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

The objective of this paper is therefore to document the contribution of clays to crop uptake compared to amorphous silica using pot experiments. Our hypothesis is that clay minerals may constitute a significant Si source because their abundance in soils (ca. 10% DW or more) may 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% SiO_2, *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 $m^2\ g^{-1}$ and 25-250 $m^2\ g^{-1}$ 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, Microméritics, adsorption measured in the BET range $0.05<p/p°<0.3$). 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% HNO_3. 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 µmol photon m^{-2} 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% Na_2CO_3 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 $m^2\ g^{-1}$ for quartz, 4.3 et 7.6 $m^2\ g^{-1}$ for the diatomite and the vermiculite respectively and, 123 and 10 $m^2\ g^{-1}$ 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 (13-33 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) $Si_{\text{shoots concentration (g/kg)}} = (m*\%\ \text{diatomite})/(k + \%\ \text{diatomite})$

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

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].

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

However, from the montmorillonite substrates, the plants extracted only part of the Si present in the soil solution indicating that the Si concentration in solution was not the limiting factor for plant uptake (Table 2). On kaolinite substrates, the Si uptake was correlated with the Si concentration in the soil solution, indicating that at this low pH value, the rice took up only a 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.

References

1. Alexandre A, Meunier J-D, Colin F, Koud JM (1997) Plant impact on the biogeochemical cycle of silicon and related weathering processes. Geochim Cosmochim Acta 61:677-682

2. Liang Y, Nikolic M, Bélanger R, Gong H, Song A (2015) Silicon in agriculture: From theory to practice. Springer 235p

3. Coskun D, Deshmukh R, Sonah H, Menzies JG, Reynolds O, Ma JF, Kronzucker HJ, Bélanger RR (2019) The controversies of silicon's role in plant biology. New Phytol 221:67–85

4. Luyckx M, Hausman J-F, Lutts S, Guerriero G (2017) Silicon and plants current knowledge and technological perspectives, Front Plant Sci 8 article 411

5. Ma J-F, Takahashi E (2002) Soil fertilizer and plant silicon research in Japan. Elsevier

6. Guntzer F, Keller C, Meunier J-D (2012) Benefits of plant silicon for crops, a review. Agron Sustain Dev 32:201-213

7. Hodson MJ, White PJ, Mead A, Broadley MR (2005) Phylogenetic variation in the silicon composition of plants. Ann Bot 96:1027-1046

8. Fraysse F, Pokrovsky OS, Schott J, Meunier J-D (2009) Surface chemistry and reactivity of plant phytoliths in aqueous solutions. Chem Geol 258:197-206

9. Conley DJ (2002) Terrestrial ecosystems and the global biogeochemical silica cycle. Global Biogeochemical Cycles 16:1121, doi:10.1029/2002GB001894

10. Keller C, Guntzer F, Barboni D, Labreuche J, Meunier J-D (2012) Impact of agriculture on the Si biogeochemical cycle: Input from phytolith studies. C R Geoscience 344:739-746

11. Cornelis J-T, Delvaux B, Georg RB, Lucas Y, Ranger J, Opfergelt S (2011) Tracing the origin of dissolved silicon transferred from various soil-plant systems towards rivers a review. Biogeosciences 8:89-112

12. Meunier J-D, Sandhya K, Prakash NB, Borschneck D, Dussouillez P (2018) pH as a proxy for estimating plant-available Si? A case study in rice fields in Karnataka (South India). Plant Soil 432:143-155

13. Sandhya K, Prakash NB, Meunier J-D (2018) Diatomaceous earth as source of silicon on the growth and yield of rice in contrasted soils of Southern India. J Soil Sci Plant Nutr 18:344-360

14. Houben D, Sonnet P, Cornelis J-T (2014) Biochar from *Miscanthus* a potential silicon fertilizer. Plant Soil 374:871–882

15. Crooks R, Prentice P (2017) Extensive investigation into field-based responses to a silica fertilizer. Silicon 9:301-304

16. Velde B, Barré P (2010) Soils, Plants and Clay Minerals: Mineral and Biologic Interactions. Springer-Verlag Berlin Heidelberg, 249p

17. Cornu S, Montagne D, Hubert F, Barré P, Caner L (2012) Evidence of short-term clay evolution in soils under human impact. CR Geoscience 344:747-757

18. Bakker E, Hubert F, Wander MM, Lancon B (2018) Soil development under continuous agriculture at the Morrow plots experimental fields from X-ray diffraction profile modelling. Soil Syst 2:46; doi103390/soilsystems2030046

19. Irfan K, Trolard F, Shahzad T, Cary L, Mouret J-M, Bourrié G (2017) Impact of 60 years of intensive rice cropping on clay minerals in soils due to Si exportation. Am J Agric For 5:40-48

20. Vandevenne FI, Barao L, Ronchi B, Govers G, Meire P, Kelly EF, Struyf E (2015) Silicon pools in human impacted soils of temperate zones. Global Biogeochemical Cycles 29: 1439-1450

21. Meunier J-D, Barboni D, Anwar-ul-Haq M, Levard C, Chaurand P, Vidal V, Grauby O, Huc R, Laffont-Schwob I, Rabier J, Keller C (2017) Effect of phytoliths for mitigating water stress in durum wheat. New Phytol 215:229-239

22. Riotte J, Meunier J-D, Zambardi T, Audry S, Barboni D, Anupama K, Prasad S, Chmeleff J, Potrasson F, Sekhar M, Braun JJ (2018) Processes controlling silicon isotopic fractionation in a forested tropical watershed : Mule Hole critical zone observatory (Southern India). Geochim. Cosmochim. Acta. doi.org/10.1016/j.gca.2018.02.046

23. Riotte J, Sandhya K, Prakash NB, Audry S, Zambardi T, Chmelef J, Buvaneshwari S, Meunier J-D (2018) Origin of silica in rice plants and contribution of diatom Earth fertilization: insights from isotopic Si mass balance in a paddy field. Plant Soil 423:481−501. https://doi.org/10.1007/s11104-017-3535-z

24. White AF, Vivit DV, Shulz MS, Bullen TD, Evett RR, Aagarwal J (2012) Biogenic and pedogenic controls on Si distributions and cycling in grasslands of the Santa Cruz soil chronosequence California. Geochim Cosmochim Acta 94:72-94

25. Alexandre A, Bouvet M, Abbadie L (2011) The role of savannas in the terrestrial Si cycle a case-study from Lamto Ivory Coast. Global Planet Changes 78:162-169

26. Loucaides S, Van Cappelen P, Behrends T (2008) Dissolution of biogenic silica from land to ocean role of salinity and pH. Limnol Oceanogr 53(4):1614-1621

27. Fraysse F, Pokrovsky OS, Schott J, Meunier J-D (2006) Surface properties, solubility and dissolution kinetics of bamboo phytoliths. Geochimica et Cosmochimica Acta 70:1939–1951

28. Sarmiento JC, Gruber N (2006) Chapter 10 Oceanic carbon cycle atmospheric CO_2 and climate. In: Ocean biogeochemical dynamics, Princeton University Press, Princeton NJ, 99p

29. Meunier J-D, Colin F, Alarcon C (1999) Biogenic silica storage in soils. Geology 27:835-838

30. Osterrieth M, Borrelli N, Alvarez MF, Fernández Honaine M (2015) Silica biogeochemical cycle in temperate ecosystems of the Pampean Plain, Argentina. Journal of South American Earth Sciences 63:172-179

31. Meunier J-D, Keller C, Guntzer F, Riotte J, Braun J-J, Anupama K (2014) Critical examination of the wet alkaline procedure used to quantify the amorphous silica fraction (ASi) in soils and continental waters. Geoderma 216:30-35

32. Guntzer F, Keller C, Meunier J-D (2010) Determination of the silicon concentration in plant material using Tiron extraction. New Phytol 188:902-906

33. Kaufhold S, Dohrmann R, Koch D, Houben G (2008) The pH of aqueous bentonite suspensions. Clays Clay Miner 56:338-343

34. Dou F, Soriano J, Tabien RE, Chen K (2016) Soil texture and cultivar effects on rice (*Oryza sativa L.*) grain yield yield components and water productivity in three water regimes. PLoS ONE 11 e0150549 doi101371/journal pone0150549

35. Merah O, Deléens E, Monneveux P (1999) Grain yield carbon isotope discrimination mineral and silicon content in durum wheat under different precipitation regimes. Physiol Plant 107:387-394

36. Narayanaswamy C, Prakash NB (2009) Calibration and categorization of plant available silicon in rice soils of South India. J Plant Nutr 32:1237-1254

37. Rozalen M, Huertas FH, Brady PV (2008) Experimental study of the effect of pH on the kinetics of montmorillonite dissolution at 25°C. Geochim Cosmochim Acta 72:4224-4253

38. Huertas FJ, Chou L, Wollast R (1999) Mechanism of kaolinite dissolution at room temperature and pressure Part II Kinetic study. Geochim Cosmochim Acta 63:3261-3275

39. Umran Dogan AU, Dogan M, Inal M, Sarikaya Y, Aburub A, Wurster DE (2006) Baseline studies of the clay minerals society source clays specific surface area by the Brunauer Emmett Teller (BET) method. Clays Clay Miner 54:62-66

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≤ 005 level. For pH, different letters indicate that the means are statistically different at the P≤ 005 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	*SD*	*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	*SD*	*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	*SD*	*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	*SD*	*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	*SD*	*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≤ 005 level, ND=not determined (no growth).

		Quartz	**Montmorillonite/Quartz (%)**			**Kaolinite/Quartz (%)**		
		100%	**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

Figures captions

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

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

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

Figure 1

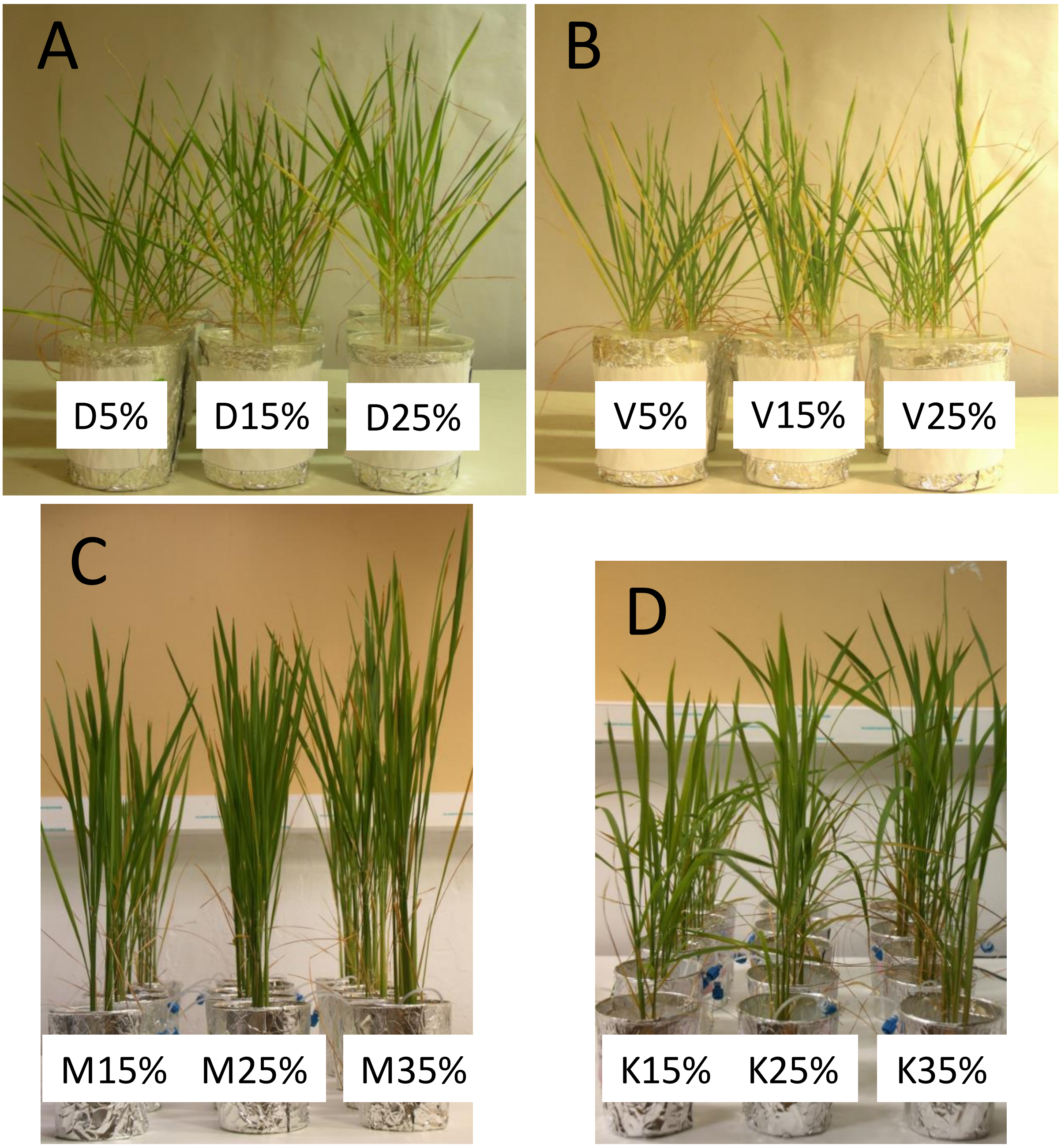


Figure 2

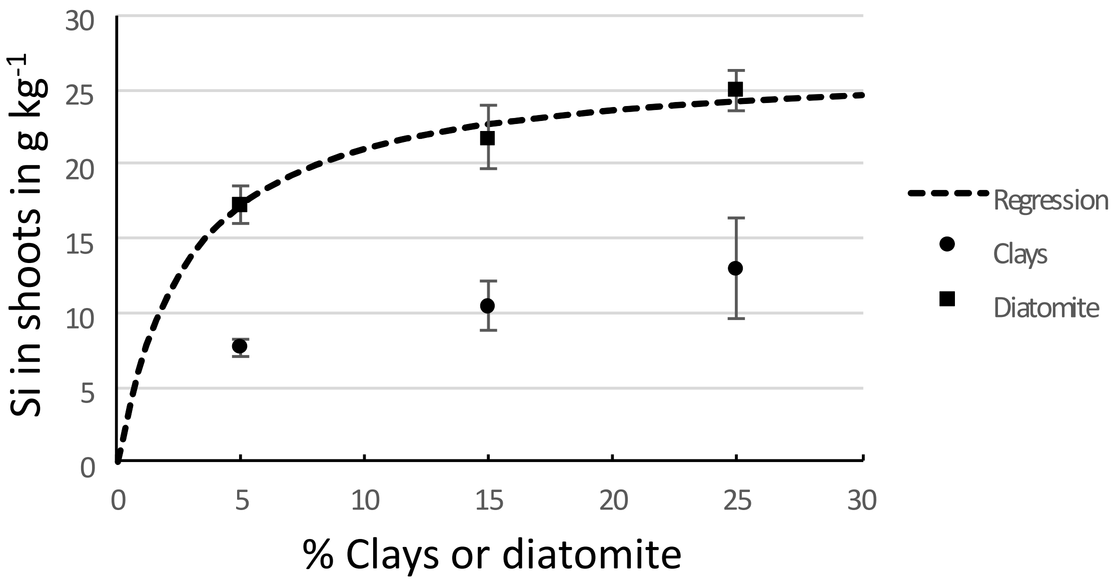
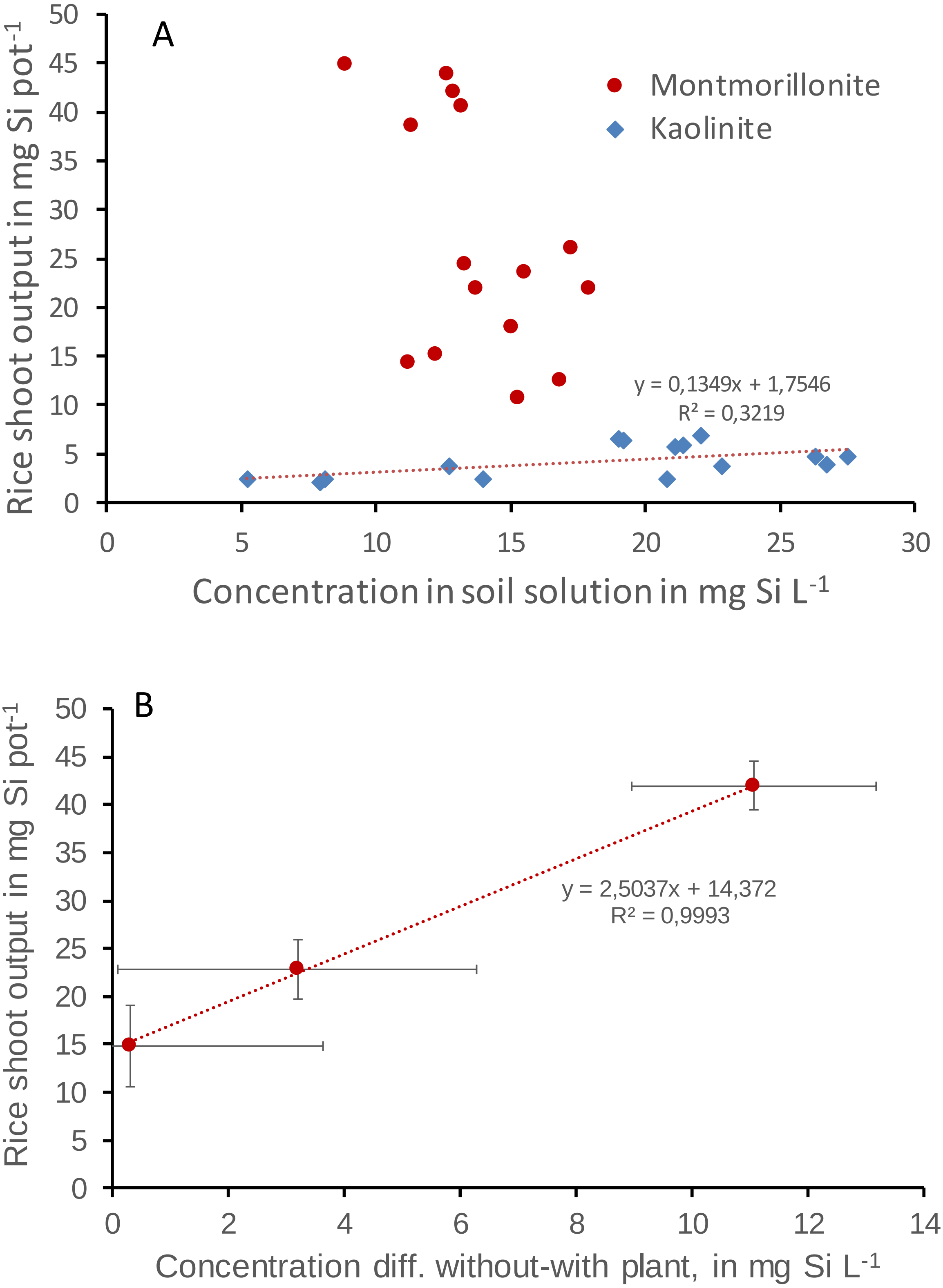

Si in shoots in g kg-1
0
5
10
15
20
25
30
0
5
10
15
20
25
30
% Clays or diatomite
Regression
Clays
Diatomite

Figure 3


A
Montmorillonite
Kaolinite
y = 0,1349x + 1,7546
R² = 0,3219
Rice shoot output in mg Si pot-1
Concentration in soil solution in mg Si L-1
0
5
10
15
20
25
30
35
40
45
50
B
y = 2,5037x + 14,372
R² = 0,9993
Rice shoot output in mg Si pot-1
Concentration diff. without-with plant, in mg Si L-1
2
4
6
8
12
14