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LAMBERS OPINION PAPER

How important is carbon sequestration in phytoliths within the soil?

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Abstract

Background and aims An overlooked fraction of the terrestrial carbon (C) pool is that associated with biogenic silica deposited in plants (phytoliths), so-called PhytOC. This fraction is small compared with the main C pools, but is of interest because it could be a long-term C sink as phytoliths may protect organic C from mineralization. However, the topic is hotly contested and unclear due to both methodological and theoretical limitations.

Scope We aim to review this topic, with specific emphasis on: (i) the range of C concentrations associated with phytoliths; (ii) soil phytolith preservation and subsequent organic C mineralization; and (iii) global estimates of C sequestration within PhytOC.

Conclusions Recent work has suggested that [PhytOC] could be much greater than currently acknowledged, but also highly variable and dependent on cell silicification types. A short case study using cryo-Scanning Electron Microscopy (cryo-SEM), X-ray microanalysis (EDX), plus Focused Ion Beam (FIB) and Scanning Transmission Electron Microscopy (STEM) on the culms of a sedge (*Schoenus caespititius*) confirmed this thinking. Understanding of both phytolith and PhytOC fates in soil is poor. We suggest that phytolith residence time should be seen as a gradient. Such a continuum is explained by different phytolith sizes, types and chemistry, which will also have contrasting PhytOC. Our estimation of C sequestration as PhytOC each year (11–190 Tg C yr^{-1}) represents between < 1% and 13% of the C that could be sequestered globally in soils (estimated at 1400 Tg C yr^{-1}). We conclude that (1) more research is needed to improve our understanding of the formation and fate of PhytOC in terrestrial ecosystems and (2) it would be unwise to put our faith in PhytOC sequestration or other related methodologies to "solve" the climate crisis.

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Climate change and soil carbon sequestration

As we write this Opinion Paper, 2023 has just been confirmed as the warmest on the instrumental record (Copernicus Climate Change Service 2024). The effects of anthropogenic climate change are becoming increasingly evident. Extreme weather events, floods, droughts, heatwaves, storms, and wildfires are being reported frequently. In his speech after the release of the IPCC synthesis report in March 2023 (IPCC 2023), UN Secretary-General António Guterres began, 'Dear friends, humanity is on thin ice — and that ice is melting fast. As today's report of the Intergovernmental Panel on Climate Change (IPCC) details, humans are responsible for virtually all global heating over the last 200 years. The rate of temperature rise in the last half century is the highest in 2,000 years. Concentrations of carbon dioxide are at their highest in at least 2 million years. The climate time-bomb is ticking' (United Nations 2023). Much of the rest of his speech concentrated on cutting carbon (C) emissions and on the decarbonization of the world's economies. However, the IPCC also spent considerable time on methodologies that could decrease the atmospheric CO_2 concentration (IPCC 2022). Many of these involve so-called 'nature-based solutions', with the planting of trees being the one that has received most public attention. The problem with such schemes is that the C sequestered is vulnerable to being released again, for example in forest fires. There are also major concerns that giving people the idea that there are ways to deal with climate change that do not involve emission cuts may lead to inaction (Mann 2021). Increased soil C sequestration has also been much touted for taking carbon dioxide out of the atmosphere.

The amount of C globally in soil, vegetation and the atmosphere is 1700, 450 and 875 Gt, respectively (IPCC 2021). Soil C stock is large, and increasing the amount stored, and thereby decreasing the CO_2 concentration in the atmosphere has been much discussed in the literature. There has been considerable debate about the efficacy of C sequestration in soil as a means of combatting climate change. Some authors are more optimistic (*e.g.*, Paustian et al. 2019; Amelung et al. 2020), while others are much less so (*e.g.*, Powlson et al. 2011; Berthelin et al. 2022; Baveye et al. 2023). Essentially, debates revolve around the finite quantity of C that can accumulate in soil, the reversibility of accumulation processes, and the problem that increased soil organic matter may cause changes in the fluxes of other greenhouse gases, including methane and nitrous oxide (Powlson et al. 2011). Clearly, anything that could increase the capacity of soil for C sequestration, slow the reversibility of storage, and/or decrease deleterious fluxes of other greenhouse gases could be advantageous. Plant biogenic silica, also called phytoliths (Greek *plant stones)*, might play an overlooked role in soil C sequestration.

A role for phytoliths in carbon sequestration?

Terrestrial plants take up silicon (Si) from the soil solution in the form of monosilicic acid. Dissolved Si is then translocated to sites of rapid transpiration, where it polymerizes as phytoliths within cell walls, in the lumen, and in extracellular (cuticular) and intercellular spaces (Piperno 1988). Overall, commelinid monocots accumulate more Si than other taxa (Hodson et al. 2005) and present well-formed phytoliths (Piperno 1988). If well-preserved in soils or sediments, phytoliths can be used to reconstruct past vegetation and ecosystem dynamics (Strömberg et al. 2018).

Parr and Sullivan (2005) suggested that organic C trapped inside the siliceous structures of phytoliths during their formation (so-called PhytOC) might be important in C sequestration at a global scale because C could be protected from mineralization over long time scales. For some years the idea gained general acceptance, but then disagreements arose, with some workers suggesting that sequestration as PhytOC was not significant (*e.g.*, Reyerson et al. 2016) while others continued calculating global estimates of PhytOC fluxes in terrestrial ecosystems (*e.g.*, Song et al. 2017). The main points of contention are the "correct" percentage of PhytOC in phytoliths and different assumptions concerning the dissolution of phytoliths returned to the soil (Hodson 2019). Here we discuss the potential importance of C sequestration in phytoliths. First, we consider how much C is present

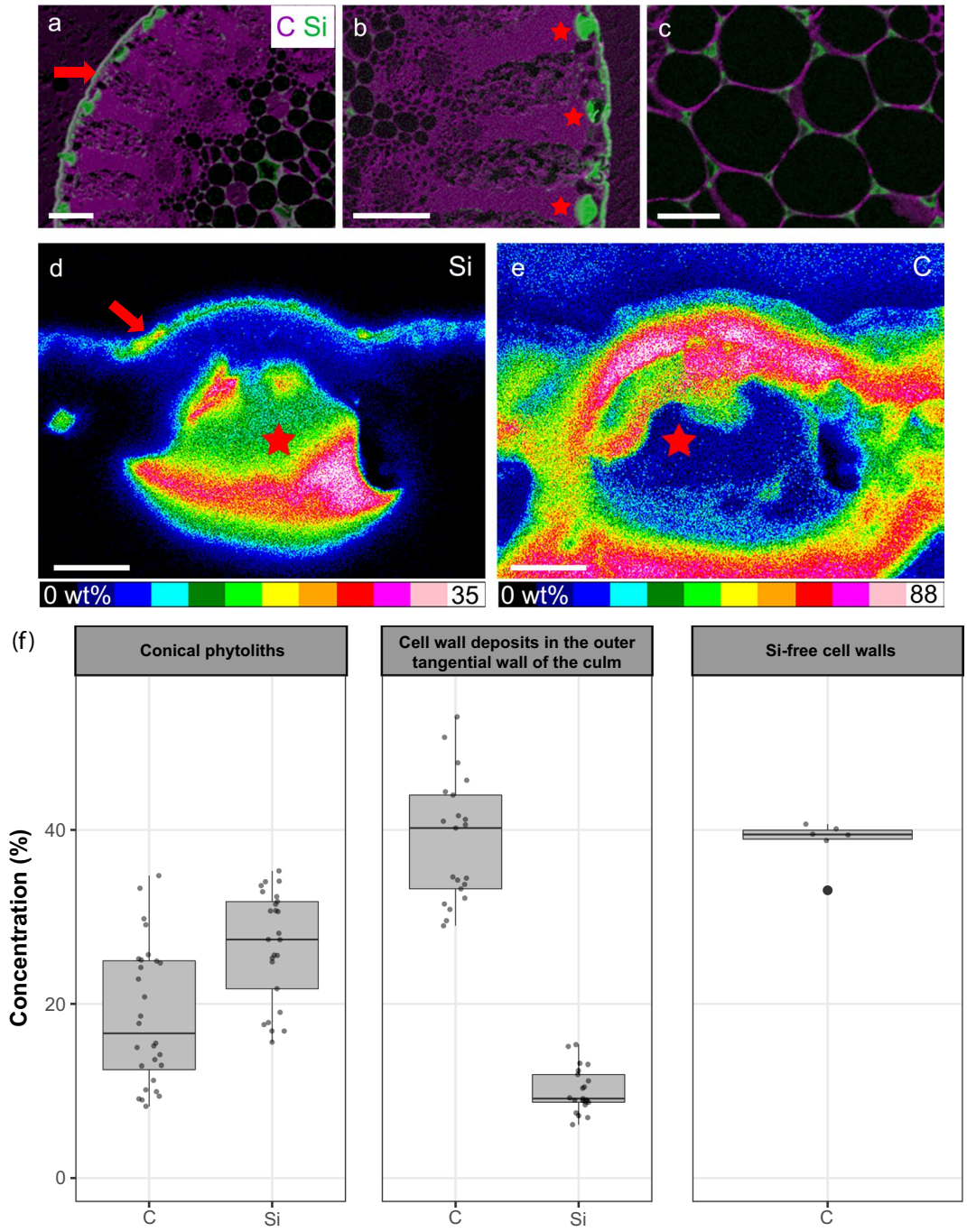
in phytoliths. We then move on to consider phytolith dissolution and subsequent C mineralization in soils and sediments. Finally, we attempt to determine global PhytOC sequestration.

Have we underestimated carbon concentrations in phytoliths?

The variation in PhytOC concentrations, hereafter [PhytOC], presented in the literature is very high – from less than 0.1% to 24.7% (Hodson 2019). Almost all estimates of [PhytOC] have relied on extraction of phytoliths from the organic matrix using dry ashing, wet ashing or microwave digestion, followed by C determination in the extracted phytoliths (Hodson 2019). If the procedure used is mild, it will leave more PhytOC within the phytoliths, but also some resistant organic material on the surface that will lead to [PhytOC] overestimation. In contrast, harsh digestion procedures will remove most of the unwanted C, but could also remove C trapped within phytoliths. Hodson (2019) raised a key difficulty with these analyses that could, at least in part, explain the discrepancy in [PhytOC] estimation: they took no account of heterogeneity in phytolith chemistry. The small amount of literature available suggests that cell wall phytoliths have much higher [PhytOC] than most lumen phytoliths, those not deposited on a carbohydrate matrix. Lumen deposition seems to be promoted by small amounts of specialised proteins (e.g. Siliplant1 in the silica cells of sorghum), but the [PhytOC] in these phytoliths is considerably lower than in those with a carbohydrate matrix (Hodson 2019; Zexer et al. 2023). The one analysis that did not involve extracting phytoliths from plant material with acid or high temperature was that for the *Phalaris canariensis* lemma macrohairs conducted by Perry et al. (1987). Hodson et al. (1984) had already conducted transmission electron microscopy (TEM) and x-ray microanalysis on ultrathin sections of these hairs. Following a developmental sequence they observed cell wall thickening and Si being deposited within it, eventually filling the whole wall. At maturity these silicified cell walls have a [PhytOC] of about 24.7% (Hodson 2019) and 18.8% Si. This [PhytOC] value is much higher than the others reported in the literature (see Hodson 2019 for a review), and suggested that PhytOC might be important for C sequestration.

Here, we conducted a short case study to better understand Si–C interactions during phytolith formation in different cell types. We considered *Schoenus caespititius*, an Australian species belonging to a major Si-accumulating family worldwide (Cyperaceae), on which we conducted in situ SEM–EDX on plant tissues and FIB-targeted nanoscale STEM-EDX analyses on a phytolith-only cross section (Figs. 1, 2) (see Supplementary Material for materials and methods). In the sedge, bulk culm [C] was determined at 44.8% and bulk culm [Si] was 1.9%. As expected, most C is present in the cell walls and is evenly distributed across the various tissues (Fig. 1a, b). We analyzed cell walls without obvious Si deposition (Fig. S1c), and their C concentrations ranged from 33.1% to 40.7% (mean: 38.6%). Silicon is much more localized in distribution, with one minor and two major sites:

1) A small amount of Si was visualized in the intercellular spaces of the cortical cells (Fig. 1c).
2) The silicified epidermal outer tangential wall (OTW) of the epidermis below the cuticle (Fig. 1a, d—arrows) had a mean C concentration of 38.7% (range 29.0% to 53.0%), and the Si concentrations ranged from 6.1% to 15.3%, with a mean of 10.1% (Fig. 1f). Although this tissue has a high C concentration, it is thin and delicate, and is highly unlikely to survive most preparative procedures, and will be quickly broken down in the soil, releasing C back to the atmosphere. This material and that from the cortical intercellular spaces is most probably analogous to the small, delicate, phytolith fragments that Puppe et al. (2017) determined made up 84% of phytogenic material.
3) The conical-shaped phytoliths observed in the epidermis that arise from secondary development of the inner tangential wall (Fig. 1b, d, e- stars). This is similar to the developmental sequence shown in Fig. 1B of Hodson (2019). These phytoliths are also called "cyperaceous type" (Mehra and Sharma 1965; Fernández Honaine et al. 2009) and they are cell-wall phytoliths, formed on a carbohydrate matrix. Mehra and Sharma (1965) noted that the conical projections were lignified, and when they were



desilicified using hydrofluoric acid, the organic matrix remained (their Fig. 13). It is therefore not surprising that the conical-shaped phytoliths have high C concentrations (range 8.3% to 34.7%; mean: 18.7%), while Si concentrations ranged from 15.6% to 35.3% (mean: 26.9%) (Fig. 1f). Provided that these analyses only include the phytolith and do not pick up X-rays from the surrounding tissues they should give an accurate representation of [PhytOC]. However, to be sure of this, we conducted STEM analyses on an ultrathin (~ 250 nm) cross section pre-

◂**Fig. 1** Culm cell-specific silicon (Si) and carbon (C) concentrations (wt%) in *Schoenus caespititius* (Cyperaceae) acquired using cryoSEM-EDX. Three regions of interest were targeted based on 12 maps coming from three biological replicates: conical phytoliths (stars), Si-rich cell walls and Si-free cell walls (see Supplementary Material for details). From (**a**) to (**c**), combined Si–C maps showing the location of Si (green) and C (purple) in the outer tangential wall of the culm (arrows), in epidermal cells forming conical phytoliths and in the intercellular space of parenchyma cells. In (**d**) and (**e**), heatmaps showing Si and C concentrations in the epidermal region, with a focus on a single conical phytolith. Scale bars: 100 µm (**a**, **b**), 50 µm (**c**), 10 µm (**d**, **e**). (**f**), boxplots showing Si and C concentrations in the different regions of interest (Supplementary Material; $n = 28$ for conical phytoliths, $n = 21$ for cell walls, $n = 6$ for Si-free cell walls). The central horizontal bar in each box shows the median, the box represents the interquartile range (IQR) and the whiskers show the location of the most extreme data points that are still within a range of 1.5 of the upper or lower quartiles. Each point indicates one region of interest

pared using FIB-SEM (Fig. S2). This allowed us to very precisely target the central area of the phytolith only, thereby avoiding any extraneous C signal, and providing structural and elemental information at the nanoscale. Low magnification confirms the sample is only from the phytolith (i.e. no cellular material) with C and Si co-localized (Fig. 2a-f). At higher magnifications, structural and chemical heterogeneity was clearly observed (Fig. 2g-l), with a low density mesh-like matrix evident throughout the Si phase. Sola-Rabada et al. (2018) used acid digestion to remove the organic matrix from phytoliths isolated from *Equisetum myriochaetum* and found that the resulting silica had a pore size of ~5 nm. It is difficult to estimate the pore size in our conical phytoliths, but the mesh-like matrix is seen to be on the nanoscale (Fig. 2j). As Hodson (2019) pointed out, pore size will almost certainly vary, and more lightly silicified material would be expected to have larger pores. With this, STEM imaging revealed a structurally-distinct area in the phytolith core (Fig. 2a, b, g) which, when analyzed using TEM–EDX (Figs. 2b, S3), indicated a mean C value of 16%, while surrounding areas contained less C (mean 6% C). These values are somewhat lower than those obtained in bulk phytoliths by cryoSEM-EDX, but still much higher than most analyses in the literature (Hodson 2019).

A detailed investigation revealed that the sedge culm only had cell wall phytoliths, and none from the lumen. As much of the discussion in the present paper concerns differences between cell wall and lumen phytoliths, we felt that it was important to include an example of an analysis from a lumen deposit, even if it was from a different species. For comparison, we also analyzed rice bulliform (lumen) phytoliths using cryoSEM-EDX (Fig. S4). As expected, the C concentration (mean = 2.5%) was much lower than that in cell-wall phytoliths (mean = 26.9%). Very recently, Negrao et al. (2024) used synchrotron scanning transmission X-ray microspectroscopy to analyse sections of BILOBATE phytoliths from sugarcane stalk epidermis. They reported 3–14% C in these lumen phytoliths, with the one higher value possibly including some of the surrounding cell wall. This is further confirmation that lumen phytoliths are lower in C than cell wall phytoliths.

The results of our microscopy work (and that of Negrao et al. 2024) suggest that in situ element analysis of phytoliths for C and Si has great potential, as does high-resolution STEM imaging of targeted FIB sections. These techniques avoid the problems of contamination and over-extraction that have bedeviled analyses using dry ashing, wet ashing, and microwave digestion, and offer opportunities to investigate [PhytOC] at previously-unconsidered scales. Moreover, cryoSEM allows us to analyze tissues that are weakly silicified (e.g., the sedge OTW), as these would normally be destroyed with conventional phytolith preparation.

Generally speaking, the C concentrations in the siliceous structures obtained here are much higher than those commonly found in the literature (Hodson 2019), but also highly variable depending on the types of silica deposits considered. Overall, evidence is accumulating that there is considerable chemical heterogeneity, both between and within phytoliths, and that cell-wall phytoliths contain more C than lumen phytoliths. It now seems highly likely that previous measurements of C concentrations underestimated the C concentrations in phytoliths which may have major implications for attempts to calculate the importance of C sequestration on a global scale. That said, it is quite possible that the C in phytoliths is rapidly mineralized in the soil.

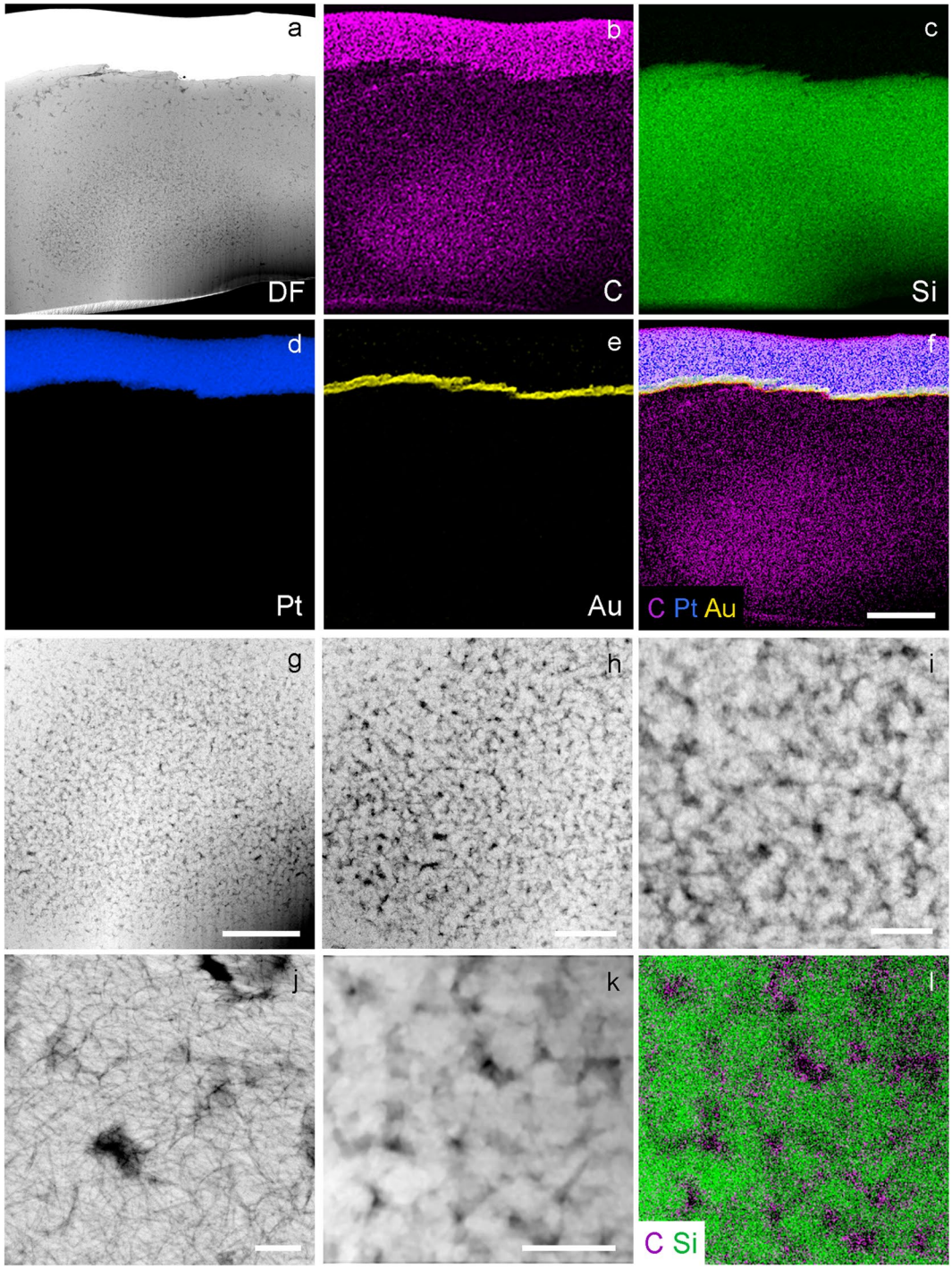


Fig. 2 High-Angle Annular Dark-Field STEM imaging and EDX analysis of a section from a conical phytolith prepared using FIB-SEM. At low magnification, the (**a**) dark-field image and (**b**-**f**) element maps show the components of the FIB section, including (**b**) a carbon (C)-rich core area within the phytolith, (**d**) the protective platinum (Pt) layer, and (**e**) the gold (Au) coating on the sample surface. At progressively higher magnifications (**g**—**j**) the low-density matrix is evident in the STEM images as dark regions with nanoscale fibers distributed throughout the brighter Si phase, which is confirmed by EDX analysis (**k**, **l**). Scale bars: 2 µm (**a** – **f**), 1 µm (**g**), 500 nm (**h**), 200 nm (**i**), 100 nm (**j**), 200 nm (**k**, **l**)

Phytoliths and PhytOC preservation in soils: the gradient hypothesis

If the question of how much C is associated with phytoliths is key, the topic of how long phytoliths will be preserved from dissolution once returned to soils and the level of protection of PhytOC from mineralization is at least equally important. It is widely accepted that phytoliths tend to have faster dissolution rates than most crystalline Si-bearing minerals. In fact, terrestrial Si cycling is strongly affected by its biological components (Alexandre et al. 1994), and numerous mass-balance calculations have reported that a significant fraction of Si in the soil solution is derived from the dissolution of the phytogenic Si pool (Bartoli 1983; Alexandre et al. 1997, 2011; Gérard et al. 2008; Sommer et al. 2013; de Tombeur et al. 2020). However, phytoliths are also used by paleo-scientists to reconstruct past vegetation (*e.g.*, Prasad et al. 2005), highlighting their partial persistence in soils and sediments in some situations.

Phytolith solubility is drastically influenced by pH, with increased dissolution rates at high pH. For instance, while dissolution rates of phytoliths are close to those of olivine at acidic pH, they are almost twice as fast at pH 8.0 (Fraysse et al. 2009). Beyond pH, increasing evidence suggests that soil aggregates can protect phytoliths from dissolution, thereby increasing their persistence (Li et al. 2020, 2022). Phytolith solubility is also influenced by other factors such as their water content, Si:Al ratios, and specific surface area (Bartoli and Wilding 1980). More importantly, isolated phytolith dissolution rates are about three times faster than for dried leaves containing the same amount of phytoliths (Bartoli and Wilding 1980), demonstrating that OM acts as a buffer to phytolith dissolution (Fraysse et al. 2010). Overall, these experimental studies demonstrate that phytolith solubility strongly depends on both soil and phytolith physicochemical properties as well as OM degradation dynamics. Phytolith preservation in soil will then depend on plant species and phytolith type, soil type, climate and weathering agents and, overall, on ecosystem properties (Cabanes and Shahack-Gross 2015; Liu et al. 2020, 2023).

Determining annual phytolith inputs along with soil phytolith stocks in a given steady-state system can yield an estimate of phytolith mean residence time (MRT) in soil (Blecker et al. 2006; Alexandre et al. 2011; White et al. 2012). Such estimates are challenging to make (Box 1), but they allow rough estimates of soil phytolith MRT: from about 200 years to more than 1000 years (Alexandre et al. 1997, 2011; Blecker et al. 2006; White et al. 2012). These numbers were used in some studies to calculate a "phytolith stability factor over 100 years", so-called PSF, in different biomes (*e.g.*, Song et al. 2017; Anjum and Nagabovanalli 2021). It was determined that between 60 and 90% of the annual PhytOC input into soil was stored over a 100-year period (PSF between 0.6 and 0.9, for phytolith MRT between 250 and 1000 years, respectively) (Song et al. 2017).

BOX 1: Extracting soil phytoliths is not a straightforward process

Extracting soil phytoliths is used for several purposes, including (1) the determination of phytolith mean residence time (MRT) in a given steady-state soil–plant system (soil phytolith pool / annual phytolith input) (*e.g.*, Blecker et al. 2006; Alexandre et al. 2011) and (2) the determination of soil [PhytOC] (*e.g.*, Pan et al. 2017; Huang et al. 2020; Lv et al. 2020). MRT is then used to calculate stability factors for soil phytoliths by some authors (*e.g.*, Song et al. 2017), to have estimates of long-term C storage through PhytOC. Here, we argue that extracting phytoliths from soil is far from straightforward, and involves several steps to properly quantify this pool (Aleman et al. 2013). For instance, removal of OM, Fe oxides, clay minerals or other types of short-range ordered aluminosilicates that could overestimate the phytolith pool is required (Aleman et al. 2013). In contrast, most of the protocols use a 5-µm filter to recover phytoliths which will remove all phytoliths < 5 µm and this may underestimate soil stocks. This is particularly important since this pool could be the bigger one in some plant species and of great importance for Si cycling (Puppe et al. 2017). Estimating [PhytOC] in soil phytoliths is even more challenging – probably more so than estimating [PhytOC] in plant phytoliths – since OC not associated with/occluded in phytoliths (OM not removed accurately enough, OC associated with clay minerals, etc.) can be quantified. Authors should check sample purity before C quantification for plant phytoliths (Corbineau et al. 2013), but also for soil phytoliths which is not always done. Overall, the methodological challenges associated with soil phytolith extraction complicate the determination of C sequestration through PhytOC compared with the assessment of "free C" pools in soil–plant systems

The use of a simple correction factor to estimate C storage through PhytOC has, however, significant limitations, in part because phytolith MRT in the literature is highly variable. In fact, comparisons of phytolith production in present-day vegetation and associated soil from paleoenvironmental studies have long demonstrated that specific phytolith

types will be preserved for longer periods than others. For instance, the conical phytoliths considered above (also called hat-shaped, cones or papillae phytoliths according to different studies; Murungi and Bamford 2020) appear to be poorly preserved, making them poor indicators of present and past Cyperaceae occurrence (Iriarte and Paz 2009; Novello et al. 2012). It also appears that thin-walled forms produced by dicots will quickly dissolve (*e.g.*, Thorn 2004). Similarly, Alexandre et al. (1994) showed that decomposition and dissolution of phytoliths is rapid and selective in tropical forest litter, with MRT values ranging from 1 to 18 months. These findings are in line with the idea that most of the phytolith input to soil is represented by small (< 5 µm) and fragile phytogenic Si that has much faster turnover rates than the reported MRT (Frayssse et al. 2009; Puppe et al. 2017; Schaller et al. 2021).

Given the tremendous variation in phytolith fates in soils, we propose that, as for soil organic C dynamics, phytolith residence time should be seen as a gradient (Dynarski et al. 2020) instead of a two-pool scenario (stable vs. non-stable phytoliths). Such a gradient will then depend on phytolith types and their resulting size, specific surface area and condensation degree (Schaller et al. 2021). Such a gradient would also likely be associated with phytoliths having different [PhytOC], which makes long-term OC storage through PhytOC particularly hard to estimate. Beyond that, studies on C storage through PhytOC assume that turnover time is equivalent to phytolith turnover time. Although it might be true for highly-protected C found in lumen phytoliths (Alexandre et al. 2015), this may not be the case for other types of PhytOC, for which phytolith dissolution and OC mineralization could be decoupled. Developing and incorporating such a gradient in our understanding, and eventual modelling, of phytoliths and PhytOC fates in soils should involve scientists from different disciplines. Only multidisciplinary approaches can gather knowledge on phytolith types in different vegetation assemblages and soils, and knowledge on PhytOC concentrations in plants and fates once returned to soils. Overall, our understanding of the fate of both soil phytoliths and PhytOC in terrestrial ecosystems is still in its infancy, and any attempts to make global estimates of C storage through PhytOC should take such uncertainty into consideration.

Towards a global estimate of PhytOC sequestration

Determining PhytOC sequestration at a global scale is fraught with difficulties, but we consider that it is worth trying, as we need to assess its overall importance in the C biogeochemical cycle relative to other potential mechanisms of sequestration in the soil. There have been several previous attempts to do this (Parr and Sullivan 2005; Reyerson et al. 2016; Song et al. 2017) and we will base some of what follows on this earlier work. We will use what we consider to be the best available data, being aware that some of our assumptions are gross simplifications, which will be improved in the future (Table 1). We have uploaded the spreadsheet with all our data, calculations, and comments in the Supplementary Information to facilitate this process.

We used the global net primary production data of Cough (2011) for seven natural biomes as the foundation of our calculations (Table 1). We then used the mean Si:C ratios determined by Carey and Fulweiler (2012) to calculate annual Si production. This could then be converted to annual phytolith production using the procedure of Blecker et al. (2006). We decided to divide plants into two types with respect to phytolith production: the grasses and cereals (crops) which have both lumen- and cell-wall phytoliths; and trees and other non-grass species that appear to only have cell-wall phytoliths (Hodson 2019). A detailed analysis of the literature suggests that this is largely (maybe even entirely) the case, but one possible exception concerns the cystoliths that are most common in the Acanthaceae, Cannabaceae, Moraceae and Urticaceae (Fernández Honaine et al. 2023). These mostly consist of calcium carbonate, but have a silicified stalk that appears to be connected to the outer cell wall. Only further high resolution TEM work will confirm whether the stalk is an ingrowth of the cell wall. At a first estimation, we assumed that the Tropical savannah and grasslands, Temperate grasslands and shrubland, Deserts, and Tundra biomes are totally dominated by grasses. These biomes will include those where bamboo is grown, and there has recently been considerable interest in these species from a carbon sequestration perspective (Zhang et al. 2019). We will assume that the Tropical, Temperate, and Boreal Forest Biomes are totally dominated by trees. For croplands, approximately half of the biomass is cereals, and the remaining half is non-cereals (FAO n.d).

Table 1 Global estimates of carbon (C) storage through phytolith C (PhytOC). Detailed data, calculations and comments can be found in a spreadsheet in Supplementary Material

	Global NPP[1]	Si:C ratio[2]	Si production[3]	Phytolith production[4]	% phytolith types[5]	[OC] in phytoliths[6]	PhytOC input[7]	Stable phytoliths[8]	Stable PhytOC[9]
Biome	Pg C yr^{-1}		Tg Si yr^{-1}	Tg phyt yr^{-1}	%	% DW	Tg C yr^{-1}	%	Tg C yr^{-1}
Tropical forests	19.6	0.006	118	289	Consideration of phytolith types (cell lumens, cell walls, fragments) based on available data. Details elsewhere.	Consideration of different [OC] for different phytolith types based on available data. Details elsewhere.	43-72	From 10% to 90%	4.3-65.1
Temperate forests	6.9	0.004	28	68			10-17		1.0-15.3
Boreal forests	3.6	0.005	18	44			7-11		0.7-10.0
Tropical savannah and grasslands	17.1	0.024	410	1010			29-64		2.9-57.2
Temperate grasslands and shrublands	5.2	0.032	166	409			12-26		1.2-23.2
Deserts	2.0	0.006	12	30			1-2		0.1-1.7
Tundra	0.8	0.023	18	45			1-3		0.1-2.6
Sub-total	*55.2*		*770*	*1895*			*104-194*		*10.4-175.0*
Croplands									
Cereals	2.2	0.029	63	154	Same	Same	4-10	Same	0.4-8.7
Other crops	2.2	0.005	11	27			4-7		0.4-6.0
Sub-total	*4.3*		*73*	*180*			*8-16*		*0.8-14.7*
TOTAL	**59.5**		**844**	**2076**			**112-211**		**11.2-189.7**
Level of understanding[10]		Reasonably High		Intermediate	Weak	Weak		Weak	
Potential for improvement[10]				High	Medium	Medium		Medium	

[1]Estimation from Cough (2011)

[2]Estimations from Carey and Fulweiler (2012). For croplands, biomass was converted into C mass with leaf [C] from a global database (de Tombeur et al. 2023)

[3]Si production = Global NPP x Si:C ratio

[4]Si was converted into biogenic Si by multiplying by 2.1392 to get SiO_2 followed by the addition of 15% of water and other elements (Blecker et al. 2006)

[5]For grass-dominated biomes: lumen 62%; cell wall phytolith 19%; cell-wall fragments,19% according to Puppe et al. (2022) (in wheat). For woody species-dominated biomes: only cell-wall phytoliths (Hodson 2019)

[6]Concentrations ranging from 0.1% to 25% depending on phytolith types and based on the literature and observations from this study. Details can be found in the main text and in the supplementary spreadsheet

[7]PhytOC input = phytolith production in cell walls x [OC] cell wall phytoliths + phytolith production in cell lumen x [OC] lumen phytoliths

[8]A 10 to 90% stability factor was applied (Alexandre et al. 1997, 2011; Puppe et al. 2017; Song et al. 2017)

[9]Stable PhytOC = PhytOC input x % stable phytoliths (from 10% to 90%)

[10]Comments on the level of understanding of each process and potential for improvement can be found in the supplementary spreadsheet

Puppe et al. (2022) provided the first estimate of the percentages of different types of phytolith in cereal (wheat) leaves: lumen, 62%; cell-wall phytolith, 19%; cell-wall fragments, 19%. We used these data for all grasses and cereals (crops), being aware that they may well vary among species. Even within grasses and cereals (crops), it seems that the culms and roots only have cell-wall silicification (Hodson 2019). For lumen phytoliths, we used a low value of 0.1% C (Reyerson et al. 2016), and a high value of 2.5% from the analyzed rice bulliform phytoliths in this study. For the C concentration of cell-wall phytoliths, we used 15% as low value based on the results obtained here (mean of 18.7% for Cryo-SEM EDX analyses, and of 16% for TEM–EDX analyses) and 25% as high value (*Phalaris canariensis* macrohairs analysed by Perry et al. 1987). Finally, for the 19% of cell-wall fragments, we estimated the C concentration at 40%, similar to that found in the sedge epidermal OTW (Fig. 1f). However, we assumed that this fraction is rapidly mineralized and does not contribute to C sequestration in the soil.

Finally, we need to account for dissolution and mineralization in the soil, as there is considerable debate over this. We decided to use two correction factors: 10% was applied as a "low stability factor", because it corresponds to the "stable phytoliths" in several articles (Alexandre et al. 1997, 2011; Puppe et al. 2017); 90% was applied as a "high stability factor", because it corresponds to the highest values found in Song et al. (2017).

The results of this analysis are shown in Table 1 and Fig. 3. For each estimation and process considered, we give the level of current understanding and

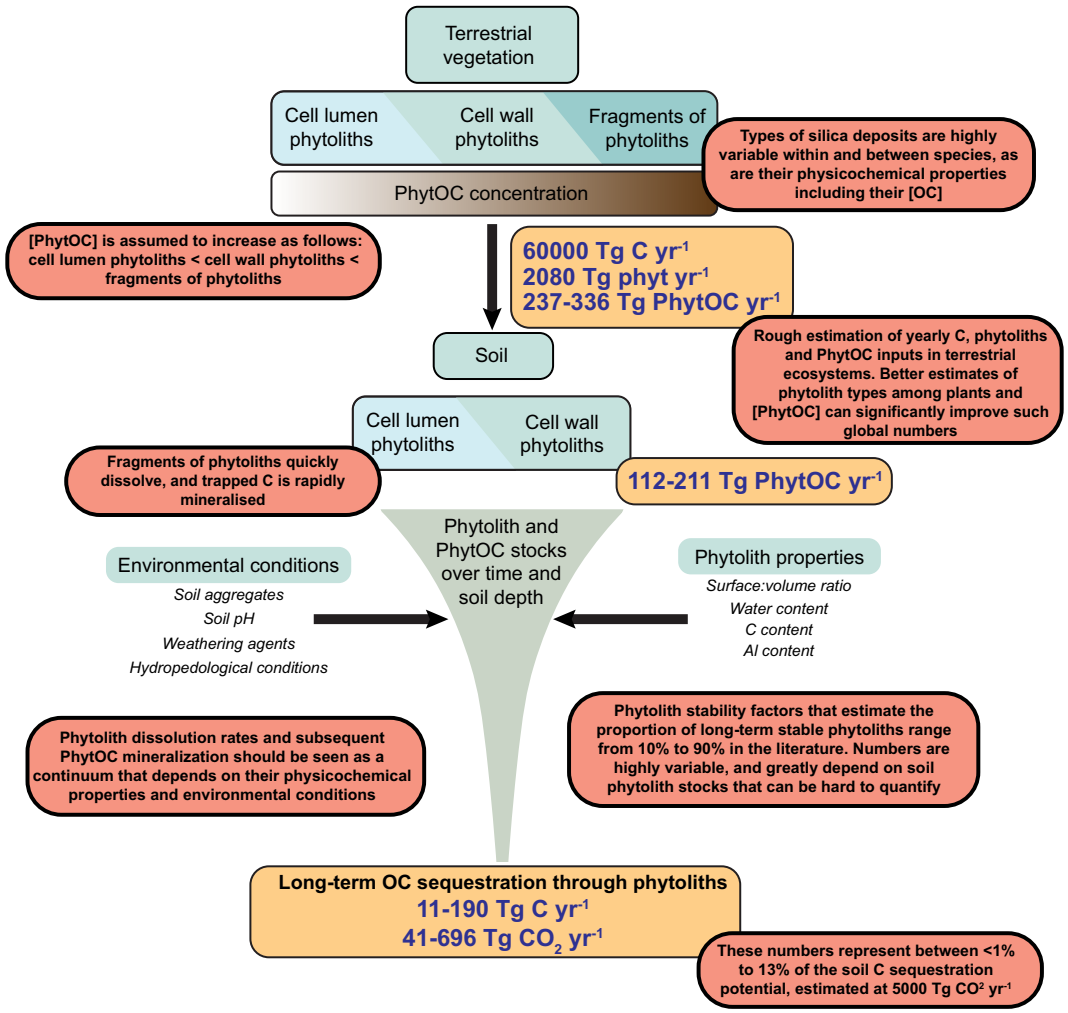


Fig. 3 Schematic representation of the pools, fluxes, and processes controlling PhytOC dynamics in soil–plant systems. Detailed calculations can be found in Table 1 and in a spreadsheet in Supplementary Material. The numbers given are informative and are expected to be improved through more research. The value for global soil carbon sequestration potential comes from Fuss et al. (2018)

level of improvement needed in the spreadsheet found in Supplementary Material, to guide further research (Table 1). It is evident that, using a "low stability factor", 11 Tg C yr^{-1} are sequestered while a "high stability factor" indicates that 190 Tg C yr^{-1} are sequestered. For comparison, Fuss et al. (2018) estimated that the soil C sequestration potential is 5000 Tg CO_2 yr^{-1}, that is around 1400 Tg C yr^{-1}. This suggests that between < 1% and 13% of the sink potential is sequestered as stable PhytOC each year, and these percentages could be higher with the implementation of specific practices (Song et al. 2017). However, we are just beginning to get some reasonable estimates for %C in phytoliths, and we have the first measurement of the percentages of different phytolith types in a cereal leaf. These values will therefore undoubtedly change in the future, as we get better estimates. One of the biggest unknowns now is the stability factor and changing the assumptions on that makes a huge difference to the overall global sequestration estimates.

Conclusion

Overall, our understanding of C sequestration through PhytOC still suffers from several problems that prevent us from making accurate global estimations. Consequently, attempts at computing global figures will lead to a wide range of long-term accumulation (Table 1, Fig. 3). Estimates could be improved by focusing on two key points:

(1) Determining [OC] associated with phytoliths remains problematic. [PhytOC] may be higher than previously reported, at least for specific types of cells, but it is also highly variable among species and between cell types. Overall, the use of one single [PhytOC] for a given biome is misleading, when [PhytOC] varies depending on cell types and plant species. More fundamental knowledge on silicification and OC occlusion/association is needed to improve [PhytOC] estimates.
(2) Estimating PhytOC turnover in terrestrial ecosystems is still highly challenging, due to our limited knowledge of phytolith dissolution dynamics and their potential to slow PhytOC mineralization. Phytolith dissolution should be seen as a continuum, rather than a two-pool view, with a stable and non-stable pool. Modeling dissolution dynamics could lead to more precise global estimates.

Of course, the big question remaining is whether PhytOC sequestration can be increased, thereby helping in the fight against climate change. Even if this is the case, it would be highly unwise to put our faith in PhytOC sequestration or indeed any other related methodology to "solve" the climate crisis. The jury is still out on whether PhytOC has any role to play in the future, but we have absolutely no doubt that a rapid decarbonization of the world economy is by far the most important aim now.

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Data Availability All the data used in this article are available online.

Declarations

Competing Interests The authors have no relevant financial or non-financial interests to disclose.

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