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1 Silicon mobilisation by root-released carboxylates

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11
12 **Keywords:** manganese; root exudates; phosphorus limitation; mycorrhiza; nutrient-
13 acquisition strategies; rhizosphere processes

14 Glossary

15 **Capillaroid roots:** roots that are covered with closely crowded persistent root hairs, which
16 attract moisture and dissolved nutrients through capillary action.

17 **Carboxylate:** the conjugate base of carboxylic acid. For example, the carboxylate citrate is
18 the conjugate base of the organic acid, citric acid.

19 **Chronosequences:** sequences of soils derived from the same parent material that differ in
20 properties primarily because of time as a soil-forming factor; can represent strong soil
21 nutrient availability gradients.

22 **Cluster roots:** bottle-brush-like or Christmas-tree-like structures in roots with a dense
23 packing of root hairs; these structures release carboxylates into the rhizosphere, thus
24 solubilising poorly available nutrients (*e.g.*, P, Mn) in the soil.

25 **Dauciform roots:** carrot-shaped roots with long root-hairs that release carboxylates into the
26 rhizosphere.

27 **Facilitation:** positive interaction that can occur between plants and results in an increase in
28 performance of at least one of the interacting species.

29 **Ligand-promoted dissolution:** release of metal cations (*e.g.*, Al, Fe, Mn) from minerals
30 promoted by chelating organic anions (*e.g.*, citrate, oxalate, EDTA)

31 **Mycorrhizal species:** plant species able to establish a symbiotic association with any type of
32 mycorrhizal fungus (from the Greek; $\mu\kappa\eta\sigma$, fungus + $\rho\iota\zeta\alpha$, root).

33 **Non-mycorrhizal species:** plant species unable to establish a symbiotic association with any
34 type of mycorrhizal fungus; examples include most species belonging to Brassicaceae
35 (cabbage family), Cyperaceae (sedge family) and Proteaceae.

36 **Phenols/phenolics:** plant secondary metabolites consisting of aromatic compounds with one
37 or more hydroxyl groups. They are broadly distributed in the plant kingdom, and protect
38 plants against stresses.

39 **Phytoliths:** hydrated amorphous silica structures precipitated in and between plant cells.
40 Useful tools in archaeology and palaeobiology, they are also thought to be responsible for the
41 Si-related stress alleviation (from the Greek; $\Phi\acute{\upsilon}\tau\omicron\nu$, plant + $\lambda\acute{\iota}\theta\omicron\varsigma$, stone).

42 **Phytosiderophores:** root-released organic substances (*e.g.*, avenic, mugineic, deoxymugineic
43 acids) produced by Poaceae species which strongly chelate metals and increase their
44 subsequent uptake (Fe, Zn, Cu, Mn, Cd).

45 **Quantitative defence compounds:** secondary plant compounds that reduce the digestibility
46 and/or palatability of the food source and invariably make up a major fraction of the biomass.
47 They are mostly phenolic compounds (phenolic acids, tannins, lignin).

48 **Sand-binding roots:** roots with a prominent dense sheath of sand particles bound together by
49 a mesh of root hairs and/or mucilaginous exudates.
50 **Silica:** silicon oxide with the chemical formula SiO_2 .
51 **Silicon transporters:** specific influx/efflux transporters that allow movement of Si from the
52 rhizosphere into roots.
53 **Sorption/sorbed ion:** chemical processes by which a dissolved ion becomes bound to the
54 surface or inside a mineral.
55 **Primary minerals:** minerals of lithogenic origin (*e.g.*, quartz, feldspars).
56 **Secondary minerals:** minerals of pedogenic origin that have been formed in soils as
57 products of weathering (*e.g.*, kaolinite, Fe/Al oxides).
58 **Trade-off:** increase of a functional trait that is inevitably associated with the decrease of
59 another.
60 **1:1 clay minerals:** phyllosilicates consisting of one tetrahedral silicate sheet bound to an
61 octahedral hydroxide sheet (*e.g.*, kaolinite).
62 **2:1 clay minerals:** phyllosilicates consisting of an octahedral hydroxide sheet bound between
63 two tetrahedral silicate sheets (*e.g.*, chlorite).
64

65 **Abstract**

66 Plants have evolved numerous strategies to acquire poorly-available nutrients from soil,
67 including the release of carboxylates from their roots. Silicon (Si) release from mineral
68 dissolution increases in the presence of chelating substances, and recent evidence shows that
69 leaf [Si] increases markedly in old phosphorus (P)-depleted soils, where many species exhibit
70 carboxylate-releasing strategies, compared with younger P-richer soils. Here, we propose that
71 root-released carboxylates, and more generally rhizosphere processes, play an overlooked
72 role in plant Si accumulation by increasing soil Si mobilisation from minerals. We suggest
73 that Si mobilisation is costly in terms of carbon, but becomes cheaper if those costs are
74 already met to acquire poorly-available P. Uptake of the mobilised Si by roots will then
75 depend on whether they express Si transporters.

76 **Manganese as a proxy for rhizosphere carboxylates**

77 In 2015, Lambers *et al.* proposed that leaf manganese concentrations ([Mn]) can be used as a
78 proxy for rhizosphere **carboxylate** (see Glossary) concentrations [1]. This tool has now been
79 used to screen native plant species growing in natural habitats [2–4] as well as genotypes of
80 chickpea (*Cicer arietinum*) under glasshouse conditions [5,6]. The tool is also valuable to
81 investigate to what extent neighbours depend on **facilitation** of their phosphorus (P) uptake
82 by carboxylate-releasing species [7,8]. Results on leaf [Mn], therefore, offer tremendous
83 potential to obtain information on rhizosphere processes that is very hard to get, especially
84 under field conditions. Not only does it allow us to find out if a particular species uses a
85 carboxylate-releasing P-mobilising strategy, but it can also provide evidence for facilitation
86 of P acquisition of neighbours of species that release carboxylates [4,9]. Carboxylate-
87 releasing strategies are particularly important on severely P-impooverished ancient soils [10]
88 and on young volcanic soils with low P availability due to strong P **sorption** onto Fe oxides
89 [11,12].

90 Recently, de Tombeur *et al.* [13,14] showed that on ancient soils along the Jurien Bay
91 **chronosequence** (south-western Australia) where many species exhibit carboxylate-releasing
92 P-mobilising strategies, leaf silicon concentrations ([Si]) are markedly higher than on
93 younger P-richer soils, despite very low plant-available [Si] in those ancient soils. This
94 pattern was found both at the community-level via species replacement across the
95 chronosequence, and also within some families and species that occur at different stages
96 along the chronosequence [13,14]. Conversely, all leaf macronutrient concentrations decrease
97 with increasing soil age [2,13,14]. In addition to a contribution of recycled soil **phytoliths**

98 (*i.e.* phytogenic **silica**) as a source of plant-available Si in these old soils [13], this
99 observation led us to explore if there is a causal relationship, with carboxylates not only
100 mobilising P and Mn, but also Si, which is abundant in soil, but not invariably readily
101 available for plants (Box 1). We propose a conceptual model (Figure 1) that explains why
102 leaf [Si] increases in some species on ancient soils. We also propose ways to test our model
103 and suggest future research directions.

104 **Silicon uptake in plants**

105 Silicon uptake in plants is predominantly an active process, and Si enters the plant from the
106 soil solution in the form of H_4SiO_4 through specific influx channels (**Si transporters**)
107 encoded by a specific gene, *OsLSi1* in rice (*Oryza sativa*), in which it is constitutively
108 expressed in the roots [15]. The gene *Lsi1* is expressed in a range of other plant species
109 including maize (*Zea mays*), barley (*Hordeum vulgare*), wheat (*Triticum aestivum*), soybean
110 (*Glycine max*), and tomato (*Solanum lycopersicum*) [16–20]. Plant species differ greatly in Si
111 accumulation, ranging from 1 to 100 g kg⁻¹ shoot dry weight [21]. The difference depends on
112 whether a species expresses transport proteins allowing Si permeability [22]. In addition to
113 actively taking up Si, plants acquire it passively [23]. Active transport is the major
114 mechanism in rice and maize (*Zea mays*), whereas passive uptake prevails in sunflower
115 (*Helianthus annuus*) and wax gourd (*Benincase hispida*) at higher external Si concentrations
116 [23]. Even in these species, active transport contributes to the total Si uptake, especially at
117 lower external Si concentrations. Silicon occurs as hydrated amorphous silica (phytoliths) in
118 specific cells of roots, stems and leaves.

119 **Silicon in plants: phytoliths**

120 Phytoliths in plants are thought to function as structural support [24] and in herbivore
121 defence, by abrading herbivore mouthparts [25]. Plant silicification also increases plant
122 resistance to water stress [26], reduces the soil-to-plant translocation of mineral toxicants
123 [22], and probably interferes with the recognition process upon pathogen infection [22].
124 Phytoliths vary widely in chemical composition. In addition to Si, carbon (C) and oxygen (O)
125 [27], some contain aluminium (Al), and this is considered a mechanism to detoxify Al
126 [28,29]. Phosphorus may also become trapped in phytoliths [30] as do a wide range of other
127 elements, both nutrients and toxic elements [29,31].

128 Silica-based defences are considered cheap alternatives for carbon-based **quantitative**
129 **defence compounds**. Raven [32] indeed calculated that, on a weight basis, the energetic cost

130 of incorporating 1 g of lignin is about 27 times greater than that of incorporating 1 g of SiO₂.
131 There also appears to be a **trade-off** between investments in silica- and C-based
132 defence/structural compounds, because numerous studies reported negative correlations
133 between leaf [Si] and concentrations of phenols or C-based structural components [33–36]. In
134 support of this, de Tombeur *et al.* [14] found a trade-off between **phenol-** and silica-based
135 defences along the Jurien Bay chronosequence that exhibits a very strong gradient of nutrient
136 availability [14,37], with a stronger expression of silica-based defences in old P-depleted
137 soils. Investing in silica-based defences, rather than phenol-based defences in nutrient-
138 depleted habitats, when resources are severely limiting, would make sense from an energetic
139 perspective [32]. Nevertheless, if silica-based defence is effective and less costly, why do not
140 all plants invest greatly in this putatively cheap defence strategy, rather than one based on
141 more costly carbon-based quantitative defence compounds? The higher density of silica
142 compared with C-based compounds might be a disadvantage to plants [32], but, as we
143 explore below, this might also be because Si-based defence involves less metabolic costs only
144 if there is plenty of plant-available Si in the rhizosphere, and involves substantial costs if Si
145 needs to be mobilised to become available for plant uptake.

146 **Silicon mobilisation by root-released carboxylates**

147 *Carboxylate effects on soil Si mobilisation*

148 Carboxylate-releasing strategies are crucial for plants growing in severely P-impooverished
149 soils [10,38], but their role for plant Si uptake in mobilising soil Si from soil minerals has
150 never been considered seriously. Yet, root-released carboxylates do not only increase soil P
151 and Mn mobilisation, but also that of Al, iron (Fe), calcium (Ca), potassium (K) and several
152 other metals [39–42]. Carboxylates mobilise P from **sorbed** forms by complexing metal ions
153 constituting the minerals that bind phosphate (*e.g.*, Fe and Al oxides), and displace P from the
154 soil solid phases as ligand exchange reactions are precursor to the dissolution reaction (Figure
155 1) [43]. This accounts for the strong increase in dissolved [Al] and [Fe] in the rhizosphere of
156 cluster roots compared with that in bulk soil [39]. Fe and Al oxides show a strong potential to
157 sorb Si [44–46], and Si can be associated with those pedogenic oxides. Therefore, release of
158 monosilicic acid after **ligand-promoted dissolution** of Al/Fe oxides is very likely (Figure 1).
159 In support of this, the Si and Fe co-released from a quartz-rich soil containing Fe oxides is
160 significantly increased by three carboxylates abundantly exuded by specialised roots, and the
161 releases of both elements are positively correlated (Figure 2A, B). Similarly, the dissolution
162 of **primary minerals** like feldspars, **2:1 clay minerals** like chlorite and **1:1 clay minerals**

163 like kaolinite are also ligand-promoted, and release monosilicic acid in solution (Figure 2C)
164 [47,48].

165 Mobilising Si from crystalline silicates via root-released carboxylates involves metal
166 complexation. In old highly-weathered soils, Si-bearing minerals are eventually dominated by
167 quartz and phytoliths, because most primary minerals and Al/Fe-containing **secondary**
168 **minerals** have been lost by dissolution (Box 1). Here, carboxylates may also play a role in
169 mobilising Si, because low-molecular-weight organic acids increase Si release from quartz
170 [49], and we may expect the same for phytoliths, especially given their order-of-magnitude
171 greater dissolution rate compared with that of most silicate minerals [50]. In support of this,
172 the release of Si from pure quartz is slightly increased by oxalate (Figure 2C), yet not by two
173 others carboxylates (malate, citrate). Nevertheless, adding carboxylates in a phytoliths and
174 pure quartz mixture with phytolith concentration commonly encountered in soils (4 g kg⁻¹;
175 *e.g.*, [13,51]) significantly increases the effect of carboxylates on Si release (Figure 2C). This
176 demonstrates the prominent influence of carboxylates on phytolith dissolution relative to
177 quartz dissolution. This process combined with the relatively high reactivity of phytoliths
178 compared with that of soil-derived minerals (Box 1) might explain why Si biocycling remains
179 intense in old soils having extremely low plant-available [Si] [13]. Many questions remain,
180 however, in particular whether the dissolution of phytoliths can be accelerated by
181 complexation of the metals they contain. Moreover, the dissolution rates of silicates exhibit a
182 typical V-shape dependent on pH, with lowest rates around pH = 5.5/6.5 [52]. Rates increase
183 with decreasing pH under acidic conditions, and also increase with increasing pH under
184 alkaline conditions [52,53]. Localised rhizosphere acidification by root activity [54] might
185 therefore also increase Si release through silicate dissolution in addition to the effect of
186 carboxylates.

187 *Evidence based on relationships between leaf [Si] and [Mn]*

188 Because leaf [Mn] can be used as a proxy for carboxylate-releasing strategies under the same
189 pedological conditions [1,3,5], similar patterns for the two elements are expected if Si is also
190 mobilised during the process (Figure 1). Interestingly, foliar [Si] and [Mn] increase along the
191 Jurien Bay chronosequence, as opposed to a decrease in concentrations of all macronutrients
192 [2,14]. For leaf [Si], such an increase is not only observed at the community-level, but also
193 within some species that occur at different stages along the chronosequence [13,14]. This
194 pattern is associated with a strong decline in soil P concentration [14], and a subsequent

195 increase in the relative cover of species with **cluster roots** or their functional equivalent [55]
196 that release carboxylates to acquire poorly-available P [10].

197 Interestingly, both leaf [Si] and leaf [Mn] are significantly greater in **non-mycorrhizal**
198 **species** than in **mycorrhizal species** across the Jurien Bay chronosequence, with most non-
199 mycorrhizal species known to release carboxylates (Figure 3A) [1,2]. This pattern was found
200 despite increased Si accumulation by mycorrhizal colonisation [56,57], and occurs across all
201 soils of the chronosequence (except for leaf [Si] at stage 1), despite wide variation in pH-
202 values (~5-8) (Figure S1) [2]. This may be because mycorrhizas appear to contribute little to
203 uptake of P on ancient soils [38]. In addition, high leaf [Si] in the mycorrhizal group ($> 5\text{g kg}^{-1}$)
204 only occur in Poaceae, which have Si transporters [15], and in *Hibbertia hypericoides*
205 individuals (Dilleniaceae) that do not release carboxylates but are typically facilitated by
206 cluster roots of neighbouring banksias (Proteaceae) [4,58]. In contrast, non-mycorrhizal
207 species with relatively low leaf [Si] ($< 5\text{g kg}^{-1}$) are dominated by Proteaceae, for which the
208 presence of Si transporters is unknown. Such similarity between leaf [Si] and [Mn] along this
209 chronosequence is supported by a positive relationship between the concentrations of both
210 elements when species from different families are considered (Figure 3B). This occurs across
211 all soils of the chronosequence, whatever the variations in soil pH (Figure S2). These
212 relationships are significant, but rather weak, as to be expected because species from different
213 families with contrasting capacities to accumulate Si are considered together in the analyses.

214 Because leaf [Si] vary greatly among terrestrial plant species [21] due to the
215 presence/absence of Si transporters [59], lower leaf [Si] among mycorrhizal species likely
216 reflects lower expression of Si transporters in this group (*e.g.*, Asparagaceae, Fabaceae,
217 Myrtaceae, Rhamnaceae) compared with non-mycorrhizal species (*e.g.*, Cyperaceae,
218 Haemodoraceae, Proteaceae, Restionaceae). Therefore, we also reanalysed data from de
219 Tombeur *et al.* [14] for family- and species-level variation. Interestingly, both nutrients are
220 positively correlated for both mycorrhizal (Fabaceae, Poaceae) and non-mycorrhizal
221 (Proteaceae, Cyperaceae) families (Figure 3C). The relationships are clearer for Poaceae and
222 Cyperaceae than for Fabaceae and Proteaceae, most likely because the first two strongly
223 express Si transporters [59]. Leaf [Si] and [Mn] are also correlated for *Desmocladius asper*
224 (Restionaceae) (Figure 3C), a non-mycorrhizal species that forms **sand-binding roots** [60]
225 and possibly **capillaroid roots** [61]. Similarly, Kothari *et al.* [62] found a highly significant
226 positive correlation between leaf [Si] and [Mn] in maize shoots. We suggest that these
227 relations between leaf [Si] and [Mn] are partly explained because both elements are

228 mobilised by carboxylates in the rhizosphere (Figure 1), and perhaps also via root-induced
229 acidification of the rhizosphere [54].

230 In environments where soil Mn availability is far greater than the very low concentration in
231 Jurien Bay, for example New Caledonia [63], Si mobilisation might be important to
232 ameliorate Mn toxicity in carboxylate-releasing species. In 1978, Horst & Marschner [64]
233 showed that *Phaseolus vulgaris* (common bean) plants treated with Si showed much greater
234 tolerance to Mn toxicity than untreated plants. In particular, 1.8 mM of Mn was toxic for
235 leaves in the absence of Si, but this critical level was 18 mM with Si addition [64]. The
236 authors explained the beneficial effect of Si on Mn toxicity by the prevention of local Mn
237 accumulation within leaf tissues and a more homogeneous distribution. This conclusion is
238 supported by more recent studies on a range of species [65–67].

239 The situation for Poaceae differs from that outlined above, because grasses tend not to
240 enhance the release of carboxylates in response to P starvation yet do accumulate both Si and
241 Mn (Figure 3C). Poaceae typically enhance the release of **phytosiderophores**, which are
242 strong chelators of Fe, in response to Fe deficiency [68–70]. Phytosiderophores also mobilise
243 zinc [71], Mn [72], and Si [73]. Gattullo *et al.* [73] showed that Fe-deficient barley (*Hordeum*
244 *vulgare*) mobilises Si, in addition to Fe, from smectite through the exudation of organic
245 ligands. Interestingly, Fe-deficient maize plants not only enhance expression of transporters
246 for Fe²⁺, but also those involved in transport of P (ZmPHT1;7 and ZmPHO1) [70]. Being
247 strong chelators, phytosiderophores are expected to mobilise P sorbed onto Fe oxides. We are
248 not aware of enhanced phytosiderophore release in response to P-starvation, but that is what
249 we might expect to account for increases in leaf [Mn] in Poaceae with decreasing P
250 availability along the Jurien Bay chronosequence [14].

251 *Decrease of leaf [Si] with fertilization*

252 In wheat, an elevated P supply reduces foliar [Si] [74], suggesting a role for chelating
253 compounds in mobilising both P and Si in this species. These might be phytosiderophores, as
254 these do mobilise Si when chelating Fe [73], whereas grasses tend not to release large
255 amounts of carboxylates. There are exceptions, however, for example oats (*Avena sativa*)
256 [75] and sorghum (*Sorghum bicolor*) [76]. Carboxylate release would be suppressed under
257 high P supply, thus reducing Si mobilisation and uptake. Similarly, leaf [Si] of *Holcus*
258 *lanatus* (Poaceae) increases under P deficiency [77], and Johnson *et al.* [78] showed that leaf
259 [Si] decreased markedly in three grass species (*Cynodon dactylon*, *Eragrostis curvula* and

260 *Microlaena stipoides*), following fertilisation (nitrogen, K, P). More generally, recent studies
261 suggest that grasses may not have evolved silica-based defences in response to extensive
262 herbivory, but in response to dry hot [79] and infertile environments [80]. In summary,
263 fertilisation, and especially P fertilisation, tends to decrease leaf [Si] in a range of Poaceae
264 which we suggest is caused by a decrease in soil Si mobilisation through the suppression of
265 exudation of chelating substances.

266 **Concluding remarks and perspectives**

267 We propose that plants growing in P-impooverished environments that express Si transporters
268 exhibit relatively higher leaf [Si] because of the mobilisation of Si by root-released
269 carboxylates or other chelators into the rhizosphere. Moreover, protons released in the
270 rhizosphere alongside carboxylates [81] might further increase Mn, P [54] and possibly Si
271 solubilisation for subsequent plant uptake. These processes are expected mainly at the family
272 or species-level, because plants exhibit great variation in their leaf [Si] due to
273 presence/absence of Si transporters [59]. At this level, correlations between leaf [Si] and
274 [Mn] are expected if species/individuals are sampled across a gradient of P availability, and
275 therefore of rhizosphere carboxylate concentrations, particularly if they exhibit Si
276 transporters. Nevertheless, an overall correlation between leaf [Si] and [Mn] when species
277 from different families are considered reveals a possible greater role of carboxylates on plant
278 Si uptake (Figure 3B). Because carboxylate-releasing P-mobilising strategies incur significant
279 C costs [82], the costs of silica-based defences might be higher than commonly realised [32]
280 if carboxylates or other root exudates are needed to mobilise Si in the rhizosphere, especially
281 when plant-available [Si] is low.

282 While many questions remain, this Opinion Paper paves the way towards the exploration of a
283 role for root exudates in soil-plant-herbivore Si dynamics, thus providing promising
284 perspectives for ecosystem Si research in both natural systems and agroecosystems (see
285 Outstanding questions) [83]. Indeed, the role of root exudates has been considered for
286 mobilisation of many essential nutrients, but ignored for Si, a beneficial element [22]. It is,
287 however, time to consider these aspects, since the significant role of Si in plant biology
288 [22,84] and ecology [85] is increasingly acknowledged. A detailed understanding of the
289 factors influencing its dynamics in soil-plant systems is therefore urgently required.

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298

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521

522 **Figure Captions**

523 **Key Figure 1.** Effects of phosphorus (P)-mobilising carboxylates on ligand-promoted
524 dissolution of minerals, thus releasing iron (Fe), aluminium (Al) and manganese (Mn), and
525 co-solubilising silicon (Si). Carboxylates (organic anions) are released via a carboxylate
526 channel. Inorganic P (P_i) is taken up by P transporters against an electrochemical potential

527 gradient, driven by a proton gradient resulting from active H^+ transport by a H^+ -pumping
528 ATPase [86]. Carboxylates chelate metal cations (*e.g.*, Fe, Al and Mn) of pedogenic oxides
529 (*e.g.*, Fe, Al and Mn oxides) and metal-containing silicates, thereby increasing their
530 dissolution. Carboxylates also increase quartz and phytolith dissolution [49] (Figure 2C),
531 although the underlying mechanisms are less clear. In Strategy 1 species, chelated Fe moves
532 to the root surface, where it is reduced, followed by uptake via a Fe^{2+} transporter [iron-
533 regulated transporter (IRT)]; this transporter is not specific and transports other
534 micronutrients, including Mn^{2+} . In Strategy 2 species, ligand exchange converts Fe to Fe^{3+} -
535 phytosiderophore (PS) complexes for root uptake via the Fe^{3+} -PS transporter [yellow stripe 1
536 (YS1) and yellow stripe-like (YSL) transporter] [87,88]. Silicon occluded in metal-containing
537 silicates as well as Si sorbed onto or co-precipitated in pedogenic oxides is subsequently
538 released into the soil solution in the form of monosilicic acid (*i.e.* H_4SiO_4) by this ligand-
539 promoted dissolution process [48,89]. Monosilicic acid can then be taken up passively or
540 actively, the latter involving Si transporters, *e.g.*, LSi1, which is highly expressed in some
541 species, *e.g.*, rice (*Oryza sativa*) [15], but not in some other species. In soils with low plant-
542 available [Si], we expect accumulation of Si in plants with high rhizosphere carboxylate
543 concentrations that highly express Si transporters. High concentrations of carboxylates in the
544 rhizosphere may be the result of release of the Si-accumulating plants themselves, as shown
545 here, or by their neighbours [7]. This figure was created using BioRender. Modified from [1].

546 **Figure 2.** Effects of a range of oxalate, citrate and malate concentrations on silicon (Si) and
547 iron (Fe) release from a quartz-rich soil containing Fe oxides (stage 4 of the Jurien Bay
548 chronosequence; [13]) (means \pm SE; $n = 3$) (A), and relation between the release of both
549 elements for the same soil and same carboxylates at similar concentrations (B). Effects of
550 same carboxylates at same concentrations on Si release from pure chlorite (purchased from
551 the Source Clays Repository, Purdue University), pure kaolinite (same manufacturer), pure
552 quartz (Supelco®), and pure quartz mixed with sugarcane phytoliths from [35] at a 0.4%
553 concentration (means \pm SE; $n = 3$) (C). Three grams of soil/reference material was shaken for
554 16 h with 30 mL of a 0.01 M KCl solution with different carboxylate concentrations (0, 125,
555 250 and 500 μ M) [90], and Si and Fe were analysed by ICP-OES after filtration. In (A) and
556 (C), bar colours indicate carboxylate concentrations, and different letters indicate significant
557 differences ($p \leq 0.05$) among carboxylate concentrations (ANOVA followed by Tukey HSD
558 tests). In (B), the black line indicates the regression line between both variables.

559 **Figure 3.** Leaf silicon (Si) and manganese (Mn) concentrations along the Jurien Bay
560 chronosequence as dependent on putative nutrient-acquisition strategy (A). Relationship
561 between leaf Si and Mn concentrations for the same individuals (B), and for Cyperaceae,
562 Poaceae, Fabaceae, Proteaceae and *Desmocladus asper* (Restionaceae) (C). All data (281
563 individuals belonging to 86 species) are from [14]. Plots in (A) show boxplots with medians,
564 25th and 75th percentiles and whiskers extended to 1.5 times the interquartile range. Data
565 presented beyond whiskers represent outliers. Both axes were log-transformed, and the p-
566 values derived from linear mixed-effects models testing the effect of nutrient-acquisition
567 strategy on leaf nutrient concentration (with species and plot as random factors). Legend
568 details: NM, non-mycorrhizal; CR, cluster roots; DR, **dauciform roots**; SB, sand-binding
569 roots. In (B) and (C), black lines indicate the regression lines between both variables, shaded
570 areas represent 95% confidence interval of the regression and circle colours (B) or symbols
571 (C) indicate nutrient-acquisition strategy or different species, respectively. In (B), both axes
572 were log-transformed. In (C), x-axes were log-transformed except for Cyperaceae, while y-
573 axes were log-transformed for Fabaceae. In (B), the p-value was derived from linear mixed-
574 effects models (with species and plot as random factors). In (C), p-values were derived from
575 Pearson tests of correlation. See also Online Supplemental Information Figures S1 & S2.

Box 1: Silicon in soils

Silicon is the second most abundant element in the Earth's crust (28.8%), after oxygen (47.2%) [91]. It is the basis for a wide range of silicate minerals which makes it ubiquitous in most soil types, but only a small fraction of soil Si is available for plant uptake [92]. During the weathering of silicate minerals, monosilicic acid is released in the soil solution and can then be taken up by plants, mobilised in the formation of secondary minerals, sorbed onto reactive soil particles (*e.g.*, Fe and Al oxides), or transferred towards the hydrosphere, where it serves as a nutrient for marine phytoplankton known as diatoms [92,93]. The concentration of dissolved Si primarily depends on the dissolution rates of primary and secondary Si-bearing minerals in soils [92,93]. During prolonged soil weathering, plant-available Si is first driven by the dissolution of primary minerals (*e.g.*, feldspars), followed by secondary 2:1 (*e.g.*, smectite), and then 1:1 (*e.g.*, kaolinite) clay minerals [93]. Plant-available [Si] decreases following this sequence, as the degree of desilication (*i.e.* Si loss by leaching) increases over time [92–94]. The lowest plant-available [Si] are typically found in old, highly-weathered soils dominated by residual sand-sized poorly-soluble [50] quartz minerals, most of primary and secondary minerals having been lost by dissolution [94]. Because the solubility of phytoliths (*i.e.* phytogenic silica) is greater than that of many primary and secondary Si-bearing minerals [50], their dissolution also contributes to plant-available Si [13,95]. Such contribution is thought to increase with increasing soil age and desilication [13,93].

576 **Text Boxes**

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