



Goethite affects phytolith dissolution through clay particle aggregation and pH regulation

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ABSTRACT

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 Yet, soil phytoliths can be protected from dissolution by entrapment in aggregates, and thus be withdrawn from the global silica cycle.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

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1. Introduction

Since the pioneer quantitative study by Bartoli (1983), the role of plants in the terrestrial cycle of silicon (Si) has been largely documented (Derry et al., 2005; Meunier et al., 2022). The original source of dissolved Si (DSi) in soil is the reserve of weatherable silicate minerals (Garrels and Christ, 1965). Dissolved Si (DSi) is taken up as monosilicic acid (H_4SiO_4) by plants where the mean Si concentration ranges between 1 and 100 g Si kg^{-1} (Epstein, 1994; Hodson et al., 2005). In plant tissues, biogenic silica (BSi) precipitates as fine 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 widespread in soils (Monger and Kelly, 2002) in which their content ranges from 1 to 10 g kg^{-1} worldwide, but may be higher locally (Meunier et al., 2014). Because of their relatively high dissolution

rate (Frayse et al., 2009), phytoliths readily contribute to the reservoir of DSi, which can be (i) absorbed by plants and other biota (Puppe, 2020), (ii) sorbed by aluminum (Al) and iron (Fe) oxides (Bowden et al., 1973; Hiemstra et al., 2007; Haynes and Zhou, 2020), (iii) precipitated into clay and/or silica minerals (Karathanasis, 2002), or (iv) leached and transferred to rivers and oceans (Bartoli, 1983; Derry et al., 2005). These processes impact the Si continent-ocean linkage, hence the global cycle of Si (Conley, 2002; Derry et al., 2005; Erhart, 1963). Since Si is beneficial to plants (Coskun et al., 2019) while Si biological cycling is critical in primary productivity and C cycling on a global scale (Conley and Carey, 2015), Si plays a major role in the supply of numerous ecosystem services (Meunier et al., 2022). Therefore, understanding the mechanisms controlling DSi is a key issue. Among these mechanisms, the processes governing the resilience of phytoliths in soils are poorly known (Cornelis and Delvaux, 2016), despite recent advances showing that DSi release from phytoliths is also mediated by ageing (Liu et al., 2023; Puppe and Leue, 2018),

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microaggregation (Li et al., 2020; Li et al., 2022) and redox-dependent surface passivation (Koebernick et al., 2022). While the latter process requires alternating redox conditions (Koebernick et al., 2022) occurring in soils covering about 5–7% of global land surface (IUSS, 2015), microaggregation of soil particles is optimized in well-aerated soils with [clay + fine silt] content above 15%, in which biological activity enhances the formation of macro- and micro-aggregates (Oades, 1984; Six et al., 2004; Totsche et al., 2018). Since well-aerated soils are, by far, largely dominant on earth (>90% of global land surface), the impact of microaggregation on Si dynamics deserves a particular attention. An ample literature is available on the crucial role of microaggregates (<250 μm) on OC stabilization and turnover (Six et al., 2004; Totsche et al., 2018). However, the role of microaggregates in soil functions and ecosystem services related to the cycling of other elements is poorly known (Totsche et al., 2018). About Si, phytoliths can be readily entrapped in microaggregates, as shown in long-term field experiments (Li et al., 2020) and short-term laboratory studies (Li et al., 2022). Aggregation reduced the release of DSi, strongly from microaggregates using allophane and ferrihydrite, but to a much lesser extent from microaggregates using kaolinite and goethite (Li et al., 2022). Allophane and ferrihydrite are only significant in some Andosols, which cover <1% of the global land surface, while crystalline mineral soils cover the majority of this surface (IUSS, 2015). Among these, soils with predominant kaolinite and goethite are widespread worldwide, since these minerals are ubiquitous (Bigham et al., 2002; White and Dixon, 2002). In particular, soils containing predominantly low activity clays (LACs), i.e., kaolinite and crystalline (Al, Fe) oxides, have a high potential to form stable aggregates at low organic matter (OM) content (Denef et al., 2002; Six et al., 2004) because kaolinite and (Al, Fe) oxides act as main binding agents (Denef et al., 2002), as does OM in permanent charge soils (Six et al., 2002). These LAC soils cover $\sim 30\%$ of the land surface at global scale and $\sim 55\%$ in the tropics (IUSS, 2015; Sanchez, 2019). So far, the effect of crystalline oxide concentration on the release of DSi from microaggregates has not been evaluated.

Clay minerals, (Al, Fe) oxides and OM are the basic blocks of microaggregates, formed via cementing, which involve primarily physicochemical and chemical interactions, and gluing in which OM and microbial activity are crucial (Deng and Dixon, 2002; Totsche et al., 2018). Here, we focus on 1:1 clay – Fe oxide microaggregation which arises notably through binding oppositely charged surfaces of oxide and kaolinite (Schwertmann, 1988). Small amounts of Fe oxides promote microaggregation while their poor crystallinity and nano size enhance it (Schwertmann, 1988; Deng and Dixon, 2002; Totsche et al., 2018; Di Iorio et al., 2022; Guo et al., 2022). For crystalline oxides, conflicting observations were mainly attributed to the large diversity of oxide crystal morphology and particle size (Schwertmann, 1988), but the impacts of oxide amount (see e.g., Di Iorio et al., 2022; Sanchez, 2019) and pH are still unclear. As kaolinite–oxide interactions are based on binding oppositely charged surfaces, increasing pH leads to surface charge change causing disaggregation (Bigham et al., 2002; Baalousha, 2009) or enhancing aggregation (Demangeat et al., 2018; Guo et al., 2022; Goldberg, 1989), likely depending on OM content (Baalousha et al., 2008).

Here, we analyzed the role of goethite-mediated aggregation in releasing DSi from phytoliths by testing two hypotheses. (i) Aggregation-induced protection of phytoliths and delayed dissolution occur at low goethite concentrations. (ii) pH change affects aggregation, thus phytolith protection and DSi release. We used aggregates incubated from mixtures made of phytoliths, OM and kaolinite in fixed proportions, quartz and goethite in variable proportions. We quantified the release of DSi as impacted by

aggregation and pH, and traced its source using the geochemical proxies Ge/Si and Al/Si molar ratios.

2. Materials and methods

2.1. Individual components

Phytoliths were extracted from rice plant (*Oryza sativa indica* IR64; IRRI) leaves (Li et al., 2019; Li et al., 2022), purified (Kelly, 1990), washed and oven-dried at 50 °C (Li et al., 2022). Quartz was supplied by Merck KGaA Co, Darmstadt, Germany, the particles being of calibrated size 330–500 μm . Organic matter (OM) was oven-dried at 45 °C and finely ground Egyptian clover (*Trifolium alexandrinum*). Charentes kaolinite (Cases et al. 1982; Cases et al., 2000; Delineau et al., 1994; Yvon et al., 1982) contained minor 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 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 and drying (Cornell and Schwertmann, 1996). As reported earlier (Li et al., 2022), the constituents exhibited characteristic morphologies and X-ray diffraction patterns as well as specific surface area (SSA), which decreased in the sequence ($\text{m}^2 \text{g}^{-1}$): phytoliths (190) > goethite (132) > kaolinite (24) > quartz (1). Besides, in the pH range 4.5–7.5, kaolinite and OM carried a negative surface charge, while goethite carried a positive surface charge as predicted from its pH value at the isoelectric point ($\text{pH}_{\text{IEP}} = 9.6$, Li et al., 2022).

2.2. Mixtures and aggregates

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

2.3. Microscopic investigations

Scanning electron microscopy (SEM) was performed on aggregates (<2 mm) without any chemical pretreatment using a field emission gun SEM (FEG-SEM; Zeiss Ultra55), equipped with an EDX system (Jeol JSM2300 with a resolution < 129 eV) to assess

the micro-scale distribution of elements: carbon (C), oxygen (O), Fe, Al, and Si. Aggregates were also visualized by Transmission Electron Microscopy (TEM) on samples sieved at 250 μm , using a LEO 922 Omega Energy Filter Transmission Electron Microscope operating at 120 kV.

2.4. Chemical analyses

Elemental analysis. Elemental analyses (Table 1) confirmed the expected value of the Al/Si ratio for kaolinite ($1.01 \text{ mol mol}^{-1}$) while the Ge/Si decreased in the order ($\mu\text{mol mol}^{-1}$): kaolinite (4.37) > quartz (2.10) > phytoliths (0.41). In this study, the total concentrations of Si, Al and Ge were measured in triplicate in the mixtures and aggregates. They were determined by Inductively Coupled Plasma - Atomic Emission Spectrometry (ICP-AES, Jarrell Ash Iris Advantage) after calcination at 500°C for 24 h, fusion in Li-metaborate + Li-tetraborate at 1000°C (Chao and Sanzalone, 1992), and then ash dissolution with a diluted 10% HNO_3 solution. Germanium (Ge) concentration was measured by ICP Mass Spectrometry (ICP-MS) in powder samples (100 mg) after alkaline fusion using sodium peroxide (Na_2O_2) in a glassy carbon crucible, heating to $600\text{--}800^\circ\text{C}$ until reaction ceased, and dissolution of the residual vitreous mass with a diluted 2% HNO_3 solution (500 ml). Accuracy and long-term repeatability of Ge analysis were well assessed. The detection limit was 0.8×10^{-3} ppb. The analytical measurement precision was $\pm 2\%$. The BHVO-2 standard (basalt rock powder) was systematically dosed every two samples in each analytical series. The C and N concentrations were measured by a Flash 2000 Elemental Analyzer (Thermo Fisher Scientific, Waltham, MA, USA).

Specific extractions from individual components, mixtures and aggregates. The Na_2CO_3 - and CaCl_2 -extractable Si and Al concentrations were determined through kinetic extractions in triplicate to assess the contents of BSi or amorphous Si (ASi) (DeMaster, 1981; Koning et al., 2002; Saccone et al., 2006) and aqueous or bioavailable Si (Haysom and Chapman, 1975; Sauer et al., 2006), respectively. As for elemental analyses, the Na_2CO_3 extraction was not repeated here for the individual components since their Na_2CO_3 extractable Si and Al contents were already discussed by Li et al. (2022). However, the CaCl_2 extraction was repeated here for the individual components and performed simultaneously with the mixtures and aggregates for comparison purposes under identical experimental conditions of temperature, pressure and ionic strength. **Na_2CO_3 extraction.** Thirty mg of sample (mixture, aggregate) was mixed in 40 ml of Na_2CO_3 0.1 M, pH = 11.2, and digested

for 5 h at 85°C . One ml of extraction solution was collected at 1, 2, 3, 4 and 5 h, then neutralized and acidified by adding 100 μl of 7 M HNO_3 to analyze dissolved Si and Al using ICP-AES. The time evolutions of extracted Si and Al (Na_2CO_3 -Si and -Al) were used to estimate the pools of ASi and amorphous Al (AAl) as described in Li et al. (2022). **CaCl_2 extraction.** As mentioned above, we carried out the CaCl_2 extractions for the individual components, mixtures and aggregates to produce experimental data in strictly identical conditions. Instead of using standard protocols, we carried out a prolonged (64d) kinetic extraction (Li et al., 2019) for the individual components, mixtures and aggregates using a solid:liquid ratio 2 g:20 ml (unbuffered 0.01 M CaCl_2) in a plastic centrifuge tube through continuously shaking under darkness at 20°C . The CaCl_2 extractant was unbuffered since buffering agents readily interact with components and interfere in colloidal interactions. Adjusting pH by adding acid or base can also impact the release of Si by mineral or phytolith dissolution. The 2:20 solid:liquid ratio was kept constant using replicates for both the extraction and analysis. At each time step (16 h, 2, 4, 8, 16, 32 and 64 days), the collected suspension (20 ml) was centrifuged at 3,000g for 20 min. The supernatant (15 ml) was filtered and separated in two aliquots to measure pH (5 ml) and solutes concentrations (10 ml). The latter extract was separated in two aliquots of 5 ml to determine, as described above, Si and Al concentration by ICP-AES and Ge concentration by ICP-MS, respectively, at each kinetic step. Each 5-ml aliquot was diluted with Milli-Q water by 10 times before assaying Si and Al, but by 2.5 times before dosing Ge. In both cases, each 5 ml aliquot was acidified by adding 50 μl 7 M HNO_3 . These determinations were aimed to quantify the release of aqueous Si as well as to trace its origin using the Al/Si and Ge/Si molar ratios. Following Houba et al. (2000), we measured dissolved OC (DOC) in the 0.01 M CaCl_2 extract at 16h with a TOC analyzer (TOC-L, CPN; Shimadzu).

3. Results

3.1. Characteristics of the materials

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

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 Na_2CO_3 -Si were not detected in quartz and OM (Fig. S3 in Li et al., 2022). The contents of amorphous Si (ASi) and Al (AAl) (Table 2) were estimated from the time evolution of Na_2CO_3 -Si and Na_2CO_3 -Al for mixtures and aggregates (Fig. S1). Largely differ-

Table 1

Total concentrations of Si, Al and Ge, Al/Si and Ge/Si molar ratio in the individual components phytolith, kaolinite, quartz and goethite, and in aggregates with increasing goethite concentration from 0 to 80 g kg^{-1} .

Material	Si g kg^{-1}	Al g kg^{-1}	Al/Si mol mol^{-1}	Ge $\mu\text{g kg}^{-1}$	Ge/Si $\mu\text{mol mol}^{-1}$
Phytolith ^a	381.29	nd ^a	nd	403.07	0.41
Kaolinite ^a	204.10	197.98	1.01	2302.92	4.36
Quartz ^a	444.11	nd	nd	2419.41	2.10
Goethite	nnd ^b	nd	–	nd	nd
^c Aggregate-0	332.07	73.21	0.23	2147.30	2.50
Aggregate-10	327.65	73.20	0.23	2126.11	2.51
Aggregate-20	323.21	73.21	0.24	2104.92	2.52
Aggregate-40	314.33	73.23	0.24	2062.53	2.54
Aggregate-60	305.44	73.22	0.25	2020.12	2.65
Aggregate-80	296.56	73.21	0.26	1977.71	2.57

^a the Si, Al and Ge concentrations are taken from Li et al. (2022) for ease of comparison.

^b nd: not detected.

^c 0–80 for aggregate refers to the goethite concentration expressed in g kg^{-1} .

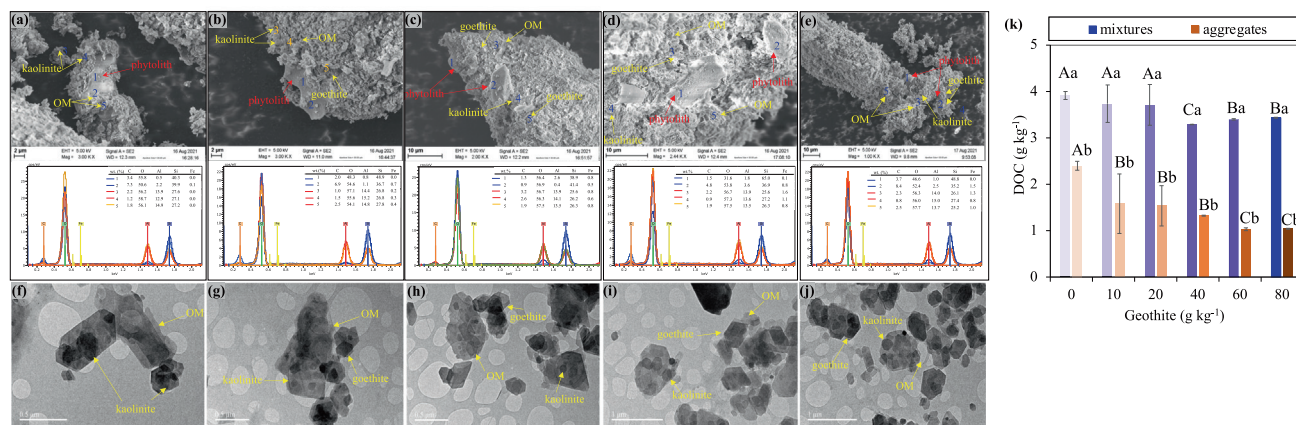


Fig. 1. (a–e) SEM micrographs and normalized mass percents (wt.%) of C, O, Fe, Al and Si, as measured by EDX on points 1–5, performed on aggregates (<2 mm) with no goethite (a) and goethite content of 10 (b), 20 (c), 40 (d) and 80 (e) g kg⁻¹. Red arrows point to phytolith particles, yellow ones to other constituents. (f–j) TEM micrographs performed on aggregates (<250 μm) with no goethite (f) and goethite content of 10 (g), 20 (h), 40 (i) and 80 (j) g kg⁻¹. Yellow arrows point to OM and mineral components, red arrows to phytoliths. (k) Dissolved organic carbon (DOC) extracted using CaCl₂ 0.01 M after 16h from both unaggregated mixtures and aggregates for each goethite content (see values in Table S1): different lowercase letter (a, b) resulting from the independent samples t-separation test, indicates a significant difference between mixtures and aggregates at a given goethite content ($p < 0.05$); different uppercase letter (A, B, C) resulting from LSD's multiple comparison test, indicates a significant difference among all mixtures or aggregates with various goethite proportion ($p < 0.05$).

Table 2

Estimated contents of amorphous Si (ASi) and Al (AAI) (and standard deviation s.d.), as quantified following DeMaster (1981) from Na₂CO₃ extractable Si (Na₂CO₃-Si) and Al (Na₂CO₃-Al) concentrations in the unaggregated mixtures and aggregates (Fig. S1) as compared to individual components. Different lowercase letter (a, b) resulting from the independent samples t-separation test, indicates a significant difference between unaggregated mixtures and aggregates at each given goethite content ($p < 0.05$); different uppercase letter (A, B, C) resulting from LSD's multiple comparison test, indicates a significant difference among unaggregated mixtures and, separately among aggregates ($p < 0.05$).

	ASi (g kg ⁻¹)		AAI (g kg ⁻¹)		AAI/ASi mol mol ⁻¹
	mean	s.d.	mean	s.d.	
Phytolith ^a	271.91	15.63	nd ^b	nd	nd
Kaolinite ^a	1.16	0.04	0.98	0.12	0.91
Quartz ^a	nd		nd		nd
Mixture-0	5.93Cb	0.24	0.67Aa	0.08	0.12Aa
Mixture-10	5.40Cb	0.14	0.58Aa	0.07	0.11Aa
Mixture-20	7.63Aa	1.47	0.42Ba	0.06	0.06Bb
Mixture-40	7.75Ba	0.33	0.64Aa	0.09	0.09Bb
Mixture-60	9.01Aa	0.42	0.76Aa	0.08	0.09Bb
Mixture-80	9.20Aa	0.78	0.44Ba	0.12	0.05Cc
Aggregate-0	6.53Aa	0.39	0.28Ab	0.09	0.04Ac
Aggregate-10	6.05Aa	0.52	0.23Ab	0.07	0.04Ac
Aggregate-20	6.65Aa	1.01	0.19Bb	0.04	0.03Bc
Aggregate-40	6.87Aa	0.61	0.17Bb	0.04	0.03Bc
Aggregate-60	6.26Ab	0.55	0.11Bb	0.03	0.02Bc
Aggregate-80	6.38Ab	0.54	0.18Bb	0.02	0.03Bc

^a The ASi and AAI concentrations are taken from Li et al. (2022) for purposes of comparison and easy reading.

^b nd: not detected.

^c 0–80 for mixture refers to the goethite concentration expressed in g kg⁻¹.

^d 0–80 for aggregate refers to the goethite concentration expressed in g kg⁻¹.

ing between phytoliths and kaolinite (272 vs 1.2 g kg⁻¹), the concentration of ASi varied from 5.9 to 9.2 g kg⁻¹ in unaggregated mixtures, where it increased with goethite content, and between 6 and 6.8 g kg⁻¹ in the aggregates. The ASi content significantly differed between mixtures and aggregates only in the absence of goethite and at goethite concentration of 60 and 80 g kg⁻¹. The AAI/ASi molar ratio was close to unity for kaolinite, but was largely below 1 for the mixtures (0.05–0.125) and aggregates (0.018–0.045). Clearly, the increase in goethite content in the mixtures (not shown) and aggregates (Table 2) led to the concomitant decrease in total Si and Ge concentrations, thus giving a Al/Si ratio increasing from 0.22 to 0.26 mol mol⁻¹ and Ge/Si ratio remaining

unchanged (2.5–2.6 μmol mol⁻¹). The Ge/Si (mmol mol⁻¹) values for phytoliths (0.41) and kaolinite (4.36) were in agreement with data reported in the literature (Li et al., 2022, and references therein). The respective Al, Si and Ge concentrations in kaolinite, phytoliths and quartz were used to compute the aggregate Al/Si and Ge/Si ratios, 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 measured values (Table 1).

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

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

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

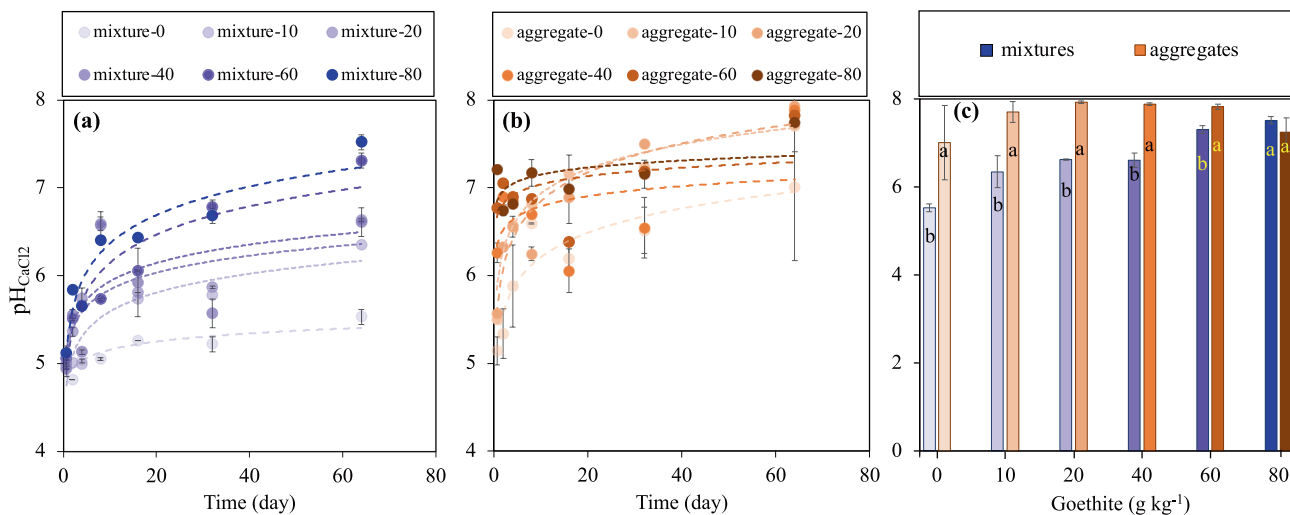


Fig. 2. (a–b) Time evolution of pH in 0.01 M CaCl₂ extracts (pH_{CaCl2}) in unaggregated mixtures (a) and aggregates (b) for each goethite content: the different mixtures and aggregates are designated by their goethite content expressed in g kg⁻¹: mixture-X and aggregate-X where X = 0, 10, 20, 40, 60 or 80 g kg⁻¹. (c) Values of pH_{CaCl2} at 64th day: different the lowercase letter (a, b) resulting from the independent samples t – separation test ($p < 0.05$) is given for comparison between unaggregated mixtures and aggregates at each goethite content.

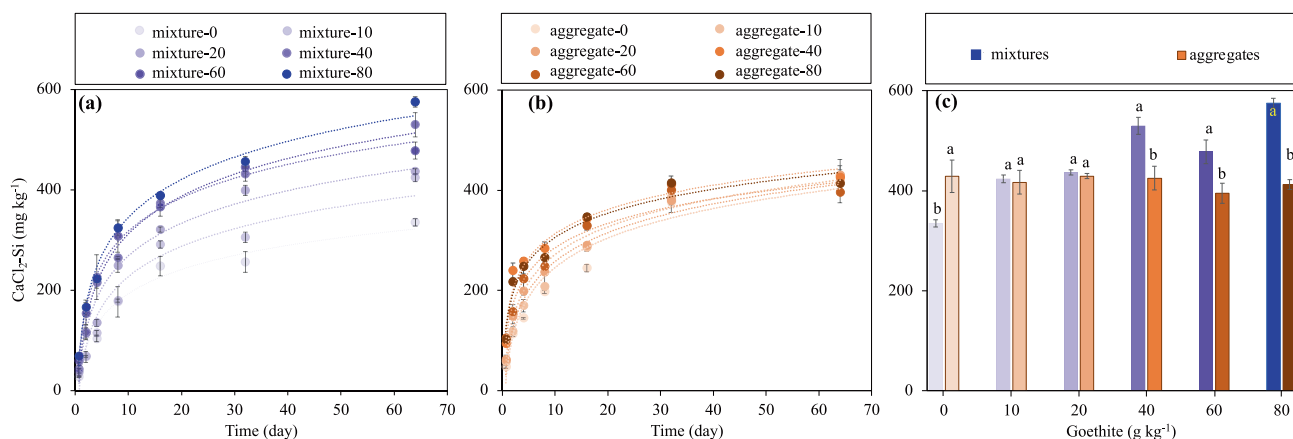


Fig. 3. Time evolution of Si in 0.01 M CaCl₂ extracts (CaCl₂-Si) in unaggregated mixtures (a) and aggregates (b) for each goethite content: the different mixtures and aggregates are designated by their goethite content expressed in g kg⁻¹: mixture-X and aggregate-X where X = 0, 10, 20, 40, 60 or 80 g kg⁻¹. (c) Values of CaCl₂-Si at 64th day: different the lowercase letter (a, b) resulting from the independent samples t – separation test ($p < 0.05$) is given for comparison between unaggregated mixtures and aggregates at each goethite content. Note: Time evolution of CaCl₂-Al was illustrated in Fig. S3 in supplementary information.

(Fig. 3c). The range of Al concentration in the CaCl₂ extracts (CaCl₂-Al) was $1.4 \cdot 10^{-6}$ – $1.9 \cdot 10^{-4}$ mol l⁻¹ in the mixtures and $0.8 \cdot 10^{-6}$ – $1.0 \cdot 10^{-4}$ mol l⁻¹ in the aggregates (Table S2) with no specific trend along increasing extraction time (Fig. S3).

For both the mixtures and aggregates (Fig. 4), the Ge concentration in the CaCl₂ extract (CaCl₂-Ge) systematically reached a maximum value at 32d. Yet, the time evolution of CaCl₂-Ge exhibited distinct patterns between mixtures and aggregates. In the mixtures, the range of CaCl₂-Ge (μmol kg⁻¹) was 0.51–1.08 at 16h and 0.06–2.12 at 64d closely depending on the goethite concentration (Fig. 4a), whereas in the 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 dependency on goethite content (Fig. 4b). As shown in Fig. 4c–d, the lower release of Ge in CaCl₂ in the aggregates was significant at 16h and 64d at goethite concentration ≥ 10 g kg⁻¹, but the reduction of CaCl₂-Ge after aggregation was much larger at the highest goethite contents (60–80 g kg⁻¹) at 64d (Fig. 4d).

The values of CaCl₂-Si, CaCl₂-Al and CaCl₂-Ge were used to compute the values of the Al/Si and Ge/Si molar ratios at each

extraction time (Table 3). The Al/Si ratio in the CaCl₂ extract (CaCl₂-Al/Si) for the mixtures and aggregates was systematically largely below that for kaolinite at each extraction time. At 64d, the range of CaCl₂-Al/Si was 0.02–0.10 and 0.018–0.03 mol mol⁻¹ for the mixtures and aggregates, respectively, compared to 0.15 for kaolinite. With increasing extraction time, the Ge/Si ratio in the CaCl₂ extract (CaCl₂-Ge/Si) decreased from 3.13 to 0.27 for phytoliths, and from 21 to 1.8 μmol mol⁻¹ for kaolinite (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 of CaCl₂-Ge/Si for the mixtures and aggregates was systematically below that for kaolinite at each extraction time. In the mixtures, CaCl₂-Ge/Si (μmol mol⁻¹) ranged from 5.25 to 10.07 at 16h; at 64d, it increased progressively from 0.11 to 0.62 with the increase in goethite concentration from 0 to 40 g kg⁻¹, and reached 1.28–1.42 at goethite concentrations of 60 and 80 g kg⁻¹. In the aggregates, the range of CaCl₂-Ge/Si was 1.86–5.84 at 16h and 0.12–0.56 mmol mol⁻¹ at 64d, with no dependency on goethite concentration.

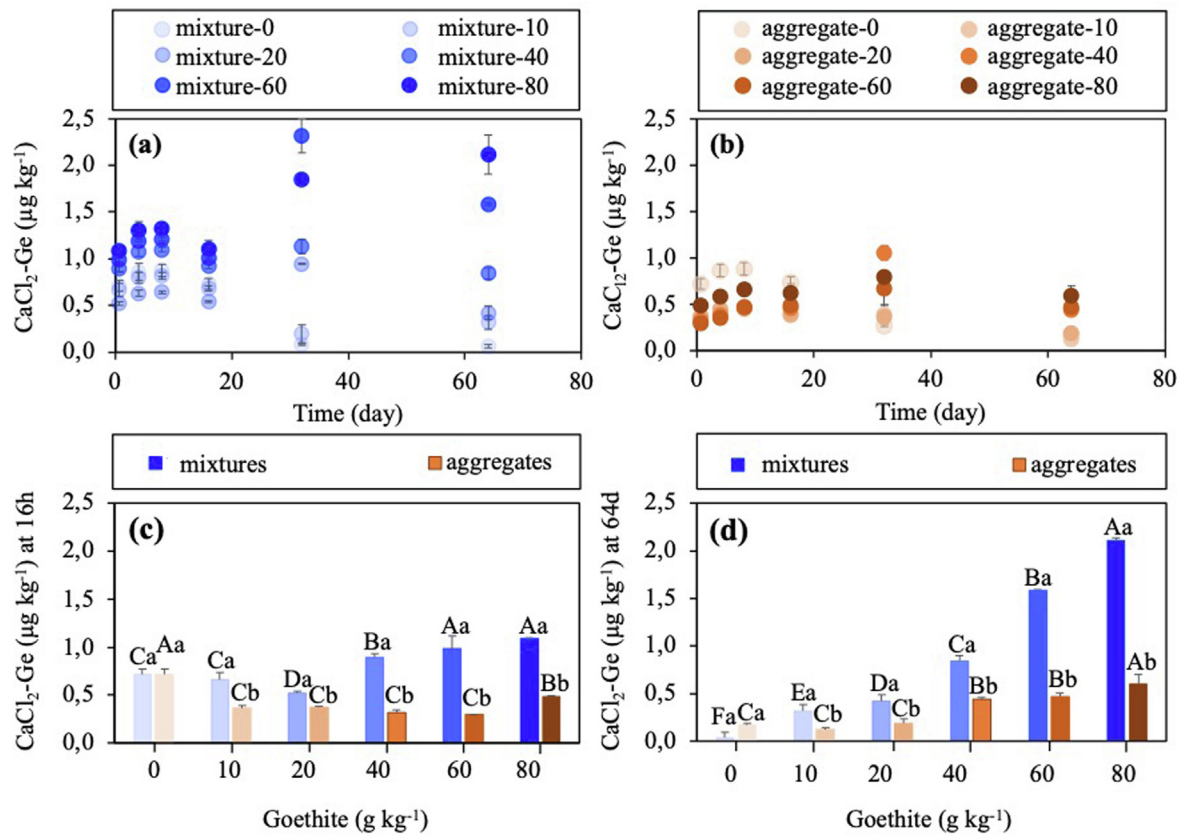


Fig. 4. Time evolution of the Ge concentration in 0.01 M CaCl₂ extracts (CaCl₂-Ge) in unaggregated mixtures (a) and aggregates (b) for each goethite content: the different mixtures and aggregates are designated by their goethite content expressed in g kg⁻¹: mixture-X and aggregate-X where X = 0, 10, 20, 40, 60 or 80 g kg⁻¹. Values of CaCl₂-Ge at 16th hour (c) and 64th day (d): different lowercase letter (a, b) resulting from the independent samples t-separation test, indicates a significant difference between the mixture and the aggregate at a given goethite content ($p < 0.05$); different uppercase letter (A-E) resulting from LSD's multiple comparison test, indicates a significant difference between mixtures and, separately, between aggregates with various goethite content ($p < 0.05$).

Table 3

Time evolution of the Al/Si (mol mol⁻¹) and Ge/Si (μmol mol⁻¹) molar ratios (and standard deviation s.d. into brackets) in 0.01 M CaCl₂ extracts for the individual components (kaolinite and phylolith), and for unaggregated mixtures and aggregates with various goethite contents (0–80 g kg⁻¹).

Time		16h	4d	8d	16d	32d	64d
Phylolith	Al/Si	0.00	0.00	0.00	0.00	0.00	0.00
	Ge/Si	3.13(0.37)	0.60(0.07)	0.83(0.03)	0.33(0.05)	0.24(0.09)	0.27(0.04)
Kaolinite	Al/Si	1.15(0.24)	0.52(0.01)	0.36(0.02)	0.21(0.01)	0.15(0.00)	0.16(0.00)
	Ge/Si	20.9(1.01)	9.15(0.32)	6.56(0.42)	3.60(0.02)	2.76(0.04)	1.78(0.05)
Mixture-0	Al/Si	0.57(0.014)	0.19(0.016)	0.20(0.029)	0.11(0.000)	0.03(0.002)	0.03(0.003)
	Ge/Si	10.07(1.01)	3.21(0.32)	1.92(0.42)	1.15(0.02)	0.12(0.04)	0.11(0.05)
Mixture-10	Al/Si	0.48(0.090)	0.12(0.003)	0.14(0.012)	0.15(0.012)	0.01(0.001)	0.06(0.006)
	Ge/Si	7.33(0.59)	2.72(0.05)	1.78(0.07)	0.92(0.07)	0.25(0.09)	0.29(0.02)
Mixture-20	Al/Si	0.39(0.003)	0.01(0.000)	0.003(0.001)	0.004(0.001)	0.003(0.000)	0.02(0.001)
	Ge/Si	5.25(0.33)	1.81(0.05)	1.01(0.05)	0.66(0.03)	0.92(0.01)	0.37(0.04)
Mixture-40	Al/Si	0.27(0.061)	0.05(0.000)	0.001(0.000)	0.04(0.000)	0.002(0.000)	0.04(0.001)
	Ge/Si	8.14(0.37)	1.94(0.07)	1.61(0.03)	0.96(0.05)	1.02(0.09)	0.62(0.04)
Mixture-60	Al/Si	0.17(0.034)	0.002(0.000)	0.002(0.000)	0.001(0.000)	0.001(0.000)	0.04(0.002)
	Ge/Si	6.48(0.11)	2.05(0.06)	1.53(0.03)	1.10(0.07)	2.01(0.11)	1.28(0.02)
Mixture-80	Al/Si	0.18(0.026)	0.003(0.000)	0.001(0.000)	0.001(0.001)	0.001(0.000)	0.09(0.011)
	Ge/Si	6.11(0.09)	2.29(0.37)	1.59(0.05)	1.11(0.11)	1.57(0.03)	1.42(0.76)
Aggregate-0	Al/Si	0.51(0.004)	0.06(0.006)	0.02(0.004)	0.008(0.001)	0.004(0.002)	0.03(0.001)
	Ge/Si	5.84(0.63)	2.33(0.29)	1.77(0.41)	1.18(0.00)	0.28(0.03)	0.15(0.08)
Aggregate-10	Al/Si	0.20(0.036)	0.006(0.001)	0.004(0.000)	0.003(0.001)	0.002(0.000)	0.03(0.005)
	Ge/Si	2.45(0.37)	0.99(0.01)	0.84(0.06)	0.52(0.06)	0.40(0.09)	0.12(0.02)
Aggregate-20	Al/Si	0.14(0.005)	0.008(0.001)	0.017(0.0001)	0.001(0.007)	0.001(0.000)	0.02(0.003)
	Ge/Si	2.35(0.21)	0.88(0.06)	0.77(0.06)	0.53(0.02)	0.35(0.01)	0.17(0.04)
Aggregate-40	Al/Si	0.008(0.005)	0.001(0.000)	0.001(0.001)	0.001(0.000)	0.001(0.000)	0.02(0.001)
	Ge/Si	1.35(0.23)	0.59(0.06)	0.65(0.11)	0.53(0.05)	1.00(0.09)	0.40(0.00)
Aggregate-60	Al/Si	0.003(0.000)	0.002(0.000)	0.002(0.000)	0.001(0.000)	0.001(0.000)	0.02(0.006)
	Ge/Si	1.10(0.07)	0.58(0.06)	0.74(0.01)	0.53(0.05)	0.64(0.11)	0.50(0.03)
Aggregate-80	Al/Si	0.006(0.001)	0.001(0.000)	0.001(0.000)	0.001(0.000)	0.001(0.000)	0.02(0.009)
	Ge/Si	1.86(0.06)	0.92(0.04)	0.97(0.04)	0.70(0.10)	0.74(0.03)	0.56(0.05)

Note: for Al/Si, 3 decimals were used when required.

4. Discussion

4.1. Aggregation reduced DOC release, while preserving kaolinite

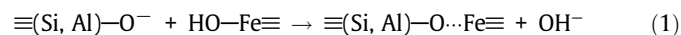
In the range of $\text{pH}_{\text{CaCl}_2}$ values, the surface charge carried by kaolinite, phytoliths and OM was negative while it was positive for goethite (Li et al., 2022). These charge discrepancies enhanced colloidal interactions and aggregation, as observed in tropical soils containing kaolinite and secondary Fe and Al oxides (Sanchez, 2019; Van Wambeke, 1992), but also in a wide range of LAC soils worldwide (IUSS, 2015). The phytoliths were embedded in aggregates (Fig. 1a–e) in which kaolinite and goethite were intimately associated and homogeneously distributed in fine-sized domains (Fig. 1f–j). Yet TEM could not distinguish whether the association consisted of kaolinite particles covered with goethite or of small clusters regularly scattered in these domains (Cambier and Prost, 1981; Schwertmann, 1988). Such clusters can combine with OM and silt-sized components to form microaggregates (Dultz et al., 2018; Kaiser and Guggenberger, 2007; Kleber et al., 2015; Six et al., 2000; Six et al., 2002). The aggregates thus readily formed after a 32-day incubation (Fig. 1), as confirmed by the DOC release, used as a test assessing the process of aggregation. The DOC release was significantly reduced after aggregation regardless the concentration of goethite (Fig. 1k, Table S1). The reduction of DOC release by aggregation occurred even at low goethite content, but was largest in aggregates with highest goethite concentrations. This reduction implied a stabilization of OM in aggregates, as shown in various soil types with predominant 2:1 or 1:1 clay minerals (Six et al., 2002).

In the aggregates the ASi content, assumed to estimate the pool of biogenic silica (DeMaster, 1981), did not differ depending on goethite concentration as it ranged between 6 and 6.8 g kg⁻¹ (Table 2) whatever the concentration of goethite. Surprisingly, the ASi content was lowest in mixtures poor in goethite (≤ 10 g kg⁻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 content ≥ 20 g kg⁻¹. Interestingly, the AAl content was significantly lower in aggregates than in mixtures, suggesting a protective effect of the aggregation process on kaolinite, which was the exclusive source of Al in our experimental model. Previous mineralogical investigations did not detect amorphous aluminosilicates in *Charentes kaolinite* (Yvon et al., 1982). Yet, they highlighted crystalline defects in kaolinite particles associated with a disorder increasing with decreasing particle size (Cases et al., 1982), likely linked to their Fe content (Mestdagh et al., 1982), and related to impurities in the crystal growth environment (Cases et al., 1982). These characteristics may have enhanced partial dissolution of fine-sized kaolinite particles in the alkaline extractant (Carroll-Webb and Walther, 1988; Devidal et al., 1997; Huertas et al., 1999; N'Guessan et al., 2021). However, the very low AAl/ASi molar ratio, 0.05–0.12 in mixtures and 0.02–0.03 in aggregates, attested to a largely dominant dissolution of an amorphous silica phase attributed to phytoliths. The dissolution of quartz, as is possible under alkaline conditions (Dove, 1994), likely did not interfere with the assessment of ASi, since the procedure did not target crystalline forms of silica (DeMaster, 1981; Sauer et al., 2006; Meunier et al., 2014).

4.2. Goethite affected phytolith dissolution through aggregation and pH regulation

The pH of the liquid phase during equilibration of the dilute CaCl_2 solution with the respective mixtures and aggregates can be regulated by various processes. These are potentially: deprotonation of hydroxyl groups in kaolinite and OM, $\text{Ca}^{2+} \leftrightarrow 2\text{H}^+$ ion

exchange, H^+ uptake by goethite surface sites, H^+ consumption by kaolinite dissolution. The latter process was limited since the CaCl_2 -Al range was $1.4 \cdot 10^{-6}$ – $1.9 \cdot 10^{-4}$ mol l⁻¹ in the mixtures and $0.8 \cdot 10^{-6}$ – $1.0 \cdot 10^{-4}$ mol l⁻¹ in the aggregates (Table S2). Note that CaCl_2 -Al was nearly systematically and significantly smaller in the aggregates than in the mixtures (Table S2, Fig. S3): this suggests that aggregation protected kaolinite. Obviously, goethite played a role in regulating pH. The prolonged (64d) equilibration with the dilute CaCl_2 solution led to a significant increase in $\text{pH}_{\text{CaCl}_2}$ from 5.5 to 7.5 with the increase in goethite concentration from 0 to 80 g kg⁻¹ (Fig. 2a). The tendency for soil pH to drift towards its pH_{IEP} value (Uehara and Gillman, 1985) had long been recognized under the principle of “isoelectric weathering” (Mattson, 1932): the higher the pH_{IEP} , the higher the soil pH, so that base-depleted, highly weathered soils rich in Al and Fe oxides can approach neutrality (Sanchez, 2019; Van Wambeke, 1992). As the pH_{IEP} value for goethite is 9.6, the increase in $\text{pH}_{\text{CaCl}_2}$ at 64d from 5.5 to 7.5 with increasing goethite content in mixtures ($r = 0.93$, $p < 0.01$) was consistent with the principle of isoelectric weathering, which involved here the release of protons by kaolinite and OM and their uptake by goethite. As reported by Arias et al. (1995), the coating of kaolinite surfaces by goethite particles changes the surface properties of kaolinite particles. Wei et al. (2014) showed that the intimate association of both minerals led to a higher pH_{IEP} than in kaolinite-goethite mixture, probably because of the coating of kaolinite surfaces by fine goethite particles (Schwertmann, 1988). From their study, a higher $\text{pH}_{\text{CaCl}_2}$ was thus expected when equilibrating the aggregates with dilute CaCl_2 compared to the mixtures, as observed here (Fig. 2). The mechanism involved is illustrated by the following reaction of deprotonated surface (Si, Al)-OH group of kaolinite with goethite hydroxyl (Wei et al., 2014):



Yet, in the absence of goethite, the higher $\text{pH}_{\text{CaCl}_2}$ in aggregate-0 than in mixture-0 (Fig. 1k) could be due to a higher retention of OM as discussed above, given that OM can be a proton donor.

In all mixtures and aggregates, the overall trend was that $\text{pH}_{\text{CaCl}_2}$ increased with increasing time up to 7.5–7.9 (Fig. 2), below the pH_{IEP} of goethite (9.6). Thus, the role of goethite in pH stabilization was moderated by other constituents with lower pH_{IEP} , as observed in soils (Sanchez, 2019), in which it may have a real effect at microsite level as illustrated here. In our experimental system, the increase in pH can have two potential consequences: (i) raising the sorption of aqueous Si on goethite surfaces (Hiemstra et al., 2007), thus removing Si from the liquid phase, (ii) enhancing phytolith dissolution (Frayse et al., 2009), hence releasing Si in the liquid phase. Our data showed that phytolith dissolution took precedence over DSi adsorption. Indeed, the time evolution of $\text{pH}_{\text{CaCl}_2}$ (Fig. 2a) and CaCl_2 -Si (Fig. 3a) suggested a major impact of pH on the release of aqueous Si from mixtures, as regulated by goethite. At 64d, CaCl_2 -Si was almost doubled (335–575 mg kg⁻¹) as pH increased from 5.5 to 7.5 with the increase in goethite content in the mixtures, whereas its range was much narrower in the aggregates (395–430 mg kg⁻¹) under small pH variation (7.2–7.9) without dependence on goethite content (Fig. 2b, Fig. 3b). Given that aggregation significantly reduced the release of aqueous Si, both the aggregation process and pH had controlled the preservation of phytoliths and their dissolution, respectively. Fig. 5 illustrated this assessment: CaCl_2 -Si increased with increasing pH, but differently before and after aggregation. At pH values close to 5, Si release was similar in both the mixtures and aggregates. Above pH 5.5, CaCl_2 -Si increased less after aggregation with increasing pH, indicating a protective effect of the phytoliths within the aggregates, thus less phytolith dissolution and, conse-

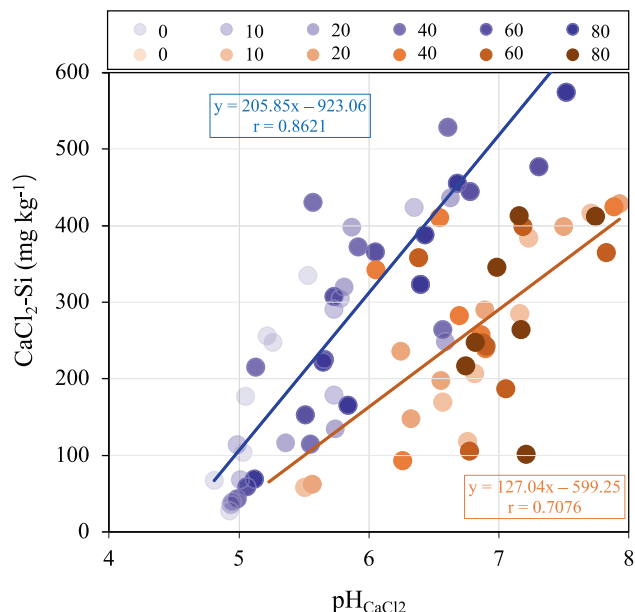


Fig. 5. Concentration of Si in CaCl_2 extracts ($\text{CaCl}_2\text{-Si}$) as plotted against pH of respective CaCl_2 extracts ($\text{pH}_{\text{CaCl}_2}$) in unaggregated mixtures (gradient blue) and aggregates (gradient orange) for each goethite content: the different mixtures and aggregates are designated by their goethite content expressed in g kg^{-1} : mixture-X and aggregate-X where X = 0, 10, 20, 40, 60 or 80 g kg^{-1} . Using the independent samples t-separation test, the values of the slopes of the two regression lines significantly differ at $p < 0.0001$.

quently, less release of Si into the aqueous phase. From Fig. 5, using the linear regression equations at $\text{pH} \geq 6$, $\text{CaCl}_2\text{-Si}$ was almost twice as small in the aggregates as in the mixtures.

To further assess the protection of phytoliths as induced by goethite-mediated aggregation, we defined its protective effect (*PrEf*) on the release of phytolithic Si using the $\text{CaCl}_2\text{-Si}$ values at 64th day as follows:

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

As shown in Fig. 6, in the absence of goethite, *PrEf* was negative (−29%). In contrast, *PrEf* within the goethite-mediated aggregates raised from ~2% at goethite content of 10–20 g kg^{-1} up to 20–30% with increasing goethite content. Thus, small amounts of goethite can have a significant effect on the protective action of aggregates on the preservation of phytoliths, hence delaying their dissolution, as noted through the release of both Si (Fig. 3) and Ge (Fig. 4). The release of Si and Ge in CaCl_2 extracts was strongly similar in two respects. Firstly, for the mixtures, both $\text{CaCl}_2\text{-Ge}$ and $\text{CaCl}_2\text{-Si}$ at 64d significantly increased with 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 ranges of $\text{CaCl}_2\text{-Ge}$ and $\text{CaCl}_2\text{-Si}$ at 64d were much narrower in aggregates than in mixtures, without any dependence on goethite content. Thus, the fates of aqueous Ge and Si were strongly similar, and likely controlled by the same source.

Since the $\text{CaCl}_2\text{-Si}$ release from quartz and OM was negligible, the only sources of aqueous Si were phytoliths and kaolinite. Molar Ge/Si and Al/Si ratios can be used as geochemical proxies to trace the source of DSi. The Ge/Si ratio highly discriminates phytoliths from clay minerals (Blecker et al., 2007; Derry et al., 2005; White et al., 2012), particularly kaolinite (Lugolobi et al., 2010; Wiche et al., 2018). The Al/Si ratio sharply distinguishes phytoliths with Al/Si ~ 0 from kaolinite exhibiting Al/Si = 1.01 (Table 1). The time

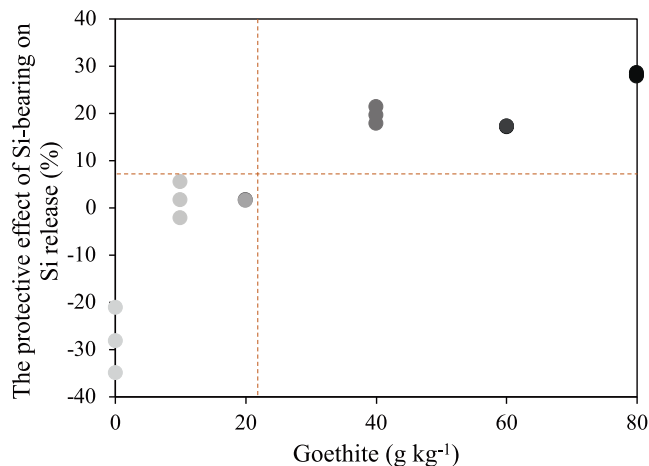


Fig. 6. Cate-Nelson plot (Cate and Nelson, 1971) illustrating the protective effect (*PrEf*, Eq. (2)) of aggregates on Si release in the goethite-mediated aggregates at the 64th day. The aggregates are designated by their goethite content expressed in 0, 10, 20, 40, 60 or 80 g kg^{-1} .

evolutions of $\text{CaCl}_2\text{-Al/Si}$ and -Ge/Si ratios for phytoliths and kaolinite (Table 3) were typical for these components (Li et al., 2022 and references therein). For mixtures and aggregates, the $\text{CaCl}_2\text{-Al/Si}$ and -Ge/Si values converged to identify the source of aqueous Si, namely phytoliths. Indeed, $\text{CaCl}_2\text{-Al/Si}$ and $\text{CaCl}_2\text{-Ge/Si}$ were systematically lower than those of kaolinite at each extraction time (Table 3), both for the mixtures and for the aggregates, but particularly for the latter. This was well illustrated in Fig. 7, showing the time evolution of the Al/Si and Ge/Si molar ratios in the CaCl_2 extracts from mixtures and aggregates. Clearly, both ratios decreased continuously to low values during prolonged equilibration with dilute CaCl_2 . The Ge/Si values were very close to those of phytoliths, as evidenced from both hydroponic (Blecker et al., 2007) and field studies (White et al., 2012). In particular, phytoliths and aggregates were clearly discriminated from kaolinite during this equilibration, using both Al/Si and Ge/Si (Fig. 7b). Plotting our 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 H_4SiO_4 activity was controlled by phytoliths in both the mixtures and aggregates. Kaolinite was unstable because of low pH (~3.8) and relative desilication with (H_4SiO_4) below 10^{-3} M . In mixtures and aggregates, the stability of kaolinite increased during the CaCl_2 extraction likely because of the increase in pH and silica activity due to phytolith dissolution. The combined use of Al/Si and Ge/Si molar ratios, pH and kinetic data thus allowed an unequivocal identification of DSi sources.

Our experimental data therefore validate our first research hypothesis. Indeed, the aggregation-induced protection of phytoliths has delayed their dissolution, thus reducing the release of DSi at low goethite concentrations ($\geq 20 \text{ g kg}^{-1}$), most probably because of oxide fine size and high SSA. However, our data somehow invalidate our second hypothesis since the increase in pH did not cause identical behavior between mixtures and aggregates (Fig. 7). This indicates that the increase in pH, as driven by increasing goethite loading, did not lead to disaggregation and a subsequent increasing release of DSi caused by the liberation of phytoliths from microaggregates. Thus, the effect of increasing pH was likely to promote the dissolution of phytoliths that were not previously trapped in microaggregates, as their dissolution rate increases by about one order of magnitude from pH 5 to 8 (Frayse et al., 2009). The poor or absent pH-induced disaggregation contrasts with earlier observations indicating disaggregation and clay dispersion upon liming highly weathered soils rich in Fe oxides

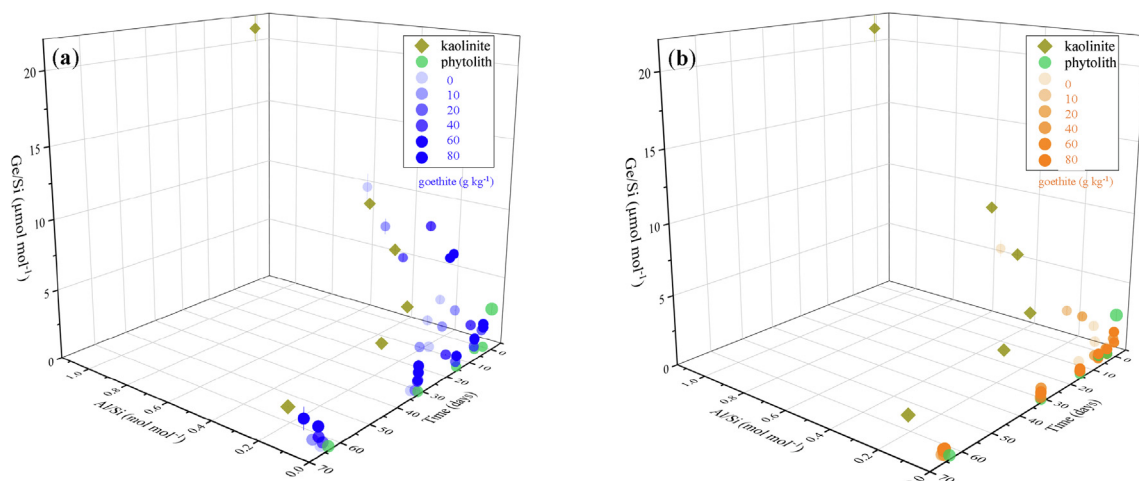


Fig. 7. Time evolution of the molar ratios Ge/Si ($\mu\text{mol mol}^{-1}$) and Al/Si (mol mol^{-1}) in 0.01 M CaCl_2 extracts in unaggregated mixtures (a) and aggregates (b) for each goethite content: the different mixtures and aggregates are designated by their goethite content expressed in g kg^{-1} : mixture-X and aggregate-X where X = 0, 10, 20, 40, 60 or 80 g kg^{-1} .

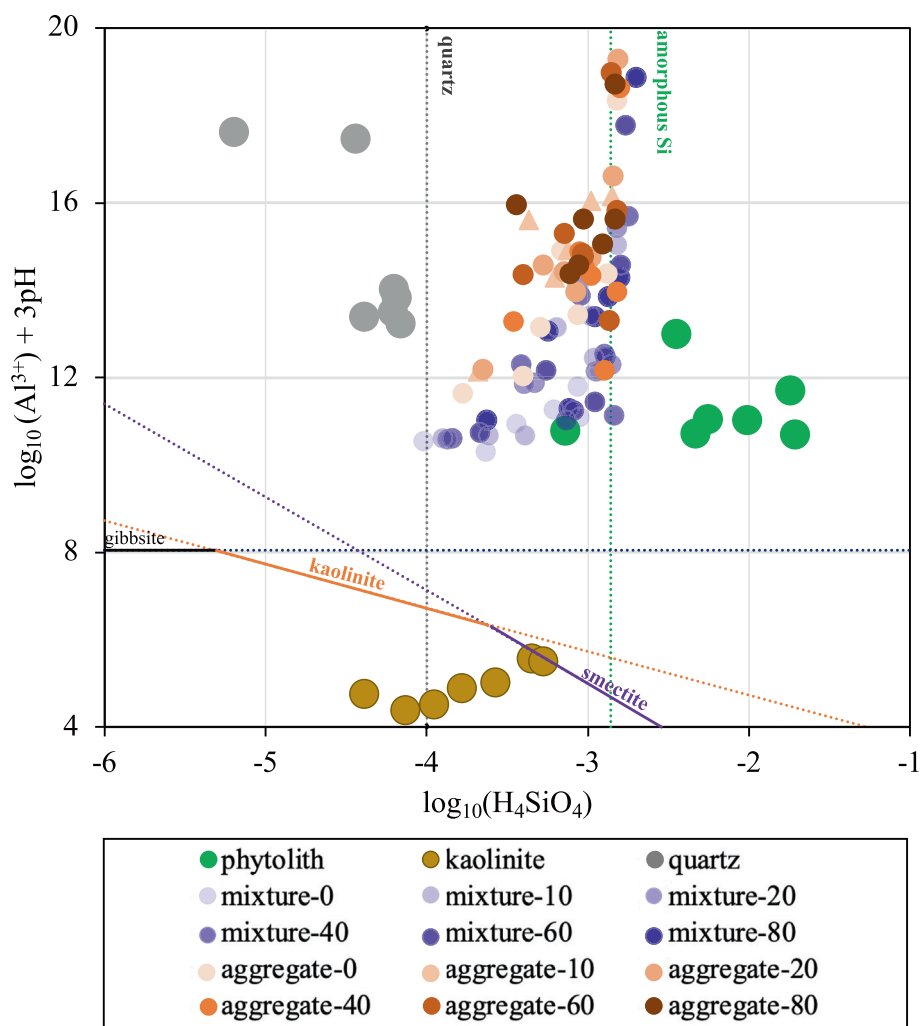


Fig. 8. Plot of the logarithmic values of experimental Al^{3+} , H^+ and H_4SiO_4 concentrations (mol l^{-1}) in CaCl_2 extracts at each kinetic step (Table S2) in the stability diagram for reference gibbsite, kaolinite and smectite in the Al_2O_3 – SiO_2 – H_2O system (Lindsay 1979).

(Bigham et al., 2002). However, it corroborates the stability of microaggregates observed in LAC soils with variable charge crystalline minerals as the soil pH drifts towards its pH_{IEP} (Goldberg, 1989). As predicted by the Derjaguin–Landau–Verwey–Overbeek (DLVO) theory, maximum aggregation should be achieved when surrounding pH approaches the particles pH_{IEP} at which surface electrical potential is minimal (Goldberg, 1989; Guo et al., 2022). This would confirm that, in our experimental scenario, the increase in pH had likely maintained or enhanced microaggregation, but promoted the dissolution of unembedded phytoliths.

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

Apart from phytolith and mineral dissolution, the sorption/desorption of DSi on secondary oxides was suggested to control DSi in soils (Cornelis et al., 2014; Meunier et al., 2018). Where soil phytoliths control DSi, as measured by $CaCl_2$ -Si, this hypothesis is questioned since, here, phytolith dissolution took precedence over Si sorption on goethite. In our experimental scenario, goethite-mediated aggregation and pH regulation actually controlled the release of DSi, despite our experimental design did not consider competing solutes for goethite sorbing sites. Although oxide surface OH groups interact specifically with H_4SiO_4 , advocating DSi sorption/desorption in natural soils could then be moderated for three reasons. (i) In soils, various solutes compete strongly with H_4SiO_4 to be adsorbed by oxides, notably organic and orthophosphate anions (Klotzbücher et al., 2020). (ii) The low reversibility of the Si sorption process may limit the additional sorption of aqueous Si (Haynes and Zhou, 2020). (iii) The change in oxide surface composition due to inner sphere complexation shifts the pH_{IEP} value downwards (Anderson and Benjamin, 1985; Kingston et al., 1972), which also reduces additional Si sorption (Bowden et al., 1973).

5. Implications and conclusion

From a geochemical perspective, soil processes impact the global fate of Si (Cornelis and Delvaux, 2016) since they control the fluxes of aqueous Si to the biosphere and hydrosphere, hence affecting the oceanic capacity to fix carbon by diatoms (Conley, 2002). In soils, phytoliths represent a major source of aqueous Si because of their relatively high dissolution rate (Frayse et al., 2009). Here we show that phytoliths can be preserved from dissolution by aggregation involving kaolinite and goethite, ubiquitous crystalline minerals with low charge and surface area. Such mineralogical pattern is typical for low activity clay (LAC) soils (Uehara and Gillman, 1985). LAC soils cover ~30% of the land surface at global scale and ~55% in the tropics. As the soil phytolith pool is a dominant, if not exclusive, contributor to the DSi pool in LAC soils (Cornelis and Delvaux, 2016; Lucas et al., 1993; Meunier et al., 1999), phytolith trapping in microaggregates is therefore a worldwide soil process that can largely impact DSi fluxes in the global Si cycle. The role of the Fe oxide is highlighted here as it mediates aggregation under continuously oxic conditions, as they occur in well-aerated soils, which are largely dominant on earth (>90% of global land surface). The protective effect of the aggregates on the preservation of phytoliths proves significant at low goethite content ($\geq 2\%$). At common pH values of the soil solution (5–6), aggregation reduced Si release by 2- to 3-fold, suggesting that phytolith preservation in soil aggregates can be more widespread than currently known, and likely more effective than Si adsorption on oxides for retaining Si. As already concluded earlier (Li et al., 2020; Li et al., 2022; Meunier et al., 2014; Vander Linden et al., 2021), the occurrence of two pools of phytoliths, namely fresh and stabilized, is also supported by our data. By using ubiquitous

clay mineral and Fe oxide, we show that microaggregation can be a widespread soil process that contributes to build up the pool of stabilized phytoliths in soils, together with other processes such as, notably, the decrease in surrounding pH (Frayse et al., 2009), ageing (Liu et al., 2023; Puppe and Leue, 2018) and surface passivation (Koebernick et al., 2022). The latter process consists of the accumulation of Fe and C on the surfaces of phytoliths, which are thus protected from dissolution (Koebernick et al., 2022). As being enhanced by alternating redox conditions, this process involving Fe dynamics can occur in waterlogged soils with alternating redox conditions. It reduces the release of DSi from the “passivated” phytoliths by 3-fold (Koebernick et al., 2022), a reduction factor similar to that observed here after aggregation under oxic conditions, which are widely prevalent in well-aerated soils.

Clearly, laboratory studies (Koebernick et al., 2022; Li et al., 2022; present study) can show higher release rates of DSi from phytoliths than in natural soils. Since unsaturated flow through soil voids limits the amount of surface exposed to water in natural conditions, the rate of Si release would be significantly lower than predicted from our laboratory studies as demonstrated earlier for weathering, precipitation-dissolution and sorption–desorption processes (Stumm and Morgan, 1996). In addition, biological activity was not considered here, although it is crucial to further enhance microaggregation. Therefore, if the release of DSi from phytoliths is so significantly reduced over short periods in laboratory conditions, as observed here, we can expect a higher impact of microaggregation on phytolith protection and DSi release reduction in natural soils. Thus, aggregation and above cited processes as well as specific properties of phytoliths (Cabanès et al., 2012; Puppe and Leue, 2018), can enhance the resilience of phytoliths in soils over Millenia (Monger and Kelly, 2002) and their use as paleo-indicators (Strömberg et al., 2018).

Declaration of Competing Interest

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

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Appendix A. Supplementary material

Supplementary material includes experimental results aimed at facilitating the understanding of data presented and discussed in the manuscript (MS). Raw data illustrated in the MS figures are in a text-based numerical format at Tables S1 and S2: organic carbon budget and DOC release (Table S1), pH, concentrations ($mol\ l^{-1}$) of H_4SiO_4 and Al as well as of Ge ($mol\ l^{-1}$) in 0.01 M $CaCl_2$ extracts as collected from 16 h to 64 d for phytoliths, quartz, kaolinite, and mixtures and aggregates (Table S2). Table S1 data are illustrated in the MS at Fig. 1 while Table S2 data are used in

all other figures, from Fig. 2 to Fig. 8 as well as in Table 3. In addition, Fig. S1 presents the Na_2CO_3 -dissolved Si and Al concentrations as measured in a kinetic extraction to estimate the contents of amorphous Si (ASi) and Al (AAl) used in Table 2 in the MS. Fig. S1 reports on CaCl_2 -extractable Si and Al that are used in the MS at Table 3, Fig. 7 and Fig. 8. Fig. S3 traces the temporal evolution of CaCl_2 extractable Al as used in the MS at Figs 7–8 and Table 3. Supplementary material to this article can be found online at <https://doi.org/10.1016/j.gca.2023.03.021>.

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