Journal of Experimental Botany, Vol. 76, No. 5 pp. 1370–1389, 2025
https://doi.org/10.1093/jxb/erae261 Advance Access Publication 7 June 2024

REVIEW PAPER

Metalloid transporters in plants: bridging the gap in molecular structure and physiological exaptation

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Received 28 February 2024; Editorial decision 29 May 2024; Accepted 6 June 2024

Editor: Robert Hancock, The James Hutton Institute, UK

Abstract

The rhizosphere contains both essential nutrients and potentially harmful substances for plant growth. Plants, as sessile organisms, must efficiently absorb the necessary nutrients while actively avoiding the uptake of toxic compounds. Metalloids, elements that exhibit properties of both metals and non-metals, can have different effects on plant growth, from being essential and beneficial to being toxic. This toxicity arises due to either the dosage of exposure or the specific elemental type. To utilize or detoxify these elements, plants have developed various transporters regulating their uptake and distribution in plants. Genomic sequence analysis suggests that such transporter families exist throughout the plant kingdom, from chlorophytes to higher plants. These transporters form defined families with related transport preferences. The isoforms within these families have evolved with specialized functions regulated by defined selectivity. Hence, understanding the chemistry of transporters to atomic detail is important to achieve the desired genetic modifications for crop improvement. We outline various adaptations in plant transport systems to deal with metalloids, including their uptake, distribution, detoxification, and homeostasis in plant tissues. Structural parallels are drawn to other nutrient transporter systems to support emerging themes of functional diversity of active sites of transporters, elucidating plant adaptations to utilize and extrude metalloid concentrations. Considering the observed physiological importance of metalloids, this review highlights the shared and disparate features in metalloid transport systems and their corresponding nutrient transporters.

Keywords: AlphaFold, arsenite, boron, crop improvement, homeostasis, metalloid, selenium, silicon, transporter.

Introduction

A plant's dire need to withstand physiological challenges has led to the evolution of several genetic adaptations (Weng *et al.*, 2021; Munns and Millar, 2023). The uptake of metalloids and their assimilation in metabolic pathways is one such example. The incorporation of metalloids in plant metabolism possibly diversified nutritional requirements in competitive environments. Boron (B) uptake, for instance, played an important role in lignified tissue development and consequent evolution of land plants (Lewis, 1980). On the other hand, silicon (Si) provides mechanical strength to plants with preferential

deposition in leaf blades (Zexer *et al.*, 2023). Although the uptake of both B and Si has been correlated with mechanical strength in plants, the specific requirement for these elements varies among evolutionary clades. *Brassicaceae*, for example, exhibit a higher B demand, whereas *Poales* require high Si and relatively lower B. The estimated cost of Si uptake is significantly lower compared with the energy required for lignin biosynthesis, which supports a shift towards Si accumulation in grasses (De Tombeur *et al.*, 2023). This multifaceted impact of metalloids on plant physiology, from structural development to metabolic processes, underscores their role in shaping plant adaptation and survival in diverse ecological niches.

Once in plants, these metalloids exert variable physiological impacts ranging from being essential, to beneficial, to toxic (Bienert *et al.*, 2008a). Environmental factors, particularly the pH and redox state of soil, directly influence metalloid speciation, impacting the predominant forms and subsequent modes of transport into plants. Si, the most abundant metalloid, is available to plants in the polyprotic state, i.e. orthosilicic acid (p*K*a=9.6), at physiological pH (Wei *et al.*, 2019) (Fig. 1). This favoured state of Si is notable in both roots and xylem vessels of plants (Ma *et al.*, 2004). Similarly, the essential micronutrient B exhibits pH-dependent speciation. At pH 7, boric acid [$B(OH)_3$] prevails, transitioning towards borate [$B(OH)^{4-}$] with increasing alkalinity (He *et al.*, 2013). The toxic metalloid arsenic (As) also demonstrates a pH-dependent shift in oxidation states, ranging from +3 to +5 under neutral conditions. In oxidizing environments, pentavalent As and oxyanionic forms are present, while trivalent As dominates under anoxic conditions (Zakhar *et al.*, 2018). Selenium (Se), yet another beneficial metalloid, is present in the soil as selenate (SeO_4^{2-}) and selenite (SeO_3^{2-}). The prevalence of selenate is observed in oxic soils, while selenite is favoured in anoxic soils (White, 2018). Given the varied responses to different metalloid species, plants must strategically acquire essential elements while keeping their concentrations below toxic levels. Achieving this delicate balance requires coordinated optimization of transport mechanisms within the plants.

On a cellular scale, the nutrient transport from root to shoot involves many transporters assisting in uptake, xylem loading, and subsequent distribution across aerial tissues. Plants utilize structural similarities of metalloids with essential nutrients to facilitate metalloid uptake. For example, nodulin 26-like intrinsic protein (NIP) aquaporins have been diversified to aid the uptake of neutral metalloid forms, while borate is transported via carbonate transporters, selenate through sulfate transporters, and arsenate via phosphate transporters (Fig. 1). Molecular subfunctionalization of these transporters for metalloids emerged early in chlorophytes and subsequently became specialized in higher plants (Wakuta *et al.*, 2015; Deshmukh *et al.*, 2020; Coskun *et al.*, 2021). The differential accumulation of metalloids in different species is explained largely by the presence of these specific transporters, their expression levels in tissues, cellular localization, polarity, and functionality (Sun *et al.*, 2020). The preservation of functional homologues across clades further supports the beneficial potential of metalloids for plants.

There is an emerging interest in understanding metalloid metabolism in plants due to their implications in terms of plant growth and abiotic and biotic stress mitigation. However, our knowledge about the mechanism of the transport process is rudimentary, creating a gap in functional gene editing efforts. Recent advances in genomics and transcriptomics resources have eased sequence comparison-based identification of transporter homologues in different plant species. The functional characterization of metalloid transport through such proteins has been validated by complementation studies, knockout mutant screens, and modulations in gene regulation. In the present review, we provide a structural overview of the potential transport systems involving the coordinate activity of influx and efflux transporters regulating metalloid uptake, distribution, and accumulation in plants. Recently, AlphaFold (Jumper *et al.*, 2021) has emerged as a new technology in molecular modelling, employing machine learning to predict protein structures. Here, we employed the holistic analysis of AlphaFold structural predictions and available crystal structures of metalloid transporters to understand structural basis of metalloid transport. A comprehensive understanding of the functional residues of these transporters will be helpful in devising schemes to combat metalloid toxicity and directing phytoremediation efforts. The manipulation of these tightly regulated influx and efflux transporters holds the potential to contribute to nutritionally safer crop production.

Metalloid influx transporters

Depending on the availability of metalloids in soil, plants can use different uptake mechanisms. Some metalloids, such as B, can diffuse across cell membranes. However, under nutrient-rich soil conditions, major intrinsic protein (MIP) family aquaporins facilitate passive uptake of metalloids. In addition, involvement of energetically demanding secondary active transporters has also been reported in metalloid influx (Ozyigit *et al.*, 2020). These secondary active transporters utilize electrochemical gradients to drive the transport of metalloids against a concentration gradient. Notably, compared with the animals that utilize sodium gradients to create electrochemical potentials, plants rely on protons for the generation of proton motive force (Andersen *et al.*, 2023). The presence of metalloid influx transporters thus provides the organism with a strategic advantage over diffusion in swiftly adapting to environmental conditions. These specialized transport proteins play a pivotal role in efficiently acquiring nutrients such as B and Si in limited or excess rhizospheric availability, balancing the nutrient uptake in dynamic environments. In the following section, we will review various specialized influx transporters with special emphasis on their structural conformations and transport mechanism.

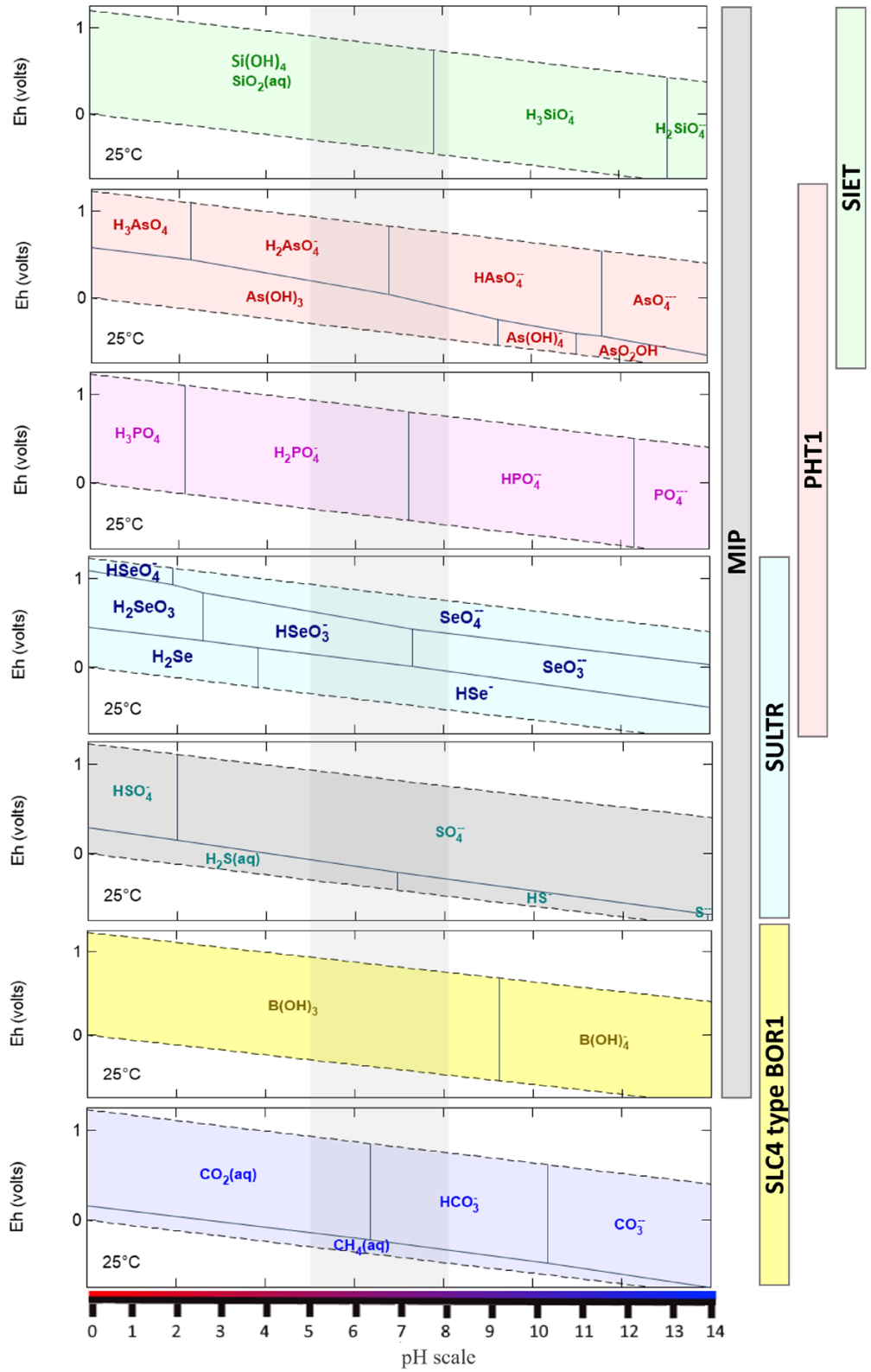

Fig. 1. The Eh–pH diagram representing the stability of various redox states of metalloids and their structural analogues across a range of pH values. The physiological pH range of plants (5–8) is indicated. The transportation of hydroxylated metalloids is facilitated by members of the major intrinsic protein (MIP) family aquaporins. Bor1 transporters exhibit structural homology with the SLC4 family carbonate transporters. Sulfate transporters (SULTRs) play pivotal roles in facilitating the transport of selenate. Additionally, phosphate transporters (PHTs) are implicated in the transport of both selenate and arsenate species. The silicon efflux transporter (SIET) Lsi2 is primarily associated with mediating the uptake of silicic acid and arsenous acid.

Nodulin26-like intrinsic proteins and their selectivity filter

The involvement of aquaporins in metalloid uptake was first identified in *Escherichia coli* (Sanders *et al.*, 1997; Meng *et al.*, 2004) and later in plants (Zardoya *et al.*, 2002; Ma *et al.*, 2006, 2008). NIPs form a subfamily of aquaporins that is present exclusively in plants (Wallace *et al.*, 2006). The amino acid diversification in this subfamily allows the uptake of small neutral molecules and metalloid oxoacids in the hydroxylated state. Based on sequential diversity, NIPs are further subdivided into NIPI, NIPII, and NIPIII aquaporins, forming defined families with related structure and substrate specificities (Mitani *et al.*, 2008). The NIPI and NIPII subgroups are present in all land plants, while NIPIII is largely restricted to silicophile species (Pommerrenig *et al.*, 2015). The sequential and functional parallels in NIP subfamilies thus indicate specificities of NIPI for lactic acid and arsenite (Beamer *et al.*, 2021), NIPII for smaller sized B and arsenous acid (Bienert *et al.*, 2008b), and NIPIII for most of the hydroxylated metalloids such as B, Si, As, Sb, and Se (Ma *et al.*, 2006, 2008; Schnurbusch *et al.*, 2010; Zhao *et al.*, 2010; Shao *et al.*, 2021).

NIPs follow the classical structure of aquaporins, having six transmembrane (TM) helices and two half-helixes constituting the NPA region in the channel (Saitoh *et al.*, 2021; van den Berg *et al.*, 2021). The structural analysis of NIPIII and NIPII class aquaporins emphasizes the unique chemistry of pore-lining residues being responsible for their metalloid uptake capabilities. Recent studies have highlighted the adaptation of wider pore diameters for NIPII and NIPIII channels consequently promoting uptake of larger solutes such as germanic acid and silicic acid (Saitoh *et al.*, 2021; van den Berg *et al.*, 2021; Beamer *et al.*, 2022; Sharma *et al.*, 2023). The high affinity of NIPIII family aquaporins for silicic acid was proposed to be determined by the hydrophilic residues that line the extracellular half of helix III in Lsi1 (Low silicon 1) (Sharma *et al.*, 2023). The comparative affinity for different metalloids is thus an interplay of the channel hydrophobicity and size of a so-called ar/R selectivity filter in the extracellular half of the protein (Box 1). Efforts have been made to modify the metalloid specificity of NIPs by altering the ar/R filter. In one such study, the selectivity filter of VvTnNIP1;1 (NIPI) and VvTnNIP6;1 (NIPII) was interchanged, which resulted in a significant impact on boric acid uptake (Sabir *et al.*, 2020). AtNIP5-1 is the major boric acid transporter in Arabidopsis root. On mutating the H5 position from the native AIGR type selectivity filter, to the NIPIII type ASGR, B uptake was reduced (Mitani-Ueno *et al.*, 2011). The H5 position is critical in NIPIII class aquaporins regulating Si uptake (Mitani-Ueno *et al.*, 2011; Sharma *et al.*, 2023). The VvTnNIP2;1 S206I mutant abolished metalloid specificity for B, Si, as well as As (Sabir *et al.*, 2020). Similarly, for rice Lsi1, a major root transporter for Si, S207I mutation abolished Si, B, and water uptake (Mitani-Ueno *et al.*, 2011). The hydrophilic H5 residue (S in NIPIII) provides better hydrogen bonding for tetrahydroxyls in the orthosilicic acid molecule, whereas the hydrophobic H5 position favours the trigonal pyramidal symmetric boric acid molecule (Beamer *et al.*, 2022; Sharma *et al.*, 2023).

The wider extracellular half of NIPII and NIPIII aquaporins compared with classical aquaporins can be attributed roughly to their helix packing. The interhelix distance of the extracellular half of NIPII and NIPIII subgroups is altered by a substitution of the aromatic H2 residue (W or F) present in orthodox aquaporins to a smaller glycine or alanine. As a result of the missing bulky side chain at the H2 position, the NIPII and NIPIII subgroup probably have a wider pore diameter and a five-residue selectivity filter (Fig. 2). The four-residue selectivity filter will thus hold for NIPI members with W at H2 position or NIP homologues with a FAAR-type selectivity filter. Even in human AQP10, the selectivity filter contains GGIR residues (Gotfryd *et al.*, 2018), which can accommodate a fifth residue and may need revisiting. The H2 position therefore provides size exclusion-based selectivity for metalloids. As a proof of concept, the substitution of H2 position T118W in NIPII-SF led to reduced boric acid uptake (Wallace and Roberts, 2005), but NIPI W86T showed increased boric acid transport (Sabir *et al.*, 2020). Similarly, a W91A mutant in AtNIP2-1 also showed 50% reduced $AlCl_3$ uptake in yeast (Y. Wang *et al.*, 2021). Due to its small molecular size and planar symmetry, transport of arsenous acid was marginally affected in

Box 1. The ar/R filter

The aromatic/arginine region of aquaporin is the size exclusion constrict, with the minimal radius localized at this region of the channel. Ironically, considering its name, certain aquaporin isoforms such as NIPII, NIPIII, and hAQP10 lack an aromatic residue in their selectivity filter, resulting in a wider extracellular half and non-single file water transport behaviour.

The conserved arginine at this region is considered the signature of aquaporins. The dynamic movement of this R residue with respect to the pore has been proposed to act as a gating mechanism. The importance of loop C in defining the open confirmation has also been discussed (Savage *et al.*, 2010; Zeng *et al.*, 2022; Sharma *et al.*, 2023). $HgCl_2$ had been used extensively for blocking the aquaporin channel. Again, the involvement of the conserved arginine in $HgCl_2$-mediated inhibition of aquaporins has been suggested (Xie *et al.*, 2022). Therefore, targeting arginine conformational switching represents a potential avenue for regulating aquaporin function. Being able to modulate aquaporin function has wide potential in terms of selective metalloid uptake and H_2O_2-mediated stress tolerance in crop species, thereby improving crop resilience and nutrients.

the majority of the mutants tested, indicating low specificity for arsenite uptake. Altogether, these observations indicate a critical role for ar/R hydrophobicity and steric hindrance in metalloid uptake through aquaporins. Lsi1, a member of NIPIII aquaporins having the widest pore diameter, showed transport activity for multiple metalloids including Si, B, As, and Se, thus highlighting the selectivity filter size as a major contributor to substrate selectivity (Ma *et al.*, 2006, 2008; Schnurbusch *et al.*, 2010; Zhao *et al.*, 2010; Shao *et al.*, 2021).

Since proteins are dynamic structures, amino acids establish contact with neighbouring residues to ultimately control functional relevance. Thus, sites other than the selectivity filter that directly influence metalloid uptake need to be reviewed. In fact, the report of Lsi1 involvement in metalloid uptake was due to a loss-of function mutation in rice *Lsi1* (Ma *et al.*, 2006). This A132T mutation in the H3 helix probably destabilized the overall structure, thus diminishing plant germanic acid uptake. Mutations can also alter the localization of a protein by affecting its localization motifs. This can result in mislocalization of the protein and impairment of its functions. For instance, a P242L variation in pumpkin has been associated with bloomless genotypes resulting from altered subcellular localization (Mitani *et al.*, 2011). Similarly, mutations effecting I18 and I285 in the N- and C-terminal regions resulted in the loss of Lsi1 polar localization and lead to retention of Lsi1 in the endoplasmic reticulum (Konishi *et al.*, 2023). Another study with CRISPR (clustered regularly interspaced palindromic repeats)-mediated editing in the C-terminus of Lsi1 showed significantly reduced Si and As uptake, which is probably attributed to regulation and localization of Lsi1 (Xu *et al.*, 2024).

Arsenate uptake by phosphate transporters: molecular analogue

Arsenate transport in plants is mediated by phosphate-specific transporters in aerobic soil conditions. The near identical p*K*as of arsenate and phosphate, similar distribution of charges, and a <4% difference in molecular radius give them striking similarities (Fig. 1) (Elias *et al.*, 2012), to the extent that they share the same transporter. In fact, arsenate has been used extensively for forward genetic screening of phosphate transporters (Kobayashi *et al.*, 2003; Catarecha *et al.*, 2007; Chen *et al.*, 2011). Based on sequence similarity and subcellular localization, phosphate transporters are largely grouped into four distinct families PHT1, PHT2, PHT3, and PHT4 (Gu *et al.*, 2016). The PHT1 family (H^+:phosphate symporter) is a high-affinity phosphate transporter, sensitive to arsenate, and localized in the plasma membrane. The PHT2 family (low-affinity H^+-dependent phosphate transporter) is localized to plastids, PHT3 (ADP/ATP carrier) is localized to mitochondria, and PHT4 (Na^+/phosphate transporter) is localized to the Golgi and thylakoid membranes. All the four gene families have distinct structural architectures, with major attention received by the PHT1 gene family having the largest number of members (Nussaume *et al.*, 2011). Phosphate binding to PHT1 occurs with both

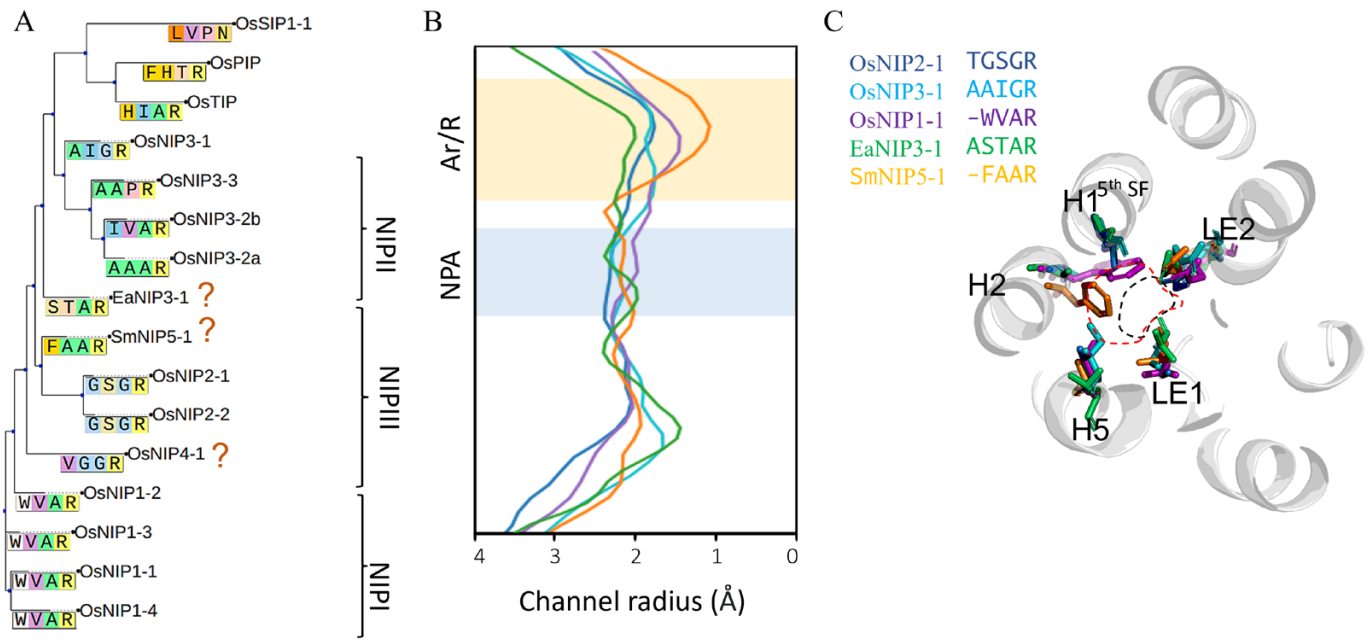

Fig. 2. The ar/R architecture shaped the functional divergence of aquaporins for metalloid uptake. (A) The diversity in the selectivity filter of NIP family aquaporins selectivity filter and (B) its relationship to the pore radius. The average pore radius was calculated from 100 ns simulations of each aquaporin individually. (C) The H2 position directly influences the size of the selectivity filter and thus the metalloid solute specificity. The radius plot and selectivity filter in (B) and (C) are identically colour coded as OsNIP2-1, blue; OsNIP3-1, cyan; OsNIP1-1, violet; EaNIP3-1, green; and SmNIP5-1, orange.

HPO_4^{2-} and $H_2PO_4^-$ states (Liu *et al.*, 2021). Similarly, As in physiological states exists as $HAsO_4^{2-}$ and $H_2AsO_4^-$.

The transport mechanisms of PHT1 transporters from the fungus *Serendipita indica* have been established (PDB:7SP5) (Pedersen *et al.*, 2013). The SiPHT1 share 34% sequence homology to the rice OsPHT1:8 transporter. The substrate-binding site of PHT1 is buried between two homologous N- and C-terminal domains and is composed of mostly conserved residues that impart negative charge to the tunnel (Fig. 3A). The key residues for phosphate and arsenate binding are the conserved aspartic acid residues in the pocket (D45 and D324) whose carboxylate interacts with the O_2 atom of the substrate, a possible key interaction for its specificity (Liu *et al.*, 2021). The protonation of these aspartate residues is proposed to be crucial for the translocation of the substrate. Substrate transport through the PHT channel is symported with H^+ ions. The channel lining is further crowded by negatively charged Asp and Glu residues, implying proton transfer to the cytosol. Overall, the negative charge accumulation in the substrate-binding cavity and proton relay through these negative residues drives a conformation transition of the PHT1 monomer and substrate release on the cytoplasmic side (Liu *et al.*, 2021).

Despite their structural similarity, both substrates (arsenate and phosphate), however, have contrasting physiological responses. Arsenate is metabolically toxic compared with indispensable phosphate. The discrimination of arsenate by phosphate transporters is therefore of paramount importance. Efforts have been made to explore available genetic variations to assess the comparative binding affinities of phosphate and arsenate. Studies in various plant species have demonstrated variation in binding affinity for arsenate and phosphate (Table 1). However, the active site residues of these transporters show high conservation, suggesting a role for other amino acids in determining the observed variation in affinity. To engineer the reduced affinity of the phosphate-binding pocket for arsenate, Elias *et al.* (2012) reported that a longer As–O_2 bond compared with P–O_2 accounted for an ~500-fold variation in phosphate specificity. Plants have also adapted regulatory feedback mechanisms to counter arsenate uptake through PHTs. Arsenate-induced calcium-mediated phosphorylation of a conserved S514 residue in AtPHT1;1 resulted in delocalization of the transporter from the membrane, eventually reducing arsenate uptake in Arabidopsis (Liu *et al.*, 2023). Overall, molecular similarities of the substrates and conserved binding interactions reinforce the overlapping uptake mechanism of phosphate and arsenate by the PHT1 transporter. Thus, further efforts in mining genetic variation for relative substrate affinity and regulatory mechanisms is needed to develop reduced arsenate uptake and consequently safer food crops.

Sulfate transporters in selenate uptake

The evolutionary trajectory indicates the divergence of the SULTR4 gene family of sulfate transporters in chlorophytes from the SULTR1/2/3/4 lineage in angiosperms (Takahashi *et al.*, 2012). The involvement of these sulfate transporters in selenate uptake was established in AtSULTR1;2, a mutant screened using selenate as a toxic analogue of sulfate (Shibagaki *et al.*, 2002; El Kassis *et al.*, 2007). AtSULTR1;2 serves as the major root SO_4^{2-} uptake contributor, which is shown by the large reduction in the root's ability to take up SO_4^{2-} and the amount of SO_4^{2-} in the shoot when *AtSULTR1;2* is mutated (Shibagaki *et al.*, 2002). Another high-affinity sulfate transporter, AtSULTR1;1, can take up selenate, but its expression is up-regulated by S deficiency (Barberon *et al.*, 2008).

Structurally, SULTR acts as homodimer with homology to the SLC26 family of Na^+/sulfate co-transporters. The recent crystal structure determination of AtSULTR4;1 (PDB:7LHV) provides insight into structure–function relationships of sulfate transporters (L. Wang *et al.*, 2021). AtSULTR1;2 shares 38% structural homology with AtSULTR4;1, with key substrate-binding residues remaining highly conserved (Fig. 3B). The binding of a charged anionic substrate— SO_4^{2-}/SeO_4^{2-}—is electrostatically supported by a conserved arginine and the dipole moment imparted by two helices (H3 and H10). A conserved, negatively charged E347 of AtSULTR4;1 significantly altered proton gradient-driven substrate transport.

Apart from the transmembrane channel, the presence of a STAS domain on the cytoplasmic side is necessary for dimerization. Deletion or mutation of the interface residues in this domain resulted in diminished substrate transport. Interestingly, two of the three point mutants of SULTR1-2 (i.e. sel1-3:G509E and sel1-8:I511T) had mutations within the STAS domain (Shibagaki *et al.*, 2002). This further emphasizes the regulatory role of the STAS domain in substrate transport and conformation switching of the SLC26-related family.

Overall, the evidence that sulfate and selenate anions have similar chemical properties, and that sulfate can inhibit selenate uptake along the proton gradient, suggests uptake through the same SULTR transporters with low selectivity for both substrates.

Metalloid efflux transporters

The metalloid efflux transporters in plants are substrate specific and rely on local proton gradients for active transport of substrate. The energetic balance of efflux is facilitated by the proton motive force generated from the acidic pH of the apoplast.

These pumps play an important role in regulating ion homeostasis via facilitating directional nutrient uptake in cooperation with influx transporters. In addition, plants can prevent metalloid accumulation to toxic levels by extrusion of high concentrations through efflux pumps.

SLC4-type BOR1 transporters

B is an essential nutrient for plant growth and development, acting primarily by maintaining the integrity of cell walls.

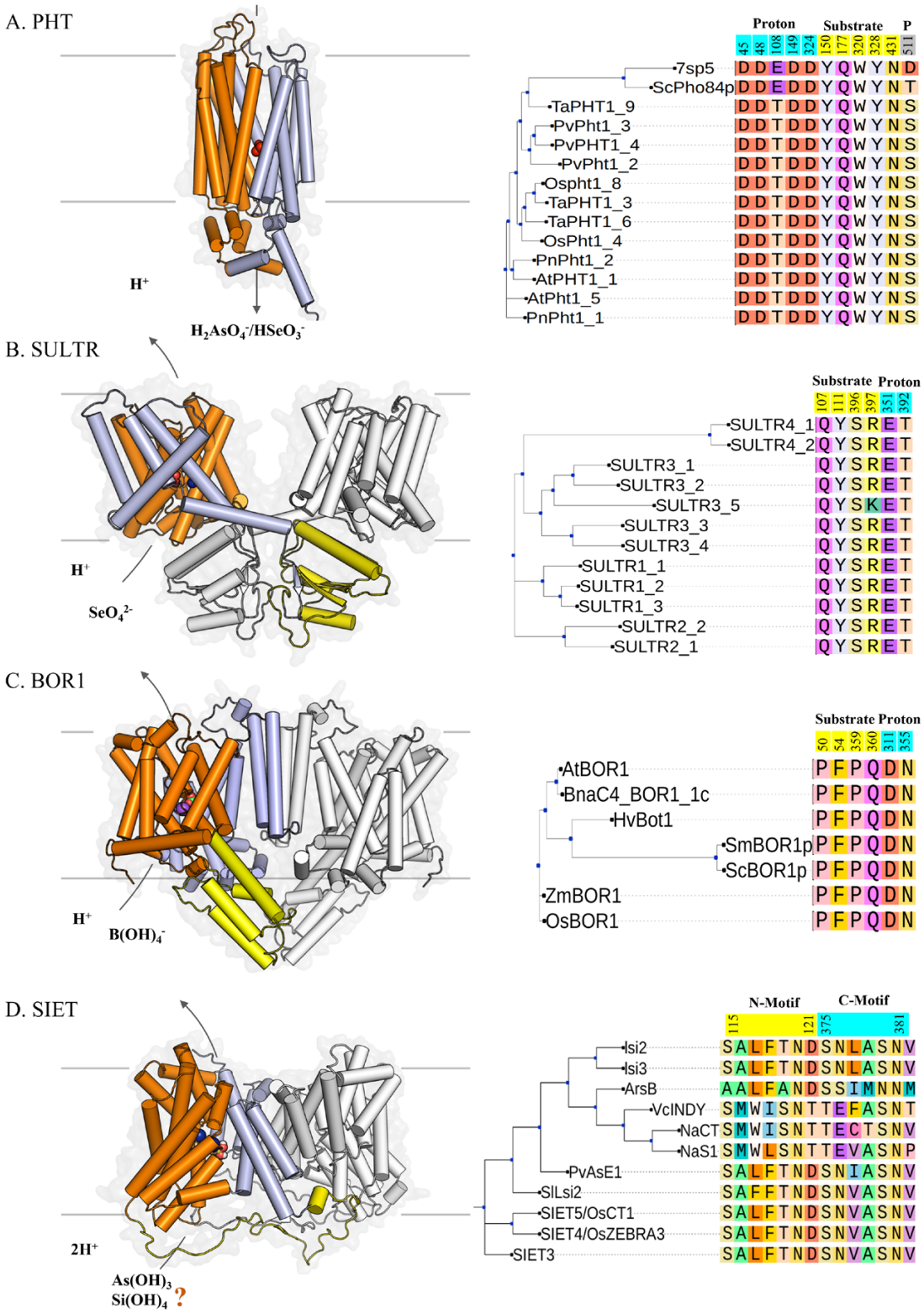

Fig. 3. The end-to-end modelled protein structures of active transporters involved in metalloid uptake. (A) Phosphate transporter (PHT), (B) sulfate transporter (SULTR), (C) borate transporter (BOR1), (D) silicon efflux transporter, Lsi2. Substrates were superimposed to illustrate a metalloid-binding pocket. The gate, core, and IDR domains are separately coloured in orange, ink, and yellow shades. The putative functional sites, including residues coupling proton transport to substrate binding, were identified and validated by a literature survey. Furthermore, the conservation of sites is shown among different homologues.

Table 1. Overview of characterized metalloid transporters and their mutants in various plant species along with their phenotypic effects

Transporter	Family	Organism	High affinity P		Mutation	Effect	Reference
AtPHT1;1	Major facilitator superfamily (MFS)	*Arabidopsis thaliana*	High affinity P	High affinity As	–	–	Catarecha *et al.* (2007)
AtPht1;5	Major facilitator superfamily (MFS)	*Arabidopsis thaliana*	High affinity P	Low affinity As	–	–	DiTusa *et al.* (2016)
OsPT4	Major facilitator superfamily (MFS)	*Oryza sativa*	–	High affinity As	–	–	Ye *et al.* (2017)
OsPT8	Major facilitator superfamily (MFS)	*Oryza sativa*	High affinity P	High affinity As	–	–	Wu *et al.* (2011)
PvPht1;2	Major facilitator superfamily (MFS)	*Pteris vittata*	Moderate affinity P	Low affinity As	–	–	Cao *et al.* (2018); Sun *et al.* (2019)
PvPht1;3	Major facilitator superfamily (MFS)	*Pteris vittata*	High affinity P	High affinity As	–	–	DiTusa *et al.* (2016)
PvPht2;1	Major facilitator superfamily (MFS)	*Pteris vittata*	Low affinity P	Low affinity As	–	–	Feng *et al.* (2021)
PnPht1;2	Major facilitator superfamily (MFS)	*Panax notoginseng*	High affinity P	Low affinity As	–	–	Cao *et al.* (2020)
PnPht1;1	Major facilitator superfamily (MFS)	*Panax notoginseng*	High affinity P	High affinity As	–	–	Cao *et al.* (2020)
TaPHT1;9	Major facilitator superfamily (MFS)	*Triticum aestivum*	High affinity P	High affinity As	–	–	Wang *et al.* (2023)
TaPHT1;6	Major facilitator superfamily (MFS)	*Triticum aestivum*	High affinity P	Moderate affinity As	–	–	Wang *et al.* (2023)
AtNIP5;1	Major intrinsic protein (MIP)	*Arabidopsis thaliana*	Boric acid	–	A117W	Reduced boron uptake	Beamer *et al.* (2022, Preprint)
AtNIP1;1	Major intrinsic protein (MIP)	*Arabidopsis thaliana*	–	–	W94A	Reduced water permeability	Beamer *et al.* (2022, Preprint)
AtNIP4;1	Major intrinsic protein (MIP)	*Arabidopsis thaliana*	–	–	W82A	Reduced water permeability	Beamer *et al.* (2022, Preprint)
VvTnNIP1;1	Major intrinsic protein (MIP)	*Vitis vinifera*	–	–	W86T	Reduced glycerol permeability	Sabir *et al.* (2020)
VvTnNIP1;1	Major intrinsic protein (MIP)	*Vitis vinifera*	–	–	V206I	Reduced glycerol permeability	Sabir *et al.* (2020)
VvTnNIP1;1	Major intrinsic protein (MIP)	*Vitis vinifera*	–	–	W86T	Higher B sensitivity	Sabir *et al.* (2020)
VvTnNIP6;1	Major intrinsic protein (MIP)	*Vitis vinifera*	Boric acid	–	T118W	Lower B sensitivity	Sabir *et al.* (2020)
OsNIP2-1	Major intrinsic protein (MIP)	*Oryza sativa*	Silicic acid	Boric acid	S207I	Low silicon transporter	Mitani-Ueno *et al.* (2011)
AtNIP5-1	Major intrinsic protein (MIP)	*Arabidopsis thaliana*	Boric acid	–	I236S	Low boron uptake	Mitani-Ueno *et al.* (2011)
OsNIP2-1	Major intrinsic protein (MIP)	*Oryza sativa*	Silicic acid	Arsenous acid	Q84N	Reduced arsenic uptake	Sharma *et al.* (2023)
OsNIP2-1	major intrinsic protein (MIP)	*Oryza sativa*	Silicic acid	Arsenous acid	S207G	Reduced arsenic uptake	Sharma *et al.* (2023)
OsNIP2-1	Major intrinsic protein (MIP)	*Oryza sativa*	Silicic acid	Arsenous acid	G155A	Reduced arsenic uptake	Sharma *et al.* (2023)
OsNIP2-1	Major intrinsic protein (MIP)	*Oryza sativa*	Silicic acid	Arsenous acid	I285	Compromised polar localization	Konishi *et al.* (2023)
OsNIP2-1	Major intrinsic protein (MIP)	*Oryza sativa*	Silicic acid	Arsenous acid	ΔF259 Q260	Small effect on shoot Si and As concentration	Xu *et al.* (2024)
AtBOR1	Anion exchanger family	*Arabidopsis thaliana*	Borate ion	–	D311A	Reduced boron efflux	Saouros *et al.* (2021); Yoshinari *et al.* (2021)
ScBOR1p	Anion exchanger family	*Saccharomyces cerevisiae*	Borate ion	–	D347A	Reduced boron efflux	Thurtle-Schmidt and Stroud (2016)
ScBOR1p	Anion exchanger family	*Saccharomyces cerevisiae*	Borate ion	–	N391A	Reduced boron efflux	Thurtle-Schmidt and Stroud (2016); Beltran *et al.* (2023)
AtBOR1	Anion exchanger family	*Arabidopsis thaliana*	Borate ion	–	P359A	Reduced boron efflux	Yoshinari *et al.* (2021)
AtBOR2	Anion exchanger family	*Arabidopsis thaliana*	Borate ion	–	Q360A	Reduced boron efflux	Yoshinari *et al.* (2021)
ScBOR1p	Anion exchanger family	*Saccharomyces cerevisiae*	Borate ion	–	Q396A	Reduced boron efflux	Thurtle-Schmidt and Stroud (2016)
ZmBOR1	Anion exchanger family	*Zea mays*	Borate ion	–	S361L	RTE-3, rotten ear phenotype	Chatterjee *et al.* (2014)
AtBOR1	Anion exchanger family	*Arabidopsis thaliana*	Borate ion	–	K590A	Abolished vacuolar transport of BOR1	Kasai *et al.* (2011)
PvASE1	Silicon efflux transporter	*Pteris vittata*	Arsenite	–	T118A	Reduced arsenic efflux	Zhenyan (2022)
PvASE1	Silicon efflux transporter	*Pteris vittata*	Arsenite	–	N119A	Reduced arsenic efflux	Zhenyan (2022)

Table 1. Continued

Transporter	Family	Organism	High affinity P		Mutation	Effect	Reference
PvASE1	Silicon efflux transporter	*Pteris vittata*	Arsenite	–	D120A	Reduced arsenic efflux	Zhenyan (2022)
PvASE1	Silicon efflux transporter	*Pteris vittata*	Arsenite	–	T121	Reduced arsenic efflux	Zhenyan (2022)
OsLsi2	Silicon efflux transporter	*Oryza sativa*	Arsenite	Silicic acid	S115N	Abolished silicon uptake	Ma *et al.* (2007)
OsZebra3/SIET4	Silicon efflux transporter	*Oryza sativa*	Silicic acid	–	S542P	Variegated leaf	Kim *et al.* (2018)
SIET4	Silicon efflux transporter	*Oryza sativa*	Silicic acid	–	KO	Silica deposition in mesophyll	Mitani-Ueno *et al.* (2023)
OsLsi2	Silicon efflux transporter	*Oryza sativa*	Arsenite	Silicic acid	12th trans-membrane helix	Reduced silicon in rice husk	Xu *et al.* (2024)
AtPIN2	PIN formed 2	*Arabidopsis thaliana*	Arsenite		KO	Arsenite hypersensitivity in roots	Ashraf *et al.* (2020)
AtSULTR1;2	Sulfate transporter family	*Arabidopsis thaliana*	Sulfate	Selenate	S96F	Resistant to selenate	Shibagaki *et al.* (2002)
AtSULTR1;2	Sulfate transporter family	*Arabidopsis thaliana*	Sulfate	Selenate	G509E	Resistant to selenate	Shibagaki *et al.* (2002)
AtSULTR1;2	Sulfate transporter family	*Arabidopsis thaliana*	Sulfate	Selenate	I511T	Resistant to selenate	Shibagaki *et al.* (2002)

The label '–' indicates that no information is available for the corresponding cells.

An inadequate supply of B leads to deficiency or toxicity in plants, affecting growth, fertility, and ultimately yield (Brdar-Jokanović, 2020). Hence, a balance of B concentration is required for plant viability. The B efflux transporters are responsible for active export of B from root cells to the xylem for further distribution or its extrusion from root to rhizosphere.

The first characterized BOR transporter was AtBOR1 (Noguchi *et al.*, 1997), a root pericycle-localized efflux transporter involved in xylem loading (Takano *et al.*, 2001). The mutant characterized had single amino acid substitutions in bor1-1 (G87E) and bor1-2 (S75E) that impaired the transport function of the protein. The charged state of the borate $B(OH_4)^-$ anion hints at its coupled co-transport with H^+ ions (Hayes and Reid, 2004; Jennings *et al.*, 2007). These transporters share structural homology with the SLC4 family which have diverse anion preferences. The typical architecture involves gate and core domains in which centralized gate domains mediate dimerization and outer core domains contain the solute-binding pocket (Thurtle-Schmidt and Stroud, 2016; Coudray *et al.*, 2017). Mechanlically, the gate domains are stable during the transport cycle while the core domains slide to generate alternative access conformations. This model supports either an elevator or a rocking-bundle mechanism of transport to carry borate across a membrane (Thurtle-Schmidt and Stroud, 2016; Coudray *et al.*, 2017).

Two crystal structures for B-specific SLC4 transporters from *Saccharomyces mikatae* (PDB:5SV9) (Coudray *et al.*, 2017) and *Arabidopsis thaliana* BOR1 (PDB:5L25) are available (Thurtle-Schmidt and Stroud, 2016). However, neither of the structures has borate bound in its active site. Due to the structural homology of AtSULTR4;1 (PDB:7LHV) and AtBOR1 protomers, a similar binding mechanism for sulfate and borate ion is expected. To evaluate this, we homology modelled AtBOR1 to PDB:7LHV. The model suggests P50, F54, P359, and Q360 to form the substrate-binding site, and D311 and N355 the proton coordination site (Fig. 3C). In support of this proposal, previous studies have shown compromised B activity in AtBOR1 and ScBOR1p when mutated at these or equivalent sites. Arabidopsis plants expressing D311A mutants of the proton-binding site in AtBOR1 exhibited reduced shoot fresh weight and typical B-deficiency symptoms (Saouros *et al.*, 2021; Yoshinari *et al.*, 2021). Additionally, positionally identical D347A mutations abolished B efflux activity in ScBOR1p yeast (Thurtle-Schmidt and Stroud, 2016). In a separate study, mutating aspartic acid to a similar amino acid, glutamic acid (D347E), resulted in decreased but significant B transport, while substitution with a positively charged glutamine residue (D347N) abolished borate transport (Beltran *et al.*, 2023). All of these results indicate a central role for D311 of AtBOR1 and D347 of ScBOR1 in B uptake, which is likely to be important for proton binding. Additionally, N355 in AtBOR1 may also facilitate ion coordination and may account for the reduced survival of the N391A mutant of ScBOR1 in yeast

complementation assays (Thurtle-Schmidt and Stroud, 2016; Beltran *et al.*, 2023).

The proposed substrate-binding site mutation P359A and Q360A in AtBOR1 significantly reduced B export activity in yeast (Yoshinari *et al.*, 2021). At the position equivalent to Q360 of AtBOR1, the Q396A mutant in ScBOR1p also showed reduced growth resulting from compromised borate binding (Thurtle-Schmidt and Stroud, 2016). Interestingly, S361L, a mutation in the classic rotten ear BOR1 mutant in maize (Chatterjee *et al.*, 2014), is also adjacent to the proposed borate-binding site, Q360. Collectively, these finding suggest that BOR1 and SULTR4;1 share monomeric structural folds with small differences and probably common solute uptake mechanisms.

AtBOR1, however, lacks structural information on the intrinsically disordered region (IDR) (371–464) unique to the plant kingdom. This IDR originated in chlorophytes and contains critical tyrosine-based AP-binding motifs and an acidic di-leucine motif for polar localization and B-dependent vacuolar sorting of BOR1 transporter (Wakuta *et al.*, 2015; Yoshinari *et al.*, 2019). Based on the presence of the acidic di-leucine motif, the BOR transporter family was classified into clades I and II, responsive to B-limited conditions and high B tolerance, respectively (Wakuta *et al.*, 2015). Also, the C-terminus of BOR1 has been shown to undergo dosage-dependent ubiquitination. A lysine residue in the C-terminus was shown to be ubiquitinated due to induction by B and to undergo endocytic degradation, highlighting its importance for vacuolar trafficking (Kasai *et al.*, 2011). Apart from amino acid variation, the tandem duplication in the B-tolerant sahara genotype of barley has been associated with higher expression of BOT1 (Sutton *et al.*, 2007).

Silicon efflux transporters in plants

Rice, being a high Si-accumulating crop (>10% of DW) has garnered an extensive research focus. High Si accumulation in rice is attributed to a perfect cooperative system of transporters which facilitate its radial transport, distribution, and deposition, and extrusion from leaves (Ma and Yamaji, 2015). Among these transporters, aquaporins serve as influx Si transporters (Ma *et al.*, 2006) while active efflux transport is facilitated by the SIET (silicon efflux transporter) family (Ma *et al.*, 2007). Structural information regarding SIETs is scarce, with homology of just 17% to SLC13 family VcINDY (PDB:6OL1) and 16.8% to NaCT (PDB:7JSK). However, transport assays do provide some hints correlating and validating AlphaFold2 predictions.

According to Alphafold, Lsi2 is a member of the SIET family and consists of 12 putative TM helices. Homologous to VcINDY, NaS1, and NaCT, the substrate-binding cavity of Lsi2 comprises residues from the TM4 and TM10 half-helices protruding to the centre of the protein from the opposite side. The active residues from TM4 are thus called the N-terminal motif while those from TM10 are called the C-terminal motif. The amino acid conservation of N- and C-terminal signature motifs in DASS family members highlights higher conservation in the N-terminal motif (SNT), the whereas C-terminal motif shows variation at the third position (SNT/V) (Sauer *et al.*, 2021). In plants, a recent study on PvASE1, an arsenic efflux transporter with 55% similarity to Lsi2, suggested Thr118–Asn119–Asp120 (TND)/Ser486–Asn487–Val488 (SNV) at the active sites (Yan *et al.*, 2022) which holds true for Si efflux transporters as well (Fig. 3D). Compared with PvASE1, the Lsi2 active site comprises residues T119, N120, D121, and S379, N380, V381. With the prerequisite of a protonable side chain to mediate H^+ coupling in plants, Lsi2 might have evolved the N-terminal motif. The N-terminal motif accommodates an aspartate at the third position of TND, instead of the sodium-specific sequence, SNT. The proton coupling of lsi2 is supported by various reports that suggest that Si transport through silicon efflux transporters is sensitive to the pH gradient, indicating proton involvement in coupled transport (Ma *et al.*, 2007; Yan *et al.*, 2022; Mitani-Ueno *et al.*, 2023). The transport activities of PvASe1, Lsi2, and SIET4 were compromised by the addition of CCCP (carbonyl cyanide *m*-chlorophenylhydrazone), a proton ionophore and uncoupler of the transmembrane proton gradient. Based on the NaCT model, the anion- and substrate-binding site are overlapping, with additional coordination of ions by residues equivalent to Lsi2's S375, A380, and S115 (PDB:60L1 and 7JSK). Notably, the first identified SIET mutant Lsi2 (Ma *et al.*, 2007) had a substitution S115N at the presumed ion-binding site, which accounts for the reduced Si uptake in Lsi2.

In addition to Si, Lsi2 mediates the efflux of arsenite towards the xylem, making it a target for As containment programmes. For instance, the alanine substitution of the TND signature sequence in the N-terminal motif of PvASE1 leads to significant reduction in arsenite uptake (Yan *et al.*, 2022). In rice, editing of Lsi2 in the 12th TM domain led to a similar pattern of reduction for both Si and As (Xu *et al.*, 2024). Similarly, S542 to proline mutation in the 12th TM domain of SIET4 in rice led to formation of leaf variegations and defective panicle coloration (Kim *et al.*, 2018). The role of SIET4 in Si deposition in leaves was recently established by a knockout study where *SIET4* knockout mutants were unable to grow in soil (Mitani-Ueno *et al.*, 2023), indicating a probable low Si transport ability in the *zebra3* mutant. Altogether, the information available so far for Si efflux transporters suggests the involvement of SIETs in Si and As efflux driven by the proton gradient. However, the exact speciation of substrates, the detailed mechanism, and the correlation of the TND signature sequence to Si specificity remain unexplained (Box 2). The predicted structure of Lsi2 further illustrates an IDR loop between TM6 and TM7 on the cytoplasmic side. The length of this IDR remained variable for homologues of Lsi2 in different plant species.

The ability of roots to take up Si is directly correlated with Si accumulation in plants (Takahashi *et al.*, 1990). Tomato

Box 2. Lsi2 substrate preference and silicon speciation in plants

Plants transport Si through symplasts as well as apoplasts. However, the apoplastic pathway is more important and most of the Si in plants is carried along the transpiration stream. Silicic acid concentration in apoplasts of rice exceeds its solubility. The probable mechanism for supersaturation of Si, even at high concentrations, is debated. The major proposal includes a high negative pressure inside the xylem and stabilization of silicic acid OH moieties by cell wall constituents such as hemicellulose. The stability of silicic acid moieties is further improved by the acidic pH of the apoplast and the availability of H^+ ions. Orthosilicic acid functions as a weak acid, undergoing protonation primarily at high pH (p*K*a=9.6). The resulting unstable silanol [$SiO(OH)_3^-$] triggers a nucleophilic attack on another silicic acid molecule, promptly converting it into a disilicate anion.

Lsi2 is an Si efflux transporter that shares low homology with NaCT citrate transporters. Indeed, the active site residues show substitution to chemically similar residues (SNT to TND). Thus, a discrepancy arises for the exact substrate of Lsi2 given the instability of the silicate ion and the low abundance of disilicate in the xylem. The question arises: does the TND substitution enable binding to neutral and smaller sized silicic acid in the active site, or are ion-mediated silanol intermediates formed at the active site? Silanol-mediated Si transport had been proposed earlier for silicic acid transporters (SITs) in diatoms (Knight *et al.*, 2016).

(*Solanum lycopersicum* L.) is a non-Si-accumulating species (Miyake and Takahashi, 1978). Compared with rice, tomato roots have much lower Si uptake (Mitani and Ma, 2005). However, the reason for this low Si uptake is not clear. A study has proposed that low Si accumulation in tomato is due to a non-functional Si transporter (Sun *et al.*, 2020). Despite the conserved proposed binding site at the active site of SlLsi2, a notable leucine to phenylalanine variation was observed in the N motif (Fig. 3D). This variation was also observed in certain homologues of Lsi2 in *Glycine max* (Fig. 4A) and thus need to be tested for functional relevance. Therefore, the structural peculiarities of Lsi2 lack information on structure–function relationship and are aptly described by the title 'Lsi2: a black box in plant silicon transport' (Coskun *et al.*, 2021).

ACR3, an arsenite efflux transporter in lower plants

ACR3, a member of the bile/arsenite/riboflavin transporter superfamily, is prevalent in bacteria and archaea (Achour *et al.*, 2007; Cai *et al.*, 2009). This plasma membrane-localized arsenite efflux transporter is a vital component in the efflux of arsenite to the extracellular space (Wysocki *et al.*, 1997). Intrestingly, while higher plants retained the arsenite reductase gene *ACR2* (Landrieu *et al.*, 2004; Duan *et al.*, 2007), the *ACR3* gene is exclusive to bacteria, fungi, and ferns (Indriolo *et al.*, 2010) (Fig. 4B). In light of the mechanism of As hyperaccumulation in ferns such as *Pteris vittata*, homologues of the *PvACR3* gene have been characterized and functionally validated (Indriolo *et al.*, 2010). Structurally ACR3s share BART family transmembrane topology and show conservation among orthologues in bacteria and ferns. The mechanism of AsIII and SbIII transport through ACR3 transporters is not well understood, but functional studies have highlighted some critical residues for transport activity of ACR3 (Maciaszczyk-Dziubinska *et al.*, 2014; Wawrzycka *et al.*, 2019; Mizio *et al.*, 2023). A conserved Cys residue, for example, is located in the centre of TM4 and had been shown to be important for transport function of ACR3 in *Saccharomyces cerevisiae*, *Corynebacterium glutamicum*, *Alkaliphilus metalliredigens*, and *Bacillus subtillis* (Maciaszczyk-Dziubinska *et al.*, 2014). In addition, a mutated E353D residue in TM9 abolished the arsenite transport activity of ScACR3, indicating involvement in substrate binding (Mizio *et al.*, 2023). In agreement with this, AtPIN1, an auxin efflux carrier from the BART family, shows binding of an auxin molecule to equivalent residue positions, and loses transport function when these positions were mutated (Yang *et al.*, 2022) (Fig. 4C). The ACR3 and AtPIN1 homology suggests the involvement of TM4/TM9 crossover along with residues from TM5 and TM10 in substrate binding. Interestingly, loss of PIN2 function itself had been associated with arsenite hypersensitivity. The *pin2* mutants had specifically high accumulation of arsenicals in Arabidopsis roots (Ashraf *et al.*, 2020), indicating the possibility that the BART superfamily is involved in arsenite transport.

In the context of As tolerance, exploiting the accumulation and sequestration properties of As hyperaccumulators such as *P. vittata* with the pivotal *ACR3* gene represents a feasible technique. Transgenic approaches, such as transferring As-resistant genes into angiosperms, show promising results for the development of low-As crops with enhanced As tolerance at the cellular level and increased As efflux (Ali *et al.*, 2012; Chen *et al.*, 2013; Pérez-Palacios *et al.*, 2019) These findings underscore ACR3's pivotal role in engineering plants for phytoremediation along with the possibility of toggling PINs for extrusion of arsenite from plants. In addition, the evolutionary analysis of ACR3 and Lsi2 hints at the convergence of distinct structural folds for the complementation of arsenite efflux function in lower and higher plants, respectively.

Evolved to be together: tales of transporter cooperativity

Efficient uptake of mineral nutrients is facilitated by coupling of influx and efflux transporters. These transporters are even

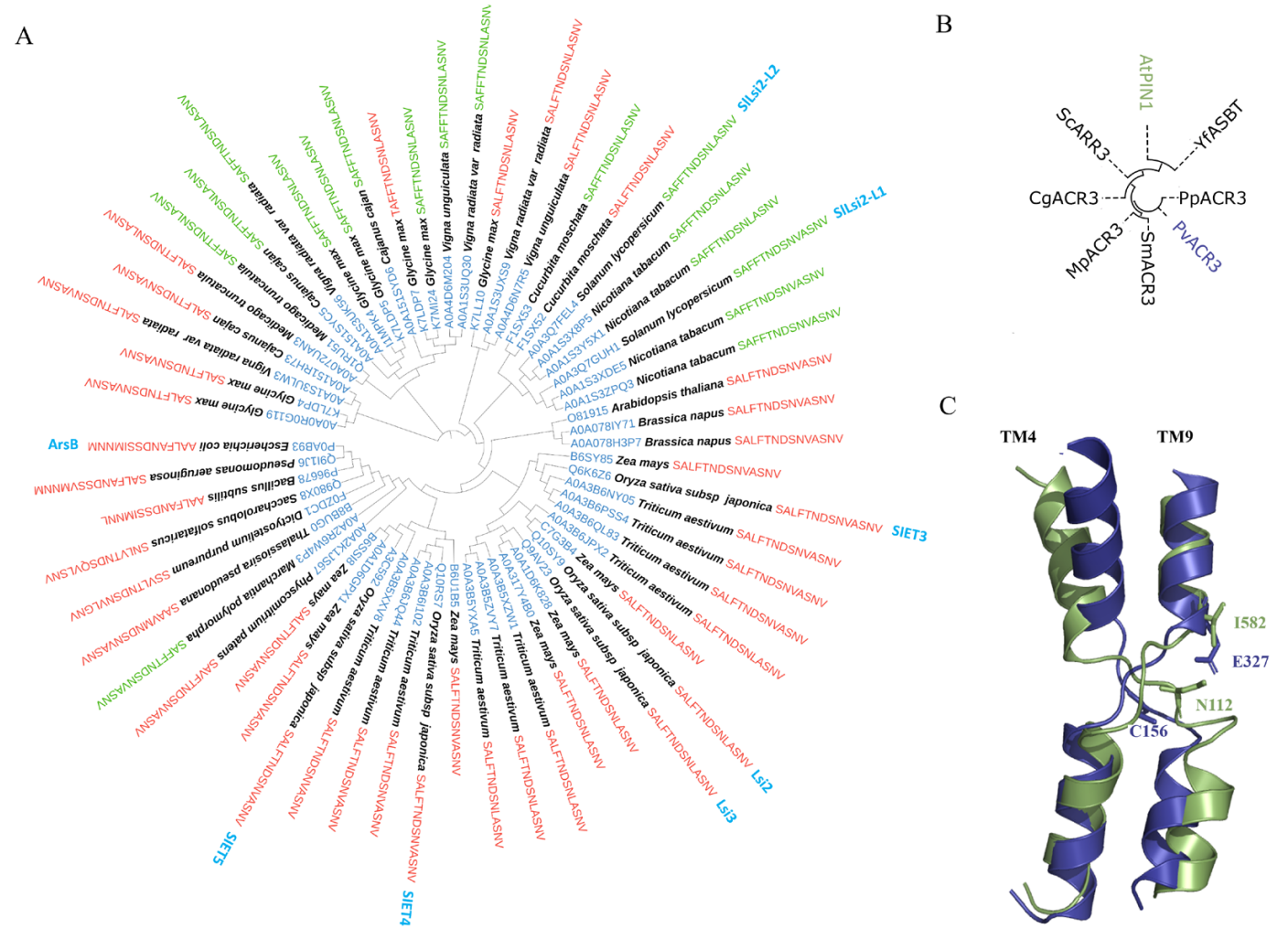

Fig. 4. Functional complementation of ACR3 and Lsi2 for the arsenite efflux role in lower and higher plants. (A) Taxonomic distribution of selected ArsB and Lsi2 homologues showing the diversity in active site residues. The labels include uniport ID, organism name, and putative substrate binding N- and C-motif. (B) Structural alignment of ACR3 homologues from *S. cerevisiae*, *C. glutamicum*, *M. polymorpha*, *S. moellendorffii*, *P. patens*, and *P. vittata* with the BART family AtPIN1 (7Y9V) and YfASBT (6LGZ). (C) PvACR3 (blue) and AtPIN1 (green) share BART family topology and key residues in substrate binding.

more crucial for plant roots where the Casparian strip is present. The Casparian strip localized at the epidermis blocks the apoplastic pathway, making it necessary for elements to pass through the symplast and thus specific channels. The presence of the Casparian strip thus maintains ion homeostasis in low/high nutrient supply (Pfister *et al.*, 2014), prevents leakage from the vascular system, and creates an apoplastic pH gradient (Martinière *et al.*, 2018). In the case of metalloids, some NIP class aquaporins serve as influx channels in anoxic conditions which is cooperated by metalloid-specific efflux channels, efficiently creating a directional transport model at various steps of loading and unloading of metalloids (Yamaji and Ma, 2021).

Plant silicon transport

With thorough investigation of rice Si biology, this crop, known for its high Si accumulation, has been established as a paradigm for studying Si uptake. OsNIP2;1 (Lsi1) is an influx transporter for Si in roots (Ma *et al.*, 2006) while SIET (Lsi2) acts as an efflux transporter (Ma *et al.*, 2007). OsLsi1 and OsLsi2 exhibit polar localization in cells of the root exodermis and endodermis, thereby creating an efficient pathway for Si transport (Ma and Yamaji, 2015). The passive influx transporter Lsi1 imports Si to the exodermis which is subsequently transferred to aerenchyma through the Lsi2 transporter. The Lsi1 influx transporters localized on the endodermis again import and target Si to the endodermis, eventually passing to the stele by Lsi2 and its homologue the Lsi3 transporter (Fig. 5) (Yamaji *et al.*, 2015). OsLsi3 in rice roots is localized to the pericycle without polarity and contributes 15% of the Si loading in the xylem, yet the contribution by Lsi2 is higher than that by Lsi3 (Huang *et al.*, 2022). Alteration in this transporter polarity reduces the Si accumulation level significantly in rice shoots (Sun *et al.*, 2018).

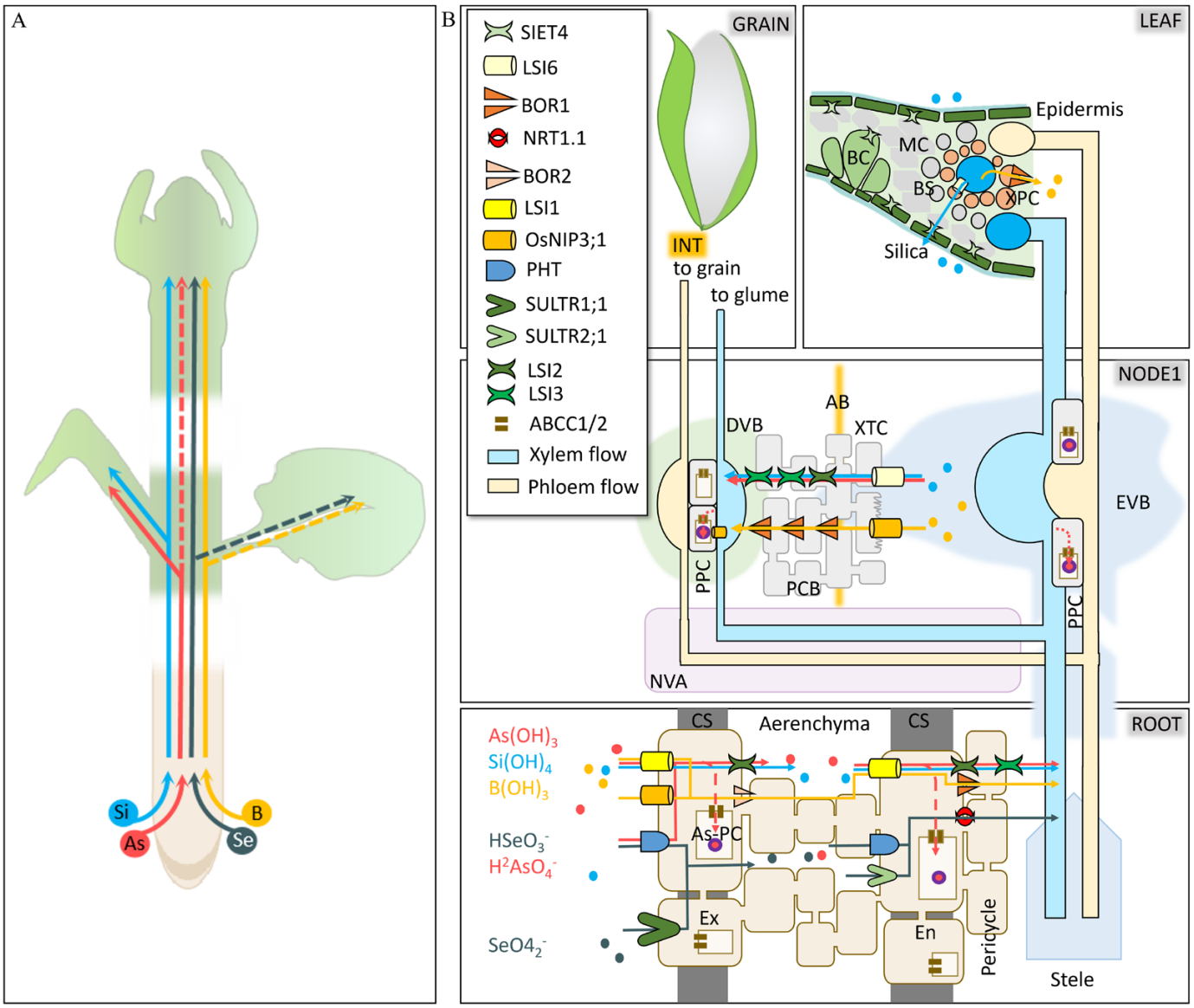

Fig. 5. The spatial distribution of metalloids and their specific transporters. (A) The distribution of metalloids within plant organs. Metalloid uptake is assisted by the maturation region in the root. In particular, silicon transport overlaps with the transpiration stream, arsenic is accumulated in leaves, whereas boron and selenium both are preferentially delivered to developing tissues. (B) Specific transporters identified for uptake, xylem loading, intervascular transfer, and subsequent deposition are shown. Ex, exodermis, En, endodermis; CS, Casparian strip; PPC, phloem parenchyma cells; EVB, enlarged vascular bundle; PCB, parenchyma cell bridge; XTC, xylem transfer cells; DVB, diffuse vascular bundle; AB, apoplastic barrier; NVA, nodal vascular anastomoses; BS, bundle sheath; BC, bulliform cells; MC, mesophyll cells; XPC, xylem parenchyma cells; INT, inositol transporter.

The Si from nodes is again distributed by Lsi6, a homologue of Lsi1. Lsi6 exhibits polarity in its subcellular localization, being restricted to the adaxial plasma membrane of the xylem parenchyma cells in both leaf sheaths and leaf blades (Yamaji *et al.*, 2008). The intervascular transfer of Si to panicles is assisted by Lsi2 and Lsi3 transporters. However, the exact mechanism of Si transfer remains uncertain due to the distinct expression patterns of Lsi2 and Lsi3 in various cell types surrounding extracellular vascular bundles (EVBs) and diffuse vascular bundles (DVBs). Specifically, Lsi3 is expressed in parenchyma cells between EVBs and DVBs, while Lsi2 is localized in the bundle sheath cell layer around EVBs. Knockout of either OsLsi6, OsLsi2, or OsLsi3 resulted in decreased distribution of Si to the panicles but increased distribution to the flag leaf (Yamaji *et al.*, 2015).

Due to the predominant retention of silicic acid in the apoplast, Si transport is facilitated by a transpiration stream (Zexer *et al.*, 2023). Thus, water loss with evaporation deposits silica as a silicified layer beneath the cuticle. The accumulation of silicic acid occurs in specialized cells of the epidermis called

silica cells and silica bodies (Hodson, 2019). These cells are lined up along the vascular bundles probably to extrude silica from the plant. A recent study found the SIET4 transporter to be localized neighbouring silica bodies and epidermal cells in the leaf. The knockout of *SIET4* spiked Si deposition in mesophyll cells and induced expression of a stress-related gene, eventually leading to plant death (Mitani-Ueno *et al.*, 2023). Again, the mechanism of silicification and biochemistry of silica cells remains an interesting unexplored chapter in silica biology (Box 2).

Plant boron transport

Plants take up B predominantly in the form of boric acid. However, whilst this small molecule is passively permeable across the bilayer (Dordas and Brown, 2000), specialized boric acid channels facilitate boric acid homeostasis in B-limited conditions. The influx of boric acid in Arabidopsis and rice is mediated by the NIP family of aquaporins. In Arabidopsis, T-DNA insertion lines of AtNIP5-1 showed growth retardation, cessation of root growth, lateral root inhibition, and reduced rosette leaves (Takano *et al.*, 2006). AtNIP5;1 is strongly up-regulated in the root elongation zone specifically in epidermal, endodermal, and cortical cells. To couple B transport, the specialized borate efflux transporter AtBOR1 is polarly localized to the stele side of the endodermis, mediating efficient xylem loading of B from the root (Takano *et al.*, 2002). BnaA3.NIP5;1 in Brassica exhibits polar localization to the distal side of the plasma membrane of the lateral root cap, mediating B influx into the root tips (He *et al.*, 2021). BnaA4.BOR2, on the other hand, showed expression in the cortex, endodermis, and stele regions of the root meristem, indicating a parallel xylem loading role (Liu *et al.*, 2024). ZmNIP3-1, an NIPII candidate, was identified as a candidate gene for tasselless mutants in rice which had *ZmNIP3-1* gene deletion and a tassel-less inflorescence phenotype (Leonard *et al.*, 2014). The polar localization pattern is retained in rice, where Lsi1 and OsBOR1 mediate efficient directional flow from the rhizosphere to the stele (Nakagawa *et al.*, 2007; Shao *et al.*, 2021) but Lsi1 expression was unaffected by fluctuations in B concentrations. The crossover between NIPII and NIPIII subfamilies for boric acid is probably due to a wider radius in NIPIIIs. However, just like Lsi1 in rice, the preference of NIPIII over NIPII for boric acid transport remains to be verified in other crops.

Plant aerial organs utilize close homologues of similar transporters in the distribution of B to developing immature leaves and inflorescence. AtNIP6-1, for instance, showed expression in nodal regions, the base of flowers, and the petioles of immature young rosette leaves, ensuring B supply to young tissues through intravascular transfer (Tanaka *et al.*, 2008). B is actively required by plants for reproductive growth, with mutants having compromised fertility, pollen architecture, and viability. Mutations in AtNIP7-1, a B influx transporter localized exclusively to the tapetum, led to defective exine walls and reduced germination (Routray *et al.*, 2018). OsNIP3-1, a homologue of AtNIP5-1, was found to be highly expressed in the node (Shao *et al.*, 2018). The collective localization of OsNIP3-1 in the xylem of EVBs and phloem of DVBs, while OsBOR1 is located to the distal side of bundle sheath cells of EVBs, indicates a similar cooperative mechanism in intervascular transfer (Shao *et al.*, 2021). For the effective distribution of B from EVBs to developing organs, various efflux transporters are reported in different plant species. A B transporter of rapeseed, BnaC4.BOR1;1c, is preferentially involved in B distribution to developing leaves and flowers (Zhang *et al.*, 2017). Similarly, the expression analysis of *SiBOR1* from *Setaria italica* showed preferential expression in the panicle, and *Sibor1* mutants had a shorter panicle, with abortive apical inflorescence (Wang *et al.*, 2022). The transcriptional variance of grapevine VvBOR1 explained berry size corelation to B concentration in cultivars such as Carménère and Cabernet Sauvignon (Pérez-Castro *et al.*, 2012). Relative to xylem, the phloem mobility of B varies considerably in plant species. B needs to be translocated to developing organs with low transpiration. The phloem mobility of B had been attributed to the production of B-complexing molecules such as polyols. The differences in sugar alcohol production in plants is thus associated with differences in B accumulation (Brown and Shelp, 1997).

Arsenic transport system

The As uptake and transport pathway in plants entirely depends on environmental conditions. Arsenate, arsenite, and methylated As are the predominant forms available to crop plants exposed to As. In anaerobic soil conditions, arsenite (p*K*a=9.2) is the major As species, existing as the neutral molecule $As(OH)_3$. Arsenous acid, having smaller size and triagonal planar symmetry, has low selectivity and is permeable through NIP, plasma membrane intrinsic protein (PIP), and tonoplast intrinsic protein (TIP) family aquaporins (Yamaji and Ma, 2021). Similar to Si, the directional transport of As in rice is assisted by OsNIP2-1 and OsLsi2 (Ma *et al.*, 2008) with competitive effect (Ma *et al.*, 2008; Tang and Zhao, 2021). However, As dynamics are more complex than those of Si considering its passive leakage through other MIP transporters. An *lsi6* mutant, for example, did not affect rice shoots, in contrast to Si (Ma *et al.*, 2008). This deviation could be due to complementation of Lsi6 function by OsNIP3;1 and other MIP aquaporins in rice roots. In addition to the *lsi1* mutant that reduced the As concentration in shoots by 50%, an OsNIP3;2 knockout decreases As levels by 20% (Chen *et al.*, 2017). The overexpression of NIP family OsNIP1;1 and OsNIP3;3 in roots also reduced As accumulation in rice attributed to compromised radial transport from roots (Sun *et al.*, 2018). In addition to arsenous acid, NIP aquaporins can also transport methylated forms of As. *Lsi1* knockout mutants absorbed 80% to 49% less

monomethylarsonous acid (MMA) and dimethylarsonous acid (DMA) than normal plants. However, the absence of the *lsi2* gene did not affect the uptake of these As compounds (Li *et al.*, 2009).

Most crops cultivated in aerobic conditions take up arsenate through phosphate transporters. In Arabidopsis, AtPHT1;1 and AtPHT1;4 are the characterized arsenate transporters. Similarly, the knockout of either OsPT4 or OsPT8 phosphate transporters reduced As concentration by ~50% in rice (Wang *et al.*, 2016; Cao *et al.*, 2017). The root to shoot transport of arsenate is facilitated by OsPT1, with knockout mutants having a 60% reduction in shoot As concentrations (Kamiya *et al.*, 2013). However, the arsenate-imposed toxicity is managed by plants at the expression level. Arsenate uptake in roots induces feedback inhibition of PT4 and PT8 transporters at the expression and post-translational modification levels (Begum *et al.*, 2016; Zhang *et al.*, 2023). Arsenate is readily converted to less toxic forms such as DMA and the As–phytochelatin (PC) complex using enzymes such as OsHAC1 and OsPCS1 (Sánchez-Bermejo *et al.*, 2014; Shi *et al.*, 2016; Hayashi *et al.*, 2017). Chemically, arsenite has the possibility of interaction with sulfhydryl groups, assisting in formation of the As–PC complex. These complexes are sequestered and compartmentalized by OsABCC1 and OsABCC7 in vacuolar structures of vascular bundles, thereby reducing arsenite availability in vascular tissues and grains (Song *et al.*, 2014; Tang *et al.*, 2019).

Due to the diverse variety of possible conjugate compounds that As can form *in planta*, a clear mechanism and the transporters involved are unknown. AtINT2 and AtINT4 showed arsenite uptake capability in oocyte and yeast assays but, considering substrate choice for INT transporters, the arsenite conjugates are more probably taken up in phloem (Duan *et al.*, 2015). In addition, rice endosperm-specific OsMATE2 transporters reduced As content in grain by 36.9–47.8% (Das *et al.*, 2018). Thus, although the transporters and genes responsive to As are widely characterized, an integrated picture is still lacking due to a paucity of knowledge regarding *in planta* diversity of arsenical species and their corresponding link with the transporters highlighted above.

Selenium transport pathways

Se absorption pathway of plants depend on their phytoavailable form. This includes selenates (SeO_4^{2-}) dominant in aerated soils, selenites (SeO_3^{2-}, $HSeO^{3-}$, and H_2SeO_3) rich in anaerobic neutral soils, and organoselenium compounds (SeCys and SeMet) present in decomposing plant reserves. Due to the low p*K*a of selenite (2.6), its uptake pathways are particularly sensitive to pH levels (Zhao *et al.*, 2010). Within the physiological range, respiratory inhibitors and low temperatures hinder selenate uptake (Ulrich and Shrift, 1968). Additionally, sulfate competes with selenate for uptake, as both are facilitated by proton gradient-sensitive sulfate transporters (Hawkesford, 2003; Sors *et al.*, 2005). Arabidopsis roots contain high affinity AtSULTR1.1 and AtSULTR1.2 isoforms which localize to the root hair epidermis and cortical cell layers and are involved in selenate uptake from the rhizosphere (Takahashi *et al.*, 2000; Hawkesford, 2003). Their homologues in rice, OsSULTR1;1 and OsSULTR1;2, are likely candidates for selenate uptake (Buchner *et al.*, 2004; Réthoré *et al.*, 2020; Zhang and Chu, 2022). Like other nutrients, selenate is taken up by root epidermal cells and transported radially to the stele via apoplastic and symplastic pathways (Takahashi *et al.*, 2000). SULTR2;1 and SULTR2;2 are located in vascular tissues on xylem parenchyma cells of leaves and roots, and therefore might be involved in stele loading and transport of selenate to above-ground tissues (Takahashi *et al.*, 2000). Selenate uptake is followed by its translocation to the leaves and incorporation into chloroplasts where it undergoes metabolic conversion by sulfate assimilation enzymes (Terry *et al.*, 2000). The SULTR3 family has been associated with transport of sulfate in chloroplasts (Cao *et al.*, 2013) and hence is likely to be involved in selenate transport as well. In chloroplasts, Se is converted to SeMet and SeCys.

At low pH, selenite uptake is sensitive to $HgCl_2$ and $AgNO_3$ which indicates involvement of aquaporins in the process (Zhang *et al.*, 2006). The neutral H_2SeO_3 is a likely candidate for MIP family aquaporins in plants. In agreement, knockout of OsNIP2-1 in rice compromised selenite uptake, demonstrating involvement of Lsi1 in selenite transport (Zhao *et al.*, 2010). However, at pH 5, selenite uptake was inhibited by phosphate (Hopper and Parker, 1999) and respiratory inhibitors (Zhang *et al.*, 2010). This evidence indicates the involvement of phosphate transporters in $HSeO_3^-$ transport (Li *et al.*, 2008). *OsPT2* knockout plants, a root epidermis- and stele-localized transporter, showed reduced selenite uptake in rice (Zhang *et al.*, 2014). However, selenite uptake through phosphate transporters shows very low accumulation in shoots (Li *et al.*, 2008). Most of the selenite in roots is readily converted to organic Se compounds such as SeMet (Yu *et al.*, 2019). Although the transport mechanism of SeMet is not well understood, overexpression of a nitrate transporter NRT1.1B in rice led to a significantly higher root to shoot ratio for SeMet suggesting SeMet transport activity and its involvement in transport from roots to shoot (Zhang *et al.*, 2019).

Conclusion

This interplay between nutrient transporters and metalloid molecules suggests a case of exaptation, where a protein sequence/structure variation is stabilized to take up new substances, facilitating survival in a new functional space within plant biology. These metalloid transporters include protein families involved in uptake of essential nutrients such as minerals and ions crucial for plant growth and development. However, due to the structural similarities between certain metalloid molecules and essential nutrients, some transporters

may have exhibited a degree of promiscuity, meaning they could also transport metalloids.

While molecular exaptation has enabled plants to adapt and evolve, the potential risk of toxic metalloid accumulation remained. Plants thus have evolved mechanisms to expel these toxic elements from their roots; however, shared pathways with essential nutrients such as phosphate and sulfate, pose challenges such as potential nutrient leakage for engineering efforts.

Exploring genetic diversity to incorporate low-affinity transporters offers a potential solution. This approach could help limit metalloid uptake in heavily contaminated soil while maintaining nutrient balance. However, this strategy may prove insufficient in nutrient-deficient soils, highlighting the need for a deeper ecological comprehension of transporter functionalities. Hence, this journey towards sustainable agriculture must be interdisciplinary with a comprehensive ecological understanding and molecular solutions that address both soil contamination and nutrient deficiencies.

Acknowledgements

The authors are grateful to the Council of Scientific and Industrial Research (CSIR) for a Senior Research Fellowship (SRF) to YS. We acknowledge the National Supercomputing Mission (NSM) through the Centre for Development of Advanced Computing (C-DAC) of the Ministry of Electronics and Information Technology (MeitY), government of India, for providing the support of high-performance computing.

Author contributions

YS, AMH, RD, and AP: conceptualization; YS: writing—original draft; YS, AMH, RD, and AP: writing—review and editing; RD and AP: supervision.

Conflict of interest

The authors declare no conflict of interest.

Funding

YS would like to acknowledge the receipt of Reasearch Fellowship recived from the Council of Scientific and Industrial Research (CSIR), Govt of India. This work was supported by the core funds received from the Department of Biotechnology, Government of India.

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