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1	Are clay minerals a significant source of Si for crops? A comparison of
2	amorphous silica and the roles of the mineral type and pH
3	Catherine Keller ¹ *, Muhammad Rizwan ² , Jean-Dominique Meunier ¹
4	
5	¹ Aix-Marseille Univ, CNRS, IRD, Coll de France, INRAE, CEREGE, Technopole de l'Environnement Arbois-
6	Méditerranée, BP80, 13 545 Aix-en-Provence, Cedex 4, France
7 8 9	² Department of Environmental Sciences and Engineering, Government College University, Faisalabad 38000, Pakistan
10	*Corresponding author: <u>keller@cerege.fr</u>
11	
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34 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.

52

53 1 Introduction

54

55 Recognition of the importance of plant cycling in the global silicon (Si) cycle [1] and the 56 increased body of evidence demonstrating that Si is a beneficial element in agriculture [2, 3] 57 have stimulated research on Si in the context of increasing food demand [4]. Silicon is not 58 considered as a nutrient but many studies show that at low Si concentration, many crops have 59 lower development and yield [2, 5, 6]. Common crops such as rice and wheat are considered as 60 Si accumulators while rice has a higher Si requirement than wheat [7]. They accumulate Si 61 mostly in the shoots through the uptake of dissolved Si from the soil. The accumulation of Si in 62 plants is therefore highly dependent on the bioavailability of Si in soil [2]. The Si bioavailability 63 ultimately depends on the reactivity (solubility and rate of dissolution) of the silicate minerals 64 present in soils, which include aluminosilicates, crystalline silica minerals (e.g. quartz) and 65 amorphous silica particles. Amorphous silica particles are mostly present as phytoliths, which 66 are the form of Si that is accumulated in plants and is reincorporated into the soil during litter 67 decomposition. Based on laboratory experiments, it has been shown that phytoliths are 2 to 4 68 orders of magnitude more reactive than primary mafic silicates and feldspar as well as 69 secondary clay minerals [8]. The higher solubility of phytoliths supports models of the terrestrial 70 biogeochemical Si cycle that show the importance of plant Si recycling [1, 9]. Typically, the 71 amount of phytoliths in soils is approximately 1% soil dry weight (DW) [10], and Si in phytoliths 72 initially originates from the slow dissolution of primary minerals at different rate depending on 73 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].

106

107 2 Materials and methods

108

109 **2.1** Pot experiment 1 (exp.1) with wheat (*Triticum turgidum* L. cv. Claudio W.)

110 Three types of materials were used, that is, quartz, vermiculite and diatomite. Quartz (99.87% 111 SiO₂, Sibelco, France), which was further cleaned and sieved with dilute nitric acid and rinsed 112 with distilled water to remove impurities, was selected as the reference inert material. The 113 cleaned quartz was mixed with a vermiculitic clay (Vermica AG, Bözen, Switzerland) or diatomite 114 (Clarcel 78, CECA) in different proportions on a % dry weight (DW) basis for (diatomite or 115 vermiculite) /quartz ratios of [25/75], [15/85], and [5/95]. Diatomite was used as a source of 116 amorphous Si and as a proxy for phytoliths based on the following assumptions: 1) the solubility 117 of phytoliths does not differ from that of amorphous Si [8]; 2) the dissolution rates of phytoliths 118 and diatomaceous lake sediments fall within the same range [26]; and 3) the specific surface 119 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 120 121 diatomite is equivalent to phytoliths in terms of the amount and form of Si, our experiments 122 using 5 to 25% diatomite over-estimated the average amount of phytoliths in the soil, which is 123 generally below 1%, but they were compatible with the cases reported in the literature [29, 30]. 124 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 clayamount found in agricultural soils.

127

128 **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].

135

136 **2.3 Experimental and analytical conditions**

137 The purity of the materials was verified using X-ray diffraction (Philips PW3710 at 30 kV and 10 138 mA). The specific surface of the initial materials was also measured (3flex, Microméritics, 139 adsorption measured in the BET range 0.05<p/p°<0.3). For both pot experiments, 400-ml plastic 140 pots were prepared, each of which contained 300 g of the prepared substrates and they were 141 tested in 3 (exp. 1) or 5 (exp. 2) replicates with 4 plants per pot and in 2 (exp. 1) or 3 (exp. 2) 142 replicates without plants. All the plastic and glassware was rinsed with 10% HNO₃. Initially, the 143 pots were seeded at a density of six seeds per pot and the seedlings were thinned to four 144 individuals per pot at five days after germination. Each pot was fertilized with a ¼ Hoagland 145 solution (without Si) and watered to keep substrates at water holding capacity (WHC). The 146 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 147 148 randomly rotated and the weeds were removed regularly when present. The plants were

149 harvested after 60 days by cutting the shoots approximately one centimeter above the 150 substrate surface. Plant samples were washed with distilled water and oven dried at 70 °C until 151 reaching a constant weight. The shoot dry weights were measured and the shoots were then 152 ground into powder. The pH values of the various substrates were measured in water before 153 and after plant growth (ratio 1:2.5). The Si concentration in the plant shoots was obtained using 154 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. 155 156 Soil solutions were collected after 4 and 7 weeks of growth, and the Si concentration (DSi) was 157 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.

162

163 **3 Results**

164

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.

172 For wheat (exp.1), the results showed that the Si was significantly higher in the shoots grown 173 on diatomite substrates than in shoots grown on vermiculite substrates (Table 1); the shoot 174 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 175 176 (Figure 1, Table 1). The uptake or mineralomass of Si (Table 1), showed that diatomite 177 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 178 179 different.

180 The pH was significantly higher on vermiculite substrates (approximately 9) than on diatomite 181 substrates (approximately 5), with pH values decreasing with increasing proportions of 182 diatomite and with plants. pH did not significantly change in the vermiculite modality. The pH 183 of vermiculite and smectite may range from acidic to alkaline. Alkaline values may be attributed 184 to impurities such as carbonates or to the types of exchangeable cations (Ca²⁺ being more acidic 185 than Na⁺ [33]). Surprisingly, the Si concentration in the wheat shoots grown on vermiculite 186 substrates was not negligible. However, the Si concentration in the shoots was significantly 187 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 188 189 (Table 1).

190

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

196 solutions of the montmorillonite substrates and all slightly lower than the respective pH of the 197 initial substrates. The plants grown on the 100% quartz substrate did not survive after 2 weeks, 198 possibly because the sandy texture was not favorable to rice growth [34] as rice requires 199 partially saturated clay soil. The silicon concentration in the soil solution increased with time in 200 the pots without plants, regardless of the clay mineral. It decreased when the pots were 201 planted, indicating Si depletion through Si uptake. However, although the plants went on 202 growing between 4 and 7 weeks, the Si concentration in the soil solution was higher after 7 203 weeks than after 4 weeks of growth, indicating continuous dissolution in both the 204 montmorillonite and the kaolinite pots.

205

206 4 Discussion

207

208 The Si concentration of the wheat shoots (experiment 1) fell within the lower range of 21 durum 209 wheats (13-33 g Si kg⁻¹) [35] although the concentrations were lower in wheat grown on 210 vermiculite. Our data confirmed that amorphous silica is a better source of Si for plant uptake 211 than clay minerals as stated by [8]. The difference between the 2 sources was explained by the 212 higher reactivity (solubility, rate of dissolution) of amorphous silica, while BET was similar. The 213 acidic pH, which resulted from the mixture of diatomite, guartz and nutrient solution, allowed 214 for amorphous silica dissolution and its uptake by plants, as shown by Sandhya et al. [13] who 215 demonstrated the positive effect of diatomaceous earth applications on acidic soils in southern 216 India for rice. The fact that the Si uptake by wheat was not significantly different between the 217 5% diatomite substrate and the 25% vermiculite substrate (Table 1) indicated that clays may 218 challenge amorphous silica as a source of Si for crops. However, 5% amorphous silica is rarely 219 found in nature. To estimate how much diatomite would be required to fit the Si concentration

220 measured on the vermiculite mixtures, a regression analysis was performed using the data from 221 the diatomite pots, assuming that at 0% diatomite (or 100% quartz), the Si concentration in the 222 shoots would be negligible.

223 The curve should pass through 0 if there were no Si source in the system. In the experiment, 224 this is not the case for several reasons: first, there is always a tiny amount of Si in seeds that 225 may be reallocated to shoots; second, we assumed that 100% of quartz is crystalline and thus 226 should not provide Si to the system. However, impurities less than 5% and amorphous Si 227 induced by grinding cannot be detected by DRX. This is indeed visible in the soil solution 228 collected in the 100% Quartz pot with rice. But we consider that the limited impact of these 229 experimental biases does not prevent calculation of a theoretical regression curve using 0 as 230 the origin for 0% diatomite.

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

232 (1) Si shoots concentration (g/kg) = (m*% diatomite)/(k + % diatomite)

with m (= 26.8) and k (= 2.79), the two constants that were calculated using the transformation

234 of eq. 1 into the following linear equation:

235 (2)
$$1/\text{Si}_{\text{shoots concentration } (g/kg)} = 1/m + (k/m)*(1/\% \text{ diatomite})$$

236

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].

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 (20–30 g Si kg⁻¹) obtained for a rice variety grown in various southern Indian soils [36]. The Si 247 248 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.

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

268 uptake from montmorillonite substrates was correlated with the difference in Si concentrations 269 in the soil solution measured between pots without and with plants, indicating that 270 solubilization was efficient at providing enough Si to the rice plants (Figure 3B). Kaolinite and 271 montmorillonite were thus able to provide significant but different amounts of Si to plants.

272

273 **5 Conclusion**

274

275 The wheat experiment showed that amorphous silica performed better than vermiculite at 276 providing Si to wheat. Clays may therefore challenge amorphous silica (phytoliths) for Si 277 provision to plants, because the usually higher proportion of clay found in soils may offset their 278 lower reactivity. The finding that the equivalence between clay and amorphous silica is more in 279 favor of clay than expected from their respective dissolution rates deserves more research. The 280 rice experiment showed that montmorillonite at or near a neutral pH was more favorable for Si 281 uptake than kaolinite at an acidic pH, as also found in the field [13]. The clay type and pH are 282 therefore two key parameters that can explain the role of clays in Si uptake by plants. 283

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Tables

377

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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.

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		Diat	omite/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, with plants	Mean SD	4.71 G <i>0.03</i>	4.95 F <i>0.04</i>	5.20 E <i>0.05</i>	9.12 A <i>0.02</i>	9.18 A <i>0.04</i>	9.01 BC <i>0.08</i>	

389Table 2 Results of the pot experiment 2 with rice grown for 60 days in substrates composed of**390**mixtures of montmorillonite or kaolinite with quartz in proportions of 35/65, 25/75 and 15/85%**391**DW. The Si concentrations and biomass are from the shoots and the pH was measured at the**392**end of the experiment in the substrates. Dissolved Si (DSi) was measured in soil solutions**393**collected 4 and 7 weeks after sowing. For each line, different letters in each column indicate**394**that the means are statistically different at the P< 005 level, ND=not determined (no growth).</td>

		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

400	
401	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	



421 Figure 2



