

Review Article

Phytolith-mediated Biocarbon Sequestration

Abstract

The sequestration of biocarbon primarily arises from natural mechanisms and is acknowledged as a critical measure in mitigating climate change. An inactive form of carbon, known as phytolith occluded carbon, is sequestered within plants and persists in soil for thousands of years following the breakdown of vegetation. Formation, distribution and storage of phytolith occluded carbon are the major factors affecting phytolith-mediated biocarbon sequestration. Crop area, crop duration, aboveground net primary productivity, crop, plant species, plant parts, age of plant, age of plant parts, cell components, phytolith morphotypes, and mean annual precipitation are some of the factors affecting the formation of phytolith occluded carbon. The stability and dissolution of phytolith occluded carbon in the soil are determined by carbon dioxide, temperature, climate zone, topography, soil, and phytolith properties characteristics. The phytolith distribution in the soil is affected by soil type and depth, tillage, bioturbulence, percolation, and phytolith morphotypes. By adopting proper soil and crop management practices phytolith mediated biocarbon sequestration can be enhanced.

Key words: Biocarbon sequestration, inert form of carbon, Phytolith, PhytOC,

1 Introduction

Since the Industrial Revolution, there has been a significant rise in the atmospheric levels of carbon dioxide (CO₂) and other greenhouse gases (GHGs), marking a notable global trend. The sixth assessment report of the Intergovernmental Panel on Climate Change (IPCC) states that global net anthropogenic greenhouse gas emissions reached 59 Gigatonnes of carbon dioxide equivalent, reflecting a 54 % increase compared to 1990 (Lynn and Peeva, 2021). The rise in greenhouse gases leading to global warming has resulted in climate changes that are impacting people's livelihoods by reducing ecosystem productivity. (Ramachandra and Bharath, 2019). Carbon dioxide (CO₂) stands out as a significant heat-trapping greenhouse gas, making a substantial contribution to global warming. In 2019, its average annual emission was measured at 409.8 ± 0.01 ppm, with an increase rate of 2.5 ppm per year. (Yadav et al. 2023). Therefore, efforts to mitigate CC require strategies aimed at either reducing emissions at their sources or decreasing the atmospheric concentration of CO₂ by utilizing carbon sinks. (Davamani et al. 2022). One such strategy to cut down the emission of CO₂ is carbon sequestration (Smith 2004; Lal, 2008; Lal et al. 2015)

Carbon sequestration refers to the process of moving and safely storing atmospheric CO₂ in alternative long-lasting carbon reservoirs, preventing its release or retention in the atmosphere (Lal 2008). Carbon sequestration involves capturing and storing atmospheric CO₂ to prevent its re-release into the air. This process can occur naturally within ecosystems or be facilitated by human-designed methods. Various approaches, including geological, oceanic, soil, and terrestrial sequestration, are employed for carbon sequestration. Terrestrial carbon sequestration also referred to as biocarbon sequestration, involves adopting conservation methods within vegetation and soil to enhance carbon retention. Biocarbon sequestration is accomplished through activities such as photosynthesis, afforestation, reforestation, bioenergy with carbon capture and storage, and agricultural practices that promote soil storage. When plants decompose, they release CO₂, but a portion of their organic matter can be integrated into the soil through various processes like microbial decomposition and physical stabilization. This process results in the long-term storage of carbon in the soil. (Margal et al. 2023).

Living organisms such as plants and microorganisms play a vital role in biocarbon sequestration, storing atmospheric carbon in vegetation, soils, woody products, and even aquatic environments. Hence, biocarbon sequestration primarily arises from natural mechanisms. (Nogia et al. 2016). An inactive carbon form, known as phytolith occluded carbon, is sequestered within plants and accumulates in soil following vegetation decomposition. (Parr and Sullivan 2005). This review article provides an in-depth examination of biocarbon sequestration through phytoliths, exploring the underlying mechanisms and factors influencing this process.

2 Phytoliths

Phytoliths are silica structures formed by plants through a process called biomineralization, by which mineral crystals are deposited in the matrix of living organisms (Rajendiran et al. 2012). The term 'phytolith' was introduced by Ruprecht in 1866. The word phytolith was derived from two Greek words, *phyto* means 'plant' and *lithos* means 'rocks', also referred to as 'plant opal', 'plant stone', 'phytolitharia', 'opal phytoliths', and 'opaline silica'. The term "opal" is employed due to the color of the particles when observed in reflected light. Similar to mineral opal formed through geological processes, phytoliths have an amorphous structure and can contain varying amounts of water. (Clarkson and Handson 1980). Phytoliths are also categorized under a broader term, 'biogenic silica,' or simply referred to as 'bioliths' (Shakoor et al. 2014). Germany emerged as the pioneering hub for phytolith research, being the first to formally observe and investigate phytoliths in plants and soils. (Madella and Zurro 2009). Phytoliths are mainly used in phylogeny, archaeology, palaeoecology, etc. due to their stability in soil environment and these having the potential for occlusion of C, phosphorus, heavy metals etc.

Because plants contain various cell types, phytoliths form in diverse shapes and sizes based on where they are deposited and the age of the plant. Phytoliths have been isolated from various plant organs such as leaves, stems, inflorescences (flowers), seeds, and roots. They can resemble recognizable cells, such as stomatal hairs or bilobate and cross forms. As a result, collections of phytolith morphotypes, whether taxonomically meaningful or not at the family, genus, or species level, are observed (Ernst et al. 1995).

3 Mechanism of phytolith formation

Phytoliths originate within plant cells through a process called bio-silicification. In this process, silicon is absorbed by plant roots in the form of mono-silicic acid and transported to various plant parts via the vascular system. The plant does not utilize silica for metabolic functions; instead, it undergoes polymerization to create silicon dioxide, which is then deposited as a siliceous gel within cavities within its structure. (Thorn 2007). As the concentration of this gel increases and it undergoes desiccation at a neutral pH, it gradually transforms into solid silt-sized particles known as phytoliths, which become enclosed within certain cell materials.

An electron probe microanalysis study on the elemental composition of phytoliths from woody bamboo species conducted by Tan et al. (2022) revealed that silicon (Si), oxygen (O), and carbon (C) were the major constituents of phytoliths. Apart from that potassium (K), calcium (Ca), magnesium (Mg), sodium (Na), chromium (Cr), iron (Fe), manganese (Mn), and aluminium (Al) were also present. A study was conducted by Watling et al. (2011) to investigate how different chemical digestion techniques affect the composition of phytoliths found in bamboo. It was found different forms of C like hydrocarbon, carboxyl C, carbonyl C, carbonate C, etc. were occluded in phytoliths to varying degrees. Phytoliths contain higher concentrations of terrigenous elements like Al, scandium (Sc), titanium (Ti), vanadium (V), caesium (Cs), Fe, and rare earth elements, while they have lower levels of major inorganic components found in plants such as K, Ca, Mg, Mn, chlorine (Cl), and bromine (Br). (Kamenik et al. 2013). The study conducted by Bujan (2013) in several Ericaceae species analyzed the abundance of Ca, Mg, Al, Fe, Mn, copper (Cu), zinc (Zn), Cr, nickel (Ni), lead (Pb), and arsenic (As) in leaf phytoliths.

4 Biocarbon sequestration via phytoliths

In the bio-silicification process, about 0.2 to 5.8% of carbon becomes trapped within it, forming what is known as phytolith occluded carbon. (Nawaz et al. 2019). Phytolith occluded carbon (PhytOC) is a substantial component of soil organic carbon. Accumulation of PhytOC is an important process in terrestrial biogeochemical carbon sequestration and is highly resistant to decomposition in the soil environment (Parr and Sullivan 2005). In terrestrial ecosystems, phytolith occluded carbon serves as a stable carbon sink and can be distributed within the organic matter that is not strongly associated with soil minerals (light fractions) or that is strongly associated with mineral particles (forming organo-mineral complexes) (heavy fractions) (Huang et al. 2020).

5 Pathway of biocarbon sequestration via phytoliths

Carbon from different sources reaches the plant. Phytolith production occurs in plant parts, hence the PhytOC formation also takes place in different parts of the plant. When the plant material decays the PhytOC

reaches the soil. Straw export and aeolian (arising from the action of wind) contributions can affect the PhytOC content reaching the soil where these can undergo mineralization and release Si and C. Soil properties and phytolith characters can influence the vertical distribution of phytoliths in soil. Pathway of phytolith-mediated biocarbon sequestration as shown in Fig. 1 occurs cyclically (Santos and Alexandre 2017).

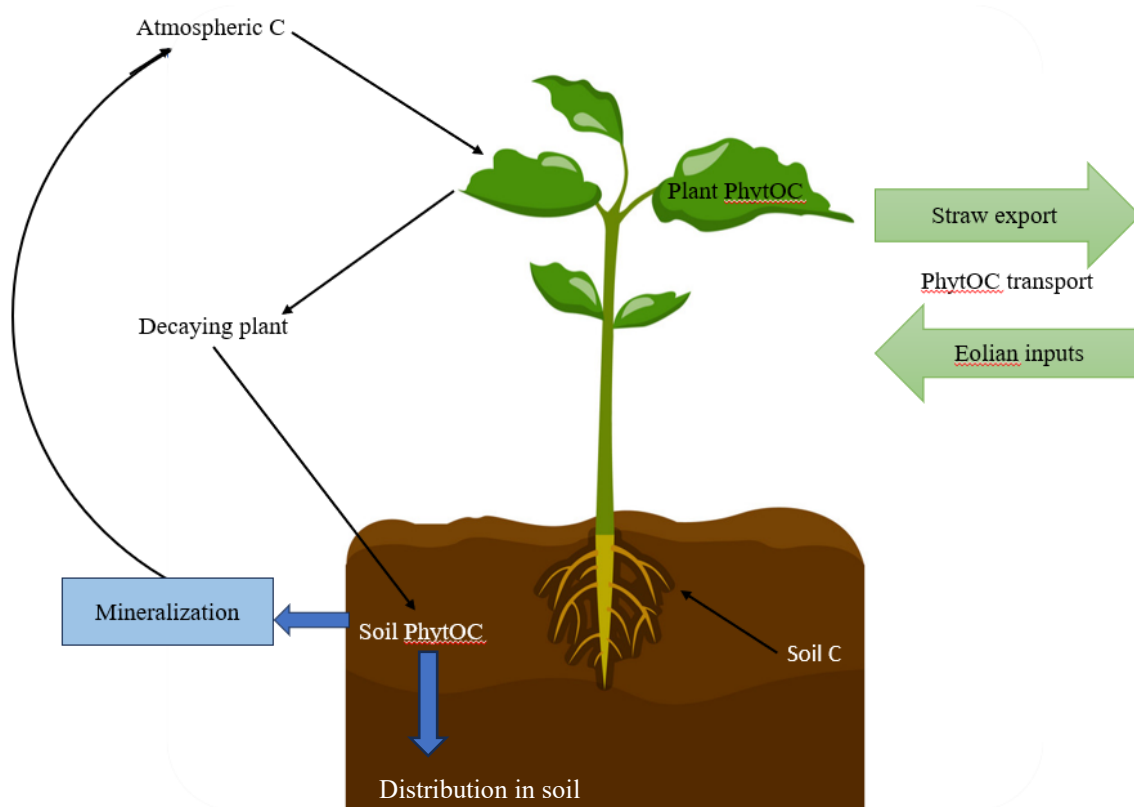


Fig. 1 Pathway of biocarbon sequestration via phytoliths (modified and adopted from Santos and Alexandre 2017)

6 Significance of phytolith-mediated biocarbon sequestration

Nearly all of the carbon found in plant biomass, roughly 97%, originates from the process of photosynthesis, wherein atmospheric CO₂ is converted (Ehleringer et al. 1997). Which is stored for a limited time. However, phytolith occluded carbon is an important stable carbon fraction in terrestrial ecosystems representing up to 82% of organic carbon in soil profiles depending on vegetation and soil conditions (Parr and Sullivan 2005). The concept of phytolith-mediated carbon sequestration, as proposed by Parr and Sullivan (2005), Parr et al. (2010), and Song et al. (2013), relies on several hypotheses: i) Phytoliths contain a high concentration of carbon (PhytOC); ii) Once carbon is enclosed within the phytolith structure (in cavities), it is shielded from mineralization; and iii) The majority of phytoliths remain intact and do not dissolve in soils for extended periods, ranging from hundreds to thousands of years. Phytolith occluded carbon accumulation occurs at a rate equivalent to 15–37% of the global average long-term (10,000 years) soil carbon sequestration rate, indicating the considerable potential of phytolith carbon sequestration in terrestrial ecosystems. (Rajendiran et al. 2012).

The stability factor of phytoliths was estimated to range from 0.8 to 1.0 across most ecosystems, as studies have shown that phytoliths remain stable for periods spanning 500 to 3000 years (Meunier et al., 1999; Parr and Sullivan, 2005; Blecker et al., 2006; Parr et al., 2010; Song et al., 2013). The maximum half-life of phytoliths in soils can be determined based on their geometric size (50 µm) and molar volume (Lasaga, 1984). This maximum half-life ranges from 25,000 years at pH = 7 to 250,000 years at pH = 4. The minimum half-life of larch and horsetail phytoliths in the soil solution between soil particles ranges from 10–12 years at pH = 2–3 to less than a year at pH levels above 6. These values are comparable to the observed mean residence time of

phytoliths in natural soil environments. (Frayse et al. 2009). Parr and Sullivan (2005) noted that in Numundo top soils, carbon fractions acquired through photosynthesis are released back into the atmosphere within approximately 100 years. In contrast, the carbon fraction trapped within phytoliths can persist in the soil for over 1000 years, highlighting the long-term stability of PhytOC in soils.

7 Phytolith-mediated biocarbon sequestration potential of different crops

A comparison of phytolith-mediated biocarbon sequestration potential of different ecosystems is given in Table 1. These ecosystems are renowned for their ability to accumulate silicon and are significant contributors to phytolith-mediated biocarbon sequestration.

Table 1 Comparing the PhytOC content in plant tissues, assessing estimated PhytOC storage fluxes (in Mg-e-CO₂ ha⁻¹ year⁻¹), and determining the global PhytOC sink rate (in Mg-e-CO₂ year⁻¹) across various plant species. (Modified from Prajapati et al. (2016)).

Crop	PhytOC contents of dry materials (mg g ⁻¹)	PhytOC sequestration fluxes (Mg-e-CO ₂ ha ⁻¹ year ⁻¹)	Global sequestration rates (Mg-e-CO ₂ -year ⁻¹)	References
Rice	0.4-2.8	0.03-0.13	1.94x10 ⁷	Li et al. (2013)
	0.04-0.28	0.03-0.13	1.75x10 ⁷	Prajapati et al. (2016)
Bamboo	2.4-5.2	0.01-0.71	1.56x10 ⁷	Parr et al. (2010)
Sugarcane	3.1-15.4	0.12-0.36	0.72x10 ⁷	Parr et al. (2009)
Wheat	0.6-6.0	0.01-0.25	5.3x10 ⁷	Parr and Sullivan (2011)
Millet	0.4-2.7	0.01-0.04	0.27x10 ⁷	Zuo and Lu (2011)
Wetlands	0.04-0.05	0.048-0.054	3.08x10 ⁷	Li et al. 2013a

8 Factors affecting biocarbon sequestration via phytoliths

Plant factors are mainly responsible for phytolith production and biocarbon sequestration within these phytoliths. These include;

8.1 Area, duration, and productivity of crop

Anjum and Nagabovanalli (2021) reported that in the rice ecosystems of India, PhytOC contribution during 1951-1980 (pre- green revolution period) was 1.34% and increased to 3.11% during 1981-2018 (post-green revolution period). This increase in PhytOC may be attributed to the effects of the green revolution which resulted in an increase in the area of cultivation along with the use of high-yielding varieties, irrigation, better crop management practices, plant protection measures, etc. Li et al. (2014) reported that expanding bamboo cultivation and choosing bamboo species with high phytolith content would enhance the sequestration of atmospheric CO₂ within bamboo phytoliths.

As the crop duration increases, the PhytOC content also increases which may be linked to the application of nitrogenous fertilizers according to the crop duration. Medium and long-duration crops require 25% and 50% more fertilizers respectively, than short-duration crops. Nitrogen-induced cell growth enhances the cell volume (affecting the size of phytoliths) and decreases surface area (reducing the phytolith dissolution) which in turn may result in a high amount of C occlusion in it and reduce the dissolution (Anjum and Nagabovanalli 2021). The

extended cultivation of Moso bamboo forests resulted in the augmentation of the soil PhytOC pool size, along with the LFOM (Light Fraction of Organic Matter) and HFOM (Heavy Fraction of Organic Matter)-PhytOC fractions (Huang et al. 2020).

A study by Arjun and Nagabovanalli (2021) in 22 rice-growing locations in the command area of Cauvery, Bhadra and Tungabhadra in Karnataka, India found that aboveground net primary productivity (ANPP) of plants was directly proportional to PhytOC. Davamani et al. (2022) opined that aboveground and belowground production of PhytOC increases as the plant age increases. A greater amount of phytoliths was found in aboveground parts and the concentration of PhytOC was greater in belowground parts. In younger plants, the distribution of PhytOC varied between different plant parts whereas it reached almost equal levels as the plant become older which can be ascribed to the variations in plant physiological properties and its adaptation to the environment.

The desertification process was found to have a considerable effect on PhytOC. It may be because of a decrease in the storage of nutrients. As desertification progresses, diverse plant communities gradually transition into simpler ones dominated by species resilient to drought. A decrease in plant biodiversity can cause a decrease in PhytOC (Ru et al. 2018). The carbon sequestration potential of forests through phytoliths can be increased by afforestation and reforestation efforts, maintaining understory vegetation, and optimizing the aboveground net primary productivity across all layers of the forest, particularly focusing on herbs that have high silicon accumulation (Yang et al. 2015).

A study was conducted by Kraushaar et al. (2021) in Spain and compared the phytolith content in four different land use systems (agricultural land, Badlands, forests, and shrublands). The phytolith content of top soils varied according to the land use. Phytolith concentration was highest in shrublands and very lowest in bad lands. Variations in plant species, net primary productivity, and management practices are attributed to this.

Soil organic carbon content, total phosphorus, available phosphorus, available potassium, and NH_4^+ -nitrogen were positively correlated with soil phytolith content. The availability of nutrients enhanced the plant growth and increased biomass which increase the phytolith production (Wang et al. 2022). Debnath et al. (2023) found that there is a direct relationship between the PhytOC content found in leaves, the overall PhytOC content in the soil, and factors such as soil phosphorus availability, elevation, nitrogen levels, potassium exchangeability, atmospheric humidity, soil organic carbon content, cation exchange capacity, and pH. A field experiment was conducted by Zhao et al. (2016) To explore the impact of applying varying levels of nitrogen externally- ranging from 0 to 50 g N m⁻² year⁻¹- between 2011 and 2013 on the potential for carbon sequestration through phytoliths in degraded grasslands, researchers conducted an analysis. The results indicated that the application of nitrogen increased the production flux of PhytOC in the severely degraded grassland from 0.003 to 0.021 tons of CO₂ ha⁻¹ year⁻¹. A study by Rehman et al. (2023) determined the effects of Si fertilization on two wheat genotypes. They found that the PhytOC yield increased four times when 500 mg l⁻¹ of Si was given to crops along with Hogland solution (T3) than Hogland solution alone (control). There was varietal difference in Si uptake and PhytOC production. Silicon fertilization increased the plant available Si (PAS) which in turn affected the phytolith production and PhytOC production. The availability of Si in soil has significant potential to improve plant growth and carbon fixation (PhytOC) by increasing the storage of Si in plants within grassland ecosystems, particularly under conditions of high salinity (Liu et al. 2020). The effects of basalt powder (BP) amendment on phytolith carbon sequestration in rice (*Oryza sativa*) were studied by Guo et al. (2015). The application of basalt powder (BP) led to elevated levels of phytolith and PhytOC in rice. This resulted in a 150% increase in the flux of carbon sequestration through phytoliths in croplands. External silicon amendments like BP amendment are identified as effective management strategies to enhance long-term biogeochemical carbon sequestration in rice cultivation. Li et al. (2013) reported that PhytOC content in reed dry biomass of the Baiyangdian reed wetland of China mainly depends on the content of the silicon taken up by the plant and the occluded carbon content of phytoliths during the plant growth.

8.2 Plant Characteristics

Phytolith mediated biocarbon sequestration potential different crops varies as shown in Table 1. Zhang et al. (2016) found that the presence of PhytOC in soil showed notable variations based on the type of crop, with the bamboo forest ecosystem exhibiting a notably greater contribution to phytolith occluded carbon sequestration compared to soils from chestnut and fir forests. This indicates that different crop types have a significant influence on the soil PhytOC storage. The PhytOC content in leaf samples collected from ten distinct clumping bamboo species of economic significance, established in trial plots for eight years, displayed variability. The carbon occluded in phytoliths differed significantly among bamboo species, attributed to variations in their phytolith production and capacity to store carbon within them (Parr et al. 2010).

Qi et al. (2017) reported that PhytOC varied among different plant species and parts of plants. The mean PhytOC was more in belowground parts than aboveground parts owing to grassy ecosystems belowground productivity is one order of magnitude greater than aboveground productivity. Phytolith content in different parts of bamboo (*Dendrocalamus ronganensis*) increases in the order; of culm, branch, raw leaves, and fallen leaves. The highest phytolith content was found in fallen leaves and there were seasonal variations in the phytolith content of raw leaves. Soil and mold had a very small amount of phytoliths compared to fallen leaves. Silica deposition varied as a function of increased transpiration within plants (Zhou et al. 2022).

Microscopic and spectroscopic analysis of winter wheat leaves revealed that PhytOC varies in different cell components of the plant. Puppe et al. (2022) found that the carbon content in silicified tissue fragments and cell wall phytoliths was more than that of lumen phytoliths, which implied that the carbon sequestration potential of silicified tissue fragments and cell wall phytoliths was more than that of lumen phytoliths. Biocarbon sequestered via phytoliths in rice cultivars mainly depends on both the content of silica (phytoliths) and the efficiency of the C occlusion within phytoliths during growth (Li et al. 2013).

The carbon content occluded in rice straw phytoliths can be categorized into three types: sub-stable PhytOC (reflecting carbon content in structurally sub-stable cell wall phytoliths), stable PhytOC (reflecting carbon content in structurally stable cell wall phytoliths), and recalcitrant PhytOC (reflecting carbon content sequestered in lumen phytoliths and the silica matrix of fragmented phytolith particles). Their estimated contributions are 63, 28, and 9% respectively. (Yang et al. 2023).

8.3 Phytolith characteristics

Phytolith morphotypes affect the volume and stability of phytoliths and hence the amount of C occluded in them. The plant community had a great influence on the phytolith morphotypes (Liu et al. 2021). The compositions and distributions of metal oxides vary across different types of phytoliths. Metal oxides are utilized as fluxing agents to lower the melting point of SiO_2 . Due to the distinct compositions and distributions of these metal elements within phytoliths, their response to heating varies (Wu et al. 2014).

8.4 Climatic conditions

A study conducted by Zhang et al. (2020) in the inner Mongolian grassland ecosystems revealed that the storage of phytoliths in soil profiles and PhytOC were positively correlated with mean annual precipitation (MAP) and negatively correlated with mean annual temperature. This can be due to increased phytolith input as a result of enhanced decomposition and higher ANPP supported by high MAP.

8.5 Lithology

Li et al. (2014) observed that the lithological composition significantly influences the presence of SiO_2 and phytolith content, likely due to the diversity in bioavailable silicon within soils developed from various parent rocks. This variance affects the absorption of silicon from the soil solution and subsequently influences the accumulation of phytoliths in leaves. Plants growing on granodiorite contain more amount of PhytOC than other lithologies (basalt, granite and shale). They suggested that management practices such as the amendment of rock powder, can enhance the production of leaf litter and the production of PhytOC. Phytolith occluded C storage in soils developed on granite was more than basalt in both the tropics and subtropics (Zhang et al. 2017). A Study

conducted by Ying et al. (2016) showed that both parent material and forest type significantly affected PhytOC concentrations in litter, and there was a significant interaction between parent material and forest type.

9 Stability and dissolution of carbon sequestered in phytoliths and factors affecting them

Dissolution is one of several taphonomic processes that can distort the interpretation of phytolith assemblages in paleoenvironmental, paleoclimatic, or taxonomic studies. It results in the creation of cavities on phytolith surfaces and the loss of delicate silica particles. Phytoliths derived from various grass species may exhibit disparate rates of dissolution. Phytolith dissolution rate (Si released by phytolith assemblages) decreases in the order plant > soil > paleosol (Liu et al. 2023). Phytolith stability is a combination of dissolution (solubility) and abrasion. Factors affecting the stability and dissolution of carbon sequestered in phytoliths are as follows;

9.1 Carbon dioxide and temperature

High temperature and low CO₂ concentration in soil favor the phytolith dissolution in soil (Nguyen et al. 2021a). At night, temperatures drop while they rise during the day. Conversely, CO₂ levels increase at night and decrease during the day. Consequently, soil phytoliths are likely more susceptible during daylight hours. Seasonal fluctuations can also impact soil phytoliths due to significant variations in temperature and CO₂ levels across different seasons. Phytolith stability is decreased during warm seasons. Under flooding, pH increases and facilitates phytolith dissolution. In soil, several processes are linked to the consumption of CO₂, such as the dissolution of soil minerals, especially those containing alkaline earth metals and silicates which increase the phytolith dissolution. Soil respiration, which generates CO₂, adds to the soil phytolith reservoir.

An experiment conducted by Nguyen et al. (2021b) on ashed phytoliths revealed that CO₂ acts to protect phytoliths by altering the solution pH. Research revealed that ashed phytoliths exhibited negatively charged surfaces and released soluble alkaline ions. This facilitated CO₂ sequestration by altering the equilibrium among H₂CO₃, HCO₃³⁻, and CO₃²⁻, favoring an increase in HCO₃³⁻ and CO₃²⁻ ions. Whereas, the increasing levels of CO₂ caused acidification of the suspensions containing phytoliths, which in turn prompted protonation of the phytolith surface. This reduced nucleophilic attacks from OH⁻ and other anions, effectively protecting the phytoliths from dissolution. Organic matter enclosed within phytoliths enhances the strength of their surface and resistance to desilicification. It was proposed that burning rice straw within a temperature range of 500 to 700 °C could be an optimal method to release more accessible silicon and phosphorus for soils and crops (Trinh et al. 2017).

9.2 Climatic characteristics

High soil phytolith content was observed in the cold temperate climatic zones than in the tropical and subtropical zones. Tropics with high temperatures and humidity reduce the biogeochemical stability of phytoliths, but the phytolith turnover rate was high in the tropics than in other climatic zones (Wang et al. 2022). Multiple investigations have indicated higher soil PhytOC storage in subtropical regions compared to tropical areas (Zhang et al. 2017; Debnath et al. 2023). Human activities, plant species present, and soil environment like pH, nutrients, water availability, etc. also account for the variation in soil phytolith content.

9.3 Topography

Yang et al. (2016) experimented to investigate the impact of topography on phytolith and PhytOC production within moso bamboo ecosystems. They observed a reduction in phytolith and PhytOC production with increasing slope steepness, with the trend being as follows: 2-5° > 5-15° > 15-35° (with a corresponding increase in production tendency from lower slope to middle slope to upper slope positions).

9.4 Soil characteristics

Soil organic carbon content, EC, clay content, oxalate extractable (non-crystalline forms) Fe and Al were positively correlated with phytolith stability while pH was negatively correlated. All these factors reduce the oxidation of phytoliths (Nguyen et al. 2019). Phytoliths exhibit a negative zeta potential at pH of 1–3 which

reflects their surface bearing a negative charge. At lower pH, protonation occurs on the negatively charged surface of phytoliths which stabilizes the phytoliths (Frayse et al. 2009).

Soil microaggregates ranging from 50 to 250 μm contribute over 75% to the phytolith pool and bioavailable silicon content. Phytolith dissolution features are rarely observed within soil aggregates. Agricultural practices like no-tillage methods and related techniques may encourage phytolith preservation in soils, slowly releasing them as they stabilize soil organic matter (SOM) over time. Soil-microaggregates act as a protective shield for phytoliths against dissolution, akin to how they safeguard SOM from biodegradation. Therefore, the entrapment of phytoliths within soil aggregates could be seen as a process supporting their longevity in soils and sediments, serving as a mechanism for biocarbon sequestration through phytoliths. (Li et al. 2020). Aggregation can protect both allophane and phytolith from dissolution and reduce the release of bioavailable Si (Li et al. 2022).

Phytolith reactivity can decline rapidly as a result of interactions with soil solution, with this decrease being notably more pronounced under alternating redox conditions compared to continuous oxic conditions. Despite the unchanged specific surface area, alterations in reactivity are likely due to chemical changes. Alternating redox conditions might facilitate the stabilization of phytoliths, preventing their dissolution (Koebernick et al. 2020).

9.5 Soil management practices

The study conducted by Majumdar and Nagabovanalli (2017) in Bangalore, Karnataka, found that phytolith content was more in surface soils for sugarcane fields, and in the case of rice fields it was more in subsurface soils. It was concluded that it may be because of the residue retention in sugarcane fields, which was removed in rice fields, and the phytolith morphotypes of rice and sugarcane. A study conducted by Nguyen and Nguyen (2019) on rice straw samples collected from the Red River Delta in Vietnam reported the practice of burning rice straw and reintroducing the resulting burned materials, including silica-rich phytoliths, into the soil is shown to be a strategy for sequestering CO_2 . This process helps buffer soil CO_2 flux and integrates CO_2 into the silicon cycle. A study by Bozarth et al. (2008) discovered that the phytoliths present in Terra Preta are not originally from their current location; instead, they originate from a disturbed context created by earthmoving activities around 1,000 years ago.

9.6 Phytolith properties

The cavate type or hollow type of phytoliths (silica deposition occurs in the primary cell wall while preserving the integrity of protoplast) cannot be destroyed by mild digestion with nitric acid but can be destroyed by intense digestion with sulphuric acid and hydrogen peroxide. But in the case of solid phytoliths, even after intense digestion, the PhytOC in the silica matrix remains unaffected (Parr and Sullivan 2014). Lumen PhytOC was more stable than silicified tissue fragments and cell wall PhytOC due to the solid nature of lumen phytoliths (Puppe et al. 2022). A study conducted by Cabanes et al. (2011) on wheat phytoliths showed that modern (not a fossil phytolith) phytolith assemblages from wheat inflorescences are less stable compared to those from leaves or stems. Burnt assemblages exhibit lower stability than unburnt ones, and a fossil phytolith assemblage dating back approximately 3000 years shows greater stability than modern wheat assemblages. The findings also emphasize that various phytolith morphotypes exhibit differing degrees of stability, and dissolution and abrasion processes may lead to morphotypes resembling each other.

Nguyen et al. (2021c) reported that the surface charge (SC) of phytoliths ranges from slightly positive at low pH to $-78.5 \text{ mmol} \cdot \text{kg}^{-1}$ at slightly alkaline pH levels, indicating their capacity to carry varying charges. This suggests that when returned to soil in substantial amounts, phytoliths could serve as a significant source of charge. Phytoliths, in combination with soil components like clay minerals, organic matter, and iron oxides, play a role in regulating the SC of paddy soils. Given their varying solubility, the SC properties of phytoliths indicate that the annual reintroduction of rice straw to paddy soils, especially post-burning, could influence the negative SC system. Consequently, the charge derived from phytoliths might impact soil cation exchange capacity, the dispersal of clay particles, and the transport of solutes.

10 Distribution of biocarbon sequestration via phytoliths

Liu et al. (2019) conducted research on the vertical movement patterns of phytoliths in 40 natural soil profiles located in Northeast China. In the majority of soil profiles studied, the distribution of phytoliths showed a consistent trend. Phytolith concentration consistently decreased with depth, ranging from the A horizon to the parent material (C horizon). Wang et al. (2022) found that Phytolith contents in soil profiles typically display an initial increase followed by a decrease. The highest phytolith contents were observed in the layer between 10 and 20 cm depth, influenced by varying soil properties at different depths. The distribution patterns and average distances traveled by phytoliths suggest that percolation plays a key role in their movement within the soil. Additionally, the formation of soil cracks enhances phytolith transport (Fishkis et al. 2010).

In a study by Liu et al. (2020c) on the vertical movement of phytoliths across 54 sites in Northeast China, it was discovered that the type of phytolith significantly influences its translocation behavior, with smaller phytoliths being preferentially transported. The deeper movement of small-sized phytoliths was observed in percolation distribution, as smaller particles have a higher likelihood of passing through narrow pore channels compared to larger ones. Phytoliths with a diameter of 5 μm were found to undergo notably deeper transport through percolation compared to phytoliths with a diameter greater than 5 μm . This size-related aspect of phytolith transport directly impacts the analysis of phytoliths in exposed soils. Therefore, if phytolith assemblages extracted from various depths within a soil profile differ primarily in the percentage of specific phytolith morphotypes, the variation in phytolith assemblages could result from unequal mobility of different morphotypes rather than changes in vegetation (Fishkis et al. 2010).

The movement of phytoliths is facilitated by earthworms through their burrowing activity. Earthworms, in conjunction with percolation, contribute to increased phytolith translocation and even distribution. Comparing the phytolith content between earthworm casts and the surrounding soil matrix can provide direct evidence of phytolith transport facilitated by earthworms (Fishkis et al. 2010).

In coarse-textured soils, which have greater continuity and a higher number of macropores, phytolith distribution is more extensive compared to sandy soils. The reported phytolith transport distance in intact Cambisol cores (2.2 ± 0.1 cm) was nearly ten times larger than that observed in repacked sand (0.3 ± 0.01 cm) (Fishkis et al. 2009).

11 Conclusion

Carbon sequestration has been recognized as a crucial step in reducing global warming. Biocarbon sequestration is one of the most promising approaches to long-term carbon storage. Biocarbon sequestration takes place in soil via phytoliths through PhytOC which can remain in the soil for millennia. Formation, distribution, and storage of phytolith occluded carbon are the major factors affecting phytolith-mediated biocarbon sequestration. Phytolith-mediated biocarbon sequestration in the soil can be affected by several factors like soil properties, management practices, crop factors, etc. Both plant factors and soil factors contribute to PhytOC. Production of PhytOC mainly depends on plant factors like crop area, crop duration, aboveground net primary productivity, crop, plant species, plant parts, age of plant, and plant parts. The amount of biomass production is directly correlated with the production of PhytOC. Phytolith morphotype is affected by cell size and shape, which in turn affect the amounts of materials silicified within phytoliths (including different forms of C) and the stability of phytoliths. Phytoliths exhibit remarkable stability within plants as Si is a quasi-essential element. When the plant dies and decomposes, the phytoliths reach the soil. Stability and distribution of phytoliths are influenced by soil factors like soil type and depth, tillage, bioturbation, percolation, etc. Phytolith morphotypes and crop management (mulching, green manuring, crop residue, etc.) can also contribute to phytolith distribution. Carbon dioxide and temperature, climate zone, and topography have a great influence on the phytolith dissolution apart from the soil factors like pH, Soil organic carbon content, EC, clay content, oxalate extractable (non-crystalline forms) Fe and Al content, etc. The relevance of phytolith-mediated biocarbon sequestration lies in the fact that even though phytoliths sequester only a tiny amount of carbon, they can endure in soil for millennia.

Disclaimer (Artificial intelligence)

Author(s) hereby declare that NO generative AI technologies such as Large Language Models (ChatGPT, COPILOT, etc.) and text-to-image generators have been used during the writing or editing of this manuscript.

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