Phytolith-associated potassium in fern

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1   **Phytolith-associated potassium in fern: Characterization, dissolution**

2   **properties and implications for slash-and-burn agriculture**

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17

18 ***Abstract***

19 In recent time, phytoliths (silicon deposition between plant cells) have been recognized as an

20 important nutrient source for crops. The work presented here aims at highlighting the

21 potential of phytolith occluded K pool in ferns. *Dicranopteris linearis* (*D. linearis*) is a

22 common fern in the humid subtropical and tropical regions. Burning of the fern *D. linearis* is,

23 in slash-and-burn regions, a common practice to prepare the soil before planting. We

24 characterised the phytolith rich ash derived from the fern *D. linearis,* and phytolith associated

25 potassium (K) (phytK), using X-ray tomographic microscopy in combination with kinetic

26 batch experiments. *D. linearis* contains up to 3.9 g K kg^{-1} d.wt, including K sub-

27 compartmented in phytoliths. X-ray tomographic microscopy visualized an inter-embedding

28 structure between organic matter and silica, particularly in leaves. Co-release of K and Si

29 observed in the batch experiments confirmed that the dissolution of ash phytoliths is one of

30 major factors controlling K release. Under heat treatment, a part of the K is made available,

31 while the remainder entrapped into phytoliths (ca. 2.0 – 3.3%) is unavailable until the

32 phytoliths are dissolved. By enhanced removal of organic phases, or forming more stable

33 silica phases, heat treatment changes dissolution properties of the phytoliths, affecting K

34 release for crops and soils. The maximum release of soluble K and Si, occurred from

35 phytoliths treated at 500 - 800 °C. For quantitative approaches for the K provision of plants

36 from the soil phytK pool in soils, factors regulating phytolith dissolution rate have to be

37 considered.

38 *Keywords*: potassium; phytolith; fern; *Dicranopteris linearis*

39 **Introduction**

40   *Dicranopteris linearis* (*D. linearis*) is one of the most common ferns in the humid

41 subtropical and tropical regions (Scott, 1969; Guariguata, 1990). *D. linearis* can tolerate low

42 soil nutritional status, occurring on shallow, immature soils, mountain ridges, precipices or in

43   severely disturbed sites such as landslides, road-cuts and degraded forest lands (Scott, 1969;

44   Guariguata, 1990), and plays an important role for ecological succession (Atkinson, 1970). It

45   contains very low contents of nitrogen and phosphorus, but silicon (Si) and potassium (K) can

46   be assimilated at significantly higher levels (Russell *et al.*, 1998; Amatangelo & Vitousek,

47   2008). While Si tends to be immobilized by polymerization, and subsequent precipitation in

48   inter- and intracellular spaces of leaves and stems to form phytoliths (Piperno & Stothert,

49   2003; Parr & Sullivan, 2005; Mazumdar, 2011), K can be re-translocated to supply the

50   appropriate ionic environment for metabolic processes throughout the plant (Leigh & Wyn

51   Jones, 1984). We hypothesize that K can be sub-compartmented in organic matter associated,

52   or even occluded, within the phytolith structure (phytK) during precipitation of Si. This

53   means that this K pool is relatively unavailable for plant uptake even if the fern residue is

54   returned to the soil and it is likely that K release is linked with the dissolution of phytoliths.

55   Overall, dissolution of phytoliths is controlled by the protonation, deprotonation, and

56   hydrolysis of surface $\equiv$Si-OH groups (Ehrlich *et al.*, 2010). This process occurs via

57   nucleophilic attack (Dove & Crerar, 1990). pH is a crucial factor in phytolith dissolution, via

58   protonation or deprotonation reactions (Fraysse *et al.*, 2009; Nguyen *et al.*, 2014), which can

59   either increase resistance of the surface or make the surface more vulnerable from

60   nucleophilic attacks (Dove & Crerar, 1990). Deprotonation of the silanol groups (Si-OH) on

61   the phytolith surface can facilitate hydrolysis of $\equiv$Si-O$^-$ bonds, which is known to be a first

62   step for dissolution (Dove & Elston, 1992; Fraysse *et al.*, 2006). Adsorption of cations from

63   aqueous solutions onto deprotonated $\equiv$Si-O$^-$ sites leads to polymerization (Weres *et al.*, 1981).

64   Therefore, the surface of phytoliths is strengthened against dissolution. Associated organic

65   matter (phytC) (Li *et al.*, 2014; Song *et al.*, 2016; Guo *et al.*, 2015), may be another factor in

66   preserving phytoliths against hydrolysis, acting as a protective barrier (Parr & Sullivan, 2005;

67   Nguyen *et al.*, 2014). PhytC can be lost upon burning, which is a common practice of field

68   preparation in the slash-and-burn farming. Little is known about the effect of heat treatment

69   on phytC loss, surface property changes and dissolution rate of the fern *D. linearis* derived

70   phytoliths.

71   Slash-and-burn farming is typical in upland north Vietnam, where *D. linearis*

72   colonises soil that is left fallow. Slash and burn causes *D. linearis* phytolith-containing ash to

73   be re-cycled to the soil, providing nutrients for subsequent crops. In this study, phytoliths

74   obtained from ashing of fern *D. linearis* plants were used to examine release of Si and K and

75   to investigate how heat interacts with the phytolith structure with respect to subsequent K

76   dissolution.

77   **Materials and methods**

78   Phytoliths obtained from 300 - 1000 °C ashing were prepared. X-ray tomographic microscopy

79   provided visualization of silicaceous structure within the phytolith. Scanning electron

80   microscopy (SEM), X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FTIR),

81   specific surface area (SSA) and chemical composition analysis were carried out to evaluate

82   transformation of phytoliths, and the effect of this transformation on Si and K release. The

83   reactivity of biogenic silica is strictly related to changes in surficial properties (Cabanes and

84   Shahack-Gross, 2015) and, in particular, loss of reactive surface sites. Therefore, surface

85   charge (SC) was also determined as it is the key electrochemical parameter of the solid-liquid

86   interface indicating ion adsorption, and ionization of surface functional groups, providing

87   important information on dissolution kinetics (Walther, 1996). Other physio-chemical

88   properties of the ashed samples, such as pH, electro-conductivity (EC) and organic carbon

89   (OC), were determined to ascertain how they relate to phytolith dissolution.

90   ***Study site and sample production***

91   *D. linearis* was collected from its natural habitat in a mountainous region (21°30′ N,

92   104°47′ E), with an elevation of ~1400 m, located in the Northwest of Vietnam (Fig. 1). The

93   soil is the Ferralic Acrisol which has developed on the basaltic rock. Slash-and-burn farming

94   in this region has been practiced for hundreds of years, where maize is cultivated after

95   burning. The average temperature is 23.5 °C, with an average relative humidity of 85%.

96   Average annual precipitation is 1700 mm, fairly evenly distributed throughout the year.

97   (Fig. 1)

98   *D. linearis* was collected by harvesting above ground biomass from three separate

99   plots (1 m x 1 m). The samples were air-dried and 1.0 mm sieved. Elemental composition

100   (Table 1) was determined by XRF spectroscopy (Rigaku, Nex CG). Ashing was conducted by

101   heating 50 g of the sample, bulked from sampling plots, in a furnace at 300, 400, 500, 600,

102   700, 800, 900 and 1000 °C, for 2 h. Phytoliths were obtained from the ash by washing 3 times

103   with deionized water, followed by centrifugation and decantation. The centrifugate phytoliths

104   were dried at 60 °C for 24 h.

105   (Table 1)

106   ***Characterization of samples***

107   The arrangement of Si and organic matter structures in dried stems and leaves of the

108   *D. linearis* was examined by synchrotron-based X-ray tomographic microscopy, at the Swiss

109   Light Source of the Paul-Scherrer-Institute in Villigen, Switzerland, using a 13 keV

110   monochromatic beam at the TOMCAT (TOmographic Microscopy and Coherent rAdiology

111   experimenTs) beamline. A sample was fixed on a centering and rotation stage in front of

112   magnifying optics and a camera detector. A series of 2D radiographic images was acquired

113   for different sample angular positions and subsequently tomographically reconstructed. A 3D-

114   rendering was generated by using YaDiV software (Friese *et al.*, 2013).

115   The chemical composition of *D. linearis,* and its ashes, was quantified by XRF

116   (Rigaku, Nex CG). The total organic carbon (TOC) in the samples was measured by wet

117   digestion with concentrated H_2SO_4 and 0.5 M $K_2Cr_2O_7$ at 170 - 180 °C. SEM-EDS using a

118   FESEM S-4800 (Hitachi Co., Tokyo, Japan) instrument, was used to map the distribution of

119   elements in ashed sample phytoliths. The presence of crystalline phases in the ash samples

120   was examined by powder X-ray diffraction (Bruker AXS D5005, Germany). The surface

121   functional groups of the ash samples were identified by FTIR spectroscopy (Nicolet^{TM} iS^{TM}5

122   FT-IR, Thermo Scientific, USA). The SSA of the samples was measured with a Gemini VII

123   2390p surface area analyzer.

124   *Kinetic batch experiments*

125   To examine K and Si solubility, each 100 mg of ash sample was mixed with 100 mL of

126   deionized water in 125-mL plastic tubes. Suspensions were gently shaken and allowed to

127   stand for 24 h at room temperature. For the samples pre-treated at 400 and 800 °C, the batch

128   experiments were extended up to 7 d, with sampling at 24 h intervals. pH and EC were

129   measured in aliquots of these suspensions by using a pH meter (Toledo, FE20, Switzerland)

130   and an electrical conductivity meter (AD3000, ADWA, Hungary), before taking samples for

131   quantification of Si and K release. The suspensions were passed through a 0.45 μm pore-size

132   cellulose acetate filter. Soluble Si and K were determined using an ICP-MS iCap Q (Thermo

133   Scientific, Bremen, Germany). All experiments were conducted in triplicates. Surface charge

134   was quantified by polyelectrolyte titration in a particle-charge detector (PCD 05, Mütek,

135   Herrsching, Germany). Suspensions were dispersed by an ultrasonic treatment for 15 s and

136   then transferred into the titration cell. The titration with the polyelectrolyte was terminated at

137   the point of zero charge where the electro-kinetic potential is zero.

138   *Statistical analysis*

139   The Pearson's test and multiple regression using SPSS 20.0 software, were used to

140   examine the correlations between parameters. Principle components analysis (PCA) was also

141   conducted, again in SPSS.

142   **Results**

143   *Sample characterization*

144   Tomographic images of leaf and stem phytoliths found high porosity, derived from

145   longitudinal vascular bundles, veins or fibers in the stem (Fig. 2a) and leaf (Fig. 2d). Based on

146   sample density, two phases of organic matter, colored with green (low density) and blue (high

147   density), and Si-rich phase colored with pink, were detected. In the stem, limited Si-phase was

148   observed (Fig. 2c), embedded into the high-density organic phase (lignin, cellulose) (Fig. 2b).

149   In the leaf, the Si-phase tends to be more porous near the leaf surface (Fig. 2d and 2e),

150   creating thin silica-rich layers (Fig. 2f), forming a protective cover for leaf veins, stabilized by

151   silicified structures in inter- and intracellular spaces.

152   (Fig. 2)

153   Heat treatment of *D. linearis* led to significant changes in chemical composition and

154   SSA (Table 2). When heating temperature changed from 300 to 1000 ºC, OC decreased from

155   10.1 to 0.2%. The total Si and K contents of the unashed sample were 2.2 and 0.3%,

156   respectively. The Si content changed from 8.7 to 15.4%, and K from 2.0 to 3.3%, between

157   300 to 1000 °C, respectively. The SSA increased from 42.5 to 161.2 m^2 g^{-1} when the

158   temperature changed from 300 to 700 ºC. A step decrease in SSA occurred above 700 ºC,

159   decreasing to 5.4 m^2 g^{-1} (Fig. 3). The SC ranged from -18.3 to -5.8 $mmol_c$ Kg^{-1}, decreasing for

160   ashed samples. This might be related to the decreasing OC content at higher temperatures and

161   to limited Si-OH represented on the surface as identified in Fig. 4b.

162   (Table 2)

163   (Fig. 3)

164   The XRD patterns of the phytolith-containing ash derived from different treatment

165   temperatures are shown in Fig. 4a. At temperatures < 800 °C, no specific reflection peak was

166   observed, suggesting that silica occurs in amorphous form. Temperatures above 800 °C can

167   favor crystallization and cause the formation of more stable silicates, i.e., leucite and zeolite.

168   Formation of zeolite might be a consequence of zeolization at high temperatures under the

169   presence of Si, Al, alkaline elements and internal water. Functional groups of the samples

170   were revealed through FTIR spectra as described in Fig. 4b. The bands at ~ 1100 cm^{-1} and

171   800 cm^{-1}, representing the stretching vibration of the SiO$_4$ tetrahedron and the bending

172   vibration of inter-tetrahedral ≡Si-O-Si≡ bonds, were apparent for almost all pretreatments.

173   The band at ~ 900 cm^{-1}, linked to Si-O stretching vibration of ≡Si-OH groups, was missing at

174   the temperatures > 800 °C. The absence of this band at high temperatures might be due to

175   transformation of ≡Si-OH to ≡Si-O-Si≡ bonds.

176   (Fig. 4)

177   ***Solubility of Si and K***

178   *Dissolution kinetics*

179   Releases of Si and K from samples derived from different treatment temperatures were

180   reflected by significant concentration increases of soluble Si and K with time (Fig. 5a). While

181   soluble K was significantly increased with time, less increase was observed for Si. After 7 d,

182   Si and K releases were 5.2 and 17.2 mg L^{-1} for the 400 °C-treated sample, 7.0 and 13.8 mg L^{-1}

183   for the 800 °C-treated sample, respectively. For both the 400 and 800 °C-treated samples, K

184   concentration showed a steep increase within the first 3 d, and minor releases after 3 days,

185   while Si concentration in the supernatant continuously increased over the period of 7 d.

186   Correlation coefficients obtained from the Pearson's test for samples treated at 400 and 800

187   °C were 0.982 and 0.986 respectively, indicating a strong relation between released Si and K

188   (Fig. 5b). A significant correlation at the 0.01 level for both the 400 and 800 °C-treated

189   samples is an obvious evidence for a strong relation between Si and K.

190   (Fig. 5)

191   *Effect of treatment temperature*

192   Solubility of Si and K in the phytoliths derived from *D. linearis* was highly affected

193   by heating temperature (Fig. 6). In general, soluble concentrations of Si were almost lower

194   than those of K over the entire temperature range from 300 to 1000 ºC. With a change in

195   treatment temperature from 300 to 600 ºC, an increase of the soluble Si and K from 1.0 to 2.1

196   mg L^{-1}, and 4.1 to 10.5 mg L^{-1}, respectively, was observed. At higher temperatures, 700 –

197   1000 ºC, the solubility of Si and K severely decreased. Lowest values of soluble Si and K

198   were 0.5 and 0.4 mg L^{-1} for the sample treated at 1000 ºC. Si and K solubility had similar

199   trends (Fig. 6a), and with maxima between 500 – 800 ºC. A scatter plot (Fig. 6b) shows the

200   correlation between the released Si and K, with R^2 of 0.724.

201   (Fig. 6)

202   PC1 versus PC2 illustrated the differentiation between treatment temperature and

203   released Si and K and other properties i.e. pH, EC, SSA, SC and OC (Fig. 7). The first PC

204   showed positive values for all parameters except SC. The second PC was strongly associated

205   to OC with positive effect and pH with negative effect, while lesser correlations were found

206   for pH, SSA, EC and released Si and K. According to the ordination of variables in the PCA

207   diagrams, released Si and K is associated with SSA, pH and EC rather than OC and SC. No

208   correlation between the treatment temperatures at 300, 900 and 1000 ºC and all variables

209   occurred. Treatment temperature of 400 ºC showed a trend to be associated with OC, whereas

210   those of 600 to 800 ºC tend to associate with SSA, pH and EC.

211   (Fig. 7)

212   **Discussion**

213   In plant tissues Si tends to be immobilized by polymerization, depositing in inter- and

214   intracellular spaces to form phytoliths (Parr & Sullivan, 2005; Nguyen *et al.*, 2014). K is more

215   mobile but can become entrapped within phytoliths. The 3D images obtained from X-ray

216   tomographic microscopy revealed inter-embedding structures between organic matter and

217   silica, particularly in leaf, in which the near-leaf-surface silica layers facilitate mechanical

218   strength and decrease transpiration (Gong *et al.*, 2003; Chen *et al.*, 2011), though this was not

219   explored here. Observation of the inter-embedding structures of phytoliths suggests that

220   precipitated silica can consolidate organic phases and sequester K. Micropores within silica

221   phases (Mohamad Remli *et al.*, 2014) could contain some occluded organic compounds and

222   K. Under heat treatment, organic phases can be removed, exposing phytolith silica.

223   Morphology of the phytoliths might also be affected (Wu *et al.*, 2012; Evett & Cuthrell,

224   2017), with melting at high temperatures resulting in a re-arrangement and crystallization of

225   silica, as deduced from XRD. Upon heating, losses of OC occurred, while K was enriched.

226   Solubility of Si increased as a result of phytolith desilification. A corresponding

227   increase of the K concentration in the supernatants suggests a relationship between K and Si

228   releases. This relationship was confirmed by scatter plots versus released Si with K (Fig. 6b).

229   Therefore, K release is related to the dissolution of phytoliths. As K is released at a faster rate

230   than Si (Fig. 6a), apart from K sequestered within phytoliths, K bound to organic matter,

231   inter-embedded with phytoliths, was also released on organic matter thermal decomposition,

232   as described by Trinh *et al.* (2017). The release of K from organic matter is likely to attribute

233   to the higher dissolution rate of K over Si. The temperature of the sample treatment may also

234   be a factor regulating phytolith desilification and K release. The maximum values of soluble

235   Si and K were observed from 500 till 800 °C, whereas lower dissolution was found at < 500

236   °C or > 800 °C. Heat treatment changed surface properties of the phytoliths, thereby affecting

237   solubility of Si and K. The ordination of variables in the PCA diagrams showed that pH and

238   SSA are factors favoring Si and K releases, whereas SC and OC have contrary effects. High

239   organic matter content of lower temperature (< 500 °C) treated samples prohibited Si and K

240   release because its coating made the phytolith surface more resistant to dissolution (Van

241   Cappellen *et al.*, 2002; Parr & Sullivan, 2005). With increasing temperature, dehydroxylation

242   of silanol groups results in more siloxane bonds and the surface becomes hydrophobic

243   (Zhuravlev, 2000). This reaction reduces adsorption of water molecules on the surface and

244   prevents the breakage of the surface siloxane bonds. It can therefore explain why less Si and

245   K were released from the phytolith samples in this case at higher temperatures. In addition,

246   the formation of stable silica at high temperatures (> 800ºC) resulted in a product with low

247   specific surface area and less activity (Kordatos *et al.*, 2008; Nguyen *et al.*, 2014), likely also

248   resulting in a decrease of Si and K release.

249   The XRD patterns indicate newly-formed crystals, leucite and zeolite, in the

250   temperature range from 900 - 1000 ºC. Occurrence of zeolite observed at high temperatures

251   was not expected since zeolite is usually formed under hydrothermal conditions (Cundy &

252   Cox, 2005). The occurrence of alkaline elements (data not shown) in combination with

253   structural water under high temperature might be initial for the nucleation from which Si and

254   Al can be polymerized to build up zeolite crystals. The newly-formed nano-size particles

255   observed on the surface (Fig. 3c) were an evidence of partial melting and re-cystallization

256   processes on the surface of phytoliths. The effect of "neo-formed" zeolite upon the releases of

257   Si and K, however, was not in focus of this study.

258   *Implications for the soil system and options for management*

259   This study relates to a more detailed understanding regarding the K pool in ferns and its

260   release properties, with the findings applicable to soil nutrient management for slash-and-burn

261   agriculture in many upland regions. Fern *D. linearis* contains up to 3.2 g K kg^{-1}, suggesting

262   that this K pool can be an additional source for soils and crops. Under heat treatment, a

263   portion of the K is readily soluble, whereas the remaining part is tightly associated with

264   phytoliths, thereby being unavailable until the phytoliths are dissolved. Co-release of K and Si

265   on heat treatment was observed in batch incubation experiments, confirming dissolution of

266   the phytoliths as one of the main factors controlling K release. The heating temperature could

267   affect K and Si releases by intensifying the removal of occluded organic matter or

268   crystallizing the silica surface of the phytoliths. The maximum values of soluble K and Si

269 release were observed in the 500 - 800 °C treatments, which suggests that the preheat-

270 treatment of the fern *D. linearis* at this temperature range is optimal toward serving as a fast

271 available K source for crops and soils. At temperatures above 900 ºC, the newly-formed

272 crystals i.e. leucite and zeolite were identified in the ashes, but their occurrence and to what

273 extent they can affect release of K, remains unclear. Phytoliths and their phytK, when

274 embedded into soils, are affected by various physico-chemical factors, which govern phytolith

275 dissolution and hereby K release to plants. Quantity values indicating the size of the soil

276 phytK pool in relation to soil properties, however, are beyond the scope of this work. They

277 will be subject of a future study employing percolation experiments.

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351

352 **Table captions**

353 Table 1. Chemical composition of the *D. linearis* above ground biomass, mean values with

354 standard deviations in brackets.

355 Table 2. pH, specific surface area (SSA), surface charge (SC), electrical conductivity (EC),

356 organic carbon (OC), Si and K content of the fern plant ash samples obtained from 300 to

357 1000 °C treatment.

358

359 **Figure captions**

360 Figure 1. Fern *D. linearis* collected from the study site at a mountainous area in the northwest

361 Vietnam.

362 Figure 2. Tomographic images revealing the location of Si phytolith phase in fern *D. linearis*:

363 cross-section (a), 3D view (b) and 3D view with only Si separated (c) of the stem; and cross-

364 section (d), 3D view (e) and 3D view with only Si separated (f) of the leaf. Phytolith Si-rich

365 phase is coloured pink, high-density organic phase is coloured with blue, and low-density

366 organic phase coloured with green.

367 Figure 3. SEM images of the ash phytoliths derived from heat treatments at 700 °C (a), 1000

368 °C (b), granules formed on the surface of ash treated at 1000 °C (c), and EDS spectra of ashes

369 treated at 700 °C (d) and 1000 °C (e).

370 Figure 4. XRD patterns (a) and IR spectra (b) of ashed fern *D. linearis* samples in the

371 temperature range from 300 - 1000 °C.

372 Figure 5. Releases of Si and K from *D. linearis* ash samples treated at 400 and 800 °C in a

373 time sequence up to 7 d (a), and their correlation (b). Data points represent mean values with

374 standard errors for 3 replicates. Error bars might be smaller than the symbol size.

375 Figure 6. Dependence of the solubility of Si and K from *D. linearis* ashes on treatment

376 temperature.

377   Figure 7. Score plots of PC1 versus PC2 indicating the differentiation of treatment

378   temperature and soluble K and Si, pH, electrical conductivity (EC), organic carbon (OC),

379   surface charge (SC) and specific surface area (SSA) for ash phytoliths.