 2007). However, direct evidence for this transport process is currently lacking. If such a mechanism exists, experimental methods that elucidated the mechanism of transporters, such as NHX1 and SOS1 (Na⁺/H⁺ antiporters; Apse et al., 1999; Qiu et al., 2002), should, hypothetically, shed light on Lsi2 functionality. The mechanism of Si deposition and accumulation is also unclear, but has recently garnered increased attention (Exley, 2015; Guerriero et al., 2016; Kumar et al., 2017b). Once the solubility of $Si(OH)_4$ is exceeded (i.e. > 2 mM), SiO_2 polymerization occurs and, for cells, this can be toxic (Iler, 1979; see also Montpetit et al., 2012; Exley, 2015); thus, it stands to reason that Si (OH)₄ transported through healthy root cells (via Lsi1 and Lsi2) must maintain a cytosolic concentration of <2 mM, although direct cytosolic measurements are currently lacking. The majority

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Fig. 3 Molecular characterization and phylogeny of the silicon (Si) channel, Lsi1. (a) Simplified two-dimensional structure of TaLsi1 from wheat showing all known features that influence solute specificity (see key). AA, amino acid; TM, transmembrane. (b) Three-dimensional model of TaLsi1. (c) Phylogenetic tree of all Nodulin 26-like intrinsic proteins (NIPs) identified in *Arabidopsis thaliana* (At), *Brassica rapa* (Br), *Brachypodium distachyon* (Bd), poplar (*Populus trichocarpa*, Pt) and rice (*Oryza sativa*, Os), highlighting the presence of NIP-IIIs (to which Lsi1 belongs) only in Si-accumulating species. (d) Taxonomic distribution of high- and low-Si-accumulating species, and their leaf Si content (in % dry weight (DW)).

of Si is found polymerized in the apoplast (e.g. around exodermal and endodermal root cells and leaf epidermal cells; Sangster *et al.*, 2001; Gong *et al.*, 2006), and cell wall constituents, such as (hemi)cellulose, callose, pectin and lignin, have been demonstrated to interact with Si(OH)₄ as 'templates' or 'scaffolding' for silicification (Guerriero *et al.*, 2016; and references therein). Si can also polymerize in specialized cells and cellular structures of some species (particularly grasses), such as leaf silica and long cells, and spikelet hairs and papillae (Rafi *et al.*, 1997), and interesting preliminary evidence for the biological control of this process has emerged (Kumar *et al.*, 2017a,b; Kumar & Elbaum, 2018).

III. The role of silicon in plants: not just a matter of semantics

Although there is no doubt that Si can be beneficial in protecting plants against stress, both biotic and abiotic (see Sections IV and V, respectively), the mechanistic underpinnings of such protection

studies have reported growth- and yield-promoting effects under such conditions, in contradiction with other reports (Table 1). It is important to reiterate, however, that Si is not an essential element for higher plants (see Section I), failing to fulfill the criteria laid out by Arnon & Stout (1939), namely: (1) deficiency in the element makes it impossible for the plant to complete its life cycle; (2) deficiency symptoms are specific to the element in question and can only be corrected by supplying the element; and (3) the element is directly involved in the nutrition of the plant and not merely correcting some unfavorable condition of the growth regime. Here, we make the case that it is specifically the third criterion that confounds much of the research on Si, that is, there is a conflation of Si-induced alleviation of stress with the postulate of a nutritional role in plants. As we shall see, the preponderance of the evidence suggests that Si per se does not promote plant growth, function or metabolic activity, but rather prevents or mitigates the strains

remain elusive. More fundamentally, however, the question of Si's

role in the absence of stress remains a contentious issue, as some

Table 1 Literature survey of the biochemical/physiological effects of silicon (Si) supplementation

Stress	Reference	Species	Growth condition (treatment)	Variable	Si effect (without stress)?	Si effect (with stress)?
Fungal disease	Cai <i>et al.</i> (2008)	Rice (Oryza sativa)	Vermiculite (± rice blast; Magnaporthe grisea)	Lignin content	No	Yes
				POD activity	No	Yes
				PPO activity	No	Yes
				PAL activity	No	Yes
	Gao <i>et al.</i> (2011)	Rice (O. sativa)	Vermiculite (\pm rice blast)	Mineral nutrient content	No	Yes
				Chlorophyll content	No	No
				$F_{\rm v}/F_{\rm m}$	No	Yes
				$F_{\rm v}/F_{\rm O}$	No	Yes
	Resende <i>et al.</i> (2012)	Sorghum (Sorghum bicolor)	Hydroponics (± anthracnose; Colletotrichum sublineolum)	A _{net}	No	Yes
				gs	No	Yes
				$C_i: C_a$	No	Yes
				E	No	Yes
				SOD activity	No	Yes
				CAT activity	No	Yes
				APX activity	No	Yes
				GR activity	No	Yes
				Leaf electrolyte leakage	No	Yes
				H_2O_2 content	No	Yes
				MDA content	No	Yes
Salinity	Zhu <i>et al.</i> (2004)	Cucumber (Cucumis sativus)	Hydroponics (\pm 50 mM NaCl)	Total DW	Yes	Yes
				Leaf soluble protein content	No	Yes
				Root electrolyte leakage	No	Yes
				Lipid peroxidation	No	Yes
				H_2O_2 content	Yes	Yes
				SOD activity	No	Yes
				GPX activity	No	Yes
				APX activity	No	Yes
				DHAR activity	No	Yes
				GR activity	No	Yes
				CAT activity	No	No
	Yin <i>et al</i> . (2016)	Sorghum (S. <i>bicolor</i>)	Hydroponics (\pm 100 mM NaCl)	Total DW	No	Yes
				Chlorophyll content	No	Yes
				Shoot Na ⁺ content	No	Yes
				Root Na ⁺ content	No	No
				Root K ⁺ content	No	No
				Total polyamine content	Yes	Yes
				Total ACC content	No	Yes
	Flam-Shepherd <i>et al.</i> (2018)	Rice (O. sativa)	Hydroponics (\pm 35 or 50 mM NaCl)	Shoot DW	Yes	Yes
				Shoot Na ⁺ content	No	Yes
				E	nd	Yes
				Apoplastic bypass flow	nd	Yes
				Root membrane electrical potential	No	No
				Na ⁺ influx	No	No
				Na ⁺ efflux	No	No

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Table 1 (Continued)

Stress	Reference	Species	Growth condition (treatment)	Variable	Si effect (without stress)?	Si effect (with stress)?
Osmotic	Hattori <i>et al.</i> (2008)	Sorghum (S. bicolor)	Hydroponics (\pm 10% PEG-6000)	Anet	No	Yes
		0		8s	No	Yes
				Ē	No	Yes
				Root hydraulic resistance	No	Yes
	Liu <i>et al.</i> (2014)	Sorghum (S. bicolor)	Hydroponics (± 10% PEG-6000)	Total DW	No	Yes
				A _{net}	No	Yes
				gs	No	Yes
				E	No	Yes
				Leaf RWC	No	Yes
				Leaf water potential	No	Yes
				K _{plant}	No	Yes
				Root xylem potential	No	No
				L _p	No	Yes
		Tamata (Calamum	the due of a star	Root surface area	No	No
	Shi et al. (2016)	lycopersicum)	(\pm 10% PEG-6000)	Total Dvv	NO	NO
				Root : shoot ratio	No	No
				A _{net}	No	Yes
				E	Yes	Yes
				Leaf water content	NO	Yes
				Lp Root electrolyte lookage	NO	Yes
				ADA contont	No	Voc
					No	Voc
				$\Pi_2 O_2$ content	No	Vec
				CAT activity	No	Vec
				Ascorbic acid content	Yes	Yes
				GSH content	No	Yes
Cd toxicity	Faroog <i>et al.</i> (2016)	Rice (O. sativa)	Hydroponics (\pm 10 µM Cd)	Total DW	No	Yes
			··· / ··· · · · · · · · · · · · · · · ·	Φρςιι	No	Yes
				Leaf H_2O_2 content	Yes	Yes
				Root H_2O_2 content	No	Yes
				Leaf ascorbate content	Yes	Yes
				Root ascorbate content	No	Yes
				Leaf GSH content	Yes	Yes
				Root GSH content	No	Yes
				Leaf NPT content	Yes	Yes
				Root NPT content	No	Yes
	Wu <i>et al.</i> (2016)	Wheat (<i>Triticum</i> aestivum)	Hydroponics (0–25 μM Cd)	Oxalate root exudation	No	Yes
As toxicity	Sanglard <i>et al.</i> (2014)	Rice (O. sativa)	Hydroponics ($\pm 25 \mu M$ As)	A _{net}	No	Yes
				gs	No	Yes
				gm	No	Yes
				V _{cmax}	No	No
				J _{max}	No	No
				J _o : J _c	No	Yes
				F _v /F _m	No	No
				$q_{\rm p}$	No	No
Min toxicity	Rögalla & Römheld (2002)	Cucumber (C. sativus)	Hydroponics (± 50 µ/M Mn)	Shoot FVV	No	Yes
				Root FW	No	Yes
		Current and Carlins		Leat Mn content	No	No
	<i>i</i> viaksimovic <i>et al.</i> (2012)	Cucumper (C. sativus)	Hydroponics (\pm 100 μ M Mn)		res	res
				Root DW	Yes	Yes
				Leaf Mn content	No	Yes
				H_2O_2 content	No	Yes
				GPX activity	Yes	Yes

Table 1 (Continued)

Stress	Reference	Species	Growth condition (treatment)	Variable	Si effect (without	Si effect (with
Al toxicity	Wang <i>et al.</i> (2004)	Maize (Zea mays)	Hydroponics	Root elongation	No	Yes
			(\pm 25 or 100 μ M Al)			
				Root length	No	Yes
				Root citrate exudation	No	No
				Root malate exudation	No	No
				Root total phenol exudation	No	No
Cu toxicity	Mateos-Naranjo et al. (2015)	Spartina densiflora	Hydroponics (\pm 15 mM Cu)	Shoot FW	No	No
				Root FW	No	Yes
				RGR	No	Yes
				No. of tillers	No	Yes
				Anet	No	Yes
				g _s	No	Yes
				C _i	No	Yes
				iWUE	No	Yes
				Φ_{PSII}	No	Yes
				Chlorophyll content	No	Yes
				Rubisco content	No	Yes
				Rubisco carbamylation	No	No
				TSP content	No	Yes
				Total respiration (O ₂ isotope fractionation)	No	No
				Total respiration (O_2 electrode)	No	Yes
K ⁺ deficiency	Chen <i>et al.</i> (2016)	Sorghum (S. bicolor)	Hydroponics (0.05 (low) or 3 mM K ⁺ (high))	Total DW	No	Yes
			0	Anet	No	Yes
				$F_{\rm v}/F_{\rm m}$	No	Yes
				Soluble protein content	No	Yes
				Chlorophyll content	No	Yes
				Chla/b	No	Yes
				Leaf K ⁺ content	No	No
				Leaf polyamine content	No	Yes
				Leaf arginine content	No	Yes
				DAO activity	No	Yes
				PAO activity	No	Yes
				H_2O_2 content	No	Yes
				SOD activity	No	Yes
				CAT activity	No	Yes
				APX activity	No	Yes

ACC, 1-aminocyclopropane-1-carboxylic acid; A_{net} , net carbon assimilation rate; APX, ascorbate peroxidase; CAT, catalase; Chla/b, chlorophyll a/b; $C_i : C_a$, internal to ambient CO₂ concentration ratio; DAO, diamine oxidase; DHAR, dehydroascorbate reductase; DW, dry weight; *E*, transpiration rate; F_v/F_0 , ratio of variable to minimum fluorescence; F_v/F_m , ratio of variable to maximum fluorescence; FW, fresh weight; g_m , mesophyll conductance; GPX, guaiacol peroxidase; GR, glutathione reductase; g_s , stomatal conductance; GSH, reduced glutathione; iWUE, instantaneous water-use efficiency; J_{max} , maximum rate of carboxylation limited by electron transport; $J_o : J_c$, ratio of electron transport rate devoted to oxygenation/carboxylation; K_{plant} , whole-plant hydraulic conductance; MDA, malondialdehyde; nd, not determined; NPT, non-protein thiols; PAL, phenylalanine ammonia-lyase; PAO, polyamine oxidase; POD, peroxidase; TSP, total soluble protein; V_{cmax} , maximum rate of carboxylation; Φ_{PSII} , steady-state quantum yield of photosystem II.

imposed by stress, and this, ultimately, is reflected in improvements in plant growth, function and metabolic activity. We believe that this is an important distinction to make, and not just a matter of semantics.

At the physiological level, most studies suggest that, in the absence of stress, Si supplementation has little or no effect. For instance, Ma & Takahashi (2002) were amongst the first to compare the photosynthetic activity of rice plants with and without Si supplementation, and could not find any differences. As Table 1 shows, the majority of studies demonstrate no effect of Si on

measures such as biomass, enzyme activity, membrane potential, ion and water transport, respiration and photosynthesis. By contrast, Si effects are quite generalized under conditions of stress, and, importantly, such effects often return physiological measures back to control levels, rather than surpassing baseline (Fig. 4a).

The advent of 'omics' technologies has offered the opportunity to investigate with unprecedented precision how Si supplementation affects a plant. Watanabe *et al.* (2004) first demonstrated that Si supplementation had essentially no effects on gene expression in rice, with only one of c. 9000 genes analyzed being significantly



Fig. 4 Silicon (Si) effects (or lack thereof) under experimentally controlled stress-free conditions. (a) Generalized representation of Si effects on biochemical/physiological variables (e.g. growth, photosynthesis, enzyme activity, etc.) under control (stress-free) and stress conditions (for details, see Sections III and V, Table 1). It should be noted that, under stress, Si effects can range from no benefit to complete recovery (see light blue bar). (b) Transcriptomic analyses of Si effects under control (C; stress-free) conditions in soybean (as measured by RNA-seq; Rasoolizadeh *et al.*, 2018) and Arabidopsis and wheat (as measured by microarray; Fauteux *et al.*, 2006; Chain *et al.*, 2009). It should be noted that, for microarray data, a cut-off of log₂ fold change was considered; thus, based on this analysis, only two (of *c*. 28 500 transcripts) and 47 (of *c*. 55 000 transcripts) differentially expressed genes (DEGs) were found in Arabidopsis and wheat, respectively (see Section III for details).

altered in its expression. Similarly, a proteomic analysis by Nwugo & Huerta (2011) showed that Si supplementation in rice resulted in statistically significant changes in the abundance of only four proteins, and another study with rice could not identify distinct metabolic pathways influenced by Si in control plants (Brunings *et al.*, 2009). Fauteux *et al.* (2006) reported the first complete transcriptomic analysis of a plant under Si supply and demonstrated that Si had no significant effect on the expression of any but

two of the c. 28 500 genes analyzed in Arabidopsis (Arabidopsis thaliana). In wheat, Chain et al. (2009) observed that, of the c. 55 000 transcripts analyzed, only 47 were significantly altered by Si supplementation, and most were downregulated stress-related genes. Interestingly, in pathogen-inoculated plants, > 3000 genes were differentially expressed, and the authors observed a nearly perfect reversal in the transcript profile when Si was supplied, suggesting that rather than being involved directly in the regulation of gene expression, Si prevented or attenuated the effects on transcription imposed by the stress. More recently, an analysis of soybean showed that Si supplementation had no effect on gene expression related to any distinct metabolic pathway, with only 50 genes altered (falling into categories of stress-related or 'hypothetical protein') of c. 55 000 analyzed under control conditions (Rasoolizadeh et al., 2018). Similar to the case with wheat, the differentially expressed genes (DEGs) in response to a pathogen challenge (c. 3000) reverted to a pattern of expression observed in non-stressed plants when Si supplementation occurred, once again supporting the notion that Si did not alter gene expression per se, but rather interfered with strains (leading to gene expression alterations) induced by stress (Fig. 4b). Interestingly, although transcriptomic studies showed little/no effect of Si on gene expression in control plants, similar analyses with essential elements vielded much larger effects. For example, the response to a 24-h deficiency in nitrogen (N), phosphorus (P) and potassium (K) resulted in 1946, 382 and 814 DEGs (of c. 27 000 loci analyzed), respectively, in rice (Takehisa et al., 2013). Taken together, these results reinforce the concept that Si has a very limited direct role on unstressed plants.

Although the majority of the studies we surveyed demonstrated a lack of an Si effect under stress-free conditions, there were some exceptions (Table 1). For example, Gong et al. (2006) and Flam-Shepherd et al. (2018) observed statistically significant gains in biomass with Si supplementation when NaCl supply was minimal in hydroponically grown rice seedlings. It was clear, however, that the beneficial effects of Si were maximal when salt stress was highest. Detmann et al. (2012) observed many benefits with Si supplementation in mature rice, including increases in crop yield, CO₂ assimilation and mesophyll conductance, in contradiction with other studies with rice (Table 1). It is unknown whether the fluctuating environmental conditions over the c. 90-d experimental period, coupled with the apparent lack of aeration of the nutrient solution, imposed unintended stresses on the plants. In transcriptomic analyses, only Van Bockhaven et al. (2015) claimed a large effect of Si on gene expression in stress-free rice in stark contrast with previous studies (Watanabe et al., 2004; Fauteux et al., 2006; Brunings et al., 2009; Chain et al., 2009; Rasoolizadeh et al., 2018; J. F. Ma et al., unpublished). Surprisingly, the number of DEGs reported (nearly 2000) even exceeds that found elsewhere under stress (e.g. Brunings et al., 2009), suggesting an influence of unaccounted stress under their experimental conditions. Nevertheless, taken as a whole, the results indicate that there is no reproducible systemic change, nor are there cascading effects (e.g. with genes part of clear metabolic or signaling pathways), associated with Si fertilization.

IV. Silicon and biotic stress: beyond mechanical barriers and defense priming

Although the benefits of Si fertilization on unstressed plants remain contentious, the same cannot be said for the expanding evidence supporting the positive role of Si in stressed plants. The initial theory concerning the mode of action of Si in plant prophylaxis involved the establishment of a mechanical barrier impeding fungal progress. This stemmed from Wagner (1940), who showed that Si offers protection against powdery mildew (Sphaerotheca fuliginea) on different host plants and was the first to suggest that the increased silicification of the host cell wall prevented penetration of the pathogen. This work laid the foundation for the mechanical barrier hypothesis that is still being conveyed to this day, despite the fact that, as early as 1965, Okuda & Takahashi (1965), citing Yoshi (1941), who measured leaf toughness, reported: 'From this result, it seemed that Si protected the rice plant against blast disease, but the increase in mechanical toughness of the plant tissue resulting from absorbed Si is not sufficient to explain the mechanism of protection'. Indeed, no observations have directly linked cell wall reinforcement with penetration failure by the fungus.

The possibility that Si played a role other than a mechanical barrier in the resistance process was first suggested by Samuels et al. (1991) and Chérif et al. (1992), who observed that plants reacted more promptly to infection by accumulating phenolic-like material that hindered the propagation of the parasite. Corroborating evidence that Si played more than a mechanical barrier role in planta was provided when the interaction between cucumber (Cucumis sativus) and powdery mildew was further analyzed at the chemical level (Fawe et al., 1998). The authors detected and identified flavonoids and phenolic acids that were specifically and strongly induced in a pattern typical of phytoalexins, as a result of Si treatment. Thus, Si was hypothesized to play an active role in disease resistance by stimulating defense mechanisms. Subsequently, through electron microscopy studies and chemical analyses of rice, Rodrigues et al. (2003, 2004) showed that plants treated with Si fended off rice blast infection through the production of electron-dense material composed of momilactones, which act as phytoalexins in rice. At the same time, similar results were obtained for wheat-powdery mildew interactions on plants supplied with Si (Bélanger et al., 2003; Rémus-Borel et al., 2009). Thereafter, numerous papers have associated the prophylactic role of Si against diseases with some form of defense response by the plant (Liang Y et al., 2015, and references therein).

For the most part, studies that have shown heightened defense responses in the presence of Si have speculated on the role of Si in the process. Hypotheses that soluble Si can act as a secondary messenger, a modulator of defense responses or a priming agent (Fawe *et al.*, 2001; Fauteux *et al.*, 2005; Van Bockhaven *et al.*, 2013) have never been fully tested in the presence of a proper genetic model, until recently. Indeed, by exploiting Arabidopsis mutants able to absorb larger quantities of Si, but deficient in the activation of the salicylic acid (SA) pathway, Vivancos *et al.* (2015) directly tested whether the protective effect of Si became null or significantly altered, given the presumed inability of the plant to mount defense reactions against powdery mildews. It was quite surprising to observe that plants transformed for high Si absorption and supplied with Si displayed resistant phenotypes in spite of having lost the ability to produce defense reactions involving the SA pathway. This meant that Si, in the form of Si (OH)₄, did not replace SA as a surrogate secondary messenger in the induction of defense reactions, as proposed previously (Fawe *et al.*, 2001). These observations strongly suggest that other factors are at play in the Si-mediated protection of plants against fungal diseases.

If the above results appear conflicting at first, they open the way to an alternative hypothesis that would unify the modes of action behind the observed phenomena. The prophylactic role of Si is overwhelmingly associated with pathogens that have a biotrophic phase (e.g. powdery mildews, oomycetes and rice blast; Table 2). For instance, powdery mildews (strict biotrophs) are particularly well controlled by Si. Among hemibiotrophs, rice blast, caused by the fungus Magnaporthe grisea, is arguably the most commonly reported disease to be controlled by Si. As such, the suggestion that Si can confer 'broad-spectrum disease resistance' (Van Bockhaven et al., 2013), notwithstanding the fact that it does not apply to nonaccumulator species, ignores the overwhelming evidence of field and experimental data associating the benefits primarily against biotrophic and hemibiotrophic pathogens, and overlooks the negative reports with necrotrophs. For instance, Rodgers-Gray & Shaw (2004) could not observe any effects against Fusarium culmorum, whilst reporting protection against powdery mildew on wheat. Other necrotrophs, such as Cercospora sojina, Pythium aphanidermatum, Bipolaris oryzae and Sclerotinia homeocarpa, have been reported to be unaffected by Si treatment (Malvick & Percich, 1993; Rodgers-Gray & Shaw, 2004; Heine et al., 2006; Nascimento et al., 2014). Also, the literature is obviously biased against reporting negative results, and our own experience has shown repeatedly that Si has no effect against typical necrotrophs, such as Botrytis cinerea and Sclerotinia sclerotiorum. Bipolaris oryzae remains an interesting intermediate model, because it is amongst the pathogens controlled by Si, albeit with less frequency and efficiency than *M. grisea*, and, although being considered a necrotroph, it produces host-selective toxins and its genome codes for effector proteins, features not typically observed for necrotrophs (Condon et al., 2013). In the last few years, the annotation of plant pathogen genomes has highlighted the presence and importance of effector proteins, most notably in the case of biotrophs and hemibiotrophs, in a compatible host-pathogen interaction. Effectors modify host cell structure, metabolism and function, and interfere with the signaling pathways required for host invasion or the triggering of host resistance (Giraldo & Valent, 2013). Fungal effectors are first released into the apoplast and can be translocated into the cytoplasm through the cell membrane or the extrahaustorial matrix (EHM) (Bozkurt et al., 2012). Interestingly, SiO₂ deposition in plants is frequently located in the apoplast and, more precisely, at the interface of the plasma membrane with the cell wall (Bauer et al., 2011; Zhang et al., 2013). In a recent review, Wang & Wang (2018) highlighted how the apoplast is a site of intense interactions of many effectors with plant targets. Indeed, the appressorium and the haustorium of powdery mildew fungi are structures of active release of effectors (Giraldo & Valent, 2013): the appressorium

Table 2 Number of studies suggesting beneficial effects of silicon (Si) indifferent plant species against biotrophic, hemibiotrophic and necrotrophicfungi

Pathogen	Number of studies ^a
Biotroph/hemibiotroph Necrotroph	100 8
Bipolaris oryzae ^b	11

 $^{\rm a}\mbox{For a detailed breakdown of the studies, refer to Supporting Information Table S1.$

^bHost-specific necrotroph.

releases effectors into the apoplast to prevent the action of plant proteases, and the haustorium releases effectors into the cytoplasm through the EHM to alter plant defenses. Given that the apoplast and the EHM are within the confines of Si deposition (Ghanmi *et al.*, 2004) and, based on our observations, it seems not only plausible but logical that Si could interfere with effectors reaching their targets or plant signals being recognized by the pathogen. This would prevent the invading fungus from inhibiting plant defenses, resulting in the expression of the complete array of defense mechanisms, or alternatively from recognizing the plant as a compatible host (Holub & Cooper, 2004; Nuernberger & Lipka, 2005). Considering the superior prophylactic role of Si against biotrophs, the heavy reliance of biotrophs on effectors to maintain their virulence and the site of Si deposition coinciding with effector release, a link between Si and effectors is strongly supported.

In an effort to test this hypothesis, Rasoolizadeh *et al.* (2018) looked at the expression of effectors of the hemibiotroph *Phytophthora sojae* and defense reactions of soybean plants grown in the absence and presence of Si. Their data clearly show a protective effect of Si in soybean, accompanied by a significant reduction in effector expression in Si-supplied plants during the biotrophic phase of *P. sojae*, together with a similarly reduced expression of plant receptors. The results support the concept that Si interferes with effector/receptor expression which, in turn, confers resistance to the plant. As the role and localization of effectors released by plant pathogens become better defined, it should become possible to investigate mechanistically whether and how Si interacts with them and affects their compatibility with the plant.

Research on Si-induced protection against herbivorous insects has followed a similar trajectory to that of fungal pathogens. For example, improved plant defense against arthropods under Si supplementation has also long suggested a mechanical form of protection (Reynolds *et al.*, 2009, 2016). As early as 1955, the reduction in damage to rice plants by the chewing herbivore *Chilo simplex* was postulated to be a result of an increased strength of the rice stem following Si accumulation (Sasamoto, 1955). More recently, a study of another chewing herbivore *Spodoptera exempta* directly showed that Si acts as a physical defense for three grasses, increasing the abrasiveness of the leaves, and leading to the increased wear of mandibles (Massey & Hartley, 2009; cf. Kvedaras & Keeping, 2007).

Also in line with fungal studies (Fauteux et al., 2005), molecularbased defenses of Si-treated plants against insects (in particular piercing–sucking types) have been proposed (Gomes *et al.*, 2005). Goussain *et al.* (2005) showed that stylet penetration of wheat aphid (*Schizaphis graminum*) was not impeded by Si in wheat plants; however, the stylet was withdrawn more often, resulting in a reduction in probing time, leading the authors to conclude that chemical changes as a result of Si absorption by the plant were probably responsible. Recently, a study in rice suggested that Si provision led to a higher level of jasmonate-mediated defenses against the rice leaffolder, *Cnaphalocrocis medinalis* (Ye *et al.*, 2013).

It has been proposed that plant-insect interactions involve a multi-layered plant defense response mediated by herbivoryassociated molecular pattern (HAMP)- and effector-triggered immunity (Hogenhout & Bos, 2011). Insect (Hemipteran) effectors are reportedly recognized by similar classes of immune receptors as those by pathogen virulence effectors (Smith & Clement, 2012; Kaloshian & Walling, 2016a). This is in line with predictions that phloem-feeding insects cause only minor tissue damage and induce defense signaling pathways resembling those activated against biotrophic and hemibiotrophic pathogens (Walling, 2001; Kusnierczyk et al., 2007). Recent evidence indicates that herbivore-associated endosymbionts (Wang et al., 2017) and the constituents of oral secretions, saliva, eggs (i.e. oviposition fluids) and frass, notably effectors, play an important role in manipulating direct and indirect plant defenses (Hilfiker et al., 2014), dramatically reshaping plant transcriptomes, proteomes and metabolomes (Wu & Baldwin, 2010). Insect effectors have been identified across a range of species, feeding guilds and for both specialists and generalists, including the Hessian fly (Mayetiola destructor; Zhao et al., 2015), brown planthopper (Nilaparvata lugens; Ji et al., 2017), tobacco hawk moth (Manducta sexta; Halitschke et al., 2001), corn earworm (Helicoverpa zea; Musser et al., 2012), cricket (Teleogryllus taiwanemma; Yoshinaga et al., 2007), vinegar fly (Drosophila melanogaster; Yoshinaga et al., 2007) and several aphid species, including pea aphid (Acyrthosiphon pisum; Carolan et al., 2011) and green peach aphid (Myzus persicae; Mugford et al., 2016). As these herbivore-associated effectors are derived from the insect or its microbial inhabitants, they are expected to be diverse in structure, function and, possibly, target protein identity (Kaloshian & Walling, 2016b).

Until recently, there was no direct evidence that insect effectors are transported into specific plant tissues and cells. Mugford et al. (2016) demonstrated, for the first time, that insect (aphid) effectors are delivered into the cytosol of plant cells during probing in the pathway phase, and other effectors are embedded within the sheaths that surround stylets in the apoplastic space of mesophyll tissue. Therefore, we might surmise that Si deposited within the apoplastic space interferes with such feeding styles. This could explain, at least in part, why, in Si-treated plants, we often observe piercing and sucking insects showing reduced probing time, although not necessarily increased mortality (Goussain et al., 2005; Costa et al., 2011). Thus, similar to the case proposed for pathogens, effectors released by insects could be trapped within the extracellular Si matrix, preventing them from impeding the plant defense response, or from recognizing the plant as a suitable host (Hogenhout & Bos, 2011).

V. Silicon and abiotic stress: a proliferation of proposed mechanisms

Remarkably, Si has been reported to alleviate a wide range of abiotic stresses, including radiation (Shen et al., 2010), lodging (Savant et al., 1997), wounding (Kim et al., 2014), temperature (Muneer et al., 2017), hypoxia (Fleck et al., 2011), salinity (Flam-Shepherd et al., 2018), drought (Liu et al., 2014), nutrient deficiency, such as that of iron (Fe; Pavlovic et al., 2016), P (Kostic et al., 2017) and K (Chen et al., 2016), and metal toxicity (e.g. cadmium (Cd), Shao et al., 2017; manganese (Mn), Che et al., 2016; arsenic (As), Sanglard et al., 2014; aluminum (Al), Wang et al., 2004; and copper (Cu), Mateos-Naranjo et al., 2015). [Correction added after online publication 14 July 2018: 'heavy' has been deleted from the preceding sentence.] Although some of these stresses are related, this is a diverse and largely disparate set of scenarios, and therefore it stands to reason that Si is providing some fundamental protection to plants that confers a wide range of benefits. Perplexingly, a survey of the relevant literature appears to suggest otherwise, with Si seemingly involved in a plethora of processes and functions, including gene expression (Manivannan & Ahn, 2017), redox homeostasis and oxidative stress (Liang et al., 2003; Zhu et al., 2004; Farooq et al., 2016), nitrogen assimilation (Pereira et al., 2013), carbohydrate metabolism (Zhu et al., 2016), cell signaling (Detmann et al., 2012, 2013), TM ion and water fluxes (Liang et al., 2006; Liu et al., 2014), hormone regulation (Liang XL et al., 2015; Markovich et al., 2017), root exudation (Kidd et al., 2001; Wu et al., 2016), metal chelation (Wang et al., 2004; Ma et al., 2015), root architecture (Gong et al., 2006; Fleck et al., 2011), transpiration (Gao et al., 2006) and photosynthesis (Shen et al., 2010; Detmann et al., 2012) (for reviews, see Epstein, 1999; Ma, 2004; Liang et al., 2007; Meharg & Meharg, 2015; Cooke & Leishman, 2016; Coskun et al., 2016; Debona et al., 2017; Frew et al., 2018). [Correction added after online publication 14 July 2018: 'heavy' has been deleted from the preceding sentence.]

Oxidative stress is a hallmark feature of stress (Mittler, 2002; Apel & Hirt, 2004; Gill & Tuteja, 2010) and its reduction by Si, by upregulating antioxidant activity, is a proposed major mode of action (Liang, 1999; Liang et al., 2003, 2006; Zhu et al., 2004; Gong et al., 2005; Gunes et al., 2007; Farooq et al., 2016; Hasanuzzaman et al., 2017; Kim et al., 2017; cf. Mateos-Naranjo et al., 2015). Consequently, several studies have linked Si with elevated shoot and root activities of antioxidants, both enzymatic (e.g. superoxide dismutase, peroxidase, catalase, ascorbate peroxidase and glutathione reductase) and non-enzymatic (e.g. ascorbate, glutathione, phenolic compounds, etc.), as well as changes in the concentrations of common markers of oxidative stress, including malondialdehyde, hydrogen peroxide (H2O2) and proline, under various abiotic stresses (for reviews, see Liang et al., 2007; Cooke & Leishman, 2016; Kim et al., 2017). Once again, however, one must be cognizant of the points of reference and the distinctions between direct and indirect effects. Indeed, compared with stress conditions without Si supplementation, Si appears to alleviate oxidative stress, which, however, does not mean that Si is directly involved in antioxidant activity, and, in fact, no such evidence presently exists. Moreover, as with other biochemical

processes (see Section III), Si has no clear or consistent effect on antioxidant activity in the absence of stress (Table 1). Thus, a more parsimonious explanation is that Si prevents or mitigates the strains imposed by stress, which is then reflected in a reduced induction of oxidative stress (Fig. 4a). This is perhaps most clearly supported by the fact that Si supply consistently reduces the root-to-shoot translocation of toxicants (e.g. Na, As, Mn and Cd), and thus their cellular accumulation in leaf tissues (Yeo *et al.*, 1999; Gong *et al.*, 2006; Sanglard *et al.*, 2014; Che *et al.*, 2016; Shao *et al.*, 2017; Flam-Shepherd *et al.*, 2018; cf. Rogalla & Römheld, 2002; Blamey *et al.*, 2018). A reduction in toxicant accumulation will obviously reduce the strains imposed on shoot tissues, and thus be reflected in reduced oxidative stress.

Reactive oxygen species (ROS) are central to cell signaling and influence a wide range of critical and cascading processes, including the expression of genes, growth, development, programmed cell death and a suite of stress responses (Mittler, 2002; Apel & Hirt, 2004; Gill & Tuteja, 2010). Thus, it is no surprise that reductions in ROS with Si provision, under stress conditions, result in numerous downstream changes (Liang Y et al., 2003, 2005, 2015; Zhu et al., 2004; Yin et al., 2016; Markovich et al., 2017); however, this should not be confused with an 'active role' of Si. For example, Si supplementation has been claimed to influence many physiological parameters based on correlations with elevated polyamine levels (e.g. spermidine, spermine and putrescine) and reduced ethylene signaling in salt-stressed sorghum (Yin et al., 2016), but such observations are far from conclusive in terms of mechanistic evidence. Likewise, claims that Si alleviates K⁺ deficiency-induced leaf chlorosis by decreasing the accumulation of putrescine are unsubstantiated (Chen et al., 2016). A similar conclusion can be drawn from a recent analysis of Si's role in the promotion of cytokinin biosynthesis and its relationship with the delay of senescence in Arabidopsis and sorghum (Markovich et al., 2017). Another common claim is that Si can influence the transport of water and ions across membranes. For example, in the context of hyperosmotic stress, increases in hydraulic conductivity with Si provision have been ascribed to increased expression of genes encoding AQPs (Liu et al., 2014). Similarly, with salinity (NaCl) stress, some studies have suggested that Si can promote the vacuolar sequestration of Na⁺, and thus protect vital cytoplasmic functions (Liang et al., 2007; and references therein). This is largely based on observations of increased H⁺-ATPase activities with Si provision (Liang, 1999; Liang et al., 2005, 2006) and speculations on downstream effects on H⁺-dependent Na⁺ fluxes (e.g. tonoplast (NHX1) or plasma membrane (SOS1) antiporters). Again, these results are correlative and only observed under stress, as opposed to control conditions, suggesting that, rather than stimulating AQP function or H⁺-ATPase activity, Si is simply mitigating their decrease (Fig. 4a). As far as we are aware, the only attempts to directly measure the effect of Si on root Na⁺ fluxes yielded no observable effects in salt-stressed rice seedlings (Malagoli et al., 2008; Flam-Shepherd et al., 2018). Similarly, electrophysiological measurements conducted in epidermal and cortical root cells demonstrated no effects of Si provision on resting membrane potentials or NaCl-induced depolarizations, suggesting that Si has no effect on TM currents (Flam-Shepherd et al., 2018). With

respect to other toxicants, claims that Si inhibits TM Cd influx and stimulates vacuolar sequestration similarly lack mechanistic evidence (Ma *et al.*, 2016). In the context of nutrient deficiency, the claim that Si increases P influx in P-deprived wheat, based on gene expression analyses (i.e. increases in expression for genes encoding P transporters) and tissue content data, does not offer evidence of a direct involvement of Si in the process (Kostic *et al.*, 2017). Although such proposals cannot be entirely ruled out, caution must always be applied when using changes in gene expression to act as a proxy for changes in protein abundance or activity without proper verification (Tian *et al.*, 2004; Schwanhausser *et al.*, 2011; Ponnala *et al.*, 2014).

What could explain such widespread effects, if they only reflect downstream (indirect) responses? In other words, what are the ultimate causes of Si-provided alleviation of abiotic stress? In the case of shoot tissues, Si deposition in cuticles has been shown to prevent water loss via evapotranspiration, protecting plants faced with water deficits (Ma et al., 2001; Ma, 2004). In roots, Si accumulates around cells expressing Si transporters, such as the exodermis and endodermis in rice (Lux et al., 2003; Gong et al., 2006; Ma & Yamaji, 2015). This is critical because Si deposition surrounding these cell layers blocks the 'apoplastic bypass route', whereby ions such as Na^+ , Cl^- and Cd^{2+} enter the transpiration stream via breaks and underdevelopments in the Casparian band (CB), and subsequently accumulate in shoots, potentially to toxic levels (Yeo et al., 1999; Ranathunge et al., 2005; Shi et al., 2005, 2013; Gong et al., 2006; Faiyue et al., 2010; Flam-Shepherd et al., 2018). Interestingly, Si appears to not only 'clog up' apoplastic bypass routes, but also to promote CB formation itself by contributing to the stimulation of suberin and lignin biosynthesis, thus further protecting plants against apoplastic bypass of toxicants (Fleck et al., 2011, 2015). The mechanism by which these changes occur are not yet clear, although it is hypothesized that Si interacts and crosslinks with phenols within cell walls or induces precipitation of phenols, leading to enhanced CB development. Lastly, the co-precipitation of Si and heavy metal toxicants, such as Al, in the extracellular matrix is another critical consideration (Kidd et al., 2001; Wang et al., 2004; Ma et al., 2015; Wu et al., 2016).

VI. The apoplastic obstruction hypothesis: a working model

Although the last 25 years have seen an unprecedented amount of research into the roles of Si in plant biology, it appears that a number of hypotheses nearly commensurate with the number of studies have been proposed, which has exacerbated the confusion. For instance, in a recent review describing the putative effects of Si, Frew *et al.* (2018) identified an inordinate amount of reported effects under various environmental conditions, including cell signaling, amino acid metabolism, photosynthesis, cell growth and division, and transcriptomic processes, which, taken as a whole, are incongruent with what we know about the properties of Si. Thus, in trying to propose a hypothesis to define the role of Si, we have taken a holistic and parsimonious approach, encompassing the various scenarios described in the literature in line with chemical and biological realities.

The first premise we considered was the evidence against a nutritional role for Si. As argued in this review, this position is supported by the vast majority of scientific papers, as well as the IPNI and most regulation agencies throughout the world. This perspective is not trivial because whether or not Si is accepted as a plant nutrient has direct repercussions on how its role is viewed in situations of stress. It is indeed unlikely that, if an element has no effect on a plant's metabolism in unstressed conditions, it would suddenly acquire unsuspected properties when a stress is imposed.

The second premise relates to the chemistry and biochemistry of Si(OH)₄, the soluble form of Si absorbed by plants. As outlined in Section I, Si(OH)₄ is uncharged and unreactive in cells (Exley, 2015); therefore, it stands to reason that there are no biochemical roles for Si(OH)₄ in terms of interactions with enzymes or other intracellular constituents; claims to this effect have been based on indirect effects and correlative evidence. As discussed here, the concept that Si(OH)₄ in planta, as a minor unpolymerized fraction, could play a cellular role was first suggested by Fawe et al. (2001), invoking the role of a secondary messenger inducing defense responses. As a result, this notion was extended to other forms of stress, but remained speculative and unsubstantiated until Vivancos et al. (2015) provided definitive evidence that Si(OH)₄ does not have a role as a signaling molecule or secondary messenger. Thus, the position that Si would have diverse and complex biochemical roles is untenable, particularly if one juxtaposes the numerous mechanistic proposals with the lack of direct evidence. It is our opinion that the expansion of mechanistic claims can largely be explained by the fallacy of conflating correlation with causation.

On the basis of these assumptions and the many benefits observed in Si-supplied plants, we conclude that the different forms of stress alleviation mediated by Si, whether biotic or abiotic, mostly stem from a common mechanism, referred to here as the apoplastic obstruction hypothesis. Under this scheme, the amorphous Si portion that deposits in the apoplast both interferes with and promotes a number of biological events leading to its beneficial role (Fig. 5). In the case of biotic stress, it interferes with the recognition process establishing the specificity between a plant and a fungal pathogen or insect, by altering the flow of the arsenal of molecules (e.g. effectors) and the establishment of structures, such as the haustorium, at the membrane interface used by a parasite to attack a plant (Fig. 5). On many levels, this explains the specificity of pathogens controlled by Si, and why those with a biotrophic phase (i.e. producing a haustorium) are particularly associated with the prophylactic properties of Si. In the case of abiotic stress, Si deposits around and fortifies apoplastic barriers surrounding the vasculature, and thus precludes the transport and accumulation of toxicants into the shoot, thereby preventing or mitigating downstream stress events (Fig. 5). Moreover, Si can coprecipitate with toxicants in the extracellular matrix, thus protecting tissues against stress (Kidd et al., 2001; Rogalla & Römheld, 2002; Wang et al., 2004; He et al., 2013, 2015; Pavlovic et al., 2013; Ma et al., 2016; Wu et al., 2016). Lastly, Si deposition in cuticles will prevent water loss, which is particularly important under osmotic stress.



VII. Perspectives and conclusions

The explanation of the roles of Si in plant biology has remained a quandary, as the mechanisms that have been proposed to explain the large number of reported beneficial effects are seemingly at odds

with its rather limited biochemical properties. There is also a disparity between its current practical exploitation in agriculture as a fertilizer and all the potential advantages it could confer, as large-scale applications are the exception rather than the norm. Accordingly, if we are to effectively benefit from its use, it is

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Fig. 5 The apoplastic obstruction hypothesis. (a) In roots, toxicants (X) can take both symplastic and apoplastic routes towards the stele (see black arrows). The apoplastic path is blocked by the Casparian band (CB), although breaks may occur which allow for bypass routes, particularly under low-silicon (–Si) conditions (Yeo *et al.*, 1999; Gong *et al.*, 2006). By contrast, high-silicon (+Si) plants have improved CB development (Fleck *et al.*, 2011), as well as apoplastic Si deposition (as silica, SiO₂; Gong *et al.*, 2006), effectively blocking bypass routes, and thus root-to-shoot translocation of toxicants. Red arrows denote symplastic and xylem transport of Si (as silicic acid, Si(OH)₄; Ma & Yamaji, 2015). (b) With abiotic stress, toxicant levels in shoots accumulate to a greater extent in –Si plants relative to +Si plants (as a function of SiO₂ deposition in roots; see (a)), resulting in elevated reactive oxygen species (ROS) and thus increased oxidative stress (e.g. decreased membrane stability (MS), decreased enzyme activity (EA), etc.), changes in gene expression, as well as decreased growth and function (e.g. photosynthesis, Ps). In +Si plants, ROS are limited and detoxified, resulting in less stress and increased growth, relative to –Si plants. Apoplastic Si deposition (SiO₂) in shoots can also aid in the prevention of ultraviolet radiation (UV) damage and water (H₂O) loss via evapotranspiration. (c) Under pathogenic fungal attack, –Si plants are susceptible to fungal invasion and development of haustorial bodies (HB), whereas +Si plants would be protected as a result of apoplastic Si deposition (SiO₂) interfering with effector (eff) release, translocation to the cytoplasm (Cyt), and/or host recognition and effector-receptor (e.g. receptor-like kinase (RK)) interactions (Rasoolizadeh *et al.*, 2018). Susceptibility in –Si conditions will correspond to effectors effectively blocking plant defense responses (DR). Micrographs under –Si and +Si panels demonstrate healthy and collapsed HB,

important to correctly understand the mechanistic underpinnings of its biological role in plants.

As detailed in this review, there are many intricacies inherent to the properties of Si and, as such, a generic acceptance of the multitude of mechanistic proposals applied to plants can only lead to confusion, unfounded expectations and negative results. First and foremost, it is important to recognize that plants differ widely in their ability to take up Si from the external environment and, concomitantly, differ widely in the benefits they derive from Si. The classification of plants on the basis of Si accumulation in the field can often lead to false conclusions, as soil properties, plant-available Si and plant development can greatly influence phenotypes. The precise description of the functional elements of Si transporters has made it possible to rely on molecular tools to classify plants as accumulators and non-accumulators, and, as genomic data become routinely available, they should be exploited to precisely categorize plants on the basis of the presence of functional Si transporters.

The preponderance of the scientific evidence is in favor of the argument that the nutritional role of Si is rather a proxy of stress alleviation, and suggests, at the very least, restraint when linking Si and nutrition. On the other hand, the benefits of Si under conditions of stress appear to be unanimously accepted. Biotic stresses have been particularly well documented in the case of fungal pathogens that possess a biotrophic phase, as well as with some insects. The fact that there is a level of specificity with respect to the parasites controlled by Si also supports arguments for a simple mode of action. In terms of abiotic stresses, the list of Si-induced protections grows continuously, which has prompted a proliferation of possible biochemical roles for Si. However, most of the roles appear to be associated with a prevention of the deregulation inherent to the stress itself, i.e. are indirect, rather than direct, effects. Given that crops in agricultural practice will always grow under some form of stress, the debate on whether the effects of Si are limited to stressed conditions may, of course, ultimately be moot, and it may well be that future recommendations to agronomists will include Si applications to fields that are deficient in the element (Liang Y et al., 2015), in particular with a view to the rapid pace of global climate change and the increased incidence of inclement and extreme weather events (Lobell et al., 2011; Cai et al., 2014; Myers et al., 2014).

Taken together, we propose a unifying model, termed the apoplastic obstruction hypothesis, by which Si can exert its

multitude of beneficial effects (Fig. 5). Through this model, our aim is to stimulate critical thinking and positive advances towards a better understanding of Si properties. Recent advances have contributed to elevate Si to the status of beneficial substance, and our hope is that continued efforts will guide research in the direction of mechanistic elucidation and biotechnological advancements for an optimal exploitation of Si in agricultural practice.

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Supporting Information

Additional Supporting Information may be found online in the Supporting Information section at the end of the article.

Table S1 Detailed list of studies reported in Table 2

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