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1 **Goethite affects phytolith dissolution through clay particle aggregation and pH regulation**

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16 *Appendix A. Supplementary Material*

17 **Abstract**

18 Formed in plant tissues as fine silica particles, phytoliths are deposited within plant debris in soils where
19 they can dissolve and feed silicon (Si) fluxes to the biosphere and hydrosphere. Yet, soil phytoliths can be
20 protected from dissolution by entrapment in aggregates, and thus be withdrawn from the global silica cycle.
21 Among clay-sized minerals interacting in stable aggregates, goethite and kaolinite are ubiquitous in soils.
22 We analyzed the impact of goethite-mediated aggregation on the release of aqueous Si from phytoliths
23 entrapped in microaggregates containing organic matter and kaolinite, with quartz and goethite at variable
24 concentrations, simulating a soil sequence with increasing contents of clay and iron oxide, as it can
25 commonly occur in terrestrial ecosystems. The microaggregates stored sizable amount of organic carbon,
26 the release of which decreased with increasing goethite concentration. Aqueous Si was assessed through a
27 kinetic extraction with dilute CaCl_2 , while pH, aluminum (Al) and germanium (Ge) concentrations were
28 measured in the CaCl_2 extracts. Our experimental data showed that phytoliths were the source of aqueous
29 Si. They also showed that the process of phytolith dissolution prevailed over Si adsorption on goethite. As
30 mediated by goethite, aggregation protected phytoliths from dissolution at goethite concentrations above 20
31 g kg^{-1} . Increasing goethite concentration enhanced aggregation on the one hand, but increased pH from 5.5
32 to 7.5 on the other. Thus, while aggregation significantly reduced the release of aqueous Si by 1.7- to 3-fold
33 at a given pH, the increase in pH enhanced it. Overall, at common soil solution pH (5-6), aggregation
34 reduced Si release by 2- 3 times. Thus, preservation of phytoliths in aggregates can be widespread in well-
35 aerated soils and more effective than Si adsorption on secondary oxides in retaining Si.

36 **Keywords:** goethite, aggregation, phytolith preservation, dissolved silicon, low activity clays (LAC) soils.

37 **1. Introduction**

38 Since the pioneer quantitative study by Bartoli (1983), the role of plants in the terrestrial cycle of silicon (Si)
39 has been largely documented (Derry et al., 2005; Meunier et al., 2022). The original source of dissolved Si
40 (DSi) in soil is the reserve of weatherable silicate minerals (Garrels and Christ, 1965). Dissolved Si (DSi)
41 is taken up as monosilicic acid (H_4SiO_4) by plants where the mean Si concentration ranges between 1 and
42 100 g Si kg^{-1} (Epstein, 1994; Hodson et al., 2005). In plant tissues, biogenic silica (BSi) precipitates as fine
43 particles of opal-A ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$), named phytoliths, which return to soil within plant debris. Phytoliths are
44 widespread in soils (Monger and Kelly, 2002) in which their content ranges from 1 to 10 g kg^{-1} worldwide,
45 but may be higher locally (Meunier et al., 2014). Because of their relatively high dissolution rate (Frayssé
46 et al., 2009), phytoliths readily contribute to the reservoir of DSi, which can be (i) absorbed by plants and
47 other biota (Puppe, 2020), (ii) sorbed by aluminum (Al) and iron (Fe) oxides (Bowden et al., 1973; Hiemstra
48 et al., 2007; Haynes and Zou, 2020), (iii) precipitated into clay and/or silica minerals (Karathanasis, 2002),
49 or (iv) leached and transferred to rivers and oceans (Bartoli, 1983; Derry et al., 2005). These processes
50 impact the Si continent-ocean linkage, hence the global cycle of Si (Conley, 2002; Derry et al., 2005; Erhart,
51 1963). Since Si is beneficial to plants (Coskun et al., 2019) while Si biological cycling is critical in primary
52 productivity and C cycling on a global scale (Conley and Carey, 2015), Si plays a major role in the supply
53 of numerous ecosystem services (Meunier et al., 2022). Therefore, understanding the mechanisms
54 controlling DSi is a key issue. Among these mechanisms, the processes governing the resilience of
55 phytoliths in soils are poorly known (Cornelis and Delvaux, 2016), despite recent advances showing that
56 DSi release from phytoliths is also mediated by ageing (Liu et al., 2023, Puppe and Leue, 2018),
57 microaggregation (Li et al., 2020; Li et al., 2022) and redox-dependent surface passivation (Koebernick et
58 al., 2022). While the latter process requires alternating redox conditions (Koebernick et al., 2022) occurring
59 in soils covering about 5-7% of global land surface (IUSS, 2015), microaggregation of soil particles is
60 optimized in well-aerated soils with [clay + fine silt] content above 15%, in which biological activity
61 enhances the formation of macro- and micro-aggregates (Oades, 1984; Six et al., 2004; Totsche et al., 2018).

62 Since well-aerated soils are, by far, largely dominant on earth (> 90% of global land surface), the impact of
63 microaggregation on Si dynamics deserves a particular attention. An ample literature is available on the
64 crucial role of microaggregates (< 250 μ m) on OC stabilization and turnover (Six et al., 2004; Totsche et al.
65 2018). However, the role of microaggregates in soil functions and ecosystem services related to the cycling
66 of other elements is poorly known (Totsche et al., 2018). About Si, phytoliths can be readily entrapped in
67 microaggregates, as shown in long-term field experiments (Li et al., 2020) and short-term laboratory studies
68 (Li et al., 2022). Aggregation reduced the release of DSi, strongly from microaggregates using allophane
69 and ferrihydrite, but to a much lesser extent from microaggregates using kaolinite and goethite (Li et al.,
70 2022). Allophane and ferrihydrite are only significant in some Andosols, which cover less than 1 percent of
71 the global land surface, while crystalline mineral soils cover the majority of this surface (IUSS, 2015).
72 Among these, soils with predominant kaolinite and goethite are widespread worldwide, since these minerals
73 are ubiquitous (Bigam et al., 2002; White and Dixon, 2002). In particular, soils containing predominantly
74 low activity clays (LACs), i.e., kaolinite and crystalline (Al, Fe) oxides, have a high potential to form stable
75 aggregates at low organic matter (OM) content (Denef et al., 2002; Six et al., 2004) because kaolinite and
76 (Al, Fe) oxides act as main binding agents (Denef et al., 2002), as does OM in permanent charge soils (Six
77 et al., 2002). These LAC soils cover ~30% of the land surface at global scale and ~55% in the tropics (IUSS,
78 2015; Sanchez, 2019). So far, the effect of crystalline oxide concentration on the release of DSi from
79 microaggregates has not been evaluated.

80 Clay minerals, (Al, Fe) oxides and OM are the basic blocks of microaggregates, formed via cementing,
81 which involve primarily physicochemical and chemical interactions, and gluing in which OM and microbial
82 activity are crucial (Deng and Dixon, 2002; Totsche et al., 2018). Here, we focus on 1:1 clay – Fe oxide
83 microaggregation which arises notably through binding oppositely charged surfaces of oxide and kaolinite
84 (Schwertmann, 1988). Small amounts of Fe oxides promote microaggregation while their poor crystallinity
85 and nano size enhance it (Schwertmann, 1988; Deng and Dixon, 2002; Totsche et al., 2018, Di Iorio et al.,
86 2022; Guo et al., 2022). For crystalline oxides, conflicting observations were mainly attributed to the large

87 diversity of oxide crystal morphology and particle size (Schwertmann, 1988), but the impacts of oxide
88 amount (see e.g., Di Iorio et al., 2022; Sanchez, 2019) and pH are still unclear. As kaolinite–oxide
89 interactions are based on binding oppositely charged surfaces, increasing pH leads to surface charge change
90 causing disaggregation (Bigham et al., 2002; Baalousha, 2009) or enhancing aggregation (Demangeat et al.,
91 2018; Guo et al., 2002; Goldberg, 1989), likely depending on OM content (Baalousha et al., 2008).

92 Here, we analyzed the role of goethite-mediated aggregation in releasing DSi from phytoliths by testing two
93 hypotheses. (i) Aggregation-induced protection of phytoliths and delayed dissolution occur at low goethite
94 concentrations. (ii) pH change affects aggregation, thus phytolith protection and DSi release. We used
95 aggregates incubated from mixtures made of phytoliths, OM and kaolinite in fixed proportions, quartz and
96 goethite in variable proportions. We quantified the release of DSi as impacted by aggregation and pH, and
97 traced its source using the geochemical proxies Ge/Si and Al/Si molar ratios.

98

99 **2. Materials and methods**

100 **2.1. Individual components**

101 *Phytoliths* were extracted from rice plant (*Oryza sativa indica* IR64; IRRI) leaves (Li et al., 2019; Li et al.,
102 2022), purified (Kelly, 1990), washed and oven-dried at 50 °C (Li et al., 2022). *Quartz* was supplied by
103 Merck KGaA Co, Darmstadt, Germany, the particles being of calibrated size 330–500 µm. *Organic matter*
104 (OM) was oven-dried at 45 °C and finely ground Egyptian clover (*Trifolium alexandrinum*). Charentes
105 *kaolinite* (Cases et al. 1982; Cases et al., 2000; Delineau et al., 1994; Yvon et al., 1982) contained minor
106 amounts of Fe ($\text{Si}_2\text{Al}_{2-x}\text{Fe}_x\text{O}_5(\text{OH})_4$, $x \leq 0.02$) (Mestdagh et al., 1982). *Goethite* was synthesized after
107 adding 5 M NaOH (70 ml) to 1 M $\text{Fe}(\text{NO}_3)_3$ (100 ml) under intense stirring and brought to pH > 12, washing
108 and drying (Cornell and Schwertmann, 1996). As reported earlier (Li et al., 2022), the constituents exhibited
109 characteristic morphologies and X-ray diffraction patterns as well as specific surface area (SSA), which
110 decreased in the sequence ($\text{m}^2 \text{g}^{-1}$): phytoliths (190) > goethite (132) > kaolinite (24) > quartz (1). Besides,

111 in the pH range 4.5-7.5, kaolinite and OM carried a negative surface charge while goethite carried a positive
112 surface charge as predicted from its pH value at the isoelectric point ($\text{pH}_{\text{IEP}} = 9.6$, Li et al., 2022).

113 **2.2. Mixtures and aggregates**

114 The individual components were mixed to prepare bulk mixtures using fixed concentrations of (g kg^{-1}): rice
115 phytoliths (20), OM (50), kaolinite (370), and variable concentrations of goethite and quartz, with the
116 goethite concentration increasing from 0 to 80 g kg^{-1} while correspondingly decreasing the quartz content
117 from 560 to 420 g kg^{-1} . Since both goethite and kaolinite used here are clay-sized, these assemblages
118 simulate a pedological continuum of LAC soils for which clay content increases from 370 to 450 g kg^{-1} with
119 the increase in Fe oxide concentration as can commonly occur in intertropical regions (Sanchez, 2019; Van
120 Wambeke, 1992). The bulk mixtures were divided into two parts, designed as *mixtures* and *aggregates*, both
121 in triplicate. The *mixtures* were in fact the initial bulk mixtures, just juxtaposing the individual components,
122 not subjected to watering and ageing. The *aggregates* were produced from bulk mixtures that were irrigated
123 with deionized water using a liquid/solid ratio 0.6/1.0 g g^{-1} , incubated in darkness at 20°C for 32 days, and
124 freeze-dried (Filimonova et al., 2016). In fact, Filimonova et al. (2016) observed well developed
125 microaggregates after 20 days, but with allophane, ferrihydrite and OM. We extended the incubation to 32
126 days in order to consider the appropriate aggregate formation times as previously estimated for soils with
127 OM and crystalline minerals (Chenu and Cosentino, 2011; De Gryze et al., 2006; Segoli et al., 2013; Totsche
128 et al., 2018). Our aggregates were then gently grinded and sieved at 2 mm. For easy reading, mixtures and
129 aggregates will be designated by their goethite concentration: mixture-X and aggregate-X where $X = 0, 10,$
130 $20, 40, 60$ or 80 g kg^{-1} .

131 **2.3. Microscopic investigations**

132 Scanning electron microscopy (SEM) was performed on aggregates ($< 2 \text{ mm}$) without any chemical
133 pretreatment using a field emission gun SEM (FEG-SEM; Zeiss Ultra55), equipped with an EDX system
134 (Jeol JSM2300 with a resolution $<129 \text{ eV}$) to assess the micro-scale distribution of elements: carbon (C),
135 oxygen (O), Fe, Al, and Si. Aggregates were also visualized by Transmission Electron Microscopy (TEM)

136 on samples sieved at 250 μm , using a LEO 922 Omega Energy Filter Transmission Electron Microscope
137 operating at 120 kV.

138 **2.4. Chemical analyses**

139 *Elemental analysis.* Elemental analyses (Table 1) confirmed the expected value of the Al/Si ratio for
140 kaolinite (1.01 mol mol⁻¹) while the Ge/Si decreased in the order ($\mu\text{mol mol}^{-1}$): kaolinite (4.37) > quartz
141 (2.10) > phytoliths (0.41). In this study, the total concentrations of Si, Al and Ge were measured in triplicate
142 in the mixtures and aggregates. They were determined by Inductively Coupled Plasma - Atomic Emission
143 Spectrometry (ICP–AES, Jarrell Ash Iris Advantage) after calcination at 500°C for 24h, fusion in Li-
144 metaborate + Li-tetraborate at 1000 °C (Chao and Sanzolone, 1992), and then ash dissolution with a diluted
145 10% HNO₃ solution. Germanium (Ge) concentration was measured by ICP Mass Spectrometry (ICP-MS)
146 in powder samples (100 mg) after alkaline fusion using sodium peroxide (Na₂O₂) in a glassy carbon crucible,
147 heating to 600–800 °C until reaction ceased, and dissolution of the residual vitreous mass with a diluted 2%
148 HNO₃ solution (500ml). Accuracy and long-term repeatability of Ge analysis were well assessed. The
149 detection limit was 0.8×10^{-3} ppb. The analytical measurement precision was $\pm 2\%$. The BHVO-2 standard
150 (basalt rock powder) was systematically dosed every two samples in each analytical series. The C and N
151 concentrations were measured by a Flash 2000 Elemental Analyzer (Thermo Fisher Scientific, Waltham,
152 MA, USA).

153 *Specific extractions from individual components, mixtures and aggregates.* The Na₂CO₃- and CaCl₂-
154 extractable Si and Al concentrations were determined through kinetic extractions in triplicate to assess the
155 contents of BSi or amorphous Si (ASi) (DeMaster, 1981; Koning et al., 2002; Saccone et al., 2006) and
156 aqueous or bioavailable Si (Haysom and Chapman, 1975; Sauer et al., 2006), respectively. As for elemental
157 analyses, the Na₂CO₃ extraction was not repeated here for the individual components since their Na₂CO₃
158 extractable Si and Al contents were already discussed by Li et al. (2022). However, the CaCl₂ extraction
159 was repeated here for the individual components and performed simultaneously with the mixtures and
160 aggregates for comparison purposes under identical experimental conditions of temperature, pressure and

161 ionic strength. *Na₂CO₃ extraction.* Thirty mg of sample (mixture, aggregate) was mixed in 40ml of Na₂CO₃
162 0.1M, pH = 11.2, and digested for 5 h at 85 °C. One ml of extraction solution was collected at 1, 2, 3, 4 and
163 5 h, then neutralized and acidified by adding 100 µl of 7M HNO₃ to analyze dissolved Si and Al using ICP–
164 AES. The time evolutions of extracted Si and Al (Na₂CO₃-Si and -Al) were used to estimate the pools of
165 ASi and amorphous Al (AAI) as described in Li et al. (2022). *CaCl₂ extraction.* As mentioned above, we
166 carried out the CaCl₂ extractions for the individual components, mixtures and aggregates to produce
167 experimental data in strictly identical conditions. Instead of using standard protocols, we carried out a
168 prolonged (64d) kinetic extraction (Li et al., 2019) for the individual components, mixtures and aggregates
169 using a solid:liquid ratio 2g:20ml (unbuffered 0.01M CaCl₂) in a plastic centrifuge tube through
170 continuously shaking under darkness at 20 °C. The CaCl₂ extractant was unbuffered since buffering agents
171 readily interact with components and interfere in colloidal interactions. Adjusting pH by adding acid or base
172 can also impact the release of Si by mineral or phytolith dissolution. The 2:20 solid:liquid ratio was kept
173 constant using replicates for both the extraction and analysis. At each time step (16h, 2, 4, 8, 16, 32 and 64
174 days), the collected suspension (20 ml) was centrifuged at 3,000g for 20 min. The supernatant (15ml) was
175 filtered and separated in two aliquots to measure pH (5 ml) and solutes concentrations (10ml). The latter
176 extract was separated in two aliquots of 5 ml to determine, as described above, Si and Al concentration by
177 ICP-AES and Ge concentration by ICP-MS, respectively, at each kinetic step. Each 5-ml aliquot was diluted
178 with Milli-Q water by 10 times before assaying Si and Al, but by 2.5 times before dosing Ge. In both cases,
179 each 5 ml aliquot was acidified by adding 50 µl 7M HNO₃. These determinations were aimed to quantify
180 the release of aqueous Si as well as to trace its origin using the Al/Si and Ge/Si molar ratios. Following
181 Houba et al. (2000), we measured dissolved OC (DOC) in the 0.01M CaCl₂ extract at 16h with a TOC
182 analyzer (TOC-L, CPN; Shimadzu).

183

184 **3. Results**

185 **3.1. Characteristics of the materials**

186 Table 1 showed, as expected, the decrease in Si and Ge concentrations in the aggregates with the increase
187 in their goethite content. Concomitantly, the Al/Si ratio increased from 0.22 to 0.26, while the Ge/Si ratio
188 remained unchanged (2.5-2.6). The SEM images showed phytolith particles embedded in aggregate matrix
189 (Fig. 1a-e), with the typical bilobate shape of rice phytoliths (ICPT, 2019; Zuo et al., 2017) associated with
190 highest contents of Si and O (Fig. 1a-e). The SEM-EDX data also showed a very close interlocking of the
191 different components within fine-sized microaggregates ($< 250 \mu\text{m}$), making it difficult to target individual
192 constituents for detecting their respective chemical compositions (Table 1). As expected, the normalized
193 mass percent of Fe increased with increasing goethite loading. The TEM micrographs illustrated intimate
194 associations of fine clay-sized kaolinite and goethite (Fig. 1g-j). Fig. 1k (see also Table S1) showed that
195 DOC release from mixtures and aggregates decreased with increasing goethite content, while for a given
196 goethite concentration, DOC was significantly lower in the aggregate relatively to the unaggregated mixture.

197 **3.2. Na_2CO_3 extractable Si and Al.** Na_2CO_3 -Al was not detected in phytoliths, while both Na_2CO_3 -Al and
198 Na_2CO_3 -Si were not detected in quartz and OM (Fig. S3 in Li et al., 2022). The contents of amorphous Si
199 (ASi) and Al (AAI) (Table 2) were estimated from the time evolution of Na_2CO_3 -Si and Na_2CO_3 -Al for
200 mixtures and aggregates (Fig. S1). Largely differing between phytoliths and kaolinite (272 vs 1.2 g kg^{-1}),
201 the concentration of ASi varied from 5.9 to 9.2 g kg^{-1} in unaggregated mixtures, where it increased with
202 goethite content, and between 6 and 6.8 g kg^{-1} in the aggregates. The ASi content significantly differed
203 between mixtures and aggregates only in the absence of goethite and at goethite concentration of 60 and 80
204 g kg^{-1} . The AAI/AASi molar ratio was close to unity for kaolinite, but was largely below 1 for the mixtures
205 (0.05-0.125) and aggregates (0.018-0.045). Clearly, the increase in goethite content in the mixtures (not
206 shown) and aggregates (Table 2) led to the concomitant decrease in total Si and Ge concentrations, thus
207 giving a Al/Si ratio increasing from 0.22 to $0.26 \text{ mol mol}^{-1}$ and Ge/Si ratio remaining unchanged (2.5-2.6
208 $\mu\text{mol mol}^{-1}$). The Ge/Si (mmol mol^{-1}) values for phytoliths (0.41) and kaolinite (4.36) were in agreement
209 with data reported in the literature (Li et al., 2022, and references therein). The respective Al, Si and Ge
210 concentrations in kaolinite, phytoliths and quartz were used to compute the aggregate Al/Si and Ge/Si ratios,

211 which ranged from 0.23 to 0.26 mol mol⁻¹ (Al/Si) and from 2.5 to 2.6 μmol mol⁻¹ (Ge/Si), in agreement with
212 measured values (Table 1).

213 3.3. CaCl₂ extractable Si, Al and Ge, and pH

214 The pH of the CaCl₂ extract (pH_{CaCl₂}) ranged between 3.5 and 3.9 for kaolinite, decreased with increasing
215 extraction time from 5.8 to 4.4 for quartz, and from 4.3 to 3.5 for phytoliths (Fig. S2, Table S2). As shown
216 in Fig. 2 (values in Table S2), pH_{CaCl₂} increased with increasing time for all mixtures from 4.9-5.1 after 16h
217 to 5.5-7.5 after 64d (Fig. 2, Table S2). At 16h timestep, pH_{CaCl₂} values (4.9-5.1, Table S2) did not
218 significantly differ between goethite loadings. However, at 64d, they significantly differ by 2 pH units, this
219 difference being related to the goethite concentration in the mixture. At 64d, the pH_{CaCl₂} value indeed
220 increased from 5.5 to 7.5 with the increase in goethite content from 0 to 80 g kg⁻¹. In contrast, for the
221 aggregates, the range of pH_{CaCl₂} was two pH units after 16h (5.2-7.2) but narrower after 64d (7.2-7.9) without
222 dependence on goethite concentration (Fig. 2).

223 As observed by Li et al. (2022), Si and Al were not detected here in the CaCl₂ extract for OM. Same as Li
224 et al. (2022), the concentration of Si in the CaCl₂ extract (CaCl₂-Si) decreased in the order (g kg⁻¹, 16h-64d):
225 phytoliths (0.2–5.6) > kaolinite (0.01–0.15) > quartz (0.001-0.02) (Fig. S2) while CaCl₂-Al was not detected
226 for phytoliths and quartz. For kaolinite, CaCl₂-Al increased from 0.9 to 0.5 × 10⁻⁶ mol l⁻¹ with increasing
227 extraction time (Table S2), giving a Al/Si ratio decreasing from 1.1 to 0.15 (Fig. S2). The kinetic curves
228 showed the release of CaCl₂-Si from the unaggregated mixtures and aggregates in Fig. 3. In the former (Fig.
229 3a), CaCl₂-Si increased to a value at 64d depending on the goethite concentration in the mixture, as CaCl₂-
230 Si at 64d increased from 335 to 575 mg Si kg⁻¹ with increasing goethite content. In contrast, the range of
231 CaCl₂-Si at 64d was narrower in the aggregates as it varied from 395 to 430 mg Si kg⁻¹, with no dependency
232 on goethite content (Fig. 3b). At goethite concentrations above 20 g kg⁻¹, CaCl₂-Si at 64d was significantly
233 lower in the aggregates than in the mixtures (Fig. 3c). The range of Al concentration in the CaCl₂ extracts
234 (CaCl₂-Al) was 1.4 × 10⁻⁶–1.9 × 10⁻⁴ mol l⁻¹ in the mixtures and 0.8 × 10⁻⁶–1.0 × 10⁻⁴ mol l⁻¹ in the
235 aggregates (Table S2) with no specific trend along increasing extraction time (Fig. S3).

236 For both the mixtures and aggregates (Fig. 4), the Ge concentration in the CaCl₂ extract (CaCl₂-Ge)
237 systematically reached a maximum value at 32d. Yet, the time evolution of CaCl₂-Ge exhibited distinct
238 patterns between mixtures and aggregates. In the mixtures, the range of CaCl₂-Ge (μmol kg⁻¹) was 0.51-
239 1.08 at 16h and 0.06-2.12 at 64d closely depending on the goethite concentration (Fig. 4a), whereas in the
240 aggregates, the range of CaCl₂-Ge (μmol kg⁻¹) was 0.29-0.71 at 16h and 0.11-0.61 at 64d with no
241 dependency on goethite content (Fig. 4b). As shown in Fig. 4c-d, the lower release of Ge in CaCl₂ in the
242 aggregates was significant at 16h and 64d at goethite concentration ≥ 10 g kg⁻¹, but the reduction of CaCl₂-
243 Ge after aggregation was much larger at the highest goethite contents (60-80 g kg⁻¹) at 64d (Fig. 4d).

244 The values of CaCl₂-Si, CaCl₂-Al and CaCl₂-Ge were used to compute the values of the Al/Si and Ge/Si
245 molar ratios at each extraction time (Table 3). The Al/Si ratio in the CaCl₂ extract (CaCl₂-Al/Si) for the
246 mixtures and aggregates was systematically largely below that for kaolinite at each extraction time. At 64d,
247 the range of CaCl₂-Al/Si was 0.02-0.10 and 0.018-0.03 mol mol⁻¹ for the mixtures and aggregates,
248 respectively, compared to 0.15 for kaolinite. With increasing extraction time, the Ge/Si ratio in the CaCl₂
249 extract (CaCl₂-Ge/Si) decreased from 3.13 to 0.27 for phytoliths, and from 21 to 1.8 μmol mol⁻¹ for kaolinite
250 (Table 3). Note that the value of CaCl₂-Ge/Si at 16h was 20.9 here against 24.7 in Li et al. (2022). The value
251 of CaCl₂-Ge/Si for the mixtures and aggregates was systematically below that for kaolinite at each extraction
252 time. In the mixtures, CaCl₂-Ge/Si (μmol mol⁻¹) ranged from 5.25 to 10.07 at 16h; at 64d, it increased
253 progressively from 0.11 to 0.62 with the increase in goethite concentration from 0 to 40 g kg⁻¹, and reached
254 1.28-1.42 at goethite concentrations of 60 and 80 g kg⁻¹. In the aggregates, the range of CaCl₂-Ge/Si was
255 1.86-5.84 at 16h and 0.12-0.56 mmol mol⁻¹ at 64d, with no dependency on goethite concentration.

256

257 **4. Discussion**

258 **4.1. Aggregation reduced DOC release, while preserving kaolinite**

259 In the range of pH_{CaCl2} values, the surface charge carried by kaolinite, phytoliths and OM was negative while
260 it was positive for goethite (Li et al., 2022). These charge discrepancies enhanced colloidal interactions and

261 aggregation, as observed in tropical soils containing kaolinite and secondary Fe and Al oxides (Sanchez,
262 2019; Van Wambeke, 1992), but also in a wide range of LAC soils worldwide (IUSS, 2015). The phytoliths
263 were embedded in aggregates (Fig. 1a-e) in which kaolinite and goethite were intimately associated and
264 homogeneously distributed in fine-sized domains (Fig. 1f-j). Yet TEM could not distinguish whether the
265 association consisted of kaolinite particles covered with goethite or of small clusters regularly scattered in
266 these domains (Cambier and Prost, 1981; Schwertmann, 1988). Such clusters can combine with OM and
267 silt-sized components to form microaggregates (Dultz et al., 2018; Kaiser and Guggenberger, 2007; Kleber
268 et al., 2015; Six et al., 2000; Six et al., 2002). The aggregates thus readily formed after a 32-day incubation
269 (Fig. 1), as confirmed by the DOC release, used as a test assessing the process of aggregation. The DOC
270 release was significantly reduced after aggregation regardless the concentration of goethite (Fig. 1k, Table
271 S1). The reduction of DOC release by aggregation occurred even at low goethite content, but was largest in
272 aggregates with highest goethite concentrations. This reduction implied a stabilization of OM in aggregates,
273 as shown in various soil types with predominant 2:1 or 1:1 clay minerals (Six et al., 2002).

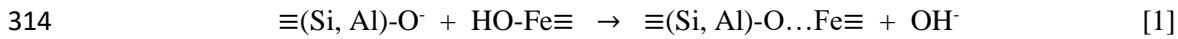
274 In the aggregates the ASi content, assumed to estimate the pool of biogenic silica (DeMaster, 1981), did not
275 differ depending on goethite concentration as it ranged between 6 and 6.8 g kg⁻¹ (Table 2) whatever the
276 concentration of goethite. Surprisingly, the ASi content was lowest in mixtures poor in goethite (≤ 10 g kg⁻¹)
277 ¹) as it was 5.4-5.9 g kg⁻¹, compared to ASi contents ranging from 7.6 to 9.2 g kg⁻¹ in mixtures with goethite
278 content ≥ 20 g kg⁻¹. Interestingly, the AAl content was significantly lower in aggregates than in mixtures,
279 suggesting a protective effect of the aggregation process on kaolinite, which was the exclusive source of Al
280 in our experimental model. Previous mineralogical investigations did not detect amorphous aluminosilicates
281 in *Charentes kaolinite* (Yvon et al., 1982). Yet, they highlighted crystalline defects in kaolinite particles
282 associated with a disorder increasing with decreasing particle size (Cases et al., 1982), likely linked to their
283 Fe content (Mestdagh et al., 1982), and related to impurities in the crystal growth environment (Cases et al.,
284 1982). These characteristics may have enhanced partial dissolution of fine-sized kaolinite particles in the
285 alkaline extractant (Carroll-Webb and Walther, 1988; Devidal et al., 1997; Huertas et al., 1999; N'Guessan

286 et al., 2021). However, the very low AAl/ASi molar ratio, 0.05-0.12 in mixtures and 0.02-0.03 in aggregates,
287 attested to a largely dominant dissolution of an amorphous silica phase attributed to phytoliths. The
288 dissolution of quartz, as is possible under alkaline conditions (Dove, 1994), likely did not interfere with the
289 assessment of ASi, since the procedure did not target crystalline forms of silica (De Master, 1981; Sauer et
290 al., 2006; Meunier et al., 2014).

291 **4.2. Goethite affected phytolith dissolution through aggregation and pH regulation**

292 The pH of the liquid phase during equilibration of the dilute CaCl₂ solution with the respective mixtures and
293 aggregates can be regulated by various processes. These are potentially: deprotonation of hydroxyl groups
294 in kaolinite and OM, Ca²⁺ ↔ 2 H⁺ ion exchange, H⁺ uptake by goethite surface sites, H⁺ consumption by
295 kaolinite dissolution. The latter process was limited since the CaCl₂-Al range was 1.4 × 10⁻⁶–1.9 × 10⁻⁴
296 mol l⁻¹ in the mixtures and 0.8 × 10⁻⁶–1.0 × 10⁻⁴ mol l⁻¹ in the aggregates (Table S2). Note that CaCl₂-Al was
297 nearly systematically and significantly smaller in the aggregates than in the mixtures (Table S2, Fig. S3):
298 this suggests that aggregation protected kaolinite. Obviously, goethite played a role in regulating pH. The
299 prolonged (64d) equilibration with the dilute CaCl₂ solution led to a significant increase in pH_{CaCl₂} from 5.5
300 to 7.5 with the increase in goethite concentration from 0 to 80 g kg⁻¹ (Fig. 2a). The tendency for soil pH to
301 drift towards its pH_{IEP} value (Uehara and Gillman, 1985) had long been recognized under the principle of
302 “isoelectric weathering” (Mattson, 1932): the higher the pH_{IEP}, the higher the soil pH, so that base-depleted,
303 highly weathered soils rich in Al and Fe oxides can approach neutrality (Sanchez, 2019; Van Wambeke,
304 1992). As the pH_{IEP} value for goethite is 9.6, the increase in pH_{CaCl₂} at 64d from 5.5 to 7.5 with increasing
305 goethite content in mixtures ($r = 0.93, p < 0.01$) was consistent with the principle of isoelectric weathering,
306 which involved here the release of protons by kaolinite and OM and their uptake by goethite. As reported
307 by Arias et al. (1995), the coating of kaolinite surfaces by goethite particles changes the surface properties
308 of kaolinite particles. Wei et al. (2014) showed that the intimate association of both minerals led to a higher
309 pH_{IEP} than in kaolinite-goethite mixture, probably because of the coating of kaolinite surfaces by fine
310 goethite particles (Schwertmann, 1988). From their study, a higher pH_{CaCl₂} was thus expected when

311 equilibrating the aggregates with dilute CaCl₂ compared to the mixtures, as observed here (Fig. 2). The
312 mechanism involved is illustrated by the following reaction of deprotonated surface (Si, Al)-OH group of
313 kaolinite with goethite hydroxyl (Wei et al., 2014):



315 Yet, in the absence of goethite, the higher pH_{CaCl₂} in aggregate-0 than in mixture-0 (Fig. 1k) could be due
316 to a higher retention of OM as discussed above, given that OM can be a proton donor.

317 In all mixtures and aggregates, the overall trend was that pH_{CaCl₂} increased with increasing time up to 7.5-
318 7.9 (Fig. 2), below the pH_{IEP} of goethite (9.6). Thus, the role of goethite in pH stabilization was moderated
319 by other constituents with lower pH_{IEP}, as observed in soils (Sanchez, 2019), in which it may have a real
320 effect at microsite level as illustrated here. In our experimental system, the increase in pH can have two
321 potential consequences: (i) raising the sorption of aqueous Si on goethite surfaces (Hiemstra et al., 2007),
322 thus removing Si from the liquid phase, (ii) enhancing phytolith dissolution (Fraysse et al., 2009), hence
323 releasing Si in the liquid phase. Our data showed that phytolith dissolution took precedence over DSi
324 adsorption. Indeed, the time evolution of pH_{CaCl₂} (Fig.2a) and CaCl₂-Si (Fig.3a) suggested a major impact
325 of pH on the release of aqueous Si from mixtures, as regulated by goethite. At 64d, CaCl₂-Si was almost
326 doubled (335-575 mg kg⁻¹) as pH increased from 5.5 to 7.5 with the increase in goethite content in the
327 mixtures, whereas its range was much narrower in the aggregates (395-430 mg kg⁻¹) under small pH
328 variation (7.2-7.9) without dependence on goethite content (Fig. 2b, Fig. 3b). Given that aggregation
329 significantly reduced the release of aqueous Si, both the aggregation process and pH had controlled the
330 preservation of phytoliths and their dissolution, respectively. Fig. 5 illustrated this assessment: CaCl₂-Si
331 increased with increasing pH, but differently before and after aggregation. At pH values close to 5, Si release
332 was similar in both the mixtures and aggregates. Above pH 5.5, CaCl₂-Si increased less after aggregation
333 with increasing pH, indicating a protective effect of the phytoliths within the aggregates, thus less phytolith
334 dissolution and, consequently, less release of Si into the aqueous phase. From Fig. 5, using the linear
335 regression equations at pH ≥ 6, CaCl₂-Si was almost twice as small in the aggregates as in the mixtures.

336 To further assess the protection of phytoliths as induced by goethite-mediated aggregation, we defined its
337 protective effect (*PrEf*) on the release of phytolithic Si using the CaCl₂-Si values at 64th day as follows:

$$338 \quad PrEf = \frac{(\text{CaCl}_2\text{-Si in mixtures}) - (\text{CaCl}_2\text{-Si in aggregates})}{(\text{CaCl}_2\text{-Si in mixtures})} \times 100\% \quad [2]$$

339 As shown in Fig. 6, in the absence of goethite, *PrEf* was negative (-29%). In contrast, *PrEf* within the
340 goethite-mediated aggregates raised from ~2% at goethite content of 10-20 g kg⁻¹ up to 20-30% with
341 increasing goethite content. Thus, small amounts of goethite can have a significant effect on the protective
342 action of aggregates on the preservation of phytoliths, hence delaying their dissolution, as noted through the
343 release of both Si (Fig. 3) and Ge (Fig. 4). The release of Si and Ge in CaCl₂ extracts was strongly similar
344 in two respects. Firstly, for the mixtures, both CaCl₂-Ge and CaCl₂-Si at 64d significantly increased with
345 the increase in goethite content from 0 to 80 g kg⁻¹ as well as in pH from 5.5 to 7.5. Secondly, both the
346 ranges of CaCl₂-Ge and CaCl₂-Si at 64d were much narrower in aggregates than in mixtures, without any
347 dependence on goethite content. Thus, the fates of aqueous Ge and Si were strongly similar, and likely
348 controlled by the same source.

349 Since the CaCl₂-Si release from quartz and OM was negligible, the only sources of aqueous Si were
350 phytoliths and kaolinite. Molar Ge/Si and Al/Si ratios can be used as geochemical proxies to trace the source
351 of DSi. The Ge/Si ratio highly discriminates phytoliths from clay minerals (Blecker et al., 2007; Derry et
352 al., 2005; White et al., 2012), particularly kaolinite (Lugolobi et al., 2010; Wiche et al., 2018). The Al/Si
353 ratio sharply distinguishes phytoliths with Al/Si ~ 0 from kaolinite exhibiting Al/Si = 1.01 (Table 1). The
354 time evolutions of CaCl₂-Al/Si and -Ge/Si ratios for phytoliths and kaolinite (Table 3) were typical for these
355 components (Li et al., 2022 and references therein). For mixtures and aggregates, the CaCl₂-Al/Si and -
356 Ge/Si values converged to identify the source of aqueous Si, namely phytoliths. Indeed, CaCl₂-Al/Si and
357 CaCl₂-Ge/Si were systematically lower than those of kaolinite at each extraction time (Table 3), both for
358 the mixtures and for the aggregates, but particularly for the latter. This was well illustrated in Fig. 7, showing
359 the time evolution of the Al/Si and Ge/Si molar ratios in the CaCl₂ extracts from mixtures and aggregates.
360 Clearly, both ratios decreased continuously to low values during prolonged equilibration with dilute CaCl₂.

361 The Ge/Si values were very close to those of phytoliths, as evidenced from both hydroponic (Blecker et al.,
362 2007) and field studies (White et al., 2012). In particular, phytoliths and aggregates were clearly
363 discriminated from kaolinite during this equilibration, using both Al/Si and Ge/Si (Fig. 7b). Plotting our
364 experimental data (Table S2) in the $\text{Al}_2\text{O}_3\text{-SiO}_2\text{-H}_2\text{O}$ stability diagram (Fig. 8) further illustrated that
365 H_4SiO_4 activity was controlled by phytoliths in both the mixtures and aggregates. Kaolinite was unstable
366 because of low pH (~ 3.8) and relative desilication with (H_4SiO_4) below 10^{-3} M. In mixtures and aggregates,
367 the stability of kaolinite increased during the CaCl_2 extraction likely because of the increase in pH and silica
368 activity due to phytolith dissolution. The combined use of Al/Si and Ge/Si molar ratios, pH and kinetic data
369 thus allowed an unequivocal identification of DSi sources.

370 Our experimental data therefore validate our first research hypothesis. Indeed, the aggregation-induced
371 protection of phytoliths has delayed their dissolution, thus reducing the release of DSi at low goethite
372 concentrations (≥ 20 g kg^{-1}), most probably because of oxide fine size and high SSA. However, our data
373 somehow invalidate our second hypothesis since the increase in pH did not cause identical behavior between
374 mixtures and aggregates (Fig. 7). This indicates that the increase in pH, as driven by increasing goethite
375 loading, did not lead to disaggregation and a subsequent increasing release of DSi caused by the liberation
376 of phytoliths from microaggregates. Thus, the effect of increasing pH was likely to be to promote the
377 dissolution of phytoliths that were not previously trapped in microaggregates, as their dissolution rate
378 increases by about one order of magnitude from pH 5 to 8 (Frayssé et al., 2009). The poor or absent pH-
379 induced disaggregation contrasts with earlier observations indicating disaggregation and clay dispersion
380 upon liming highly weathered soils rich in Fe oxides (Bigham et al., 2002). However, it corroborates the
381 stability of microaggregates observed in LAC soils with variable charge crystalline minerals as the soil pH
382 drifts towards its pH_{IEP} (Goldberg, 1989). As predicted by the Derjaguin–Landau–Verwey–Overbeek
383 (DLVO) theory, maximum aggregation should be achieved when surrounding pH approaches the particles
384 pH_{IEP} at which surface electrical potential is minimal (Goldberg, 1989; Guo et al., 2022). This would confirm

385 that, in our experimental scenario, the increase in pH had likely maintained or enhanced microaggregation,
386 but promoted the dissolution of unembedded phytoliths.

387 **4.3. How does the Si sorption/desorption control DSi?**

388 Apart from phytolith and mineral dissolution, the sorption/desorption of DSi on secondary oxides was
389 suggested to control DSi in soils (Cornelis et al., 2014; Meunier et al., 2018). Where soil phytoliths control
390 DSi, as measured by $\text{CaCl}_2\text{-Si}$, this hypothesis is questioned since, here, phytolith dissolution took
391 precedence over Si sorption on goethite. In our experimental scenario, goethite-mediated aggregation and
392 pH regulation actually controlled the release of DSi, despite our experimental design did not consider
393 competing solutes for goethite sorbing sites. Although oxide surface OH groups interact specifically with
394 H_4SiO_4 , advocating DSi sorption/desorption in natural soils could then be moderated for three reasons. (i)
395 In soils, various solutes compete strongly with H_4SiO_4 to be adsorbed by oxides, notably organic and
396 orthophosphate anions (Klotzbücher et al., 2020). (ii) The low reversibility of the Si sorption process may
397 limit the additional sorption of aqueous Si (Haynes and Zou, 2020). (iii) The change in oxide surface
398 composition due to inner sphere complexation shifts the pH_{IEP} value downwards (Anderson and Benjamin,
399 1985; Kingston et al., 1972), which also reduces additional Si sorption (Bowden et al., 1973).

400

401 **5. Implications and conclusion**

402 From a geochemical perspective, soil processes impact the global fate of Si (Cornelis and Delvaux, 2016)
403 since they control the fluxes of aqueous Si to the biosphere and hydrosphere, hence affecting the oceanic
404 capacity to fix carbon by diatoms (Conley, 2002). In soils, phytoliths represent a major source of aqueous
405 Si because of their relatively high dissolution rate (Frayse et al., 2009). Here we show that phytoliths can
406 be preserved from dissolution by aggregation involving kaolinite and goethite, ubiquitous crystalline
407 minerals with low charge and surface area. Such mineralogical pattern is typical for low activity clay (LAC)
408 soils (Uehara and Gillman, 1985). LAC soils cover ~30% of the land surface at global scale and ~55% in
409 the tropics. As the soil phytolith pool is a dominant, if not exclusive, contributor to the DSi pool in LAC

410 soils (Cornelis and Delvaux, 2016; Lucas et al., 1993; Meunier et al., 1999), phytolith trapping in
411 microaggregates is therefore a worldwide soil process that can largely impact DSi fluxes in the global Si
412 cycle. The role of the Fe oxide is highlighted here as it mediates aggregation under continuously oxic
413 conditions, as they occur in well-aerated soils, which are largely dominant on earth (> 90% of global land
414 surface). The protective effect of the aggregates on the preservation of phytoliths proves significant at low
415 goethite content ($\geq 2\%$). At common pH values of the soil solution (5-6), aggregation reduced Si release by
416 2- to 3-fold, suggesting that phytolith preservation in soil aggregates can be more widespread than currently
417 known, and likely more effective than Si adsorption on oxides for retaining Si. As already concluded earlier
418 (Li et al., 2020; Li et al., 2022; Meunier et al., 2014; Vander Linden et al., 2021), the occurrence of two
419 pools of phytoliths, namely fresh and stabilized, is also supported by our data. By using ubiquitous clay
420 mineral and Fe oxide, we show that microaggregation can be a widespread soil process that contributes to
421 build up the pool of stabilized phytoliths in soils, together with other processes such as, notably, the decrease
422 in surrounding pH (Frayse et al., 2009), ageing (Liu et al., 2003; Puppe and Leue, 2018) and surface
423 passivation (Koebernick et al., 2022). The latter process consists of the accumulation of Fe and C on the
424 surfaces of phytoliths, which are thus protected from dissolution (Koebernick et al., 2022). As being
425 enhanced by alternating redox conditions, this process involving Fe dynamics can occur in waterlogged
426 soils with alternating redox conditions. It reduces the release of DSi from the “passivated” phytoliths by 3-
427 fold (Koebernick et al., 2022), a reduction factor similar to that observed here after aggregation under oxic
428 conditions, which are widely prevalent in well-aerated soils.

429 Clearly, laboratory studies (Koebernick et al., 2022; Li et al., 2022; present study) can show higher release
430 rates of DSi from phytoliths than in natural soils. Since unsaturated flow through soil voids limits the amount
431 of surface exposed to water in natural conditions, the rate of Si release would be significantly lower than
432 predicted from our laboratory studies as demonstrated earlier for weathering, precipitation-dissolution and
433 sorption-desorption processes (Stumm and Morgan, 1996). In addition, biological activity was not
434 considered here, although it is crucial to further enhance microaggregation. Therefore, if the release of DSi

435 from phytoliths is so significantly reduced over short periods in laboratory conditions, as observed here, we
436 can expect a higher impact of microaggregation on phytolith protection and DSi release reduction in natural
437 soils. Thus, aggregation and above cited processes as well as specific properties of phytoliths (Cabanes et
438 al, 2012; Puppe and Leue, 2018), can enhance the resilience of phytoliths in soils over Millenia (Monger
439 and Kelly, 2002) and their use as paleo-indicators (Strömberg et al., 2018).

440

441 **Declaration of Competing Interest**

442 The authors declare that they have no known competing financial interests or personal relationships that
443 could have appeared to influence the work reported in this paper.

444

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453

454 **Appendix A. Supplementary material**

455 Supplementary material includes experimental results aimed at facilitating the understanding of data
456 presented and discussed in the manuscript (MS).

457 Raw data illustrated in the MS figures are in a text-based numerical format at Tables S1 and S2: organic
458 carbon budget and DOC release (Table S1), pH, concentrations (mol l^{-1}) of H_4SiO_4 and Al as well as of Ge
459 ($\mu\text{mol l}^{-1}$) in 0.01 M CaCl_2 extracts as collected from 16 h to 64 d for phytoliths, quartz, kaolinite, and
460 mixtures and aggregates (Table S2). Table S1 data are illustrated in the MS at Fig.1 while Table S2 data are
461 used in all other figures, from Fig.2 to Fig.8 as well as in Table 3.

462 In addition, Fig. S1 presents the Na_2CO_3 -dissolved Si and Al concentrations as measured in a kinetic
463 extraction to estimate the contents of amorphous Si (ASi) and Al (AAl) used in Table 2 in the MS. Figure
464 S1 reports on CaCl_2 -extractable Si and Al that are used in the MS at Table 3, Fig. 7 and Fig. 8. Figure S3
465 traces the temporal evolution of CaCl_2 extractable Al as used in the MS at Fig. 7-8 and Table 3.

466

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