ABSTRACT

Phytoliths are formed from silica carried up from groundwater and some plants. The weathering of silicate minerals at the Earth’s surface provides large amounts of soluble silica, some of which is absorbed by growing plants. In solution, silica exists as mono silicic acid $\text{Si} (\text{OH})_4$ with pH values of 2–9. It is carried upward in the vascular system and becomes concentrated during transpiration around the leaf stomata. The supersaturated solution begins to polymerize or gel then solidifies and forms solid opaline silica ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) bodies (phytoliths) within and between some of the plant tissues.
1. INTRODUCTION

Phytoliths (from the Greek ‘plant stone’) are rigid, microscopic structures made of silica, found in some plant tissues. Plants take up silica from the soil, whereupon it is deposited within different intracellular and extracellular structures of the plant. Phytoliths survive the decomposition and humification of organic tissues and can thus accumulate in the soil. Most of them are part of the textural silt fraction. Although some use ‘phytolith’ to refer to all mineral secretions by plants, it more commonly refers to siliceous plant remains.

Monosilicic acid (H$_4$O$_2$Si) is absorbed by plant roots, transported through the plant body and deposited as solid hydrated silica polymers (SiO$_2$ * nH$_2$O; opal-A) inside and around cells when they are still alive [1]. This uptake and transport occur both as passive and active (energy-demanding) processes, depending on the plant and the environmental availability of silica [2]. Thus, transpiration appears to be an important factor in pulling water with dissolved silicic acid into the leaves of plants, but cannot fully explain patterns, rates, and timing of silica deposition [1]. Recent work suggests that specific biomolecules may catalyze precipitation of silicic acid as tiny granules of opal-A [3,1]. The silica bodies (phytoliths) that result from the aggregation of these granules are microscopic, ranging from infillings of cell walls to cell lumen, partial or full infillings of individual cells to entire silica skeletons encompassing tens or hundreds of cells [3].

Silicon (Si) is the second most abundant mineral element in soil comprising approximately 28% of the earth’s crust. In warm sub-humid and humid tropical ecoregions a high degree of weathering, mainly as desilication, has resulted in the development of soil orders high iron and aluminium oxides and low in nutrient bases and Si. Many plants can absorb Si depending upon the species in the biomass can range from 10 to greater than 100 g Si kg$^{-1}$. Plant species are considered Si accumulators when the concentration of Si is greater than 1 g/kg. Relative to monocots, dicots such as tomato, cucumber and soybean are considered to be poor accumulators of Si with values less than 1 g/kg in their biomass. Dryland grasses such as wheat, oat, rye, barley, sorghum, corn, and sugarcane contain about 10 g/kg in their biomass, while aquatic grasses have Si content up to 50 g/kg [2]. Plants’ uptake of Si is often greater than nitrogen and potassium. Despite high concentration in plants, Si is striving for the status of essential element. Among terrestrial plants, only horsetails have been conclusively shown to require Si as an essential nutrient. Depending upon the Si concentration in tissue, plants are classified as silicon accumulators or non-accumulators. Normally most dicots are silicon non-accumulators except cucumber and watermelon that have Si concentration less than 0.5 per cent while most of the grass family members (particularly rice and sugarcane) are Si accumulators having Si concentration of more than five per cent.

A great many functions have been proposed for silica and silicon inside the plant body. Many of these functions relate to silicon as a biologically active element and include stimulation of photosynthesis, mitigation of stresses, both physical (e.g., radiation damage, water deficit, wind, cold temperatures) and chemical (e.g., nutrient deficiency and excess, low or high soil pH, and metal toxicity), as well as pathogen resistance [4]. In addition, there is evidence that silica in solid form (as phytoliths) acts as structural support and/or mechanical defense against insect and small mammalian herbivores in extant plants [e.g., 5,6]. In contrast, a recent study found little evidence for the longstanding notion that phytoliths in modern grasses deter large mammalian herbivores, and challenged the
idea that grass phytoliths evolved for this purpose.

2. PHYTOLITHS FORMATION

Phytoliths are formed from silica carried up from groundwater. The weathering of silicate minerals at the Earth's surface provides large amounts of soluble silica, some of which is absorbed by growing plants. In solution, silica exists as monosilicic acid \( \text{Si(OH)}_4 \) with \( \text{pH} \) values of 2–9. It is carried upward in the vascular system and becomes concentrated during transpiration around the leaf stomata. The supersaturated solution begins to polymerize or gel then solidifies and forms solid opaline silica \( \text{SiO}_2 \cdot n\text{H}_2\text{O} \) bodies (phytoliths) within and between some of the plant cells. The obvious relationship between transpiration and deposition of phytoliths remains poorly understood. However, it has been discovered that the number of phytoliths and their morphology is largely underdetermined by genetic control [9]. Nevertheless, it should be noted that not all plant species (or their individuals) produce phytoliths and the reason for this is not clear.

Phytoliths are found in nearly all plant structures; stems, leaves, roots, and inflorescences. In general, more phytoliths form in the aerial tissue than subterranean tissue, but in some plants, phytoliths are equally spread throughout. Patterns of phytolith formation appear to be consistent within families and species, however, only a fraction of the global flora has been investigated for their phytolith presence (Fig. 1) the formation of phytoliths in monocotyledons often involves the filling of a cell interior. Cell interiors act as moulds, producing solid phytoliths of different but repeatable three-dimensional shapes. Solid phytoliths are extremely resistant to decomposition and are therefore more frequently recovered from soils and sediments than those produced by woody species. Phytoliths from woody plant species have until recently been largely ignored. One problem in the interpretation of phytoliths from trees and shrubs has been the poor preservation of the most common phytoliths (polyhedral) produced in the epidermal cell walls of leaves of these plants. These phytoliths are poorly preserved because of their fragile plate-like structure. However, spherical phytoliths are produced in large numbers in the centre of groups of silicified epidermal cells of trees and shrubs that tend to be well preserved [8].

![Fig. 1. Patterns of phytoliths formation in soil and plants](image-url)
Fig. 2. Distribution and turnover of phytoliths in soil. A. Schematic representation of phytolith distribution in soils, showing how the abundance of plant-derived silica decreases with depth in the soil. Labile and stable pools differentiated, with question marks showing the potential decrease with depth of the stable phytoliths pool [9]. B. Turnover rates of phytoliths in soils under different types of vegetation. Bars mark the error in turnover rate estimates; arrows indicate minimum estimates.

3. PHYTOLITHS COMPOSITION, CHARACTERISTICS AND FUNCTION

Phytoliths are in general composed of amorphous (non-crystalline) silicon dioxide ($\text{SiO}_2$) and about 4–9% water. However, measurable amounts of microcrystalline structures have been reported within phytoliths, creating the possibility of direct dating using optically stimulated luminescence (OSL) methods [10]. Phytoliths are optically isotropic with refractive indices between 1.41 and 1.47 and have a specific gravity range between 1.5 and 2.3. They range in color under transmitted light from colorless to light brown to opaque.

Phytoliths can also contain significant amounts of occluded, chemisorbed, or solid solution impurities such as aluminums, iron, titanium, manganese, phosphorus, copper, nitrogen, and carbon. It is thought that the presence of carbon within phytoliths is the result of the trapping of plant cellular material during phytoliths formation within living cells. In addition, it has been demonstrated that more than 50% of this encapsulated carbon is protected from oxidation, and thus provides another source of paleoenvironmental and paleoclimatic information [11].

The development of accelerator mass spectrometry (AMS) radiocarbon techniques using very small samples permits the dating of phytolith carbon [12]. Moreover, carbon isotope analysis can also be used to provide additional information about the photosynthetic pathway of
plants. For example, knowledge as to whether C$_3$ and C$_4$ grasses dominated a given environment is an indication of climate at the time those plants were growing [13]. Carbon isotope analysis of phytolith-occluded carbon has recently been used to generate a late Quaternary isotopic record of atmospheric carbon dioxide (CO$_2$). In addition to providing generalized patterns of vegetation history from the analysis of phytolith morphologies, phytoliths are unique in being able to be directly dated and provide evidence of changes in the ratios of atmospheric CO$_2$, from the same material. Moreover, because phytolith-occluded carbon is of plant cellular origin, it is theoretically possible that deoxyribonucleic acid (DNA) is present and could provide direct evidence of floral origin. Stromberg et al. [6] is developing methods to extract and analyze DNA from phytolith-occluded carbon. The functional significance of silica is not obvious, and to some extent, the mechanism of phytolith formation appears passive and they represent no more than ‘waste products’ [14] alternatively, phytoliths provide mechanical support, preventing the collapse of cell walls under tension during transpiration. Moreover, phytoliths provide plants with increased resistance to browsing by herbivores and insects and attack by pathogenic fungi. Research has also shown that in some situations plants actively incorporate solid silica into their structures. Despite incomplete understanding as to why some plants secrete silicon and some do not, it does appear that silicon is an essential element in the development of some species [7].

4. PHYTOLITHS MORPHOLOGY

At the heart of phytolith analysis is the understanding of how the shapes of phytoliths extracted from sediments and seen under a microscope, relate to the species or family of plants in which they formed.

4.1 Representativeness and Preservation

Phytolith analysis is a developing discipline and there are still identification problems to be resolved. These are of multiplicity when many different phytoliths are found in a single taxon, and redundancy, when the same form can occur in many taxa. Another problem is associated with the lack of representation of some phytoliths forms in assemblages extracted from sediments. As mentioned above, some phytoliths produced by plants do not persist or are poorly represented in sediments and soils. However, these problems are being resolved as more reference collections of modern phytoliths and soil assemblages are compiled. One such example is the reference collection produced by Wallis [15] who documented the occurrence of distinctive phytoliths from the leaves of 177 non-Poaceae plant species from northwest Australia. The study showed that although only 50% of the specimens examined were phytoliths producers, there was enough morphological variability to distinguish between fossil phytoliths assemblages from the region.

5. TERMINOLOGY AND CLASSIFICATION

Historically, the terminology and classification of phytoliths have been of a fragmented and individual nature. Many independent schemes were devised which were used to deal with phytoliths extracted from plants or sediments, generally from a specific region. There was a certain amount of overlap between these schemes and over the years many attempts have been made to develop a universally accepted standard classification scheme. To bring standards and to harmonize the naming and description of phytoliths a working group has been formed that has developed a standard protocol for naming phytolith types and a glossary of descriptors: ‘The first international code for phytoliths nomenclature 1.0’ [16]. It is suggested that when naming a particular phytoliths type, there should be up to three descriptors. The first descriptor should be the two- or three-dimensional shape. The second descriptor should be texture and/or ornamentation and should be added if they are characteristic or diagnostic. A third descriptor can be added when the anatomical origin is clear and beyond doubt. For example, bulliform is an established botanical term used to describe a particular type of cell found in grass leaf epidermis. For this particular case, the word conveys both an anatomical and a descriptive meaning. It is expected that as the scheme is adopted, it would undergo many changes as more phytoliths are discovered and described (Table 1).
Table 1. Schematic drawings of phytoliths

| Schematic drawings | ICPN names                  | Former nicknames                      |
|---------------------|-----------------------------|---------------------------------------|
| Bilobate short cell | Dumbbell or bilobate        |                                       |
| Trapeziform short cell | Square or rectangle    |                                       |
| Cylindrical polylobate | Polylobate                 |                                       |
| Trapeziform polylobate | Polylobate                 |                                       |
| Trapeziform sinuate |                              |                                       |
| Elongate echinate long cell | Elongate spiny or elongate sinuous |                                       |
| Cuneiform bulliform cell | Bulliform or fan-shaped |                                       |
| Parallelepiped bulliform cell | Bulliform                 |                                       |
| Acicular hair cell | Point-shaped                |                                       |
| Unciform hair cell | Point-shaped                |                                       |
| Globular granulate | Spherical rugose            |                                       |
| Globular echinate | Spherical crenate           |                                       |
| Cylindric sulcate tracheid | Tracheid                  |                                       |
6. PALEOENVIRONMENTAL RECONSTRUCTION USING PHYTOLITH ANALYSIS

Many paleoenvironmental reconstructions involving phytolith analysis have used qualitative or semiquantitative methods. For example, Carter and Lian [17] used the morphological differences in phytoliths assemblages extracted from a well-dated 6.4 meter loess core to indicate changes in the relative abundance of forest versus grass cover. The record showed a correlation between the tree–shrub phytolith fluctuations and the oxygen isotope curve of between Marine Oxygen Isotope Stages (MIS) 1 and 5, suggesting that changes in the ratio of arboreal to nonarboreal phytoliths directly result from climate changes (Fig. 3). Many other such studies have been conducted from all continents and most regions of the world. However, in addition to being used successfully as a broad measure of paleoenvironmental and paleoclimatic change, phytoliths have greater potential as a proxy for changes to past environments and climates. Powers-Jones and Padmore [18] saw much progress in putting phytoliths analysis on a more quantitative footing. These techniques include the development of suitable statistical methods, dating techniques, chemical, and isotopic analytical methods.

Much as for palynomorphs and leaf fossils, the characteristics of phytoliths as a source of paleoecological information depend in large part on their production patterns among and between plants and the differential preservation potential for different morphotypes, which to some extent follows taxonomic lines (Table 2) [e.g., 19,20,7]. Most major groups of land plants contain taxa that deposit substantial numbers of phytoliths in their tissues, but far from all plants are active phytolith accumulators [21]. Broadly speaking, the consistently highest silica accumulator’s fall in the monocotyledons, with grasses and palms as prime examples, ferns, and the sole extant genus in horsetails, Equisetum [7,22]. Non-angiosperm seed plants, such as conifers, cycads, and Gnetales generally do not accumulate much silica, although exceptions exist (e.g., Picea) [22,6]. Within non-monocotyledonous angiosperms, several families deposit abundant phytoliths, particularly among tropical trees, vines, and herbs (e.g., Chrysobalanaceae, Cucurbitaceae, Moraceae), but many groups are low producers (e.g., Fabaceae, Solanaceae). In addition, within monocotyledons, several clades exist that do not accumulate much silica (e.g., Juncaceae, Liliaceae) [e.g., 3, 23]. Above all, even within clades that contain some of the highest producers, some subclades or genera do not produce (e.g., ferns within the Pteridaceae, [24]. These patterns indicate that even though the genetic framework for active uptake and deposition of silica existed early on land plants [22], active accumulation of silica evolved in parallel or convergently in many clades much later on, perhaps as part of adaptation to particular biotic or abiotic environments [6]. The existing variation means that some low-producing or silica excluding taxa are underrepresented or “silent” in the phytoliths record whereas others, such as grasses, can be overrepresented [8,25,6]. This bias can be compared to the rarity of pollen from insect-pollinated plants relative to wind-pollinated conifers in the palynological record, or the relative absence of herbaceous plants in the leaf fossil record (Table 2).

For example, to establish a more quantifiable corresponding relationship between vegetation and phytoliths assemblages, various statistical quantitative methods have been applied, such as constrained classification techniques; cluster analysis and correspondence analysis (see reviews of phytoliths statistical methods in Pearsall and Piperno [26] and Pearsall [27]). To find the most suitable statistical methods for phytolith analysis compared many methodologies. Bobrov et al., [28] were able to demonstrate that by using cluster and canonical correspondence techniques they were able to distinguish between the phytoliths from 69 Cyperaceae and Poaceae species. A transfer function technique was used by Prebble et al., [29] to quantify the relationship between modern phytolith assemblages and environmental parameters for the quantification of a long late Quaternary paleoenvironmental record.

Phytoliths are incorporated into soils or subaerial sediments when leaf litter and plants decay on the surface, or belowground in the case of roots and rhizomes [30]. In addition, phytoliths are deposited on the land surface as part of sediment-water suspension (e.g., through overbank flooding) or windblown dust [31,32,33]. Empirical data show that the concentration of biogenic silica is very high near the soil surface but typically decreases drastically below about 30–80 cm (Fig. 4) [11,32]. Deeper in the soil profile, the phytoliths concentrations appear to be stabilized [9]. This distributional pattern results in...
from a combination of (bio) chemical dissolution and vertical transport of phytoliths. Specifically, in the top part of the soil, biologically mediated mineralization of organic matter occurs rapidly and the most soluble phytoliths are dissolved; this silica is in large part recycled through (re-)uptake by living plants (Figs. 3, 4) [32]. This “labile” pool of recycled silica ranges from 69% of the total soil silica in short grass prairie to 92% in tropical forest, a variation that suggests a strong dependence on climate [32,34]. The intensity of chemical dissolution is visible as more marked etching or pitting of phytolith morphotypes further down in the soil column [32,35]. Conversely, pedogenic secondary silica (see below), thought to result from dissolved and mobilized amorphous silica from the O and A horizons of the soil, increases with depth [32].

| Table 2. Characteristics of paleobotanical evidence used for paleoecological reconstruction |
|---------------------------------------------|---------------------------------|---------------------------------|
| Production bias                            | Overrepresented taxa            | Wind-pollinated taxa (e.g., conifers, grasses), some aquatic taxa |
|                                            | Underrepresented taxa           | Animal-pollinated taxa          |
| Preservation bias                           | Overrepresented taxa            | Taxa with thick-walled pollen/spores (e.g., conifers, elms, ferns) |
|                                            | Underrepresented taxa           | Taxa with thin-walled pollen/spores (e.g., grasses, aquatic) |
|                                            | Overrepresented environment     | Lakes, swamps, lagoons (low pH, negative Eh) |
|                                            | Underrepresented environment    | Soils and deposits on e.g., floodplains, arid environments (high pH, positive Eh) |
| Taxonomic resolution                       | Well resolved                   | Woody taxa (trees and shrubs) |
|                                            | Poorly resolved                 | Grasses |
| Temporal resolution                        | 1-many years                   | 1–10^3 years |
| Typical spatial resolution                 | Regional                       | Local – regional |

Deciduous trees/shrubs

Herbs, evergreen trees/shrubs

Sclerophyllous leaves with thick cuticle

Thin leaves with thin cuticles (e.g., aquatic plants, herbs)

Lakes, swamps, lagoons (low pH, negative Eh); levees (rapid burial)

Soils and deposits on e.g., floodplains, arid environments (high pH, positive Eh)

Many plants (e.g., many angiosperms, conifers, ferns)

Grasses and (many) other parallel-veined monocotyledons

Day(s) – years
The stable pool of phytoliths is subject to vertical transport through bioturbation and illuviation (Fig. 3), although the roles of different factors affecting these movements, such as downward water percolation, degree and type of bioturbation, and soil grain size are still debated [16]. Vertical dispersal is thought to typically result in temporally averaged phytolith assemblages across the soil profile. However, several studies involving radiocarbon (C-14) dating of phytoliths in soil profiles (for discussion of the use of phytolith C-14, see [7]) have indicated that stratification of the biosilica pool can occur in soils, such that the phytolith record is more temporally resolved than the soil overall. Phytolith assemblage formation in soils, with influences on phytolith assemblage composition marked with thick arrows (Fig. 3). Note that such influences include both the factor that is of interest to the researcher (plant community composition; green bolded box) and factors that obscure this influence and that therefore may bias the vegetation inference (yellow bolded box). The latter factors relate to plant type (e.g., differential phytolith production among plant taxa), climate, soil/sediment type (both influencing e.g., soil chemistry affecting dissolution), and analytical protocol.

Fig. 3. Schematic of phytoliths assemblage formation in soils
7. PHYTOLITHS AND CHRONOLOGY

7.1 Radiocarbon

An important aspect of late quaternary research is being able to reliably date changes in the relevant sequences and processes. In addition to providing vegetation information, phytoliths contain radiometrically datable carbon. Moreover, because phytoliths-occluded carbon is effectively sealed against post-deposition contamination at the time of the phytoliths formation, they provide an almost ideal time capsule. Wilding [36] was the first to determine a radiocarbon age from phytoliths-occluded carbon. However, because of the large samples needed (45 kg of sediment), it became impractical. Following the development of AMS dating, more dates have been obtained [12]. As with most new techniques, many issues have been raised about preparation, accuracy, and reliability. These methods are in the process of being further developed and tested [37].

7.2 Optically Stimulated Luminescence

Despite being generally described as amorphous, phytoliths appear to contain microcrystal structures. Theoretically, these microcrystal structures should be able to trap electrons and as such offer potential material for thermoluminescence (TL) dating. Rowlett and Pearsall [10] examined the feasibility of TL analysis of phytoliths. They dated many phytoliths from sediments associated with ceramics of known cultural affiliation and radiocarbon-dated organic material. However, while their TL dates were in general agreement with the previously accepted ages, indicating its potential, the phytoliths matrix was shown to be unstable at high temperatures.

More recently Reiser et al., (2015) have measured strong luminescence light emission from phytoliths following both infrared and green light stimulation using the optically stimulated luminescence (OSL) method. This team is continuing with experiments to confirm and refine the technique and is using both AMS 14C and OSL techniques to date the same phytolith material. Once the reliability of OSL dating of phytoliths is established with 14C, then the older range of OSL will allow the dating of longer records.

7.3 Phytoliths Chemical Analysis

In recent years, previously unrecordable components of phytoliths and their occlusions have been analyzed and documented following the development of new instruments and techniques. Instruments such as the inductively coupled plasma source mass spectroscope (ICP/MS) capable of measuring elements in parts per billion has opened up the possibility of measuring trace elements present in only minute quantities in phytoliths. Hart [38] used this technique to examine trace elements present within phytoliths from the leaves of Actinotis helantheri and Triodia mitchelli. She was able to confirm the presence of more than double the previously documented number of phytoliths occluded trace elements. Smith and Anderson [39] used tetramethylammonium (TMAH) thermochemolysis and gas chromatography-mass spectrometry (GC-MS) to characterize the organic compounds in C3 and C4 phytoliths.

In an attempt to improve on phytolith taxonomic resolution, Carnelli et al., [40] have proposed a new method of distinguishing between similar morphological forms from different taxa. Using X-ray analysis paired with phytolith morphology they have been able to demonstrate that aluminium in phytoliths from ericaceous and conifers were significantly higher than in Cyperaceae and Poaceae. The technique will require further investigations of different taxa to confirm that the co-deposition of aluminium and silicon in phytoliths is more frequent in woody plants than herbaceous plants.

7.4 Phytoliths Stable Isotope Analysis

It has been demonstrated that the stable isotope analysis of phytoliths can contribute considerable paleoenvironmental and paleoclimate evidence [11,31,39]. Tests carried out by Kelly et al., [11] confirmed that the carbon occluded within phytoliths is protected by the nonporous glass-like microstructure of the silica body and is, therefore, unlikely to be vulnerable to decay.

7.5 Oxygen

Information about climatic conditions during plant growth is preserved by the oxygen isotope composition of phytoliths [41]. They hypothesised that climate factors that affect the isotopic composition of oxygen of water (H2O) within
Growing plants should leave a record in the oxygen isotopic ratios of phytoliths silica. They were able to determine that the plant growing temperature is recorded in the 180 phytoliths formed within the non-transpiring tissue of grasses. However, the signal from non-transpiring tissue can be masked by phytoliths from transpiring tissue, which in contrast are variably enriched in depending on relative humidity.

7.6 Carbon

Phytoliths trap trace amounts of organic carbon (0.09–1.3%; Kelly et al., 2001). Organic compounds can be attached to the silicates by hydrogen bonding, or parts of the cytoplasm may become occluded within the phytoliths as they silicify [31]. Wilding [36] isolation and radiocarbon analysis of phytoliths carbon created the opportunity to extract more paleo information. Fredlund [31] demonstrated that careful analysis of phytolith-occluded carbon had the potential for reconstructing a record of the range, variability, and changes of $^{13}$C and $^{18}$O, of past grassland ecosystems. However, Smith and Anderson [39] showed that the method was limited by the compression of the phytoliths $^{13}$C scale (6.6‰) relative to the whole-plant scale (11.2‰). Their study demonstrated that it was possible to characterize the phytolith organic compounds in C₃ and C₄ grass phytoliths using TMAH and GC-MS analysis. These analyses record the presence of lipids, which are generally depleted in $^{13}$C, and suggested, therefore, that lipid presence explains the depletion in $^{13}$C in phytoliths carbon relative to whole plant $^{13}$C. Moreover, they suggested that the isotopic differences in C₃ and C₄ grass phytoliths were most likely caused by differential fractionation associated with the formation of lipids in C₃ and C₄ plants. Smith and White [13] have gone on to resolve some modern calibration issues raised in previous work, and showed that the carbon isotope ratios of fossil phytoliths presented a unique tool for reconstructing the proportion of C₃ and C₄ grasses in ancient grasslands.

The occluded carbon within phytoliths is formed by photosynthesis from atmospheric CO$_2$ when the host plant was growing. Therefore, it should be possible to relate the carbon isotope analysis of phytolith-occluded carbon with carbon isotope concentration in atmospheric CO$_2$. Carter [42] has extracted a last glacial cycle record from phytoliths extracted from a 120,000-year-old loess core. Phytoliths were extracted from the 7.4 meter loess core and analyzed morphologically and isotopically from the occluded carbon. Rates of isotopic fractionation between plant and phytoliths were determined by measurements from many modern tree, fern, and grass species. There was little correlation between the $^{13}$C record and the phytolith morphological assemblages, suggesting that the $^{13}$C signal from occluded carbon was largely determined by the atmospheric CO$_2$ carbon isotopic ratio.

8. SILICON IN SOILS

Silicon is the second most abundant element in the crust of the earth after oxygen, with a mean content of 28.8 % (weight) and an occurrence that ranges from 0.52 to 47 % [43]. In rocks, the concentrations of silicon range from 23 % (e.g., basalt) to 46.5 % (e.g., orthoquartzite) [44]. Trace amounts of silicon are also in carbonaceous rocks such as the limestones and the carbonates. The silicates are the component of derived soils that contain significant amounts of silicon (as high as 46 %). The amount of silicon in the petrocalcic horizon is much lower than (8 %) than in the silicates and the amount of silicon in the minerals found in some highly weathered oxisols such as bauxites is even less.

Silicon (Si) is abundant in nature, and as such, the total silicon content of soils, plants and materials suitable for use as soil amendments for agricultural purposes, can be high. In soil, Si exists in a wide variety of forms and stabilities. It is estimated to represent about 28 per cent of the earth’s crust, and alumino-silicates and quartz can be as much as 75 to 95 per cent of the inorganic fraction of soil [45]. Silica (SiO$_2$) can occur in different crystalline forms, of which quartz is the most common, or as amorphous Si-containing substances. Also present in soils are amorphous forms of Si, including aliphane, a non-crystalline Si-containing colloidal mineral substance, and the hydrated forms of silica (SiO$_2$.nH$_2$O), commonly known as phytoliths, resulting from plant decomposition in sponge spicules. Phytoliths can be relatively stable and usually concentrate in the surface horizon of soils. Amounts of opal phytoliths commonly range from <1 to 30 g/kg on a total soil basis [46].

While Si compounds such as quartz, various crystalline silicate minerals, silicate clays and amorphous silica compounds dominate the solid
phase of all soils, the soluble forms in the soil solution consist of monosilicic acid ($\text{Si(OH)}_4$) and polysilicon acids, and complexes with organic and inorganic compounds. The total Si content of soils can have little relationship to the concentration of soluble Si in soils, which is the component important for plant growth. The concentration of soluble Si in soils is dynamic. Monosilicic acid will remain in solution in the monomeric state in neutral and weakly acid solutions. However, a rapid polymerization occurs at high solution concentrations, with increasing soil pH and in the presence of oxides and hydroxides of aluminium and iron [47].

Fig. 4. Schematic diagram the solid, liquid and adsorbed phases of silicon are the key components of the silicon cycle in soil
9. SILICON CYCLE IN SOIL

The solid, liquid and adsorbed phases of silicon are the key components of the silicon cycle in soil (Fig. 4.). The liquid silicon phase consists of $\text{H}_4\text{SiO}_4$ and the polymerized and complexed silicic acid in soil solution, and the uncharged form of $\text{H}_4\text{SiO}_4$ is the only form that is absorbed by plants and microorganisms. The absorbed silicon is later deposited as polymerized silica within the plant tissues or the cell structure of the microorganisms. These polymerized silica bodies return to the topsoil in the litterfall and the remains of microorganisms and eventually enter the highly soluble biogenic silica pool that contributes to the silicon in the soil solution [48]. The estimated that 60–200 Tonns moles silicon per year is stored in plants. Silicon is also added to soils with applications of manure and compost, and the decomposition of silicon-rich manure can increase the level of available soil silicon. The silicon rarely interacts with dissolved organic matter but does form colloidal aluminium-silicon polymers (Fig.5) at many soil solution pH values [49,50].

Fig. 5. Silicon rarely interacts with dissolved organic matter
10. FUNCTIONS OF SILICON IN PLANTS

Silicon is classified as a “beneficial nutrient” in plant biology. Under controlled hydroponic conditions, Si does not meet the classical definition of an essential nutrient. However, in the real world where plants are exposed to multiple stresses, Si plays an important role in plant health. One major contribution of Si is the reinforcement of cell walls by deposition of solid silica. It is translocated from the roots as silicic acid through the xylem until it deposits under the cuticle and in intercellular spaces. These silica bodies are called phytoliths, or plant opal. These structures are very resistant to decomposition. Many persist in soils as “plant fossils” for very long periods, which is useful in archaeological and paleoecological research.

Silicon represents a major mineral constituent of plants and is present in plants in concentrations similar to that of the other macronutrients. At 0.1 per cent, Si is equivalent to the levels of macronutrients, Ca, Mg, P and S; while the upper levels of 10 per cent exceed the concentrations of the minor nutrients like K and N [51]. However, the Si content of different plants, and various plant parts, is extremely variable. Different plant species differ in both their concentrations of Si and their accumulation of Si from the soil solution. Jones and Handreck [52] divided plants into three major groups according to the SiO₂ per cent of the leaf tissue on a dry weight basis. “Wetland” grasses (e.g., paddy-grown rice) have the highest levels at 5 - 15% “dryland” grasses having intermediate levels of 1 - 3% and the dicotyledons generally having the lowest levels of less than 1%.

11. SOIL FACTORS AFFECTING SILICON AVAILABILITY

Plants growing in soils with high percentages of sand tend to have low Si concentrations. Although the sand is largely composed of Silicon dioxide, this material provides very little soluble or plant-available Si. Sandy soils also usually have good drainage, which prevents Si accumulation. Thus, it is not unusual for crops grown on sandy soils to benefit from applications of soluble Si. Silicon availability to plants does not change markedly across the soil pH range where most crops are grown. Many of the commonly used Si fertilizer materials also serve as liming agents and their application results in the neutralization of soil acidity.

There are many types of silicate materials suitable for use as soil amendments/fertilizers, however, their effectiveness is more dependent on their reactivity rather than total Si content. An excellent review of sources suitable for agriculture is provided by Gascho [53]. As mentioned plant material can have high concentrations of Si, and crop residues (e.g., rice hulls and sugar mill wastes) are commonly used, although high rates are usually necessary. There are a few naturally occurring mineral materials, such as wollastonite (CaSiO₃), olivine (MgSiO₃) and diatomaceous earth, which can have total silicon contents of approximately 55%, 30% and >70% SiO₂ respectively. By far the most common forms of silicate materials used as soil amendments are various industrial by-products, for example, calcium silicate slag, a by-product from the production of elemental phosphorus.

12. SILICON UPTAKES, TRANSFER AND DEPOSITION IN PLANT

Plants uptake silicon from the soil solution in the form of H₄SiO₄ and is commonly found at concentrations that range from 0.1 to 0.6 mM at the pH levels found in most agricultural soils [54]. According to Doucet et al., [55], the lateral roots of rice are involved in the uptake of silicon. The different mechanisms by which the silicon is absorbed by plants, i.e., active, passive and rejective (Table 3) [56-57].

The plants in the high-accumulator category have a silicon content in the shoots that ranges from 1.0% to 10% dry weight and are primarily monocotyledons such as bamboo (Bambuseae), barley (Hordeum vulgare), rice (Oryza sativa), sorghum (Sorghum bicolor), sugarcane (Saccharum officinarum), and wheat (Triticum aestivum) (Ma et al., 2011). The intermediate accumulator plants are mostly dryland Gramineae with shoot silicon contents that range between 0.5% and 1.5% dry weight (Table 4).

The SiO₂ precipitation in plants occurs at concentrations of H₄SiO₄ greater than 2 mol m⁻³ (Liang et al., 2017) and occurs primarily in the epidermis of the shoots, in addition to the vascular system and the endodermis of roots of some plant species (Osuna-Canizales et al., 2001). The deposited silica is immobile and is not transferred to actively growing or meristematic tissues (Reaven, 2003; Saccone et al., 2017). Transpiration remains a viable option as one of the primary drivers in silicon transport and
deposition in plants, and therefore, the duration of plant growth significantly affects the concentration of silicon; for example, older leaves contain more silicon than younger leaves [51]. Based on earlier research, the SiO$_2$·nH$_2$O framework possibly binds with organic components (De Saussure 2004). Conversely, the studies by Lanning, (2003); Henriet et al., (2006) confirmed that only the monosilicic acids and di-silicic acids but no organosilicon complexes were found in the xylem exudates of rice.

Table 3. Silicon is absorbed by plants

| Mode of uptake               | Examples                      |
|-----------------------------|-------------------------------|
| Accumulator type (active uptake) | Rice, wheat, barley          |
| Intermediate type (passive uptake) | Cucurbits, soybean           |
| Excluder type (rejective):   | Tomato, French bean, black gram |

Table 4. Si concentration in species

| Name of the species                  | Si concentration | Examples          |
|--------------------------------------|-------------------|-------------------|
| Wetland species of Gramineae         | 10–15%            | Rice              |
| Dryland species of Gramineae and a few dicots | 1–3%              | Wheat, sugarcane  |
| Most dicots                          | < 0.5%            | Especially legumes|

Fig. 6. Application of silica fertilizer enhances the mechanical strength of rice
13. **FUNCTIONS OF SILICON ON RICE CROP**

Increasing canopy photosynthetic efficiency by keeping leaves erect and compact rice uses chlorophyll to fix atmospheric carbon dioxide and water to form carbohydrates. Rice yield is directly proportional to the accumulation of photosynthetic formed in the process of photosynthesis [21]. Appropriate plant density and fertilizer management are essential for achieving an optimal leaf area index for photosynthesis. The application of silica fertilizer enhances the mechanical strength of epidermal cells on the rice leaf surface, keeping the rice leaves erect and avoiding mutual shading (Fig. 6).

Silicon is accumulated at levels equal to or greater than essential nutrients in plant species belonging to the families Poaceae, Equisetaceae, and Cyperaceae. In rice, for example, Si accumulation is about 100% greater than that of nitrogen. It is estimated that a rice crop producing a total grain yield of 5000 kg/ha will remove Si at 230 to 470 kg/ha from the soil. Therefore, applications of calcium silicate at 5000 kg/ha (Si at 1000 kg/ha) appear to be sufficient for supplying enough Si to the plant so that the tissue content will be 3% or greater. Concentrations between 3 and 5% may be the minimum tissue levels needed for disease control [21].

14. **INCREASING RESISTANCE TO INSECT PESTS AND DISEASES**

Silicon helps to strengthen cells of rice leaf, stem, and roots. Epidermal cells accumulate the most amount of silicon absorbed from the soil. In the intercellular spaces, silicon is oxidized to form silicon dioxide (silica gel). Their presence enhances the plant's resistance to insect pests and disease pathogens (Table 5). The reduction in disease infection and pest's infestation is principal because silicon promotes ammonium assimilation. This chemical process inhibits the accumulation of unstable amino acids and amides in cells which provide nutrients to pests and pathogens [21].

**Table 5. Enhances the plant's resistance towards insect pests and disease pathogens**

| Crops       | Disease          | Pest               |
|-------------|------------------|--------------------|
| Rice        | Brown spots,     | Green leafhopper,  |
|             | Grain discolouration, | Brown plant hopper and Stem borer |
|             | Stem rot, Leaf and neck blast. | Stem borer and Stem borer |
| Sugarcane   | Sugar rust and Ringspot | Stalk borer and Stem borer |
| Grape       | Powdery mildew | Fruit cracking |
| Cucumber    | Root rot         |                    |

15. **CONCLUSIONS**

Phytoliths were preserved as fossils in rocks for many millions of years. Various shapes and sizes of phytoliths due to their inorganic nature and their persistence to decomposition. Carbon sequestration is a potentially important way to limit atmospheric greenhouse gas concentrations in the long term with the use of phytoliths. It is an amorphous biogenic form of silicon. Silicon in fewer amounts can be beneficial in increasing grain yield and growth of cereal crops. The nutrient absorption capacity of the plant can be improved further and the nutrient deficient soil can also be effectively used for enhancing the productivity of rice. Si play important role in drought tolerance, pest and disease resistance.

16. **FUTURE THRUST**

Phytoliths size and length aspect ratio should be considered in studies of phytoliths translocation. The role of phytoliths occluded carbon of crop plants for enhancing soil carbon sequestration in agro-ecosystems need to be studied. The soil it's a very incomplete type of the processes involved in phytoliths dissolution, which needs to be explored. Phytoliths chemistry and formation at a molecular level right up to biogeochemical cycles and groundwater level should be given focus.

**COMPETING INTERESTS**

Authors have declared that no competing interests exist.
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