



**QUEEN'S
UNIVERSITY
BELFAST**

Characterization and dissolution properties of phytolith occluded phosphorus in rice straw

Trinh, T. K., Nguyen, T. T. H., Nguyen, T. N., Wu, T. Y., Meharg, A. A., & Nguyen, M. N. (2017). Characterization and dissolution properties of phytolith occluded phosphorus in rice straw. *Soil and Tillage Research*, 171, 19-24. <https://doi.org/10.1016/j.still.2017.04.002>, <https://doi.org/10.1016/j.still.2017.04.002>

Published in:
Soil and Tillage Research

Document Version:
Peer reviewed version

Queen's University Belfast - Research Portal:
[Link to publication record in Queen's University Belfast Research Portal](#)

Publisher rights

© 2017 Elsevier Ltd. This manuscript version is made available under the CC-BY-NC-ND 4.0 license <http://creativecommons.org/licenses/by-nc-nd/4.0/>, which permits distribution and reproduction for non-commercial purposes, provided the author and source are cited.

General rights

Copyright for the publications made accessible via the Queen's University Belfast Research Portal is retained by the author(s) and / or other copyright owners and it is a condition of accessing these publications that users recognise and abide by the legal requirements associated with these rights.

Take down policy

The Research Portal is Queen's institutional repository that provides access to Queen's research output. Every effort has been made to ensure that content in the Research Portal does not infringe any person's rights, or applicable UK laws. If you discover content in the Research Portal that you believe breaches copyright or violates any law, please contact openaccess@qub.ac.uk.

Open Access

This research has been made openly available by Queen's academics and its Open Research team. We would love to hear how access to this research benefits you. – Share your feedback with us: <http://go.qub.ac.uk/oa-feedback>

Characterization and dissolution properties of phytolith occluded phosphorus in rice straw

Trang K. Trinh¹, Thinh T. H. Nguyen², Tu N. Nguyen³, Ta Yeong Wu⁴,

Andrew A. Meharg⁵, Minh N. Nguyen^{*1,5}

¹ Faculty of Environmental Science, VNU University of Science, Vietnam National University, Hanoi (VNU), 334 Nguyen Trai, Thanh Xuan, Hanoi, Viet Nam.

² Institute for Nuclear Science and Technology, 179 Hoang Quoc Viet, Hanoi, Viet Nam.

³ Faculty of Environment, Vietnam National University of Agriculture, Trau Quy, Gia Lam, Hanoi, Viet Nam.

⁴ Chemical Engineering Discipline, School of Engineering, Monash University, Jalan Lagoon Selatan, 47500 Bandar Sunway, Selangor Darul Ehsan, Malaysia.

⁵ Institute for Global Food Security, Queen's University Belfast, David Keir Building, Malone Road, BT9 5BN, Northern Ireland, UK.

* Correspondence: Dr. Minh N. Nguyen, E-mail: minhnn@vnu.edu.vn

1. Introduction

Rice straw derived phytolith, a siliceous structure formed through Si precipitation in rice plant tissues (Parr and Sullivan, 2005), has been widely known as a potential source to sustain soil Si nutrient pools when it is cycled to soils (Dobermann and Fairhurst, 2000; Nguyen et al., 2014; Nguyen et al., 2015; Seyfferth et al., 2013). However, there has been a lack of systematic information on the fate of rice straw derived phytolith in soils, and to what extent this nutrient pool can benefit crops. Phosphorus (P) is among the most important nutrient elements in rice. P is taken up from the soil solution by root absorption, transport across cell membranes and compartmentation, and redistribute within different parts of rice plant (Agarie et al., 1996; Schachtman et al., 1998; Yamaji et al., 2008). During rice growth,

26 P can be re-translocated through rice's xylem/phloem system (Schachtman et al., 1998), and
27 some parts might be trapped within phytolith structure (so-called phytOP) when Si
28 precipitates. This means that even if rice straw is cycled to soil, this P pool might still exist
29 inside phytolith and unavailable for plant uptakes. There has been a knowledge gap and lack
30 of experimental evidence for the fate of phytOP and its capacity to serve as an additional P
31 source for crops.

32 Generally, dissolution of phytolith is regulated by the desilification in aqueous
33 solution. This process occurs via hydrolysis of $\equiv\text{Si-O-Si}\equiv$ bonds of the silica surface in which
34 water molecules orient their electronegative pole towards the Si atoms in silica structure,
35 resulting in a transfer of electron density to the $\equiv\text{Si-O-Si}\equiv$ bonds, thereby raising their length
36 and consequently breaking them (Dove and Crerar, 1990). pH is well understood as a crucial
37 factor driving phytolith dissolution kinetics via protonation or deprotonation reactions
38 (Frayse et al., 2009; Nguyen et al., 2014) which can either increase resistance of the surface
39 or make the surface more vulnerable from nucleophilic attacks (Dove and Crerar, 1990). On
40 the other hand, occluded organic matter can be another factor in preserving phytolith since it
41 may act as a protective shield against hydrolysis of the silica (Nguyen et al., 2014; Parr and
42 Sullivan, 2005). In this study, the release of P was inspected in considering the dissolution
43 rate of phytolith's silica body and influence of occluded organic matter content.

44 Open-field burning of rice straw after harvesting is a conventional method of disposal
45 of straw to return nutrients to the soils in many rice-based countries. Although this method
46 causes significant emission of greenhouse gases (e.g. CO_2 , CO, NO_x), losses of nutrients (e.g.
47 N, K, P,) and contributes to air pollution (Andreae and Merlet, 2001; Bijay et al., 2008;
48 Dobermann and Fairhurst, 2000), it is the easiest way of returning most nutrients to the soils,
49 and at present rice growers have little incentive to change this method. As burning of rice
50 straw at different temperatures might result in various degrees of dehydroxylation of biogenic

51 silica and organic matter contents, rice straw phytolith ash samples which were obtained from
52 300 to 1000°C ashing temperatures were used to examine the release of P in batch
53 experiments. X-ray tomographic microscopy (Marone, 2010), provided a visualization for
54 siliceous structure of phytolith. Scanning electron microscopy (SEM), X-ray diffraction
55 (XRD), Fourier transform infrared spectroscopy (FTIR), specific surface area (SSA) and
56 chemical composition analysis were carried out to evaluate transformation of phytolith and its
57 effect on P release. Statistical analysis using Pearson's test can help to provide an additional
58 information of correlation between the released Si and P. Based on the identification of
59 relation between the release of P and dissolution of rice-straw phytolith, this study clarifies
60 the dynamics of the phytOP and suggest possible management options on one hand to
61 maximize the use of this phytOP pool, and on the other hand to adjust fertilization strategy.

62 **2. Materials and Methods**

63 ***2.1. Study site and sample production***

64 Rice-straw was collected from a paddy field (105°44' E long, 20°59' N lat) in the Red
65 River Delta (RRD), a second largest delta in Vietnam. In the RRD, approx. 12 tons ha⁻¹ of the
66 rice straw can be annually burnt and returned to the fields which serves as large amount of
67 phytolith for paddy soils. The rice-straw was air-dried, milled and passed through a 1.0-mm
68 sieve. Ashing was conducted by heating the rice straw sample in an furnace at a target
69 temperature range between 300 and 1000°C for 2 h. The derived phytolith containing ash was
70 washed with DI water, followed by centrifugation and decantation, and finally were dried at
71 60°C in an oven for 24 h. The samples from pretreatments at 300, 400, 500, 600, 700, 800,
72 900 and 1000°C were used for chemical analysis, mineralogical characterizations, SSA
73 analysis and batch dissolution experiments. For kinetic experiments, the samples treated at
74 400, 700 and 1000°C were selected.

75 ***2.2. Sample characterization***

76 *Tomographic and morphological analysis:* a 3D image of the siliceous structures of a rice
77 plant was built by using YaDiV software (Friese et al., 2013), and input data from X-ray
78 tomographic microscopy by TOMCAT (TOMographic Microscopy and Coherent rAdiology
79 experimenTs) beamline at the Swiss Light Source, Paul Scherrer Institute, Villigen,
80 Switzerland. Dry rice leaf was scanned under monochromatic beam from a 2.9 T
81 superbending magnet at an energy of 11.1 keV. Micromorphology of the sample was
82 inspected by using SEM (FEI Quanta 600 FEG, USA).

83 *Chemical composition:* To examine chemical composition, the samples derived from
84 pretreatments at 300 to 1000°C were examined using the Particle Induced X-Ray Emission
85 (5SDH-2 Pelletron accelerator system, USA). Total organic carbon (TOC) in the samples was
86 measured by wet digestion with concentrated H₂SO₄ and 0.5 M K₂Cr₂O₇ at 170 – 180 °C.

87 *X-ray diffraction, FTIR and surface area analysis:* Silica phases of the ash samples were
88 examined by powder X-ray diffraction (Bruker AXS D5005, Germany). The surface groups
89 of the ash samples were identified by using FTIR measurements (Nicolet™ iS™5 FT-IR,
90 Thermo Scientific, USA). The SSA of the samples was measured with a Gemini VII 2390p
91 surface area analyzer.

92 **2.3. Kinetic batch experiments**

93 To examine P and Si solubility, 300 mg of sample was mixed with 300 mL of DI
94 water in 500-mL plastic tubes. Suspensions were gently shaken and allowed to stand for 24 h
95 at room temperature. For the samples pre-treated at 400, 700 and 1000°C, the batch
96 experiments were in triplicates and extended up to 6 d with sampling at 24 h intervals. The
97 suspensions were passed through a 0.45 µm filter paper. Soluble P was determined using ion
98 chromatography (DX-600, Dionex-Thermo, USA) while soluble Si was examined by
99 molybdate blue method with a Spectrophotometer UV-Vis (L-VIS-400, Labnics, USA). Since
100 the ash samples still contain certain amounts of OC, dissolution of the OC might affect

101 releases of Si and P by changing phytolith exposure to solution. In all kinetic experiments,
102 DOC was also analysed using a TOC Analyzer (VCPH, Shimadzu), to identify whether the
103 released P was related to dissolution of occluded organic matter. Correlations between the
104 released Si and P derived from all dissolution kinetic experiments were also evaluated by
105 Pearson's test using SPSS 20.0 software program. The strength of correlation can be
106 evaluated by using two levels of significance 0.01 and 0.05, representing relations between
107 the released Si and P occurring by chance are 1 and 5%, respectively.

108 **3. Results**

109 **3.1. Sample characterization**

110 The arrangement of phytolith's siliceous structure in the rice leaf was visualized in
111 Fig. 1. A high-porosity system with various size holes which might represent longitudinal
112 vascular bundles, veins or fibers of the rice plant (Botha, 2013). Si covers, throughout,
113 internal- and external surfaces of the vascular system to form a coating layer, coloured
114 yellow, as shown in Fig. 1a. This layer is known as silica-rich epidermis which is developed
115 to become the main strengthening tissue in the stem and leaf (Islam et al., 2009; Yamanaka et
116 al., 2009). The holes can be fulfilled by organic matter which appears in violet (Fig. 1b).
117 Excessive precipitation of Si can likely to form "closed holes" within the vascular bundles,
118 capturing embedded organic matter, as well other occluded substances including P.

119 (Figure 1)

120 Heat treatments of the rice straw resulted in significant changes in chemical
121 composition and SSA as shown in Tab. 1. The organic carbon was almost completely
122 removed by heating at >800 °C, whereas, only less than 30% of TOC was removed at 300 °C.
123 In rice straw the total P and Si contents were 1.02 and 73.6 g kg⁻¹, respectively. However, the
124 contents of P changed from 1.21 to 2.55 g kg⁻¹ and those of Si varied from 87.6 to 184.2 g kg⁻¹,
125 when the heating temperatures of rice straw increased from 300 to 1000°C. A severe

126 decrease of the SSA was obtained with increasing heating temperature. The SSA decreased
127 from 36.2 to 0.22 m² g⁻¹ with an increase of heating temperature from 300 to 1000°C,
128 indicating an enhanced condensation of silica structures at higher temperatures as shown in
129 Fig. 2.

130 (Table 1)

131 (Figure 2)

132 The XRD for phytolith derived from different treatment temperatures is shown in Fig.
133 3a. At temperatures < 700°C, no specific reflection was observed, suggesting that silica
134 occurs in amorphous form. Temperatures > 800°C can favor crystallization and cause the
135 formation of more stable silica crystalline structures, i.e., cristobalite and tridymite (Kordatos
136 et al., 2008). Functional groups of the samples were revealed through FTIR spectra as
137 described in Fig. 3b. The bands at ~1100 cm⁻¹ and 800 cm⁻¹, representing for the stretching
138 vibration of the SiO₄ tetrahedron and the bending vibration of inter-tetrahedral ≡Si-O-Si≡
139 bonds, were apparent for almost all pretreatments.

140 (Figure 3)

141 **3.2. Solubility of Si and P**

142 *Dissolution kinetics*

143 Batch experiments for the samples derived from different heat-treatments showed that
144 the concentration of soluble P and Si significantly increased with time at different rates for
145 400 and 700°C -treated samples, whereas trivial increases of soluble P and Si were observed
146 for 1000°C -treated sample (Fig. 4a, b). After 6 d, P and Si releases were 1.2 and 41.0 mg L⁻¹
147 for the 400°C treated sample, 2.0 and 55.0 mg L⁻¹ for the 700°C -treated sample, and 0.04 and
148 3.3 mg L⁻¹ for the 1000°C -treated sample, respectively. For 400 and 700°C -treated samples,
149 P concentration showed a remarkable increase within the first day, and minor increases after

150 day 1 while Si concentration in the supernatant continuously increased over 6 d. The releases
151 of DOM in batch experiments were also examined, but no clear trend has been observed.
152 (Figure 4)

153 Correlation coefficients obtained from Pearson's test for samples treated at 400 and
154 700°C were 0.968 and 0.878 (respectively), indicating a relation between released Si and P. In
155 contrary, a correlation coefficient of -0.504 implies that no clear relation exists between
156 released Si and P for the sample treated at 1000°C. For the samples treated at 400 and 700°C,
157 a significant correlation at the 0.01 level is an obvious evidence for a strong relation between
158 Si and P, suggesting that release of P relates to the dissolution of phytolith. For the sample
159 treated at 1000°C, the relation between released Si and P cannot be affirmed due to a very low
160 solubility of phytolith. A normalized correlation coefficient of 0.922 was obtained when
161 Pearson's test was executed for all the samples together, and this correlation showed a
162 significance at 0.01 level.

163 *Effect of treatment temperature*

164 The solubility of P and Si of the phytolith samples showed a strong dependence on
165 heating temperature (Fig. 5). When the heating temperature was changed from 300 to 600°C,
166 increases of the soluble P and Si from 0.4 to 1.3 mg L⁻¹ and 7.2 to 13.5 mg L⁻¹, respectively,
167 were observed. At >700°C, the solubility of P and Si was readily reduced. The lowest values
168 of soluble P and Si were 0.04 and 0.27 mg L⁻¹ (respectively) for the sample treated at 1000°C.
169 Over the entire range of heating temperature from 300 to 1000°C, P showed a relatively lower
170 solubility as compared to Si. It can be recognized that soluble P and Si showed similar "peak
171 shape" trends as depicted in Fig. 5, and the highest values were at ~600°C. This phenomenon
172 suggested that a similar mechanism drove the dissolution of P and Si from the samples.
173 (Figure 5)

174 **4. Discussion**

175 Si and P assimilated from soil are transferred to rice leaf and stem. While Si tends to
176 be immobilized by precipitation that forms siliceous phytolith structure (Nguyen et al.,
177 2014; Parr and Sullivan, 2005), it is likely that P is more mobile in plant. P stored in older
178 leaves can be readily re-translocated to both young leaves and growing roots via the xylem
179 and phloem systems (Jeschke et al., 1997). X-ray tomographic microscopy revealed various
180 holes within the phytolith and these holes were filled with occluded organic substances (Fig.
181 1). However, these holes as well as morphology of the phytolith can be strongly affected by
182 heat-treatment as shown in Fig. 2, in which high treatment temperatures resulted in a re-
183 arrangement and followed by crystallization of silica in phytolith structure as deduced from
184 XRD spectra in Fig. 3a. As P is dominant in the transport sap (Schachtman et al., 1998), P and
185 organic compounds might also be trapped inside siliceous structure of phytolith when
186 precipitation of Si forms phytolith. Chemical analysis revealed that phytOP contents of the
187 samples obtained from various treatment temperatures were up to 2.55 g kg⁻¹.

188 Six-day extractions of the samples treated at 400 and 700°C resulted in Si
189 concentrations of 41 and 55 mg L⁻¹, respectively, which were both equivalent to ~31 % of the
190 total Si introduced in the experiment. This result is in between the findings of
191 Wickramasinghe and Rowell (2006), Nguyen et al. (2014) and Wilding et al. (1979), who
192 measured a Si extractability of 20-38%, 46% and 50-75%, respectively. It can be inferred that
193 burning process resulted in robust destruction of the rice straw and produced a structure with
194 low resistance to dissolution. In contrast, soluble amount of the sample treated at 1000°C was
195 less than 2 % indicating its high resistance against dissolution. This implies that burning rice
196 straw at high temperatures (> 800°C) can lead to a long-term stabilization of rice straw
197 phytoliths under actual soil conditions.

198 In the kinetic experiments, the solubility of Si was increased with time as a
199 consequence of phytolith desilification, and a corresponding increase in the P concentration

200 suggested a relationship between the released Si and P. Scatter plots as shown in Fig. 6
201 demonstrate a strong correlation between the released Si and P amounts. A positive
202 correlation, $R^2 = 0.847$, indicates ~85% of the variance in the soluble P is related to soluble
203 Si. Also, strong correlation coefficients at the 0.01 level obtained from Pearson's test allow
204 generalizing a relation between P and Si, in which the P release is regulated by the dissolution
205 of the phytolith and treatment temperature appears as a primary factor driving this process.
206 (Figure 6)

207 Changes in the removal rate of occluded organic matter and transformation of the
208 silica phases during the heating were recognized as two of the major factors directing Si and P
209 release from rice straw phytoliths. High organic matter content in the samples heated at low
210 temperature is likely a major factor to inhibit Si and P liberates. It might be because the
211 heating treatments resulted in an inter-embedded organic-silica structure and this matter acts
212 as a "two-surface shield", by which each of organic matter and phytolith silica can be
213 preserved from the other. As a consequence, the presence of occluded organic matter can
214 decrease of dissolution rate of the phytolith and phytOP as well. The present result is in
215 agreement with other findings (Nguyen et al., 2014; Parr and Sullivan, 2005) in which it was
216 stated that occluded organic matter "strengthens" the phytolith surface and its resistance to
217 desilification. When heating temperature increases, dehydroxylation of silanol groups will
218 favor a formation of siloxane bonds (Fig. 2a), and the surface is hydrophobic (Zhuravlev,
219 2000). This reaction diminishes adsorption of water molecules on the surface and decreases
220 the breakage of the surface $\equiv\text{Si-O-Si}\equiv$ bonds (Parr and Sullivan, 2005). It can, therefore,
221 explain why lesser Si and P were liberated from the phytoliths in this case. Additionally, the
222 formation of stable silica phases at high temperature favored a product with low SSA and less
223 activity (Kordatos et al., 2008), likely also resulting in a decline of P and Si release. An
224 illustration for the effects of occluded organic matter, SSA and crystallization degree together

225 on co-release of Si and P was depicted in Fig. 7. Burning rice straw at a temperature range
226 from 500 to 700°C was suggested as an optimal practice toward serving more available Si and
227 P for soils and crops.

228 (Figure 7)

229 **5. Conclusions**

230 Rice straw phytoliths contain up to 2.5 g P kg⁻¹, indicating that this P-pool can be an
231 additional source for crops when the straw is returned to the soils. By integrating the results
232 from batch experiments, chemical analysis, and X-ray tomographic microscopy, this study
233 revealed that P in the phytolith structure might be unavailable for plants prior to desilification
234 of the phytolith structure. Co-release of P and Si was observed and the dissolution of the
235 phytolith could be concluded as the main factor controlling P release. The heating temperature
236 of the rice straw could affect P and Si releases by intensifying the removal of occluded
237 organic matter or crystallizing the silica surface of the phytolith. The maximum values of
238 soluble P and Si observed from 500 till 700°C recommended that the pretreatment of the rice
239 straw at this temperature range is optimal in serving as available P and Si for crops and soils.
240 As it is still unclear to what extent organic-P can be transformed to inorganic P accompanying
241 with heat treatment of the rice straw, this process and its relation to P-release will be
242 considered in future works.

243 **Acknowledgements**

244 This research was funded by the Vietnam National Foundation for Science & Technology
245 Development (Project 105.09-2015.01).

246 **References**

247 Agarie, S., Agata, W., Uchida, H., Kubota, F., Kaufman, P.B., 1996. Function of silica bodies
248 in the epidermal system of rice (*Oryza sativa* L.): testing the window hypothesis. *Journal*
249 *of Experimental Botany* 47, 655 - 660.

- 250 Andraea, M.O., Merlet, P., 2001. Emission of trace gases and aerosols from biomass burning.
251 Global Biogeochemical Cycles 15, 955-966.
- 252 Bijay, S., Shan, Y.H., Johnson-Beebout, S.E., Yadvinder, S., Buresh, R.J., 2008. Chapter 3
253 Crop Residue Management for Lowland Rice-Based Cropping Systems in Asia,
254 Advances in Agronomy. Academic Press, pp. 117-199.
- 255 Botha, T., 2013. A tale of two neglected systems—structure and function of the thin- and
256 thick-walled sieve tubes in monocotyledonous leaves. *Frontiers in Plant Science* 4.
- 257 Dobermann, A., Fairhurst, T., 2000. Rice. Nutrient disorders and management, Handbook
258 series. Potash and Phosphate, Singapore.
- 259 Dove, P.M., Crerar, D.A., 1990. Kinetics of quartz dissolution in electrolyte solutions using a
260 hydrothermal mixed flow reactor. *Geochim. Cosmochim. Acta* 54, 955-969.
- 261 Fraysse, F., Pokrovsky, O.S., Schott, J., Meunier, J.-D., 2009. Surface chemistry and
262 reactivity of plant phytoliths in aqueous solutions. *Chemical Geology* 258, 197-206.
- 263 Friese, K.I., Cichy, S.B., Wolters, F.E., Botcharnikov, R.E., 2013. Analysis of tomographic
264 mineralogical data using YaDiV—Overview and practical case study. *Comp. Geosci.* 56,
265 92-103.
- 266 Islam, M.T., Sarwar, A.K.M.G., Begum, H.H., Ito, T., 2009. Epidermal features of rice leaf
267 CV. BRRI Dhan29. *Bangladesh Journal of Plant Taxonomy* 16, 4.
- 268 Jeschke, W.D., Kirkby, E.A., Peuke, A.D., Pate, J.S., Hartung, W., 1997. Effects of P
269 deficiency on assimilation and transport of nitrate and phosphate in intact plants of castor
270 bean (*Ricinus communis* L.). *Journal of Experimental Botany* 48, 75-91.
- 271 Kordatos, K., Gavela, S., Ntziouni, A., Pistiolas, K.N., Kyritsi, A., Kasselouri-Rigopoulou,
272 V., 2008. Synthesis of highly siliceous ZSM-5 zeolite using silica from rice husk ash.
273 *Microporous and Mesoporous Materials* 115, 189-196.

- 274 Marone, F.M., R; Modregger, P; Fife, J; Pinzer, B; Thüring, T; Mader, K; Mikuljan, G;
275 Isenegger, A; Stampanoni, M 2010. Present and Future X-ray Tomographic Microscopy
276 at TOMCAT., 10th International Conference on X-Ray Microscopy, Chicago, Illinois,
277 (USA), 15 August 2010 - 20 August 2010, 116-119.
- 278 Nguyen, N.M., Dultz, S., Guggenberger, G., 2014. Effects of pretreatment and solution
279 chemistry on solubility of rice-straw phytoliths. *Journal of Plant Nutrition and Soil*
280 *Science* 177, 349-359.
- 281 Nguyen, N.M., Dultz, S., Picardal, F., Bui, T.K.A., Pham, Q.V., Schieber, J., 2015. Release of
282 potassium accompanying the dissolution of rice straw phytolith. *Chemosphere* 119, 371-
283 376.
- 284 Parr, J.F., Sullivan, L.A., 2005. Soil carbon sequestration in phytoliths. *Soil Biol. Biochem.*
285 37, 117-124.
- 286 Schachtman, D.P., Reid, R.J., Ayling, S.M., 1998. Phosphorus uptake by plants: from soil to
287 cell. *Plant Physiology* 2, 447-453.
- 288 Seyfferth, A.L., Kocar, B.D., Lee, J.A., Fendorf, S., 2013. Seasonal dynamics of dissolved
289 silicon in a rice cropping system after straw incorporation. *Geochimica et Cosmochimica*
290 *Acta* 123, 120-133.
- 291 Wickramasinghe, D.B., Rowell, D.L., 2006. The release of silicon from amorphous silica and
292 rice straw in Sri Lankan soils. *Biol Fertil Soils* 42, 231-240.
- 293 Wilding, L.P., Hallmark, C.T., Smeck, N.E., 1979. Dissolution and Stability of Biogenic
294 Opal1. *Soil Sci. Soc. Am. J.* 43, 800-802.
- 295 Yamaji, N., Mitatni, N., Ma, J.F., 2008. A Transporter Regulating Silicon Distribution in Rice
296 Shoots. *The Plant Cell* 20, 1381-1389.

- 297 Yamanaka, S., Takeda, H., Komatsubara, S., Ito, F., Usami, H., Togawa, E., Yoshino, K.,
298 2009. Structures and physiological functions of silica bodies in the epidermis of rice
299 plants. *Applied Physics Letters* 95, 1-3.
- 300 Zhuravlev, L.T., 2000. The surface chemistry of amorphous silica. Zhuravlev model. *Colloids*
301 *and Surfaces A: Physicochemical and Engineering Aspects* 173, 1-38.
- 302

303 **Table caption**

304 Table 1. Specific surface area (SSA), chemical composition of the rice straw and its phytolith
305 ash samples obtained from 300 to 1000°C ashing temperatures.

306

307 **Figure captions**

308 Figure 1. 3D images of the phytolith's siliceous structure (a) and it is embedded by organic
309 matter (b)

310 Figure 2. SEM images of a leaf fragment in treated rice-straw samples: 400°C (a), 700°C (b)

311 Figure 3. XRD patterns (a) and IR spectra (b) of rice-straw samples treated at different
312 temperatures

313 Figure 4. Release of Si (a) and P (b) from rice straw samples treated at 400°C, 700°C and
314 1000°C in a time sequence up to 6 d. Data points represent mean values with standard
315 deviations for 3 replicates. Error bars might be smaller than the symbol size.

316 Figure 5. Solubility dependence of Si and P on treatment temperature. Data points represent
317 mean values with standard deviations for 3 replicates. Error bars are smaller than the symbol
318 size.

319 Figure 6. Correlation between soluble Si and P in the supernatant of 400°C-, 700°C-, and
320 1000°C-treated samples in the kinetic experiments. Where not visible, error bars are smaller
321 than the symbol size.

322 Figure 7. Illustration of temperature effect on P and Si co-release from rice straw derived
323 phytolith via changing occluded organic matter content, surface area and crystallization
324 degree.