Aluminium–silicon interactions in higher plants: an update

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Abstract

Aluminium (Al) and silicon (Si) are abundant in soils, but their availability for plant uptake is limited by low solubility. However, Al toxicity is a major problem in naturally occurring acid soils and in soils affected by acidic precipitation. When, in 1995, we reviewed this topic for the Journal of Experimental Botany, it was clear that under certain circumstances soluble Si could ameliorate the toxic effects of Al, an effect mirrored in organisms beyond the plant kingdom. In the 25 years since our review, it has become evident that the amelioration phenomenon occurs in the root apoplast, with the formation of hydroxyaluminosilicates being part of the mechanism. A much better knowledge of the molecular basis for Si and Al uptake by plants and of Al toxicity mechanisms has been developed. However, relating this work to amelioration by Si is at an early stage. It is now clear that co-deposition of Al and Si in phytoliths is a fairly common phenomenon in the plant kingdom, and this may be important in detoxification of Al. Relatively little work on Al–Si interactions in field situations has been done in the last 25 years, and this is a key area for future development.

Keywords: Aluminium toxicity, co-deposition, hydroxyaluminosilicates, silicon, phytolith, X-ray microanalysis.

Introduction

Silicon (Si) is, at 27.7%, the second most abundant element after oxygen in the Earth’s crust, whilst aluminium (Al) is the third most abundant at 8.2% (Exley, 1998). In many soils, aluminosilicates form a very significant component of the solid mineral matter. However, both Si and Al have relatively low solubility, with Si at around a maximum of 2000 µmol l−1, and the solubility of Al is highly affected by pH. The uptake of both is dependent on molecular form. Uptake of Si is as Si(OH)4 in aqueous solution (Raven, 1983; Epstein, 1994). It is understood to travel through the plant as Si(OH)4 in the transpiration flow and until deposited (usually as SiO2: Casey et al., 2003; Mitani et al., 2005; Ma and Yamaji, 2015; Coskun et al., 2019). Silica is deposited in the lumen, cell wall, and intercellular spaces, and the deposits are known as phytoliths. Al uptake is strongly pH dependent and is predominantly as Al3+ which is only available below pH 4.5 (Marion et al., 1976).

There is a wide variation in the extent to which different species take up Si. It has been suggested that Si accumulators should be defined as those species whose Si content is >1.0% and where the Si/Ca ratio is >1.0 (Ma and Takahashi, 2002). Hodson et al. (2005) conducted a meta-analysis of data for Si content in leaves and non-woody material in 735 species. The horsetails and non-vascular plant species accumulated more Si than the ferns, gymnosperms, and angiosperms. Within the angiosperms, dicots tended to be low Si accumulators, while the commelinid monocot orders Poales (including the cereals and grasses) and Arecales accumulated substantially more Si than other monocots. In the heavy accumulators, some tissues

Abbreviations. ABC, ATP-binding cassette; HAS, hydroxyaluminosilicate; NIPIII, Nodulin 26-like intrinsic protein 3-1; REE, rare Earth element; VB, vascular bundle.

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and organs (e.g. the inflorescence bracts of the grasses) accumulate Si to very high levels. For most plants, Si is usually seen as a beneficial element, rather than essential, but it has important roles in defence against pathogens and grazers, and in decreasing abiotic stresses.

As with Si, there is a wide range of uptake of Al. For most plants, Al is toxic, and it is an important factor in acid soils around the world, where it often seriously limits plant growth. In most plants, it is excluded from the root (for a recent review, see Bojorquez-Quninal et al., 2017). There are also a small number of Al accumulators, for which Al is beneficial (e.g. tea, Camellia sinensis; Matsumoto et al., 1976). The exclusion of Al from the root is most frequently achieved by the secretion of organic acids through transporters induced in the presence of Al. The Al accumulator species transport Al to the shoot, where it is chelated, often with organic acids (Ma et al., 1997a, b).

We last reviewed this topic 25 years ago (Hodson and Evans, 1995), and it seems timely to bring it up to date now. Considerable progress has been made during this time. We have a much better knowledge of the solution chemistry underlying Al–Si interactions, and of the mechanism whereby Al toxicity is ameliorated in root systems. We now have a good understanding of the molecular basis of Al and Si transport, and of co-deposition within the plant. In this review we will consider first the state of knowledge of the field when we last reviewed it in 1995, and then the advances made in the study of Al–Si interactions and evidence for molecular mechanisms. Finally we will re-evaluate the significance of this for agriculture and understanding of plant responses to Al in soils.

What was known in 1995

When we reviewed the topic in 1995, the amelioration of Al toxicity by Si had already been investigated in eight species, all in hydroponic solutions. Of these, half of the investigations (for rice, wheat, cotton, and pea) showed little or no amelioration, while the other half (for sorghum, barley, teosinte, and soybean) showed a marked effect. At the time it was unclear why this was the case, and there seemed to be both plant species effects and solution effects. It was highly uncertain whether amelioration effects were to be found entirely in bulk solutions, within the plants, or a combination of the two.

In 1995 it was very well known that Al was more available for plant uptake, and more toxic, at low pH. It was not then clear, however, that pH also affected the interactions between Al and Si in solution, impacting plant growth. At that time, Baylis et al. (1994) had only recently published their work on amelioration of Al toxicity by Si in soybean. They showed that higher concentrations of Si were required for amelioration at lower pH, and concluded that, ‘These results support the hypothesis that the pH–dependent affinity of Si for Al in dilute solutions, and the consequent formation of sub-colloidal inert hydroxyluminosilicate species, is the basis for the alleviation of Al toxicity by Si.’ Although we were aware that pH had an effect on hydroxyluminosilicate (HAS) formation, it was only after this work (Baylis et al., 1994) that plant scientists began to investigate the phenomenon. Birchall, Exley, and their colleagues had already investigated the chemistry of Al–Si interactions in solution, and particularly the formation of HAS (Exley and Birchall, 1992, 1993). HAS formation involved the inhibition of aluminium hydroxide nucleation. This resulted from silicic acid exchanging with hydroxylated Al at growth sites on the lattices of aluminium hydroxide. The effect depended on solution pH and the concentration of silicic acid.

It was already clear that there were several distinct groups of plants with respect to Al–Si interactions (Hodson and Evans, 1995). The grasses and cereals transported large amounts of Si to the shoot (see ‘Si transport mechanisms’ below), but mostly prevented Al transport beyond the root. Thus, most of the interest in Al– Si interactions in these species was focused on the roots. Most of the dicots excluded both elements from the shoots, and there was already some evidence (Baylis et al., 1994) that Si could ameliorate Al toxicity under some conditions in these plants. It seemed that the conifers could transport moderate amounts of both Al and Si to the shoot. The first microanalytical study that demonstrated Al–Si co-deposition in conifer needles was that of Godde et al. (1988). They investigated spruce that was suffering from dieback in Germany, and found that Al and Si were co-located in the transfusion tissue of the needles. By 1995 it was already evident that there was no relationship between the uptake of Si and tolerance to Al, and that a variety of mechanisms and processes were involved.

After 1995 we chose to work on Al–Si interactions in the cereals and the conifers. Both are economically important groups, and they appeared to cope with Al toxicity, and to use Si in amelioration of the toxicity, in somewhat different ways. Other scientists joined us in these investigations, and yet others continued the work on Al hyperaccumulators. Progress since 1995 has focused on three main areas: the amelioration of Al toxicity by Si in root systems; Al and Si transport at the cellular level; and the co-deposition of Al and Si in phytoliths.

The amelioration of Al toxicity by Si in root systems

Since our 1995 paper there have been many reports of Al toxicity being ameliorated by Si (e.g. Hammond et al., 1995; Corrales et al., 1997; Hara et al., 1999; Liang et al., 2001; Singh et al., 2011; Pontigo et al., 2017) and we will not catalogue these in detail here. Rather we will highlight work that elucidates the mechanism(s) behind the amelioration effect.

The crucial effect of pH

It was soon found that even relatively small changes in solution pH can have a very marked effect on amelioration of Al toxicity by Si. Cocker et al. (1997), working on wheat, observed amelioration at pH 4.6, but not at 4.2 (with 100 µmol l⁻¹ Al
and 2000 µmol l\(^{-1}\) Si. Similarly, Ryder et al. (2003) found that Si (1000 µmol l\(^{-1}\) or 2000 µmol l\(^{-1}\)) did not ameliorate toxic effects of Al (with 100 µmol l\(^{-1}\)) on root growth of spruce at pH 4.00, 4.25, and 4.50, while apparently complete amelioration was found at pH 4.75 and 5.00. It became obvious that the early papers that reported no amelioration by Si were almost certainly using a solution pH that was too low for the effect to be observed. The importance of pH change of culture solutions during plant growth experiments was also recognized, with later work mostly being carried out in highly controlled flowing culture systems.

Solution chemistry

It is now recognized that the chemistry of the interaction between Al and Si in solution is complex, and more complex than we had thought 25 years ago. Computer modelling of speciation has helped, and the constants used have been continually improved. Ryder et al. (2003) used an equilibrium speciation model (EQ3NR) to predict the behaviour of Al and Si in growth solutions over the pH range 4.0–5.0. As might be expected, addition of Si (1000 µmol l\(^{-1}\) to Al (100 µmol l\(^{-1}\)) solutions caused a decrease in Al\(^{3+}\). At pH 4.00, Al\(^{3+}\) decreased from 92.4% to 83.3%, and at pH 5.00 the fall was from 54.6% to 17.7%. The decline in Al\(^{3+}\) was considered to be due to the formation of HAS species. One of the complexities in using such equilibrium speciation models is that they assume that solutions have come to equilibrium, and this may not always be the case. The most detailed recent explanation of the formation of HAS was provided by Beardsmore et al. (2016). The authors used computational chemistry to recognize and describe the significant reaction steps. Density-functional theory combined with solvent continuum models were used to confirm that the reactants were an aluminium hydroxide dimer and silicic acid. The reaction products were two HAS species, HAS\(_A\) and HAS\(_B\). According to Beardsmore et al. (2016), HAS\(_A\) dominates in solutions where the concentration of Si(OH)\(_4\) is less than or equal to the total Al. However, HAS\(_B\) is dominant when the concentration of Si(OH)\(_4\) is at least double that of Al. This means that we would expect HAS\(_B\) to be the dominant species in almost all of the experiments conducted on plants, as in nearly all cases Si exceeds Al by a factor of 10. HAS\(_A\) and HAS\(_B\) are then precursors of much more insoluble HAS species.

A solution effect or in planta?

It is now certain that at least some of the ameliorative effects of Si on Al toxicity occur in solution, with the formation of non-toxic HAS species. However, evidence has accumulated since 1995 that part of the amelioration occurs within the plant (‘in planta’). Later we will consider cases where Al is co-deposited with Si as a solid, decreasing the availability of Al within the plant. Here we will only look at situations where there is no obvious co-deposition, mostly concerning experimental work on root systems.

Corrales et al. (1997), working on maize, showed that pretreatment of roots with 1000 µmol l\(^{-1}\) Si markedly increased growth of plants that were then exposed to Al (using a range of concentrations up to 100 µmol l\(^{-1}\)). Obviously, this effect could not be due to HAS formation in the bulk solutions as Al and Si were not present in the solutions at the same time. The authors showed that the presence of Si decreased the uptake of Al into the root, and suggested that this was the reason for the better growth in the plants pre-treated with Si. A second example where solution effects could be ruled out was provided by the work of Cocker et al. (1998a) who studied the Al-ultrasensitive wheat cultivar, Scout 66. A low concentration of 1.5 µmol l\(^{-1}\) Al inhibited the root growth, but amelioration was observed with only 5 µmol l\(^{-1}\) Si. These low concentrations of Al and Si are well below those where the formation of HAS species has been observed. Again this is highly suggestive that in this case in planta effects are involved.

Cocker et al. (1998a) also worked on the Atlas 66 cultivar of wheat, where Al-induced malate exudation from roots was already known to be involved in Al tolerance. It was found that 2000 µmol l\(^{-1}\) Si ameliorated the toxicity of Al (100 µmol l\(^{-1}\)) in this cultivar at pH 4.6. Under these conditions, malate exudation was very similar to that found in plants treated with just 100 µmol l\(^{-1}\) Al. However, addition of citrate, a well-known chelator of Al, decreased malate exudation at 5–40 µmol l\(^{-1}\) and completely inhibited it at 100 µmol l\(^{-1}\). These findings strongly indicate that the formation of HAS in the bulk solution was not the reason for the amelioration of Al toxicity, and that this must take place in planta. We were then able to put together all of the available data and to form a hypothesis that the root cell walls were the main sites of Al detoxification, and that HAS species or aluminosilicates formed there as the primary mechanism (Cocker et al., 1998b). A number of factors were believed to be responsible: high apoplastic pH; organic substances such as malate; and local concentrations of Al and Si on or within the cell wall.

The most detailed investigation of the amelioration phenomenon published so far was that of Wang et al. (2004), and this provided further confirmation of the role of HAS formation in the root cell wall. They worked on an Al-sensitive maize cultivar, Lixis, using short exposure times (25 µmol l\(^{-1}\) Al with or without 1400 µmol l\(^{-1}\) Si). Monomeric Al concentrations were not reduced by Si, implying that there were no interactions in the bulk solutions, and yet significant amelioration was observed. Greater than 85% of Al was bound within the cell wall in 1 cm root apices. Al content of root apices, which were treated with Si, were no different from those with no treatment for the apoplastic sap, the symplastic sap, and the cell wall. Confirming the results of Cocker et al. (1998a), Si had no effect on exudation of organic acids and phenols that were induced by Al treatment. The major effect of Al treatment was to increase accumulation of Si in the cell wall fraction. This decreased mobility of Al in the apoplast, and appeared to be the reason for the amelioration effects.

Additional evidence that HAS formation in the root cell wall was involved in the amelioration of Al toxicity was provided by Kopittke et al. (2017). These authors used low energy X-ray fluorescence (LEXRF) to examine Al and Si distribution in the sorghum root apex. They found that Al and Si were co-localized in the mucigel and outer apoplast of the root.
It seems clear that the hypothesis that we (Cocker et al., 1998b) proposed has been confirmed by further work over nearly 20 years. In planta co-deposition of Al with Si and the formation of HAS within the root apoplast does appear to be the mechanism behind amelioration. Very recently, Coskun et al. (2019) proposed their ‘apoplastic obstruction hypothesis’, suggesting that Si in the apoplast is involved in the reduction of a wide range of abiotic and biotic stresses. Although they did not consider the topic in detail, it does appear that work on the amelioration of Al toxicity by Si in plants fits reasonably well with their ideas.

Al and Si transport at the cellular level

One of the greatest advances since our previous review has been in the identification and characterization of transporters for Si and Al at the molecular level. The presence of membrane proteins (usually modified water channels, aquaporins) facilitates uptake and transport. Exley and Guerriero (2019) suggest these are channels, rather than active transporters (though there is a suggestion that at least one Si transporter is a proton-linked antiporter; Ma et al., 2007; Coskun et al., 2019; see below). They therefore suggest that directionality of transport is due to the concentration gradients of soluble Si(OH)₄ created by water flow and the removal of Si from solution, usually as SiO₂. As different species take up Si to different extents (see above), it would be expected that uptake would correlate with the presence and activity of transporters. Bélanger et al. (2016) demonstrated that Si uptake was dependent on root stock rather than transpiration rates in a soybean grafting experiment, suggesting that the characteristics of root cells were more important than the transpiration rate. Exley (2015) also noted the significance of guttation—the active exudation of aqueous solutes—which may include Si(OH)₄ from the plant surface in some circumstances, though this may be considered as a variant of passive movement in the water flow.

Si transport mechanisms

Si transporters to date have been characterized as influx and efflux carriers suggested to provide directional transport to regions of high accumulation. First to be identified (Ma et al., 2006) was an Si influx protein, named Lsi1 (for low silicon protein 1, due to its absence in a low Si-accumulating rice), an aquaporin. Lsi1 is localized to the distal side of endodermal and exodermal cells of the root. This was followed by identification of an Si efflux protein, Lsi2 (Ma et al., 2007), located in the root exodermis and endodermis, but, in contrast to Lsi1, on the proximal side of these two layers. Ma et al. (2007) therefore suggested that movement of Si in rice is through a transport pathway traversing the endodermis and exodermis, to the xylem and the shoot. In silico modelling reveals that their location at the endodermis and exodermis coupled with the presence of the impermeable Casparian strip is required for effective movement of Si to the shoot (Skurai et al., 2015).

Lsi1 is a member of the membrane intrinsic [MIP (major intrinsic protein) and NIPIII (Nodulin 26-like intrinsic protein 3-1)] family of aquaporins. Specificity for Si is achieved by an hourglass–like configuration of the protein, with six transmembrane domains and two half helices projecting into a central pore. This constriction, with two NPA (asparagine, proline, and alanine) domains is close to a second constriction, the selectivity filter, which determines specificity for Si. The key amino acids for Si are glycine–serine–glycine–arginine (GSGR; Hove and Bhave, 2011). The spacing of the two NPA domains is important for transport, as this renders the pore permeable to Si(OH)₄; high Si accumulators have a 108 amino acid separation (Deshmukh et al., 2015). Lsi1 also transports methylated arsenic species (Li et al., 2009). Lsi2 resembles a bacterial arsenite transporter and is thought to be an Si(OH)₄/H⁺ antipporter, though direct evidence for this is lacking (Ma et al., 2007; Coskun et al., 2019). It belongs to the arsenite–antimonite (ArsB) efflux (TC 2.A.45) family. Si transport activity was demonstrated using Xenopus oocytes pre-loaded with Si, which showed Si efflux activity (Ma et al., 2007). Pommerrenig et al. (2020) have recently provided evidence that the NIP family of transporters originated from bacterial arsenic efflux channels through a horizontal gene transfer followed by evolution to higher plant Si and boron transporters.

The tissue location of Si transport proteins has been shown to be important for movement to different areas of the shoot and contributes to areas of high accumulation (Yamaji et al., 2015). Rice accumulates >10% Si (dry weight basis) in the husk, which protects the grain from biotic and abiotic stress. In addition to Lsi1 and Lsi2, Lsi6 is a plasma membrane-localized Si transporter expressed in roots and shoots, and is located at nodes involved in Si distribution from xylem to leaf tissue (Yamaji et al., 2008). In these and subsequent experiments, Yamaji et al. (2015) observed that Lsi2 is polarly localized under bundle sheath cells around enlarged vascular bundles (VBs). Lsi6 is localized in a xylem transfer cell layer adjacent to this; Lsi3 is in the parenchyma between VBs. Knockout of these two reduces Si in panicles and increases it in the flag leaf. Yamaji et al. (2015) modelled this to show that an apoplastic barrier at the bundle sheath and development of the enlarged VBs in the node are needed for Si hyperaccumulation in the husk.

While rice Si transport is the best studied system, Si transporters have been identified in a number of other species based on sequence homology and, in some instances, function. These are summarized in Table 1. They include Si influx transporters in wheat, Tritium aestivum, TaLsi1 (Montpetit et al., 2012); barley, HvLsi1 (Chiba et al., 2009; Mitani et al., 2009), and Si influx and efflux channels in cucumber, CmLsi1 and CmLsi3 (Mitani et al., 2011); maize, NIP2-1 and ZmLsi2 (Mitani et al., 2009), perennial ryegrass, Lolium perenne, Lsi1 and Lsi2; (Pontigo et al., 2017), and a barley homologue of Lsi6 involved in Si distribution, HvSi6 (Yamaji et al., 2012). Channels predicted to allow Si movement have also been identified in castor bean, wild soybean, mung bean, date palm, red clover, pearl millet, sorghum, grape vine, and barley medic (see Supplementary Table S1 at JXB online). While maize and barley show similar Si transporters to rice, the work of Mitani et al. (2009) suggests a different transport mechanism, as the Lsi2 homologue is
Horsetails are primitive plants with a very high Si content (Hodson et al., 2005), that require Si to complete their life cycle (Chen and Lewin, 1969; Miyake and Takahashi, 1976) and provide evidence of a distinct family of Si transporters (Grégoire et al., 2012). These are members of the NIP2 subfamily and, in place of the GSGR Ar/R filter, possess a STAR (serine–threonine–alanine–arginine) filter predicted to have a pore large enough to permit passage of silicic acid (Grégoire et al., 2012). Three horsetail transporter subgroups were identified, and EaNIP3;1, EaNIP3;3, and EaNIP3;4 are all efficient Si transporters in the Xenopus oocyte system and showed strong expression in roots. When EaNIP3;1 was expressed in Arabidopsis, it resulted in accumulation of Si in Arabidopsis shoots. A study of date palm (Bokor et al., 2019) resulted in characterization of an aquaporin Si transporter, also possessing the GSGR Ar/R selectivity filter, PdNIP2-1. Si transport was demonstrated using Xenopus oocytes.

Table 1. Plant Si transporters in plant membranes with supporting references (Uniprot Consortium, 2019)

| Entry   | Protein names                  | Gene names                  | Organism          | Length | Reference          |
|---------|--------------------------------|-----------------------------|-------------------|--------|--------------------|
| Q62T3   | Aquaporin NIP2-1 (Low silicon protein) | NIP2-1 LS1 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 298    | Ma et al. (2006)   |
| Q10S9Y  | Aquaporin NIP2-2 (Low silicon protein) | NIP2-2 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 472    | Ma et al. (2007)   |
| Q67WJ8  | Aquaporin NIP2-6 (Low silicon protein) | NIP2-6 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 298    | Yamaji et al. (2008) |
| Q9AV23  | Aquaporin NIP2-3 (Low silicon protein) | NIP2-3 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 485    | Yamaji et al. (2015) |
| G0WXH5  | Silicon transporter protein    | TaLS1 Triticum aestivum (wheat) | Hordeum vulgare (barley) | 295    | Montpetit et al. (2012) |
| B9X078  | Aquaporin NIP2-2 (Low silicon protein) | NIP2-2 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 295    | Chiba et al. (2009) |
| Q19KC1  | Aquaporin NIP2-1 (Low silicon protein) | NIP2-1 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 295    | Mitani et al. (2009) |
| C6KYS1  | Silicon transporter protein    | HvLSi6 Hordeum vulgare (barley) | Hordeum vulgare (barley) | 300    | Yamaji et al. (2012) |
| F1SX51  | Aquaporin NIP2-1 (Low silicon protein) | NIP2-1 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 295    | Mitani et al. (2011) |
| C7G3B4  | Aquaporin NIP2-1 (Low silicon protein) | NIP2-1 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 295    | Mitani et al. (2009) |
| F1SX50  | Aquaporin NIP2-1 (Low silicon protein) | NIP2-1 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 295    | Mitani et al. (2011) |
| I4IY30  | Aquaporin NIP2-1 (Low silicon protein) | NIP2-1 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 295    | Mitani et al. (2011) |
| I4IY32  | Aquaporin NIP2-1 (Low silicon protein) | NIP2-1 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 295    | Mitani et al. (2011) |
| I4IY33  | Aquaporin NIP2-1 (Low silicon protein) | NIP2-1 LS12 SIT1 Oryza sativa subsp. japonica (rice) | Oryza sativa subsp. japonica (rice) | 295    | Mitani et al. (2011) |
| XP_008802606 | Aquaporin silicon transporter | PdNIP2-1 Phoenix dactylifera (date palm) | Phoenix dactylifera (date palm) | 290    | Bokor et al. (2019) |
| XP_004240725.1 | Si influx transporter (active) | SIIS2-L1 Solanum esculentum (tomato) | Solanum esculentum (tomato) | 528    | Sun et al. (2019) |
| XP_010317628.1 | Si efflux transporter (inactive) | SIIS2-L2 Solanum esculentum (tomato) | Solanum esculentum (tomato) | 516    | Sun et al. (2019) |

See Supplementary Table S1 for a full list including putative Si transporters identified from genome database annotation.

located at the endodermis but immunostaining does not reveal the polarity exhibited by Ls1 and Ls2 in rice. The importance of Ls2 in transport, however, is demonstrated by a correlation between expression levels and Si uptake and its ability to recover uptake in a low Si rice mutant. Studies on the Si influx transporter in two cultivars of pumpkin (Cucurbita sativa), one a high Si accumulator, the other a low accumulator, reveal that a change of one amino acid—Pro242 to lysine—results in loss of Si accumulation and relocation of the transporter from the plasma membrane to the endoplasmic reticulum (Mitani et al., 2011). Sun et al. (2019), in a study of tomato root Si transporters, demonstrate that while there are two Si transporter homologues present (SiLS1, a homologue of the rice Ls1 influx transporter; and SiLS2, a homologue of the rice Ls2 efflux transporter), only SiLS1 is active. They suggest that the absence of active SiLS2 explains the low levels of Si accumulation in this species.
Al transport mechanisms

Al transporters have also been characterized for the first time in plants since we wrote our previous review, though this remains a much less well explored area than Si transporters and much of the progress has been in identifying transporters for compounds such as organic acids induced under Al stress. Table 2 presents a listing of proteins suggested to be Al transporters, together with associated references. Zhang et al. (2019) recently reviewed evidence for Al transporters in plants, and readers are directed to this review for detailed consideration; evidence for Al transport has been associated with plasma membrane and tonoplast proteins and with proteins of the ATP-binding cassette (ABC), aquaporin, and natural resistance-associated macrophage protein (Nramp) families. These include ABC partial homologues AtALS3 and AtSTAR1 in Arabidopsis with homologues OsSTAR1 and OsSTAR2 in rice (Larsen et al., 2005, 2007; Huang et al., 2009, 2012). AtALS3 encodes a single domain homologous to a bacterial ABC protein, while the two rice proteins contain the nucleotide-binding domain (OsSTAR1) and transmembrane domain (OsSTAR2) also of a bacterial-type ABC transporter (Huang et al., 2009). However, when co-expressed in the oocyte transport assay system, OsSTAR1 and OsSTAR2 form a functional UDP-glucose transporter. The transporter Nrat1 (Nramp-natural resistance-associated macrophage protein aluminium transporter 1) was described by Xia et al. (2010) in rice and provided evidence that Nrat1 is specific for trivalent Al, localized to the plasma membrane of root tip cells other than the epidermis, and has a role in detoxifying Al in the vacuole; Nrat1 knockouts have enhanced Al sensitivity and increased cell wall Al. Providing evidence for aquaporin family transporters, Negishi et al. (2012, 2013) explored Al transport in the Al hyperaccumulator hydrangea where they identified both plasma membrane (PALT1) and tonoplast (VALT) Al transporters in the sepal. Both PALT1 and VALT are members of the aquaporin family. Expression in arabidopsis confers Al sensitivity (PALT) and tolerance (VALT), suggesting they are part of a pathway of Al detoxification in the vacuole.

The exclusion of Al from the root is most frequently achieved by the secretion of organic acids through transporters induced in the presence of Al. Two families of transporters have been identified, designated MATEs (multidrug and toxic compound extrusion) and ALMTs (aluminium-activated malate transporters) (Bojorquez-Quininal et al., 2017; Yang et al., 2019; Zhang et al., 2019). As well as preventing Al uptake, other species transport Al to the shoot, where it is chelated. In high Al accumulators, such as hydrangea, buckwheat, and tea (Ma et al., 1997a; Carr et al., 2003; Shen et al., 2004), chelation by small organic compounds is key to detoxification; in buckwheat, this is oxalate, with Al-citrates being the mobile form in the xylem (Ma et al., 1997b; Shen et al., 2004). In hydrangea sepal, the chelator is delphinidin 3-glucoside and is 3-cafeoylquinic and citrate in the leaves (Ma et al., 1997a). The chelator in tea has been shown to be catechin (Nagata et al., 1992).

Table 2. Putative aluminium transporters with supporting publications listed (UniProt Consortium, 2019)

| Entry     | Entry name       | Protein names                                           | Gene names                                      | Organism                                      | Length | Reference         |
|-----------|------------------|---------------------------------------------------------|------------------------------------------------|-----------------------------------------------|--------|-------------------|
| Q92UT3    | ALS3_ARATH       | Protein ALUMINUM SENSITIVE 3 ABC family member, but lacking ATP binding cassette. | ALS3 ABC16, At2g37330, F3G5.12                 | Arabidopsis thaliana (mouse-ear cress)       | 273    | Larsen et al. (2005) |
| K02Y9     | K02Y9_HYDMC      | Plasma membrane aluminium transporter Aquaporin family | PALT1                                           | Hydrangea macrophylla (bigleaf hydrangea) (Viburnum macrophyllum) | 304    | Negishi et al. (2012) |
| Q0WML0    | AB27B_ARATH      | ABC transporter B family member                          | ABCB27 ALS1, TAP2, At1g39040, MXF12.50        | Arabidopsis thaliana (mouse-ear cress)       | 644    | Larsen et al. (2007) |
| Q9FNU2    | AB25B_ORYSJ      | ABC transporter B family member                          | ABCB25 ALS1, Os03g0755100, LOC_Os03g54790, OSJNBb0081K01.19 | Oryza sativa subsp. japonica (rice)          | 641    | Verrier et al. (2008) |
| K09T1     | K09T1_HYDMC      | Vacuolar aluminium transporter Aquaporin family         | VALT                                            | Hydrangea macrophylla (bigleaf hydrangea) (Viburnum macrophyllum) | 252    | Negishi et al. (2012) |
| Q0D9V6    | STAR1_ORYSJ      | Protein STAR1 Partial ABC transporter; when expressed with STAR2 transports UDP glucose. | STAR1 ABC12, ALS1, Os06g0695800, LOC_Os06g48060, P0622F03.26 | Oryza sativa subsp. japonica (rice)          | 346    | Huang et al. (2009) |
| Q5W7C1    | STAR2_ORYSJ      | UFP0014 membrane protein STAR2 partial ABC transporter | STAR2 Os05g0119000, LOC_Os05g02750, P0496H07.22 | Oryza sativa subsp. japonica (rice)          | 285    | Huang et al. (2009) |
| Q62G85    | NRAT1_ORYSJ      | Metal transporter NRAT1                                  | NRAT1 Os02g0131800, LOC_Os02g03900, OJ1007.D04.24, Oa1_05257 | Oryza sativa subsp. japonica (rice)          | 545    | Xia et al. (2010)  |
and Lsi1 and Lsi2 genes were both down-regulated in roots in the presence of Al and Si, applied singly. However, application of Si to Al-treated plants resulted in an up-regulation of both transporter genes. The authors suggest that this is indicative of an increased Si requirement by the tissue in Al toxicity. Bhat et al. (2019) have recently reviewed the importance of Si in ameliorating heavy metal toxicity. In rice, down-regulation of heavy metal transporter genes (OsHMA2 and OsHMA3), and up-regulation of Si transporter genes (OsLSi1 and OsLSi2) has been observed with Si supplementation (Kim et al., 2014). Similarly, the enhanced expression of phytochelatin synthase 1 (PGS1) and decreased expression of the metallothionein gene (MT1a) was associated with Si supplementation in Arabidopsis under copper stress (Khandekar and Leisner, 2011). Likewise, Si up-regulates OsLSi1 and down-regulates the cadmium (Cd) transporter Nramp5 in Cd stress (Ma et al., 2015). While results like these for heavy metals may shed some light on the role of transporters in amelioration, it is clear additional data are needed before their role is fully understood.

Co-deposition of aluminium and silicon

We have seen that the formation of HAS in the root apoplast appears to be part of the mechanism whereby Al toxicity is ameliorated by Si. However, as Beardmore et al. (2016) point out, HASA and HASB are precursors of much more insoluble HAS species. It would therefore seem quite likely that we would find solid deposits containing both Al and Si in plants. When we wrote our previous review of this topic (Hodson and Evans, 1995), relatively little was known about the co-deposition of Al and Si in plants. We considered two methodologies for studying this: chemical analysis and microanalysis. There has been less work since that time using chemical analysis, as the difficulties in obtaining samples of phytoliths that were not contaminated with minerals from non-mineralized plant tissue have become apparent. For example, Kameník et al. (2013) used three different extraction methodologies to isolate phytoliths from barley: acid digestion, dry ashing, and acid digestion followed by incineration. They did not recommend just using acid digestion as it left organic matter in the phytoliths, but even the other two methods gave somewhat different results. In all cases, terrigenous elements, including Al, were enriched in the phytoliths compared with the plant material. For the rest of this discussion, we will only consider microanalytical work. In 1995 we could only locate five microanalytical investigations that had concerned this topic. We now have a much better understanding of the scale of Al and Si co-deposition, although it is still far from clear how significant this is in the amelioration of Al toxicity. We will now assess the progress that has been made in this area under four headings: roots; conifers; broad-leaved woody plants (including Al accumulators); and others.

Roots

As we have seen, the grasses and cereals seem to largely exclude Al from their shoots, and so we would expect most of the interest in Al–Si interactions in these species to be in the roots. That does appear to be the case (Cocker et al., 1998b), but these interactions seem mostly to involve soluble HAS complexes, and there have only been two cases where Al and Si co-deposition has been observed. In both sorghum (Hodson and Sangster, 1993) and wheat (Cocker et al., 1997) plants grown in hydroponic culture, deposits containing Al and Si were located in the root epidermal cell walls. The authors speculated that this co-deposition may prevent some Al from penetrating further into the root cortex. As we noted above, Kopittke et al. (2017) used LEXRF and found that Al and Si were co-localized in the mucigel and outer apoplast in the sorghum root apex, a similar location to that observed by Hodson and Sangster (1993) for the same species. LEXRF is a more sensitive technique than X-ray microanalysis, and it is possible that it was detecting more soluble HAS in addition to deposited material.

Until recently, the only example of Al and Si co-deposition in roots that we are aware of outside the grasses was from Norway spruce (Hodson and Wilkins, 1991) where the phenomenon was observed in the cortical cell walls. One slightly unusual example of Al and Si co-deposition comes from the work of Feng et al. (2019) working on the root border cells of pea. They were able to produce an extracellular silica nanocoat formed by layer-by-layer self-assembly on the surface of these cells. When they were then treated with Al, the coating adsorbed Al on its surface preventing it from penetrating into the cells, and thereby decreasing toxicity. The authors suggested that this approach might be used to solve the global Al toxicity problem, but we suspect that much more research will be needed before it can be applied in field situations.

Conifer needles

Carnelli et al. (2002) included five conifers in their study of Al in the phytoliths isolated from plants growing in the Valaisan Swiss Alps. All of the phytoliths from wood contained Al, and the element was also detected in the needles of three species (Juniperus nana, Pinus cembra, and Pinus mugo). Phytoliths containing Al were also common in woody dicots, but very rarely in grasses and other monocots. These findings led the authors to suggest that Al and Si co-deposition in phytoliths could be used as a marker for woody species in palaeoecological investigations.

Following our review in 1995, one of us (MJH) was involved in a whole series of studies investigating mineral localization in the needles of conifers. The species investigated were: white spruce (Hodson and Sangster, 1998); balsam fir (Hodson and Sangster, 1999); American larch and European larch (Sangster et al., 2001); white pine (Hodson and Sangster, 1999, 2000, 2002); Douglas fir (Sangster et al., 2007); and Eastern hemlock (Sangster et al., 2009). These studies gave us a much better idea of the extent of Al and Si co-deposition, its locations, and the environmental factors that affect it. The co-deposition of Al and Si occurred in all the species investigated, but the phenomenon was more pronounced in white pine, Eastern hemlock, balsam fir, and the larch species, and less so in white spruce and Douglas fir. The major locations for Al and Si co-deposition...
in the needles were the epidermis and the transfusion tissue. Epidermal deposition was most pronounced in white spruce, balsam fir, and the larch species. Al and Si co-deposition in the transfusion tissue was noted particularly towards the tips of the needles in white pine and Eastern hemlock. It was also evident from these investigations that Al and Si co-deposition was only found when the plants were growing in acidic soils. This was most clearly shown in white pine (Table 3) where both Al and Si accumulate in the transfusion tissue near the tips of the needles, but more of both elements are present in soils with a pH below 4.2. It appears that the idea of Carnelli et al. (2002) that Al in phytoliths could be used as a marker for woody species is only likely to work if all of the plants are growing on acidic soils with reasonable Al availability.

Broad-leaved woody plants

As we saw above, Carnelli et al. (2002) included seven woody shrub species in their study of Al and Si co-deposition in phytoliths from plants growing in the Swiss Alps. In all cases, Al was detected in phytoliths from leaves and wood. Turnau et al. (2007) conducted a detailed investigation of metal uptake in Erica andevalensis growing on a highly acidic pyrite mine in southeastern Portugal. Using microanalysis they showed that both iron and Al were co-localized with Si in the epidermis and glandular hairs of the leaves. They also found the elements associated with a fungal root endosymbiont, Hymenoscyphus ericae. The authors suggested that the endosymbiont is involved in restricting the entry of toxic metals into the roots, while co-deposition of Al with Si in the leaf epidermis was seen as a detoxification mechanism.

In our 1995 review, we wrote that, ‘It would appear that heavy Al accumulation and heavy Si accumulation are mutually exclusive.’ This statement has proven to be largely correct, but it does now appear that some Al accumulator species potentially use Si in detoxification. The best example of this phenomenon is the Al accumulator, Faramea marginata (Rubiaceae), which was studied by Britez et al. (2002). This species is not an Si accumulator, and the authors described it as ‘no more than an intermediate or weak Si accumulator’, and it does not form phytoliths. However, Britez et al. presented very persuasive evidence that Al and Si form complexes, probably including HAS, in their shoot tissues. Most Al accumulators use organic ligands and form complexes with Al (see above), and this was thought to be the first example where an inorganic ligand was used for detoxification. So this appears to be a case where Al and Si co-deposition does not occur, but Si is involved in reducing the availability of Al in the shoot. More recently, Malta et al. (2016) investigated Rudbecka viburnoides, another Al accumulator in the Rubiaceae, and using X-ray microanalysis found that Al and Si were co-localized in the roots, stems, and leaves, mostly in the epidermis.

Probably the most famous Al accumulator plant is tea (Camellia sinensis) and, according to Matsumoto et al. (1976), it can accumulate >3% Al in its older leaves. These authors used light microscopy and X-ray microanalysis, and located Al in the epidermal cells, but did not consider Si. It appears that there is some uncertainty with regards to Al and Si co-localization in this species. Whilst Tolrà et al. (2011) reported that the two elements were not co-deposited, Haruyama et al. (2019) found that this occurred in the leaf epidermis. The latter suggested that the reason for the different distributions was possibly due to the conditions under which the plants grew and the ages of the leaves.

Other plants

For completeness, we should also point out that Al and Si co-localization has been observed in species beyond the Angiosperms. Liu et al. (2019) worked on Dicranopteris linearis, a fern which is an Al hyperaccumulator in China. They showed co-deposition of Si with Al and rare Earth elements (REEs). This is the one case we are aware of where a species is both an Al accumulator (up to 9660 mg kg⁻¹) and an Si accumulator (up to 20 300 mg kg⁻¹). Dicranopteris linearis also accumulates high concentrations of REEs (up to 3830 mg kg⁻¹). How this species is capable of doing something that few, if any, others can do is a mystery.

Finally, Pressel et al. (2011) found what they considered was the first example of Al and Si co-localization in the bryophytes. Working on the thalloid liverwort, Mizutania riccardoides, they found that the outer part of the wall consisted of irregular blocks of dense material, containing high concentrations of Al and Si.

What questions remain?

Having assessed 25 years of research on Al–Si interactions in plants what are the topics that still need further research?

In the key area of the amelioration of Al toxicity by Si in the root, it seems that our hypothesis stated in Cocker et al. (1998b) is largely correct, and the formation of HAS within the apoplast is at least a major part of the mechanism. Although

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Table 3. A comparison between microanalysis results from three sites for Al and Si in the transfusion cells of 2-year-old white pine needles

| Needle zone | Al (mmol kg⁻¹) | Si (mmol kg⁻¹) |
|-------------|----------------|----------------|
|             | Glendon pH 6.7* | Muskoka pH 4.2 | Sudbury pH 3.5–4.0 | Glendon pH 6.7 | Muskoka pH 4.2 | Sudbury pH 3.5–4.0 |
| Base        | 9.6            | 12.7           | 14               | 29.2           | 13            | 16.6            |
| Middle      | 13.9           | 30.2           | 11.1             | 13.1           | 19.5          | 25              |
| Tip         | 9.1            | 44.5           | 61.4             | 611            | 5838          | 4282            |

Data from Hodson and Sangster (1999, 2000, 2002).
* Soil pH at 40 cm.
there has been considerable progress in determining the molecular basis for both Al and Si transport, we have only just begun to investigate the effect of Al on Si transport or of Si on Al transport (Pontigo et al., 2017). It will be some time before we can determine how important these processes are in the amelioration effect. Is the in planta amelioration, often observed, solely due to phenomena in the apoplast which prevent Al uptake, or is it more complex than that?

A number of studies have shown that Si has a general effect on plant responses to abiotic stress (for reviews, see Kim et al., 2017; Etesami and Jeong, 2018). Application of Si in-creases stress tolerance by reducing the generation of reactive oxygen species (ROS). These effects were seen for a wide range of abiotic stresses, including the heavy metals Cd (Shi et al., 2010), manganese (Maksimović et al., 2007), and chromium (Tripathi et al., 2015), but evidence for Al/Si is limited. In a study of the effect of Si nanoparticles (SNPs) on Al toxicity in maize growing in an artificial soil system, de Sousa et al. (2019) demonstrated (amongst other effects) that while Al uptake remained the same as in the absence of SNPs, ROS production was reduced, as was oxidative damage. Antioxidant enzymes and metabolites were enhanced in leaves and roots. In a similar way, Dorneles et al. (2019) showed that Si was partially able to ameliorate Al toxicity in two potato genotypes. The authors related this to increased activity of antioxidant enzymes and mitigation of Al-induced damage to membrane lipids.

One of the more disappointing aspects of our review of Al–Si interactions 25 years on is how little research on agricultural systems is recorded in the literature. In fact there have been very few investigations carried out in soil systems. Morikawa and Saigusa (2002) studied the impacts of Si fertilization on Al toxicity in barley plants growing in two andosols soils. They found that addition of silica gel and sodium metasilicate to the soils was ineffective in amelioration of Al toxicity despite the treatments causing an increase in soil Si concentration. Waste porous hydrated calcium silicate did lead to amelioration of Al toxicity but the authors considered that this was probably due to the increase in soil pH. Although the paper by Morikawa and Saigusa has, according to Google Scholar, been cited 31 times (in January 2020), none of the citations refer specifically to further experiments conducted in soil to investigate Al–Si interactions. In the study by de Sousa (2019; see above) on the effect of silicon dioxide nanoparticles on Al toxicity, amelioration but not a reduction in Al accumulation was observed. The overall effect was suggested to result from stimulation of organic exudation in the roots. It may be that the paucity of studies in this area is due to the complexities of the chemistry, particularly in soil. So at present we have definite ameliorative effects in hydroponics, but uncertainty as to whether the findings can be transferred to field situations and under what conditions. The overall beneficial effect of Si on stress and Si soil treatments on pH suggest that this is worth further exploration.

We now know much more about Al and Si co-deposition than we did, particularly in the confiers. However, it is unclear whether this is part of a detoxification mechanism or is just coincidental. Al as Al$^{3+}$ is toxic to plant cells, and precipitation in a solid form should decrease toxicity, but we have no direct experimental evidence that proves this.

**General conclusions**

Our knowledge of Al–Si interactions in plants has markedly increased in the last 25 years. We have determined a mechanism for the amelioration effect in roots that has withstood detailed investigation. This mechanism shows the importance of the apoplast in the amelioration phenomenon. We now have greatly increased knowledge of Al and Si transporters but have yet to ascertain whether these have a role in amelioration. It appears that Al and Si co-deposition is quite common in some plant groups, but its functional significance is not certain. We still have relatively little knowledge concerning the importance of amelioration effects in the field, and hopefully this will be a focus of the next 25 years of research.

**Supplementary data**

Supplementary data are available at JXB online.

Table S1. The plant membrane proteins that have been identified as Si transporters from either publications or genome database annotation.

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