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Are clay minerals a significant source of Si for crops? A comparison of amorphous silica and the roles of the mineral type and pH

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32

33

Abstract

Identifying the source(s) of silicon (Si) for plant is a key issue in understanding the terrestrial cycle of Si and for deciphering the reservoir of bioavailable Si to Si accumulating crops. In soils, amorphous Si, one of the most bioavailable source, is mostly present as phytoliths and has been suggested for use as a Si fertilizer by diatomite application. Although clay minerals are known to contribute to plant nutrition, their role as a major source of silica for plants has not been fully addressed. We aim at evaluating the efficiency of clay minerals as a source of Si for crops.

We conducted two pot experiments: one wheat-growing experiment to compare a clay (vermiculitic) mineral and amorphous silica particles (diatomite, which is used as a phytolith substitute), and one rice-growing experiment to compare two types of clay (kaolinite vs montmorillonite) common in rice cultivation.

We confirmed that the amorphous silica was more efficient than vermiculite for Si uptake by wheat. However, the Si uptake was not significantly different between the 5% diatomite substrate and the 25% vermiculite substrate indicating that clays may challenge amorphous silica, as a source of Si for crops. The kaolinite probably delivered less Si to the rice than the montmorillonite because of the lower specific surface area and lower pH of kaolinite substrates. Because clays are generally much more abundant in soils than amorphous silica, we concluded that clays may be a substantial Si source for plants, depending on the clay mineralogy.

1 Introduction

Recognition of the importance of plant cycling in the global silicon (Si) cycle [1] and the increased body of evidence demonstrating that Si is a beneficial element in agriculture [2, 3] have stimulated research on Si in the context of increasing food demand [4]. Silicon is not considered as a nutrient but many studies show that at low Si concentration, many crops have lower development and yield [2, 5, 6]. Common crops such as rice and wheat are considered as Si accumulators while rice has a higher Si requirement than wheat [7]. They accumulate Si mostly in the shoots through the uptake of dissolved Si from the soil. The accumulation of Si in plants is therefore highly dependent on the bioavailability of Si in soil [2]. The Si bioavailability ultimately depends on the reactivity (solubility and rate of dissolution) of the silicate minerals present in soils, which include aluminosilicates, crystalline silica minerals (e.g. quartz) and amorphous silica particles. Amorphous silica particles are mostly present as phytoliths, which are the form of Si that is accumulated in plants and is reincorporated into the soil during litter decomposition. Based on laboratory experiments, it has been shown that phytoliths are 2 to 4 orders of magnitude more reactive than primary mafic silicates and feldspar as well as secondary clay minerals [8]. The higher solubility of phytoliths supports models of the terrestrial biogeochemical Si cycle that show the importance of plant Si recycling [1, 9]. Typically, the amount of phytoliths in soils is approximately 1% soil dry weight (DW) [10], and Si in phytoliths initially originates from the slow dissolution of primary minerals at different rate depending on the environmental conditions including the soil type [11].

In some parts of the world soils may be acidic and depleted in primary silicate minerals leading to low values of phytoavailable Si [12] and/or croppings may have led to exhaustion of phytoavailable Si [5]. In this type of situation, Si fertilization has been found to increase crop

77 yields [2, 5, 13]. The materials used as Si fertilizers are varied, but some contain or are composed
78 of amorphous silica either as phytoliths (e.g. biochar see [14]) or as diatomite [13, 15]. Clay
79 minerals are present in various amounts and in different types in cultivated soils depending on
80 the degree of soil weathering and the climate [11]. They play a major role in plant nutrition by
81 providing large specific surface areas that can fix nutrients [16]. There is evidence in the
82 literature that clay mineral structures may be affected by plants. *Cornu* et al. [17] compared the
83 evolution of the clay composition between forested and cultivated soils and showed that the
84 lower pH under forest led to quicker clay dissolution and aluminum release. More recently, it
85 was shown at Morrow plot experiment field (USA) that continuous cropping for 110 years led
86 to an increase in fine clay particles (<0.05 mm) [18], which is an indicator of clay mineral
87 dissolution. In a rice paddy field in Camargue (France), the decreased crystallinity of smectite
88 was attributed to rice cultivation and its subsequent Si uptake [19]. However, no associated Si
89 concentrations in plants were reported in that study, or in the other abovementioned studies.
90 Some data show that Si bioavailability was correlated with clay content [2, 20], although a
91 recent study in South India did not confirm this statement [21]. Si isotopes were used to trace
92 the origin of Si in southern Indian soil solution from forested and cultivated areas, and the
93 authors found that input from clays could be neglected compared to amorphous silica [22, 23].
94 It has been found that natural prairie ecosystems in California extracted larger proportion of
95 biogenic Si (Si solubilized from phytoliths) from the topsoil but also took up Si from poorly
96 crystalline secondary silicates that were solubilized at depth [24].
97 The objective of this paper is therefore to document the contribution of clays to crop uptake
98 compared to amorphous silica using pot experiments. Our hypothesis is that clay minerals may
99 constitute a significant Si source because their abundance in soils (ca. 10% DW or more) may
100 compensate for their lower solubility compared to phytoliths, the abundance of which is

generally low (below 1%) [25]. For this purpose, we conducted two pot experiments using rice and wheat, first, to compare the Si uptake from quartz (as an inert material), a clay mineral and an amorphous Si substrate (diatomite), and second, to evaluate the roles of two clay minerals, kaolinite and smectite, which are typical clay minerals in acidic and neutral soils, respectively, that are used to cultivate rice [12].

2 Materials and methods

2.1 Pot experiment 1 (exp.1) with wheat (*Triticum turgidum* L. cv. Claudio W.)

Three types of materials were used, that is, quartz, vermiculite and diatomite. Quartz (99.87% SiO₂, Sibelco, France), which was further cleaned and sieved with dilute nitric acid and rinsed with distilled water to remove impurities, was selected as the reference inert material. The cleaned quartz was mixed with a vermiculitic clay (Vermica AG, Bözen, Switzerland) or diatomite (Clarcel 78, CECA) in different proportions on a % dry weight (DW) basis for (diatomite or vermiculite) /quartz ratios of [25/75], [15/85], and [5/95]. Diatomite was used as a source of amorphous Si and as a proxy for phytoliths based on the following assumptions: 1) the solubility of phytoliths does not differ from that of amorphous Si [8]; 2) the dissolution rates of phytoliths and diatomaceous lake sediments fall within the same range [26]; and 3) the specific surface areas of phytoliths and diatoms, although highly variables, fall within the same ranges of 5-315 m² g⁻¹ and 25-250 m² g⁻¹ for phytoliths [8, 27] and diatoms [28], respectively. Assuming that diatomite is equivalent to phytoliths in terms of the amount and form of Si, our experiments using 5 to 25% diatomite over-estimated the average amount of phytoliths in the soil, which is generally below 1%, but they were compatible with the cases reported in the literature [29, 30]. We chose 5% as a minimum value in our experiment because using 1% diatomite would have

been difficult to mix homogeneously while the % of clay used was within the range of the clay amount found in agricultural soils.

2.2 Pot experiment 2 (exp.2) with rice (*Oryza sativa* L., cv. Anagha)

Three types of silicate were used, namely quartz (similar to experiment 1), which was mixed with 2 different clay minerals: montmorillonite was used because it is a common mineral in the smectite group (natural montmorillonite, Aroma-Zone, France) and kaolinite (Merck, Germany). We tried to grow rice on a substrate containing only quartz, and we used mixtures of clays with quartz in the following proportions: (vermiculite or kaolinite)/quartz in DW % = [35/65], [25/75] and [15/85].

2.3 Experimental and analytical conditions

The purity of the materials was verified using X-ray diffraction (Philips PW3710 at 30 kV and 10 mA). The specific surface of the initial materials was also measured (3flex, Micromeritics, adsorption measured in the BET range $0.05 < p/p^0 < 0.3$). For both pot experiments, 400-ml plastic pots were prepared, each of which contained 300 g of the prepared substrates and they were tested in 3 (exp. 1) or 5 (exp. 2) replicates with 4 plants per pot and in 2 (exp. 1) or 3 (exp. 2) replicates without plants. All the plastic and glassware was rinsed with 10% HNO₃. Initially, the pots were seeded at a density of six seeds per pot and the seedlings were thinned to four individuals per pot at five days after germination. Each pot was fertilized with a ¼ Hoagland solution (without Si) and watered to keep substrates at water holding capacity (WHC). The plants were grown under controlled conditions with a short-day cycle (8/16 h 23 °C/20 °C day/night), 70% humidity and 187 $\mu\text{mol photon m}^{-2} \text{ s}^{-1}$ of light intensity. The pots were randomly rotated and the weeds were removed regularly when present. The plants were

harvested after 60 days by cutting the shoots approximately one centimeter above the substrate surface. Plant samples were washed with distilled water and oven dried at 70 °C until reaching a constant weight. The shoot dry weights were measured and the shoots were then ground into powder. The pH values of the various substrates were measured in water before and after plant growth (ratio 1:2.5). The Si concentration in the plant shoots was obtained using 1% Na₂CO₃ extraction followed by colorimetric determination [31] or using Tiron extraction [32]. For exp. 2, one Rhizon® (Rhizosphere Research Products bv, NL) was installed in each pot. Soil solutions were collected after 4 and 7 weeks of growth, and the Si concentration (DSi) was measured by colorimetry [31].

All the data were statistically analyzed using a one-way ANOVA. Then, a post-hoc test of pairwise multiple comparisons of Fisher (LSD) was performed on the different parameters to assess if their various levels were significantly different from each other, at a significance level of $P < 0.05$ with XLSTAT software for Windows.

3 Results

The X-ray diffractogram showed no impurities in the quartz material, while the vermiculite clay was composed of a mixture of vermiculite with vermiculite-illite, regular smectite-illite interlayers and irregular illite-smectite interlayers. The presence of smectite and quartz was detected in the diatomite, feldspar, quartz and illite were detected in the kaolinite material and illite, feldspar, carbonates and gypsum were found in the montmorillonite material. The specific surfaces were 0.01 m² g⁻¹ for quartz, 4.3 et 7.6 m² g⁻¹ for the diatomite and the vermiculite respectively and, 123 and 10 m² g⁻¹ for the montmorillonite and the kaolinite, respectively.

For wheat (exp.1), the results showed that the Si was significantly higher in the shoots grown on diatomite substrates than in shoots grown on vermiculite substrates (Table 1); the shoot biomass was significantly higher on the 25% diatomite substrate than on other substrates showing that below 25% diatomite, the nature of the substrate had no effect on the biomass (Figure 1, Table 1). The uptake or mineralomass of Si (Table 1), showed that diatomite substrates accumulated more Si than vermiculite substrates in general. However, the Si uptake from the 5% diatomite substrate and on the 25% vermiculite substrate were not significantly different.

The pH was significantly higher on vermiculite substrates (approximately 9) than on diatomite substrates (approximately 5), with pH values decreasing with increasing proportions of diatomite and with plants. pH did not significantly change in the vermiculite modality. The pH of vermiculite and smectite may range from acidic to alkaline. Alkaline values may be attributed to impurities such as carbonates or to the types of exchangeable cations (Ca^{2+} being more acidic than Na^+ [33]). Surprisingly, the Si concentration in the wheat shoots grown on vermiculite substrates was not negligible. However, the Si concentration in the shoots was significantly higher on the diatomite substrates (17-25 g Si kg⁻¹) than on those containing vermiculite (8-13 g Si kg⁻¹) with a trend towards higher values at higher proportions of diatomite or vermiculite (Table 1).

For rice (exp. 2), the results showed a significantly higher Si concentration and Si uptake in shoots grown on the montmorillonite substrates than in the shoots grown on kaolinite substrates (Table 2). The shoot biomass was the highest on the 35% montmorillonite substrates and on the 35% kaolinite substrate (Figure 1). The pH was acidic in the soil solutions of the kaolinite substrates, near neutral in that of the 100% quartz substrate and alkaline in the soil

solutions of the montmorillonite substrates and all slightly lower than the respective pH of the initial substrates. The plants grown on the 100% quartz substrate did not survive after 2 weeks, possibly because the sandy texture was not favorable to rice growth [34] as rice requires partially saturated clay soil. The silicon concentration in the soil solution increased with time in the pots without plants, regardless of the clay mineral. It decreased when the pots were planted, indicating Si depletion through Si uptake. However, although the plants went on growing between 4 and 7 weeks, the Si concentration in the soil solution was higher after 7 weeks than after 4 weeks of growth, indicating continuous dissolution in both the montmorillonite and the kaolinite pots.

4 Discussion

The Si concentration of the wheat shoots (experiment 1) fell within the lower range of 21 durum wheats ($13\text{--}33\text{ g Si kg}^{-1}$) [35] although the concentrations were lower in wheat grown on vermiculite. Our data confirmed that amorphous silica is a better source of Si for plant uptake than clay minerals as stated by [8]. The difference between the 2 sources was explained by the higher reactivity (solubility, rate of dissolution) of amorphous silica, while BET was similar. The acidic pH, which resulted from the mixture of diatomite, quartz and nutrient solution, allowed for amorphous silica dissolution and its uptake by plants, as shown by *Sandhya* et al. [13] who demonstrated the positive effect of diatomaceous earth applications on acidic soils in southern India for rice. The fact that the Si uptake by wheat was not significantly different between the 5% diatomite substrate and the 25% vermiculite substrate (Table 1) indicated that clays may challenge amorphous silica as a source of Si for crops. However, 5% amorphous silica is rarely found in nature. To estimate how much diatomite would be required to fit the Si concentration

measured on the vermiculite mixtures, a regression analysis was performed using the data from the diatomite pots, assuming that at 0% diatomite (or 100% quartz), the Si concentration in the shoots would be negligible.

The curve should pass through 0 if there were no Si source in the system. In the experiment, this is not the case for several reasons: first, there is always a tiny amount of Si in seeds that may be reallocated to shoots; second, we assumed that 100% of quartz is crystalline and thus should not provide Si to the system. However, impurities less than 5% and amorphous Si induced by grinding cannot be detected by DRX. This is indeed visible in the soil solution collected in the 100% Quartz pot with rice. But we consider that the limited impact of these experimental biases does not prevent calculation of a theoretical regression curve using 0 as the origin for 0% diatomite.

We found that the data fitted a hyperbola-type regression (Figure 2) described as follows:

$$(1) \quad \text{Si}_{\text{shoots concentration (g/kg)}} = (m * \% \text{ diatomite}) / (k + \% \text{ diatomite})$$

with $m (= 26.8)$ and $k (= 2.79)$, the two constants that were calculated using the transformation of eq . 1 into the following linear equation:

$$(2) \quad 1/\text{Si}_{\text{shoots concentration (g/kg)}} = 1/m + (k/m) * (1/\% \text{ diatomite})$$

Accordingly, to obtain the equivalent of 13 g Si kg⁻¹ in shoot, which was the maximum concentration found using 25% vermiculite (Table 1, Figure 2), we estimated that 2.6% diatomite would be required. Following the same line of reasoning, we calculated the amount of vermiculite required to match 1% phytoliths, a current concentration found in soils, assuming that diatomite is a proxy for phytoliths. We obtained 5% vermiculite for a concentration of 7.7 g Si kg⁻¹ in shoot. The 5/1 ratio between vermiculite and phytoliths is approximately the same as the ratio expected from the dissolution rates of clays and phytoliths [8].

244

245 In experiment 2, all the Si concentrations obtained for rice were lower than the average value
246 of 31.7 g Si kg⁻¹ [7], but those in rice grown on montmorillonite fell within the range of values
247 (20–30 g Si kg⁻¹) obtained for a rice variety grown in various southern Indian soils [36]. The Si
248 concentrations in rice shoots grown on kaolinite substrates were one order of magnitude lower
249 than most of the values found in the literature but they were within the same order of
250 magnitude as the value (2.6 g Si kg⁻¹) found for a mutant rice variety that was defective in Si
251 uptake [5]. The higher Si uptake on montmorillonite substrates compared to kaolinite was
252 explained by a higher montmorillonite dissolution rate, as indicated by the higher Si
253 concentrations in the soil solution. However, Si is released from both minerals at similar rates,
254 with a similar U pattern according to the pH, and with minimum rates at approximately pH 7–8
255 and maximum rates under acidic conditions [37, 38]. Because the pH in the kaolinite substrates
256 was lower than it was in the montmorillonite substrates, while kaolinite released less Si, pH was
257 not responsible for the larger Si release by montmorillonite. However, the reactivity also
258 depends on the surface area, which was larger for the montmorillonite (123 m² g⁻¹) than for the
259 kaolinite (10 m² g⁻¹) as reported in the literature [39]. The larger Si uptake from the
260 montmorillonite substrates relative to the kaolinite substrates may therefore be attributed to
261 the higher specific surface of montmorillonite particles that are releasing larger amounts of Si
262 combined with near-neutral pH conditions favorable to rice growth.

263 However, from the montmorillonite substrates, the plants extracted only part of the Si present
264 in the soil solution indicating that the Si concentration in solution was not the limiting factor for
265 plant uptake (Table 2). On kaolinite substrates, the Si uptake was correlated with the Si
266 concentration in the soil solution, indicating that at this low pH value, the rice took up only a
267 limited amount of Si due to the unfavorable growth conditions (Figure 3A). By contrast, the

uptake from montmorillonite substrates was correlated with the difference in Si concentrations in the soil solution measured between pots without and with plants, indicating that solubilization was efficient at providing enough Si to the rice plants (Figure 3B). Kaolinite and montmorillonite were thus able to provide significant but different amounts of Si to plants.

5 Conclusion

The wheat experiment showed that amorphous silica performed better than vermiculite at providing Si to wheat. Clays may therefore challenge amorphous silica (phytoliths) for Si provision to plants, because the usually higher proportion of clay found in soils may offset their lower reactivity. The finding that the equivalence between clay and amorphous silica is more in favor of clay than expected from their respective dissolution rates deserves more research. The rice experiment showed that montmorillonite at or near a neutral pH was more favorable for Si uptake than kaolinite at an acidic pH, as also found in the field [13]. The clay type and pH are therefore two key parameters that can explain the role of clays in Si uptake by plants.

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Tables

Table 1 Results of the pot experiment 1 using wheat grown for 60 days on substrates composed of mixtures of diatomite or vermiculite with quartz in the proportions of 25/75, 15/85 and 5/95% DW. The Si concentration and biomass are from the shoots and the pH was measured at the end of the experiment in the substrates. For each line except for pH, different letters indicate that the means are statistically different at the $P \leq 0.05$ level. For pH, different letters indicate that the means are statistically different at the $P \leq 0.05$ level considering all modalities, with and without plants.

		Diatomite/Quartz (%)			Vermiculite/Quartz (%)		
		25/75	15/85	5/95	25/75	15/85	5/95
Shoot [Si]	Mean	24.92 A	21.80 A	17.28 B	13.02 C	10.46 CD	7.67 D
g Si kg ⁻¹ , n=3	<i>SD</i>	1.42	2.16	1.27	3.38	1.71	0.62
Shoot biomass	Mean	0.71 A	0.55 B	0.48 B	0.45 B	0.45 B	0.44 B
g DW pot ⁻¹ , n=3	<i>SD</i>	0.1	0.11	0.06	0.08	0.09	0.04
Shoot Si uptake	Mean	17.71 A	11.88 B	8.28 C	5.81 CD	4.61 D	3.36 D
mg Si pot ⁻¹ , n=3	<i>SD</i>	2.25	2.40	0.95	1.13	0.40	0.13
pH of initial substrates		6.37	6.30	6.54	8.79	8.89	9.00
pH substrate, n= 2	Mean	5.01 F	5.13 E	5.76 D	8.93 C	9.09 AB	9.00 BC
without plants	<i>SD</i>	0.04	0.01	0.02	0.01	0.00	0.13
pH substrate, n= 3,	Mean	4.71 G	4.95 F	5.20 E	9.12 A	9.18 A	9.01 BC
with plants	<i>SD</i>	0.03	0.04	0.05	0.02	0.04	0.08

Table 2 Results of the pot experiment 2 with rice grown for 60 days in substrates composed of mixtures of montmorillonite or kaolinite with quartz in proportions of 35/65, 25/75 and 15/85% DW. The Si concentrations and biomass are from the shoots and the pH was measured at the end of the experiment in the substrates. Dissolved Si (DSi) was measured in soil solutions collected 4 and 7 weeks after sowing. For each line, different letters in each column indicate that the means are statistically different at the $P \leq 0.05$ level, ND=not determined (no growth).

			Quartz 100%	Montmorillonite/Quartz (%)			Kaolinite/Quartz (%)		
				35/65	25/75	15/85	35/65	25/75	15/85
Shoot [Si]	Mean	ND		29.23 A	24.92 B	23.62 B	5.54 C	5.27 C	3.54 C
g Si kg ⁻¹ , n=3	SD	-		3.67	1.42	3.123	0.73	0.56	0.25
Shoot biomass	Mean	ND		1.45 A	0.92 C	0.58 E	1.15 B	0.79 CD	0.66 DE
g DW pot ⁻¹ , n=3	SD	-		0.11	0.14	0.18	0.21	0.12	0.05
Shoot Si uptake	Mean	ND		41.98 A	22.77 B	14.86 C	6.23 D	4.12 DE	2.33 E
mg Si pot ⁻¹ , n=3	SD	-		2.23	2.75	3.82	0.45	0.45	0.18
pH of initial substrates		6.92		8.39	8.54	9.07	5.49	5.71	6.05
pH soil solution n=3	Mean	6.26 B		7.87 A	7.90 A	7.88 A	3.70 F	3.77 EF	4.10 DEF
without plants	SD	0.02		0.05	0.01	0.02	0.05	0.04	0.14
pH soil solution n=5	Mean	6.55 B^(a)		7.79 A	7.88 A	7.89 A	4.89 C	4.40 CDE	4.50 CD
with plants	SD	0.16		0.06	0.06	0.02	1.15	0.72	0.36
[DSi], mg Si L ⁻¹ , 4 weeks	Mean	2.3 G		11.1 BC	11.2 BC	11.0 BC	17.6 A	13.7 B	7.1 EF
n= 3, without plants	SD	0.2		0.6	1.0	0.3	1.6	4.5	3.6
[DSi], mg Si L ⁻¹ , 4 weeks	Mean	ND		8.3 DE	10.2 CD	9.3 CDE	16.5 A	10.0 CD	4.7 F
n= 5, with plants	SD	-		1.3	1.2	0.9	1.4	1.3	1.3
[DSi], mg Si L ⁻¹ , 7 weeks,	Mean	7.96 D		22.9 BC	18.2 CD	15.0 CD	39.5 A	35.9 AB	13.7 CD
n= 3, without plants	SD	0.55		2.1	1.1	1.6	4.9	17.8	4.2
[DSi], mg Si L ⁻¹ , 7 weeks,	Mean	ND		11.8 B	15.0 B	14.7 B	20.6 A	23.2 A	11.2 B
n= 5, with plants	SD	-		1.8	1.6	2.9	1.4	6.1	6.2

^(a): pH in pots initially with plants but measured after plants had died

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Figures captions

402

403 **Fig 1** Photographs of the pot experiments 1 and 2 before harvesting for wheat (A, B) and rice
404 (C, D) showing the variation of plant height according to the proportion (% dry weight) of
405 diatomite (D) vermiculite (V), montmorillonite (M) and kaolinite (K) mixed with quartz

406

407 **Fig 2** Plots of the data from experiment 1 with a hyperbola-type regression model for diatomite
408 mixtures used to estimate the amount of diatomite required (below 5%) to match the Si
409 concentration in shoots grown on clay mineral (V) mixtures

410

411 **Fig 3** Relationship between Si exportations by rice and Si concentrations in soil solution in
412 experiment 2 A: silicon exportation by rice shoots for the 2 types of clay minerals,
413 montmorillonite and kaolinite; B: for montmorillonite only, silicon exportation by rice shoots in
414 relation to the difference in Si concentration measured in the soil solution after 7 weeks of
415 growth between pots without and with plants

416

417 **Figure 1**

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421 **Figure 2**

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424 **Figure 3**

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