

# Characterization and dissolution properties of phytolith occluded phosphorus in rice straw

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1	Characterization and dissolution properties of phytolith occluded
2	phosphorus in rice straw
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15	
16	1. Introduction
17	Rice straw derived phytolith, a silicaceous structure formed through Si precipitation in
18	rice plant tissues (Parr and Sullivan, 2005), has been widely known as a potential source to
19	sustain soil Si nutrient pools when it is cycled to soils (Dobermann and Fairhurst, 2000;
20	Nguyen et al., 2014; Nguyen et al., 2015; Seyfferth et al., 2013). However, there has been a
21	lack of systematic information on the fate of rice straw derived phytolith in soils, and to what
22	extent this nutrient pool can benefit crops. Phosphorus (P) is among the most important
23	nutrient elements in rice. P is taken up from the soil solution by root absorption, transport
24	across cell membranes and compartmentation, and redistribute within different parts of rice
25	plant (Agarie et al., 1996; Schachtman et al., 1998; Yamaji et al., 2008). During rice growth,

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

32 Generally, dissolution of phytolith is regulated by the desilification in aqueous 33 solution. This process occurs via hydrolysis of =Si-O-Si= bonds of the silica surface in which 34 water molecules orient their electronegative pole towards the Si atoms in silica structure, resulting in a transfer of electron density to the =Si-O-Si= bonds, thereby raising their length 35 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 (Fraysse 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.

Open-field burning of rice straw after harvesting is a conventional method of disposal of straw to return nutrients to the soils in many rice-based countries. Although this method causes significant emission of greenhouse gases (e.g. CO<sub>2</sub>, CO, NO<sub>x</sub>), losses of nutrients (e.g. N, K, P,) and contributes to air pollution (Andreae and Merlet, 2001; Bijay et al., 2008; Dobermann and Fairhurst, 2000), it is the easiest way of returning most nutrients to the soils, and at present rice growers have little incentive to change this method. As burning of rice straw at different temperatures might result in various degrees of dehydroxylation of biogenic

silica and organic matter contents, rice straw phytolith ash samples which were obtained from 51 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 silicaceous 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 the dynamics of the phytOP and suggest possible management options on one hand to 60 maximize the use of this phytOP pool, and on the other hand to adjust fertilization strategy. 61

62 2. Materials and Methods

## 63 2.1. Study site and sample production

Rice-straw was collected from a paddy field (105°44' E long, 20°59' N lat) in the Red 64 River Delta (RRD), a second largest delta in Vietnam. In the RRD, approx. 12 tons ha<sup>-1</sup> of the 65 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

*Tomographic and morphological analysis:* a 3D image of the silicaceous structures of a rice plant was built by using YaDiV software (Friese et al., 2013), and input data from X-ray tomographic microscopy by TOMCAT (TOmographic Microscopy and Coherent rAdiology experimenTs) beamline at the Swiss Light Source, Paul Scherrer Institute, Villigen, Switzerland. Dry rice leaf was scanned under monochromatic beam from a 2.9 T superbending magnet at an energy of 11.1 keV. Micromorphology of the sample was 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 H<sub>2</sub>SO<sub>4</sub> and 0.5 M K<sub>2</sub>Cr<sub>2</sub>O<sub>7</sub> at 170 – 180 °C.

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

Heat treatments of the rice straw resulted in significant changes in chemical composition and SSA as shown in Tab. 1. The organic carbon was almost completely removed by heating at >800 °C, whereas, only less than 30% of TOC was removed at 300 °C. In rice straw the total P and Si contents were 1.02 and 73.6 g kg<sup>-1</sup>, respectively. However, the contents of P changed from 1.21 to 2.55 g kg<sup>-1</sup> and those of Si varied from 87.6 to 184.2 g kg<sup>-1</sup>, when the heating temperatures of rice straw increased from 300 to 1000°C. A severe decrease of the SSA was obtained with increasing heating temperature. The SSA decreased from 36.2 to 0.22 m<sup>2</sup> g<sup>-1</sup> with an increase of heating temperature from 300 to 1000°C, 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  $< 700^{\circ}$ C, no specific reflection was observed, suggesting that silica 134 occurs in amorphous form. Temperatures > 800°C can favor crystalization and cause the formation of more stable silica crystaline structures, i.e., cristobalite and trydimite (Kordatos 135 136 et al., 2008). Functional groups of the samples were revealed through FTIR spectra as described in Fig. 3b. The bands at ~1100 cm<sup>-1</sup> and 800 cm<sup>-1</sup>, representing for the stretching 137 138 vibration of the SiO<sub>4</sub> 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* 

Batch experiments for the samples derived from different heat-treatments showed that the concentration of soluble P and Si significantly increased with time at different rates for 400 and 700°C -treated samples, whereas trivial increases of soluble P and Si were observed for 1000°C -treated sample (Fig. 4a, b). After 6 d, P and Si releases were 1.2 and 41.0 mg L<sup>-1</sup> for the 400°C treated sample, 2.0 and 55.0 mg L<sup>-1</sup> for the 700°C -treated sample, and 0.04 and 3.3 mg L<sup>-1</sup> for the 1000°C -treated sample, respectively. For 400 and 700°C -treated samples, 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 solubility of phytolith. A normalized correlation coefficient of 0.922 was obtained when 160 161 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. increases of the soluble P and Si from 0.4 to 1.3 mg L<sup>-1</sup> and 7.2 to 13.5 mg L<sup>-1</sup>, respectively, 166 167 were observed. At  $>700^{\circ}$ C, the solubility of P and Si was readily reduced. The lowest values of soluble P and Si were 0.04 and 0.27 mg L<sup>-1</sup> (respectively) for the sample treated at 1000°C. 168 169 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 silicaceous 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 XRD spectra in Fig. 3a. As P is dominant in the transport sap (Schachtman et al., 1998), P and 184 185 organic compounds might also be trapped inside silicaceous structure of phytolith when 186 precipitation of Si forms phytolith. Chemical analysis revealed that phytOP contents of the samples obtained from various treatment temperatures were up to  $2.55 \text{ g kg}^{-1}$ . 187

188 Six-day extractions of the samples treated at 400 and 700°C resulted in Si concentrations of 41 and 55 mg  $L^{-1}$ , respectively, which were both equivalent to ~31 % of the 189 190 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

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suggested a relationship between the released Si and P. Scatter plots as shown in Fig. 6 demonstrate a strong correlation between the released Si and P amounts. A positive correlation,  $R^2 = 0.847$ , indicates ~85% of the variance in the soluble P is related to soluble Si. Also, strong correlation coefficients at the 0.01 level obtained from Pearson's test allow generalizing a relation between P and Si, in which the P release is regulated by the dissolution 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 =Si-O-Si= bonds (Parr and Sullivan, 2005). It can, therefore, explain why lesser Si and P were liberated from the phytoliths in this case. Additionally, the 221 222 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 crystalization degree together on co-release of Si and P was depecited in Fig. 7. Burning rice straw at a temperature range
from 500 to 700°C was suggested as an optimal practice toward serving more available Si and
P for soils and crops.

228 (Figure 7)

## 229 **5.** Conclusions

Rice straw phytoliths contain up to 2.5 g P kg<sup>-1</sup>, indicating that this P-pool can be an 230 231 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 of the phytolith structure. Co-release of P and Si was observed and the dissolution of the 234 235 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 organic matter or crystallizing the silica surface of the phytolith. The maximum values of 237 238 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.

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302

# 303 **Table caption**

- Table 1. Specific surface area (SSA), chemical composition of the rice straw and its phytolith
  ash samples obtained from 300 to 1000°C ashing temperatures.
- 306

## **307** Figure captions

- Figure 1. 3D images of the phytolith's silicaceous structure (a) and it is embedded by organicmatter (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
- Figure 4. Release of Si (a) and P (b) from rice straw samples treated at 400°C, 700°C and 1000°C in a time sequence up to 6 d. Data points represent mean values with standard 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 symbol318 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
- than the symbol size.
- Figure 7. Illustration of temperature effect on P and Si co-release from rice straw derived
  phytolith via changing occluded organic matter content, surface area and crystallization
  degree.