

The role of silicon in the supply of terrestrial ecosystem services

Jean-Dominique Meunier, Sophie S. Cornu, Catherine Keller, Doris Barboni

▶ To cite this version:

Jean-Dominique Meunier, Sophie S. Cornu, Catherine Keller, Doris Barboni. The role of silicon in the supply of terrestrial ecosystem services. Environmental Chemistry Letters, 2022, 20 (3), 10.1007/s10311-021-01376-8. hal-03661575

HAL Id: hal-03661575 https://hal.science/hal-03661575

Submitted on 7 Oct 2022

HAL is a multi-disciplinary open access archive for the deposit and dissemination of scientific research documents, whether they are published or not. The documents may come from teaching and research institutions in France or abroad, or from public or private research centers. L'archive ouverte pluridisciplinaire **HAL**, est destinée au dépôt et à la diffusion de documents scientifiques de niveau recherche, publiés ou non, émanant des établissements d'enseignement et de recherche français ou étrangers, des laboratoires publics ou privés.

Title: The role of silicon in the supply of terrestrial ecosystem services for food security and environmental concerns

Authors: Jean-Dominique Meunier, Sophie Cornu, Catherine Keller, Doris Barboni

Address: CEREGE Aix-Marseille Univ, CNRS, IRD, INRAE, 13545 Aix en Provence, France e-mails: <u>meunier@cerege.fr;</u> sophie.<u>cornu@inrae.fr;</u> <u>keller@cerege.fr;</u> barboni@cerege.fr

Abstract

In everyday life, silicon (Si) is omnipresent in manufactured objects such as electronic chips or cosmetic products. However, a growing number of studies on Si in plants and soils highlight its interest in today's environmental concerns such as food security, carbon regulation or cultural heritage. Here we review the state of knowledge of the Earth's terrestrial silicon cycle and show its importance in the framework of the ecosystem services concept. We show that silicon can participate in the inherent and manageable properties involved in all ecosystem services. As records of the past, phytoliths can be useful parameters in cultural services. Si is involved in provisioning services because it may influence the production of food and fibers. Si is also involved in regulating services may be improved through Si management not only by the application of Si fertilizer to soil but also by foliar application in the field. The soil and plant silicon status should be considered in assessment of ecosystem services as much as essential nutrients are considered, and the cost-benefit balance of Si remains poorly quantified.

Keywords Silicon. Terrestrial ecosystems. Phytoliths. Provisioning ecosystem services. Regulating ecosystem services. Cultural ecosystem services

Content

- 1.Introduction
- 2. The Si biogeochemical cycle: A supporting process
- 2.1 Terrestrial Si cycling at a glance

2.2 Si status, an inherent and manageable soil property fully involved in soil pedogenesis

- 3.Cultural services
- 4.Regulation services
- 5. Provisioning services
- 5.1 Si and nutrient uptake
- 5.2 Si and abiotic stress
- 5.3 Si and soil contamination
- 5.4 Si and biotic stress
- 6. Management of ecosystem services
- 6.1 Crop and soil management
- 6.2 Foliar application
- 7. Conclusion

References

1. Introduction

In everyday life, silicon (Si) is a major component of everyday manufactured products as evidenced by glass, electronic chips, silicones or more recently nanoparticles (Pradha et al. 2021). As a natural element, silicon is also known as a major constituent of beach sand and dust that cause silicosis. The benefits of Si in major environmental issues remains however largely underestimated. Silicon is the second-most common element on the Earth's surface, after oxygen. It is an essential nutrient for aquatic microorganisms such as diatoms that are of utmost importance in the aquatic food chain and play a major role in global biogeochemical cycles (Tréguer and Della Rocha, 2013). The Si biogeochemical cycle in aquatic ecosystems is strongly dependent on the terrestrial biogeochemical cycle (Struyf et al. 2009), as the supply of Si for diatom development depends on the processes that occur on land, particularly in soils where Si-bearing solid phases are weathered and transfer Si to rivers, lakes and seas. While marine diatoms sequester 240 Tmol Si yr⁻¹ (Tréguer et al. 1995), the amount of Si fixed by terrestrial biomes is estimated to be 84 Tmol Si yr-¹ with 35% in cultivated lands (Carey and Fullweiler 2012) because the most important crops such as cereals are Si accumulators (Guntzer et al. 2012a).

In plants, the first measurements of Si concentrations were performed by de Saussure (1804), who suggested that Si was an essential nutrient because of its high concentration in grasses. Si, however, was not considered as an essential element in the first inventories of the elements that are essential for the growth and survival of plants (Sachs 1865). Since the 20th century, the benefits of Si have been particularly well documented for crops such as rice, wheat, sugarcane, soybean, tomato, and cucumber (Liang et al. 2015) and for fibers such as hemp (Luycks et al. 2017), bamboo (Collin et al. 2014) and cotton (Rodriguez and Datnoff 2015; Fichhof et al. 2018).

3

Although the role of Si in plants deserves more research (Klotzbücher et al. 2017), a large body of empirical literature has shown its benefits and attracted the interest of agrobusiness (International Plant Nutrition Institute: Nutri-Facts Sheet: Silicon ref. #14#15056).

Ecosystem services are defined as "the benefits that people obtain from ecosystems". Although diatoms are well recognized as providers of ecosystem services in aquatic ecosystems because they impact many human beneficiaries (Rhodes et al. 2017), Si is not mentioned in the framework of terrestrial ecosystem services and related utmost important issues such as food security or carbon sequestration. Indeed, Si is not mentioned in the "key soil properties" that are related to soil-based ecosystem services (Adhikari et al. 2016) or in the list of soil quality indicators (Drobnik et al. 2018; Bünemann et al. 2018). The concept of ecosystem services has been largely popularized in recent decades since the seminal papers of Costanza et al. (1997) and Daily et al. (1997). The services provided by ecosystems are complex and have been classified into three main categories (CICES, 2011): 1) provisioning e.g. food, water, timber, fiber, and fuel production, 2) regulating and maintenance e.g. carbon sequestration, water and waste recycling, and 3) cultural e.g. recreational, aesthetic and spiritual; a fourth category of ecosystem services, namely, supporting services, is often added to the list (Millennium Ecosystem Assessment, 2005). Here we review the importance of Si in the framework of terrestrial ecosystem services (Dominati et al. 2010; CICES, 2011; MEA, 2005). We describe how the Si biogeochemical cycle is part of the supporting processes as defined by Dominati et al. (2010) and discuss the Si contribution to different ecosystem services, namely, cultural, regulation and provisioning services. Finally, we show how Si should be added to soil and plants to manage or improve ecosystem services.

4

2. The Si biogeochemical cycle: A supporting process

According to the Millennium Ecosystem Assessment (2005), supporting services are necessary to produce all other ecosystem services. Unravelling the terrestrial biogeochemical cycle of Si makes it possible to characterize the factors that control Si fluxes and the transfer between ecosystem compartments and hence its bioavailability (Figure 1) and impact on ecosystem services.

2.1 Terrestrial Si cycling at a glance

Si is found in the various biotic and abiotic compartments of terrestrial ecosystems (Figure 1). The input of Si by rainfall and dust is generally small and neglected in the Si budget (Sommer et al. 2006). In the solid soil phase, Si is included in primary minerals such as quartz, feldspar, in secondary minerals e.g. phyllosilicates and short range-ordered aluminosilicates and amorphous biogenic silica from plants namely phytoliths and microorganisms e.g. testate amoebae, diatoms, sponges. It is also adsorbed on soil particles such as Fe oxides (Cornelis et al. 2011) or clays (Nguyen et al. 2017). Weathering of the solid phase results in the release of Si in solutions, referred below as DSi, most generally in the form of silicic acid Si(OH)₄. The dissolution of silicate depends on the solid phase properties e.g. solubility, kinetics, grain size, on edaphic factors e.g. pH, ionic strength, biota and on climate. The pH level has contrasting effects on the dissolution of silicates: quartz and biogenic silica dissolution is higher under alkaline conditions, while aluminosilicates are more soluble at low pH levels (Fraysse et al. 2009).

Si solubilization can also be mediated by biological activities (Figure 1). Terrestrial plants and microorganisms can extract their essential nutrients from the dissolution of minerals through the release of organic compounds (Banfield et al. 1999; Neaman et al. 2006). Some bacteria, for example, have been found to specifically solubilize silicates (Sheng et al. 2008), resulting in an increased dissolution rate of minerals as resistant as quartz when colonized by cyanobacteria (Brehm et al. 2005). The role of fungi in increasing the release of Si from silicates is also well documented. The fungi attack silicates to varying degrees (Henderson and Duff 1963). For example, *Verticillium leptobactrum* extracted more Si from chrysotile than did *Fusarium oxysporum* (Daghino et al. 2009); *Penicillium simplissimum* solubilized 31% of Si from

powdered rocks after 7 days of incubation (Silverman 1970); and the presence of a mycorrhizal fungus in the soil significantly increased the release of Si into drainage water (Van Hees et al. 2004). The presence of lichens resulted in a fourfold increase in the Si flux compared to bare mica-schist, as shown in laboratory experiments (Aghamiri and Schwartzman, 2002).

Soil fauna and megafauna also modify the Si cycle by ingesting minerals, which results in an increase in Si solubilization. Bityutskii et al. (2016) showed that the concentration of water-extractable Si in earthworm casts was higher than that in bulk soil. Bioavailable Si, extracted by CaCl₂, was higher in termite mounds than in bulk soil (Jouquet et al. 2020). Vandevenne et al. (2013) showed that the feces of various herbivores produced a higher release of Si than that of fresh hay and concluded that grazers likely play a significant role in enhancing the availability of Si in the soil.

Once in the soil solution, DSi is either lost through drainage, sorbed onto mineral surfaces or taken up by plant roots or microorganisms. In plants, as DSi reaches the leaves, water evaporates through the stomata, creating an ascendant sap flux, while silicon accumulates in leaf and stem cells, polymerizing and forming solid clusters called phytoliths. Phytoliths play a major role in the Si cycle (Alexandre et al. 1997; Sommer et al. 2013; Yang and Zhang 2018). Indeed, the dissolution of 0.1% to 1% of the soil phytolith pool is enough to explain the Si concentrations in surface waters (Fraysse et al. 2010). Si uptake by testate amoebae can significantly lower the amount of Si released into solutions, as shown by Aoki et al. (2007). Sommer et al. (2013) measured a 17 kg Si ha⁻¹ uptake by testate amoebae, accounting for approximately half of the annual Si uptake by plants (35 kg Si ha⁻¹).

The Si budget in cultivated areas is still poorly documented. It may be impacted when irrigation and Si fertilizers are applied (Desplanques et al. 2006; Riotte et al. 2018) and when plant residues are exported. Indeed, if the removal of Si by plant exportation is not compensated, the soil may be depleted of phytoliths (Desplanques et al. 2006; Vandevenne et al. 2011; Clymans et al. 2011; Guntzer et al. 2012b). Assuming that the phytoliths are the only source of Si for crops, a simple calculation shows that the phytolith pool would be depleted within a few decades, considering an export of 50-100 kg Si ha⁻¹ yr⁻¹ and an initial pool of Si from phytoliths of 1000 kg Si ha⁻¹ (Keller et al. 2012). The situation is more complex when considering soluble Si: while Ma and Takahashi (2002) found soluble Si depletion in 250-yr-old paddy fields in Japan, Caubet et al. (2020) observed an increase in CaCl₂-extracted Si in temperate,

aerobic, cultivated soils that developed on sedimentary rocks due to pH variations. Cultivation may increase the pedogenic silica pool that is related to the clay fraction (Vandevenne et al. 2015; Caubet et al. 2020; Keller et al. 2021).

2.2 Si status, an inherent and manageable soil property fully involved in soil pedogenesis

To evaluate soils, Dominati et al. (2010) defined the concept of natural capital. This natural capital is formed and maintained by supporting processes and is characterized by two main groups of properties: the inherent properties that are stable over decadal to century time scales and the manageable properties that may change on an infradecadal time scale (Figure 2). The Si status belonging to both categories depends on its form (Figure 2). The main procedures that are currently available to quantify the various pools of Si forms are summarized in Table 1. For the quantification of Si in minerals and plants, the procedure may take place in 2 steps: the first step consists of destroying the material and releasing Si in a solution, which is generally alkaline, and the second step consists of measuring the concentration of dissolved Si, generally by spectrophotometry. Other nondestructive methods are also available, such as MIRS or portable X-ray fluorescence (Table 2). For the analysis of phytoliths, the extraction procedures require the destruction of the matrix (plants or soils) and separation using heavy liquid flotation. While Si is involved in minerals that evolve over the long term (Rounsvell et al. 1999), the Si soluble pool may depend on agricultural management e.g., liming, crop type and therefore may evolve on a much shorter time scale with yet to be defined kinetics.

3. Cultural services

"Cultural services include all non-material ecosystem outputs that have symbolic, cultural or intellectual significance" (CICES, 2011). Phytolith records such as pollen records provide "scientific" service type benefits from the "Intellectual and experiential" class (Figure 2). Indeed, phytolith assemblages that are preserved from dissolution in paleosols containing hominin fossils or human artifacts such as stone tools, pottery, grinding stones, and hearths are now widely studied, as they help document the early history of the human lineage, cultural behaviors and practices, plant domestication and early agricultural and pastoral practices. Thanks to their recognizable shapes, some phytoliths allow the identification of certain plant taxa. They are particularly diagnostic of the Poaceae, Cyperaceae, Arecaceae, Commelinaceae, conifers, ferns, Musaceae, and Cucurbitaceae (Piperno, 2006; Eichhorn et al. 2010; Ball et al. 2016).

At paleoanthropological sites, phytoliths have helped to characterize the paleovegetation associated with some of the earliest hominins known to date (Figure 3) (Novello et al. 2017; WoldeGabriel et al. 2009) and have shown that the first bipedal human ancestors lived in savannah-covered landscapes, but their habitat was restricted to forested environments located along rivers, lakeshores or springs (Barboni et al. 2019). At Olduvai Gorge, a World Cultural Heritage archaeological site in Tanzania, phytoliths have helped document the paleoenvironmental context associated with the emergence of early cultural practices: hunting and stone tool use at Olduvai 1.8 million years ago may have occurred because freshwater springs attracted prey and carnivores that were easily hunted by Homo species hiding in easyto-climb palm trees. Phytoliths have also proven useful for documenting the beginning of crop domestication such as rice in China (Luo et al. 2016; Ma et al. 2016) and maize and squash in Central and South America (Lombardo et al. 2020; Piperno et al. 2009; Ranere et al. 2009), and the grinding of wild grasses in West Africa (Radomski and Neumann 2011) during the Holocene. Phytolith studies are also applied to identify and characterize agro-pastoral activities and economies (Ball et al. 2016; Roberts and Rosen 2009; Rosen and Weiner 1994). Although less reliable, phytolith assemblages trapped in dental calculus were tentatively used for documenting the paleodiet of australopithecines (Henry et al. 2012).

4. Regulation services

Regulation services include "all the ways in which ecosystems control or modify biotic or abiotic parameters that define the environment of people, i.e., all aspects of the 'ambient' environment". Here, we document that Si is involved in the "C sequestration" service (CICES 2011) (Figure 2). Indeed, Si weathering may help remove atmospheric CO₂. Soils are the main place where weathering takes place. At the geological scale, weathering links the Si and C cycles because the chemical alteration of silicates consumes CO₂ from the atmosphere and produces dissolved acid carbonate that is eventually deposited in the ocean as Ca or Mg carbonates by streams

(Krissansen-Totton and Catling 2020). The chemical reactions in soils (1) and in the ocean (2) can be respectively written as:

(1) $CaAl_2Si_2O_8 + 3H_2O + 2CO_2 \rightarrow Al_2SiO_2(OH)_2 + Ca^{2+} + 2HCO_3^{-}$ Anorthite Kaolinite

(2) $Ca^{2+} + 2HCO_3^{-} -> CO_2 + H_2O + CaCO_3$

Calcite

The budget of (1) and (2) shows that one mole of anorthite can pump one mole of CO_2 . Based on this principle, the application of powdered silicate rock on agricultural lands has been suggested to actively remove CO_2 from the atmosphere (Hartmann et al., 2013). Amann et al. (2020) conducted a one-year experiment on mesocosms using dunite rock containing 90% olivine. Based on Mg measurements, they found that the CO_2 capture was low compared to theoretical estimates, but they pointed out the release of potentially harmful metals such as Ni or Cr. This geoengineering experiment indicated that other silicates have to be tested before they are applied in the field.

Parr and Sullivan (2005) suggested that the phytoliths stored in the soil may also be a significant C sink. This principle implies that phytolith particles are not entirely made of Si, O and H but also contain impurities, including C, which, when sequestered during amorphous silica precipitation, may contribute to 10-37% of the long-term soil carbon accumulation rates. However, based on the critical examination of the techniques used for measuring phytolith carbon sequestration, referred below as Phyt C, and for global estimation, Santos and Alexandre (2017) concluded that Phyt C was not a major source of C sequestration. Hence, despite the abundant literature on the subject, the quantitative role of phytoliths in C sequestration remains speculative.

5. Provisioning services

Provisioning services include "all material and energetic outputs from ecosystems; they are tangible things that can be exchanged or traded, as well as consumed or used directly by people in manufacturing" (CICES, 2011). In terrestrial ecosystems, provisioning services mainly consist of the production of food, timber, fiber, water and fuel. Just as Si plays a role on the global scale in provisioning an essential nutrient to aquatic microorganisms such as diatoms, Si also plays a role in

providing services at the terrestrial scale if we consider crops as "material outputs". Hereafter, we show how Si benefits crops and how this benefit depends on the soil Si status and environmental stressors.

5.1 Si and nutrient uptake

Ma and Takahashi (2002) showed that Si had a positive effect on rice growth under phosphate deficiency stress. They attributed the effect of Si to the enhanced availability of internal P due to the reduced uptake of excess Fe and Mn. In addition, when P was supplied at a high concentration, a chlorosis effect on rice leaves was not observed in the presence of Si. However, the mechanisms involved were not clear. The role of Si in mobilizing P was shown in Arctic soils, where a positive correlation between P and Si availabilities was found (Shaller et al. 2019). A decrease in the Fe(II)-phosphate phase was found after Si addition, indicating a mobilization of P from the mineral phase. Adsorption of both silicic acid and phosphate ions on the soil depended on the pH (Hingston et al. 1972; Obihara et al. 1972), but while the maximum Si adsorption peaked at a pH of approximately 8-9, the adsorption of P decreased when the pH increased. If the level of adsorbed phosphate was very low in neutral and alkaline soils, Si adsorbed and displaced P in solution, leading to its uptake by plants (Obihara et al. 1972). Iron III oxides and hydroxides were important sinks and regulators of dissolved Si and phosphate (Sigg and Stumm 1980). These results on soils have been confirmed in plants with evidence of the effect of Si on the P uptake and plant growth in aquatic plants (Schaller et al. 2012) and grasses (Neu et al. 2017). Other experiments, which applied different combinations of Si and P rates, showed that increases in rice yield were not straightforward (Li et al. 2020). Crusciol et al. (2015) showed that the application of silicate and phosphogypsum on Brazilian upland rice affected the number of panicles per m² but not the weight of 1000 grains. More research is required to decipher the complex interaction between Si and P in soils and plants (Matichenkov et al. 2017; Haynes and Zhou 2018). The effect of Si on N nutrition remains poorly understood; for example, Detmann et al. (2012) showed an increase in yield and in harvest index (grain/total biomass ratio) but not in grain N. The availability of other nutrients, such as K and Fe, was found to be positively affected by Si (Tubana and Heckman 2015; Liang et al. 2016).

5.2 Si and abiotic stress

The benefits of silicon on plants that are subjected to drought have been observed for many crops, including rice, sorghum, wheat, and maize (Haynes 2017). Chen et al. (2018) suggested several possible mechanisms at the root level: Si could block reactive oxygen species that inhibit the activity of aquaporins, which are proteins that promote the passage of water molecules; Si could improve the accumulation of soluble substances e.g. sugars and amino acids in xylem sap by osmoregulation; and finally, Si could adjust the growth of the roots and increase the root/stem ratio, which, combined with the improvement in the aquaporins' efficiency and the osmotic motive force, could contribute to the improvement in the hydraulic conductance of the roots. Meunier et al. (2017) showed that silicon attenuated the effects of drought by reinforcing the structure of leaves through preferential phytolith accumulation above the veins. Amorphous silica in the soil may also reduce plant stress by increasing the soil water holding capacity and plant water availability (Schaller et al. 2020; Kuhla et al. 2021). In addition to water stress, the beneficial effect of Si has also been documented for other abiotic stressors such as an excess of salt or UV radiation (Liang et al. 2015).

5.3 Si and soil contamination

Si addition can also be beneficial when organic or inorganic soil contamination induces deleterious effects on crops including rice, corn, and wheat (Tunaba and Heckman 2015; Haynes 2017; Rizwan et al. 2016). The mitigation processes, though still poorly understood, may occur in the soil and at the root or shoot levels. For instance, Rizwan et al. (2016) suggested that in durum wheat, Si reduced the rootshoot translocation of Cd by armoring the root surface with Si. Greger et al. (2016) showed that Si downregulated heavy metal ATPases, which regulated Cd transport from the roots to the shoots in wheat. Silicic acid also decreased the As concentration in rice shoots because the arsenide transported in the roots was shown to share the same high affinity transporter as Si and thus competed with it, indicating that sufficiently available Si in soil would be efficient at reducing As accumulation in rice shoots (Ma et al. 2008). Si can also reduce the transport of Cu from roots to shoots in grasses (Keller et al. 2015; Viera Filho and Monteiro 2020; Collin et al. 2014). Si mitigation may also play a role in the shoots. For instance, Al can be sequestered in phytoliths by codeposition with Si (Hodson and Evans 2020). Delplace et al. (2020) also showed that sequestration of metals in phytoliths may occur for As, Cu, Mn and

Pb in reeds. A more comprehensive review on the silicon-mediated alleviation of heavy metal toxicity in plants can be found in Adrees et al. (2015).

5.4 Si and biotic stress

Si has been shown to be beneficial for many crops such as rice, wheat, sugarcane, soybean corn, and tomato that are affected by herbivores, insects, and fungi (Liang et al. 2015; Rodrigues and Datnoff 2015). In Japan, the effects of Si on rice were discovered at the beginning of the 20th century, with studies showing that Si-rich rice leaves were less infected by blast, a fungal disease, than were Si-poor leaves. However, there is no consensus for explaining the role of Si in plants under biotic stress. Two scenarios are plausible. One scenario involves a physical barrier where a silica layer formed in the cell wall enhances a plant's resistance to biotic stress. According to Coskun et al. (2019), amorphous Si deposited in the apoplast interferes with effectors in case of a parasitic attack, or in the case of abiotic stress, it fortifies barriers around the vasculature, thus preventing the transport of toxicants into the shoots. The second scenario involves a biochemical barrier where Si could stimulate the expression of genes involved in the production of defense enzymes e.g. polyphenol oxidase, glucanase, peroxidase, phenylalanine ammonia-lyase, antimicrobial compounds e.g. phenolic, flavonoids, phytoalexins, pathogenesis-related proteins in plants, or substances that play a role in the signal transduction pathways involved in immune defenses e.g., salicylic acid, jasmonic acid, ethylene; cytokinin (Wang et al. 2017; Markovich et al. 2017).

6. Management of ecosystem services

Si management may improve the regulating and provisioning services not only through better crop management and the application of Si fertilizer to soil but also by foliar application in the field.

6.1 Crop and soil management

Si spreading on soil is directly involved in regulation (and maintenance) services. Indeed, the results from a long-term experiment in Germany showed that approximately 43-60% of Si exports could be prevented by crop straw recycling (Puppe

et al. 2021). Si addition may simply consist of keeping organic residues that are rich in Si in the field, as was done in traditional agriculture for centuries but has been largely abandoned in recent decades in "conventional" practices where removal of residues is common. Song et al. (2021) studied a 39-year-old paddy field amended by a long-term straw return. They showed that the bioavailable Si and rice yield significantly increased when compared to NPK fertilization alone by 29.9 % to 61.6 % and 14.5 % to 23.6 %, respectively. Other plant materials, such as silica-rich biochars, have also been shown to be potential Si fertilizers (Nguyen et al. 2021).

Si fertilization may also consist of applying silicates that have kinetic properties that are compatible with the growth duration of crops, such as silicate materials originating from geological sites, or from industrial byproducts (Liang et al. 2015). For instance, the application of Si as diatomite containing amorphous silica, in a pot experiment using soil from south Indian paddy (rice) fields, led to an increase in rice grain yield in acidic soils using the recommended doses of N, P, and K (Sandhya et al. 2018). Hence, Si may be a limiting element for crops, and Si fertilizer may be recommended for rice in certain soil types. Acidic soils that are depleted in nutrients and silica are common in tropical regions where heavy rainfalls and high temperatures lead to intense weathering (Cornelis and Delvaux 2016).

Except for some slags that may contain high levels of metal contaminants, silicate fertilizers are considered to be environmentally friendly and, depending on their cost, may constitute a positive investment. The cost-benefit calculations on integrating calcium silicates as fertilizers in agricultural practices have been estimated to provide savings of approximately \$74 ha yr⁻¹ assuming a yield increase of 12% for rice production in Florida, USA (Alvarez and Datnoff 2001). Because Si application may eliminate the need for fungicides and pesticides in managing rice diseases and may reduce the application of other fertilizers and lime, extra savings of \$50–272 ha yr⁻¹ were estimated (Alvarez and Datnoff 2001). Cost-benefit calculations should require more studies that consider the large variety of crops and soils around the world and the cost and availability of Si fertilizers that are produced from byproducts or specifically formulated.

The fraction of soil Si that is available to plants can be empirically measured in an extracting solution mixed with soil (Table 1). If a positive correlation is obtained between soluble Si extracted by the procedure and the Si concentration in plants growing in the same soil, then the procedure can be used as a proxy for the measurement of plant bioavailable Si (referred below as PAS). Owing to the importance of quantifying bioavailable Si, many extractants have been proposed (Table 1), as well as the associated thresholds to identify critical levels of bioavailable Si. If the PAS is below the critical level, Si fertilization may be required. Based on 200 soil samples from rice fields in southern India and Si extraction using a 0.01 M CaCl₂ solution and 0.5 M acetate-acetic acid, Meunier et al. (2018) estimated that between 38 % and 88 % of the soils were below critical levels and could be considered depleted in PAS. In China, a chronological study from 1990 to 2010 on rice field soils showed a significant decline of 14.1 % in PAS values using 1 M acetic acid- sodium acetate buffer at pH 4 (Yang et al. 2021). In French soils, Caubet et al. (2020) showed that 4 % of the soils cultivated for wheat are below the critical level of 20 mg kg⁻¹ using a 0.01 M CaCl₂ and could be considered deficient in PAS and would benefit from Si addition.

6.2 Foliar application

Compared to Si application on soil, relatively few studies document the beneficial effects of foliar Si on plants, and the underlying mechanisms are rarely discussed. Among these, Guevel et al. (2007), who studied powdery mildew on wheat, showed that both root and foliar Si application were beneficial, but foliar application was less effective. They concluded that foliar application did not lead to a significant absorption of Si by the plant and that the prophylactic effect was not directly attributable to Si but to a deleterious effect that the product deposited on the leaf had on the fungus. In their review on foliar Si application, Puppe and Sommer (2018) showed numerous examples of the positive effects of foliar Si application on mitigating the effect of diseases on crops, but in the absence of biotic or abiotic stress, the effects were not systematically observed. Foliar application of Si nanoparticles has also been tested and shown to be beneficial, especially for mitigating the effect of Cd (Wang et al. 2015). Foliar application deserves more research, especially since it may be used instead of synthetic chemical compounds such as pesticides, whose deleterious effects on the environment and health are recognized.

7. Conclusion

We have shown that Si, despite its status as a nonessential element, is an important component of both terrestrial and aquatic ecosystems. In terms of soil

capital, Si is both an inherent property e.g., phytoliths, total Si, Si minerals and a manageable property e.g. PAS. Under its available form, Si is beneficial to plants such as commercial crops and fibers and therefore contributes to provisioning services. In the form of phytoliths, Si becomes a record of the past and therefore contributes to cultural services. Si also contributes to climate regulation through silicate weathering. This makes Si an important natural element to consider when defining soil indicators for ecosystem services, and its status needs to be assessed in addition to those of other soil properties. Since long-term cultivation could deplete the soil to a point where a PAS deficiency can be recorded, it has become a challenge to maintain high levels of bioavailable Si in cultivated fields. The costs and benefits of Si application in agricultural management are, however, still poorly documented.

Acknowledgements

The authors are grateful to Lina Höhener for the drawing of figure 1.

References

Adhikari K, Hartemink AE (2016) Linking soils to ecosystem services-A global review. Geoderma 262, 101-111. https://doi.org/10.1016/j.geoderma.2015.08.009

Adrees M, Ali SA, Rizwan M, Zia-ur-Rehman M, Ibrahim M, Abbas F, Farid M, Qayyum MF, Irshad MK (2015) Mechanisms of silicon-mediated alleviation of heavy metal toxicity: a review. Ecotox Environm Safety 119, 186-197. https://doi.org/10.1007/s11356-015-5305-x

Aghamiri R., Schwartzman DW (2002) Weathering rates of bedrock by lichens: a mini watershed study. Chem. Geol. 188, 249–259. https://doi.org/10.1016/S0009-2541(02)00105-5

Alexandre A, Meunier JD, Colin F, Koud JM (1997) Plant impact on the biogeochemical cycle of silicon and related weathering processes, Geochim. et Cosmochim. Acta, 61, 677-682. https://doi.org/10.1016/S0016-7037(97)00001-X

Alvarez J, Datnoff LE (2005) The economic potential of silicon for integrated management and sustainable rice production. Crop Protection 20, 43-48. https://doi.org/10.1016/S0261-2194(00)00051-X

Amann T, Hartmann J, Struyf E, de Oliveira Garcia W, Fischer EK, Janssens I, Meire P, Schoelynck J (2020) Enhanced weathering and related element fluxes – a cropland mesocosm approach. Biogeosciences 17, 103-119. https://doi.org/10.5194/bg-17-103-2020

Aoki Y, Hoshino M, Matsubara T (2007) Silica and testate amoebae in a soil under pineoak forest. Geoderma 142, 29-35. https://doi.org/10.1016/j.geoderma.2007.07.009

Aureli F, Ciprotti M, D'Amato M, do Nascimento da Silva E, Nisi S, Passeri D, Sorbo A, Raggi A, Rossi M, Cubadda F (2020) Determination of total silicon and SiO2 particles using an ICP-MS based analytical platform for toxicokinetic studies of synthetic amorphous silica. Nanomaterials, 10, 888; doi:10.3390/nano10050888. DOI: 10.3390/nano10050888

Ball T, Chandler-Ezell K, Dickau R, Duncan N., Hart TC, Iriarte J, Lentfer C, Logan A, Lu H, Madella M, Pearsall DM, Piperno DR, R A, Vrydagh L, Weisskopf A, Zhang J (2016)

Phytoliths as a tool for investigations of agricultural origins and dispersals around the world. Journal of Archaeological Science 68, 32–45. https://doi.org/10.1016/j.jas.2015.08.010

Banfield, J.F., Barker, W.W., Welch, S.A., Taunton, A., 1999. Biological impact on mineral dissolution: application of the lichen model to understanding mineral weathering in the rhizosphere. Proceedings of the National Academy of Sciences of the United States of America 96, 3404–3411. https://doi.org/10.1073/pnas.96.7.3404

Barao L, Vandevenne F, Clymans W, Frings P, Ragueneau O, Meire P, V_Conley DJ, Struyf E (2015) Alkaline-extractable silicon from land to ocean: A challenge for biogenic silicon determination. Limnology and Oceanography: Methods 13(7), 329-344. https://lup.lub.lu.se/record/7984984

Barboni D (2014) Vegetation of Northern Tanzania during the Plio-Pleistocene: A synthesis of the paleobotanical evidences from Laetoli, Olduvai, and Peninj hominin sites. Quaternary Int. 322-323, 264-276. https://doi.org/10.1016/j.quaint.2014.01.016

Bityutskii N, Kaidun P, Yakkonen K (2016) Earthworns can increase mobility and bioavailabnility of silicon in soil. Soil Biol. Biochem. 99, 47-53. https://doi.org/10.1016/j.soilbio.2016.04.022

Brehm U, Gorbushima A, Mottershead D (2005) The role of microoganisms and biofilms in the breakdown and dissolution of quartz and glass. Pal. Pal. Pal. 219, 117-129. https://doi.org/10.1016/j.palaeo.2004.10.017

Bünemann EK, Bongiorno G, Bai, Creamer RE, De Deyn G, de Goede R, Fleskens L, Geissen V, Kuyper TW, Mäder P, Pulleman M, Sukkel W, van Groenigen JW, Brussaard L, (2018) Soil quality – A critical review. Soil Biology and Biochemistry, 120: 105-125. doi.org/10.1016/j.soilbio.2018.01.030

Carey JC, Fulweiler RW (2012) The Terrestrial Silica Pump. PLoS ONE 7(12): e52932. doi:10.1371/journal.pone.0052932

Caubet M, Cornu S, Saby NPA, Meunier JD (2020) Agriculture increases the bioavailability of silicon, a beneficial element for crop, in temperate soils. Scientific Reports, 10, Article number: 19999. https://doi.org/10.1038/s41598-020-77059-1

Chen J, Blume, HP, Beyer, L (2000) Weathering of rocks induced by lichen colonization — a review. Catena 39, 121–14. https://doi.org/10.1016/S0341-8162(99)00085-5

CICES (2011) Common International Classification of Ecosystem Services: 2011 Update. Paper prepared for discussion at the expert meeting on ecosystem accounts organised by the UNSD, the EEA and the World Bank, London, December 2011(Contract No:No. EEA/BSS/07/007). The University of Nottingham.

Clymans W, Struyf E, Govers G, Vandevenne F, and Conley DJ (2011) Anthropogenic impact on amorphous silica pools in temperate soils. Biogeosciences, 8, 2281–2293, 2011. https://doi.org/10.5194/bg-8-2281-2011

Collin B, Doelsch E, Keller C, Cazevieille P, Tella M, Chaurand P, Panfili F, Hazemann JL, Meunier JD (2014) Evidence of sulfur-bound reduced copper in bamboo exposed to high silicon and copper concentrations. Environm. Pollution 187, 22-30. https://doi.org/10.1016/j.envpol.2013.12.024

Corbineau R, Reyerson PE, Alexandre A, Santos GM (2013) Towards producing pure phytolith concentrates from plants that are suitable for carbon isotopic analysis. Review of Palaeobotany and Palynology 197 (2013) 179–185. http://dx.doi.org/10.1016/j.revpalbo.2013.06.001

Cornelis JT, Delvaux B, Giorg RB, Lucas Y, Ranger J, Opfergelt S (2011) Tracing the origin of dissolved silicon transferred from various soil-plant systems towards rivers: a review. Biogeosciences, 8, 89–112, 2011. https://doi.org/10.5194/bg-8-89-2011

Cornelis JT, Delvaux B (2016) Soil processes drive the biological silicon feedback loop. Functional Ecology 2016, 30, 1298–1310. https://doi.org/10.1111/1365-2435.12704 Coskun D, Deshmukh R, Sonah H, Menzies JG, Reynolds O, Ma JF, Kronzucker HJ, Belanger RB (2019) The controversies of silicon's role in plant biology-Tansley review. New Phytologist 221: 67–85. https://doi.org/10.1111/nph.15343

Costanza R, d'Arge R, DeGroot R, Farber S, Grasso M, Hannon B, Limburg K, Naeem S, O'Neill RV, Paruelo J, Raskin RG, Sutton P, vandenBelt M 1(997) The value of the world's ecosystem services and natural capital. Nature 387 (6630), 253–260. https://doi.org/10.1038/387253a0

Crusciol CAC, Artigiani ACCA, Arf O, Carmeis Filho ACAC, Soratto RP, Nascente AS, Alvarez RCF (2015) Soil fertility, plant nutrition, and grain yield of upland rice affected by surface application of lime, silicate, and phosphogypsum in a tropical no-till system. Catena 137, 87-99. https://doi.org/10.1016/j.catena.2015.09.009

Daghino S, Turci F, Tomatis M, Girlanda M, Fubini B, Perotto S (2009) Weathering of chrysotile asbestos by the serpentine rock-inhabiting fungus *Verticillium leptobactrum*. FEMS Microbniol Ecol 69, 132-141. https://doi.org/10.1111/j.1574-6941.2009.00695.x

Daily GC, Matson PA, Vitousek PM (1997) Ecosystem services supplied by soil. In: Daily GC (Ed.), Nature Services: Societal Dependence on Natural Ecosystems. Island Press, Washington DC, pp. 113–132.

De Souza PF, Santos D, de Carvalho GGA, Nunes, LC, Gomes MD, Guerra MBB, Krug FJ (2013) Determination of silicon in plant materials by laser-induced breakdown spectroscopy. Spectrochimica Acta part B Atomic Spectroscopy 83-84, 61-65. DOI:10.1016/j.sab.2013.02.004

Detmann KC, L, Araujo WJ, Martins SCV, Sanglard LMVP, Reis JV, Detmann E, Rodrigues FA, Nunes-Nesi A, Fernie AR, DaMatta FM (2012)Silicon nutrition increases grain yield, which, in turn, exerts a feed-forward stimulation of photosynthetic rates via enhanced mesophyll conductance and alters primary metabolism in rice. New Phytologist 196, 752–762.doi: 10.1111/j.1469-8137.2012.04299.x

Delplace G, Schreck E, Pokrovsky OS, Zouiten C, Blondet I, Darrozes J, Viers J (2020) Accumulation of heavy metals in phytoliths from reeds growing on mining environments in Southern Europe. STOTEN 712, 135595. https://doi.org/10.1016/j.scitotenv.2019.135595

Dominati E, Patterson M, Mackay A (2010) A framework for classifying and quantifying the natural capital and ecosystem services of soils. Ecological Economics 69, 1858-1868. oi:10.1016/j.ecolecon.2010.05.002

De Saussure NT (1804) Recherches chimiques sur la végétation. Chez la veuve Nyon, Paris.

Desplanques V, Cary L, Mouret JC, Trolard F, Bourrié G, Grauby O, Meunier JD (2006) Silicon transfers in a rice field in Camargue (France). Journal of Geochemical Exploration, 88, 190-193. https://doi.org/10.1016/j.gexplo.2005.08.036

Drobnik T, Greiner L, Keller A, Grêt-Regamey A (2018) Soil quality indicators – From soil functions to ecosystem services. Ecological Indicators 94, 151–169. https://doi.org/10.1016/j.ecolind.2018.06.052

Eichhorn B, Neumann K, Garnier A (2010) Seed phytoliths in West African Commelinaceae and their potential for palaeoecological studies. Palaeogeography, Palaeoclimatology, Palaeoecology 298, 300–310. https://doi.org/10.1016/j.palaeo.2010.10.004

Elliott CL, Snyder GH (1991) Autoclave-induced digestion for the colorimetric determination of silicon in rice straw. J. Agric. Food Chem. 39, 1118-1119. DOI: 10.1021/jf00006a024.

Fichhof WH, de A. Silva R, de Oliveira LS, da Silva RM (2018) Management of Biostimulant and Silicon in Mineral Nutrition and Quality of Cotton Fiber. Journal of Agricultural Science Vol 10 No. 10, 476-484. https://doi.org/10.5539/jas.v10n10p476

Fraysse F, Pokrovsky OS, Schott J, Meunier JD (2009) Surface Chemistry and reactivity of plant phytoltihs in aqueous solutions. Chemical Geology, 258, 197-206. https://doi.org/10.1016/j.chemgeo.2008.10.003

Fraysse F, Pokrovsky OS, Meunier JD (2010) Experimental study of terrestrial plant litter interaction with aqueous solutions. Geochimica et Cosmochimica Acta., 74, 70-84. https://doi.org/10.1016/j.gca.2009.09.002

Germanique JC (1994) Major, trace and rare-earth elements in fourteen GSL reference Samples. Determination by x-ray fluorescence spectrometry and inductively coupled Plasma optical emission spectrometry. Geostand. Newslett. 18, 91-100.

Greger M, Kabir AH, Landberg T, Maity PJ, Lindberg S (2016) Silicate reduces cadmium uptake into cells of wheat. Env. Poll.211, 90-97. https://doi.org/10.1016/j.envpol.2015.12.027

Guevel MH, Menzies JG, Bélanger RR (2007) Effect of root and foliar applications of soluble silicon on powdery mildew control and growth of wheat plants. Eur J Plant Pathol. 119:429–436. https://doi.org/10.1007/s10658-007-9181-1

Guntzer F, Keller C, Meunier JD (2010) Determination of the silicon concentration in plant material using Tiron extraction. New Phytologist 188, 902-906. DOI: 10.1111/j.1469-8137.2010.03416.x

Guntzer F, Keller C, Meunier JD (2012) Benefits of plan silicon for crops : a review. Agronomy Sust. Developm. 32, 201-213. https://doi.org/10.1007/s13593-011-0039-8

Guntzer F, Keller C, Poulton PR, McGrath SP, Meunier JD (2012b) Long-term removal of wheat straw decreases soil amorphous silica at Broadbalk, Rothamsted. Plant and Soil 352, 173-184. https://doi.org/10.1007/s13593-011-0039-8

Hartmann J, West J, Renforth P, Köhler P, De La Rocha CL, Wolf-Gladrow DA, Dürr HH, Scheffran J (2013) Enhanced chemical weathering as a geoengineering strategy to reduce atmospheric carbon dioxide, supply nutrients, and mitigate ocean acidification. Rev. Geophys. 51, 113–149. Doi :10.1002/rog.20004

Haynes RJ (2017) Significance and role of Si in crop production. Advances in Agronomy Volume 146, 83-166. http://dx.doi.org/10.1016/bs.agron.2017.06.001

Haynes RJ, Zhou YF (2018) Competitive and non-competitive adsorption of silicate and phosphate by two Si-deficient soils and their effects on P and Si extractability. Soil Sci. Plant Nutr. 64, 535–541. https://doi.org/10.1080/00380768.2018.1473008

Haysom MBC, Chapman LS (1975) Some aspects of the calcium silicate trials at Mackay. Proc Qld Soc Sugar Cane Technol 42:117–122

Henderson MEK, Duff RB (1963) The release of metallic and silicate ions from minerals, rocks, and soils by fungal activity. J Soil Science 14, 236-246. https://doi.org/10.1111/j.1365-2389.1963.tb00949.x

Henry AG, Ungar PS, Passey BH, Spnheimer M, Rossouw L, Bamford M, Sandberg P, de Ruiter DJ, Berger L (2012) The diet of *Australopithecus sediba*. Nature 487, 90-93. https://doi.org/10.1038/nature11185

Hingston FJ, Posner AM, Quirk JP (1972) Anion adsorption by goethite and gibbsite. I The role of the proton in determining adsorption envelopes. J Soil Sci 23:177–192. https://doi.org/10.1111/j.1365-2389.1972.tb01652.x

Hodson MJ, Evans DE (2020) Aluminium/silicon interactions in higher plants-an update. J Exp Bot 71, 6719-6729. https://doi.org/10.1093/jxb/eraa024

Jouquet P, Jamoteau F, Majumdar S, Podwojewski P, Nagabovanalli P, Caner L, Barboni D, Meunier JD (2020) The distribution of silicon in soil is influenced by termite bioturbation in South Indian forest soils. Geoderma. https://doi.org/10.1016/j.groderma.2020.114362. Kameník J, Mizera J, Řanda, Z (2013) Chemical composition of plant silica phytoliths. Environ Chem Lett 11, 189–195. <u>https://doi.org/10.1007/s10311-012-0396-9</u>

Keller C, Guntzer F, Barboni D, Labreuche J, Meunier JD (2012) Impact of agriculture on the Si biogeochemical cycle: input from phytolith studies. Comptes Rendus Geoscience 344, 739-746. https://doi.org/10.1016/j.crte.2012.10.004

Keller C, Rizwan M, Davidian JC, Pokrovsky OS, Bovet N, Chaurand P, Meunier JD (2015) Effect of silicon on wheat seedlings (*Triticum turgidum L.*) grown in hydroponics and exposed to 0 to 30µM Cu. Planta 241, 847-860. DOI: 10.1007/s00425-014-2220-1

Keller C, Rizwan M, Meunier JD (2021) Are clay minerals a significant source of Si for crops? A comparison of amorphous silica and the roles of the minerals type and pH. Silicon. https://doi.org/10.1007/s12633-020-00877-5

Kendrick KJ, Graham RC (2004) Pedogenic silica accumulation in chronosequence soils, southern California. Soil Science Society of America Journal 68: 1295–1303. DOI:10.2136/sssaj2004.1295

Klotzbücher A, Klotzbücher T, Jahn R, Xuan LD, Cuong LQ, Chien HV, Hinrichs M, Sann C, Vetterlein D (2017) Effects of Si fertilization on Si in soil solution, Si uptake by rice, and resistance of rice to biotic stresses in Southern Vietnam. Paddy Water Environ. doi 10.1007/s10333-017-0610-2

Korndorfer GH, Snyder GH, Ulloa M, Datnoff LE (2001) Calibration of soil and plant silicon for rice production. J Plant Nutr 24:1071–1084. https://doi.org/10.1081/PLN-100103804

Krissansen-Totton J, Catling DC (2020) A coupled carbon-silicon cycle model over Earth history: Reverse weathering as a possible explanation of a warm mid-Proterozoic climate. EPSL 537, 116181. https://doi.org/10.1016/j.epsl.2020.116181

Kuhla J, Pausch J, Schaller J (2021) Effect on soil water availability, rather than silicon uptake by plants, explains the beneficial effect of silicon on rice during drought. Plant, Cell & Environment 44 (10), 3336-3346. https://doi.org/10.1111/pce.14155.

Landré A, Saby NPA, Barthès BG, Ratié C, Guerin A, Etayo A, Minasny B, Bardy M, Meunier JD, Cornu S (2018) Prediction of total silicon concentrations in French soils using pedotransfer functions from mid-infrared spectrum and pedological attributes. Geoderma 331, 70-80. DOI:10.1016/j.geoderma.2018.06.007

Lentfer CJ, Boyd WE (1998) A comparison of three methods for the extraction of phytoliths from sediments. Journal of Archaeological Science 25, 1159–1183. https://doi.org/10.1006/jasc.1998.0286

Li Z, Cornelis JT, Song Z, Wang X, Delvaux B (2020) Combined silicon-phosphorus fertilization affects the biomass and phytolith stock of rice plants. Front. Plant Sci. 11:67. https://doi.org/10.3389/fpls.2020.00067

Liang Y, Nikolic M, Bélanger R, Gong H, Song A (2015) Silicon in Agriculture. Springer Netherlands.

Luo W, Yang Y, Yao L, Chen Z, Li J, Yin C, Zhang J, Lin L, Gan H (2016) Phytolith records of rice agriculture during the Middle Neolithic in the middle reaches of Huai River region, China. Quaternary International 426, 133-40. https://doi.org/10.1016/j.quaint.2016.03.010

Lombardo U, Iriarte J, Hilbert L, Ruiz-Pérez J, Capriles JM, Veit H (2020) Early Holocene Crop Cultivation and Landscape Modification in Amazonia. Nature 581, no 7807, 190-93. https://doi.org/10.1038/s41586-020-2162-7

Luyckx M, Hausman J-F, Lutts S, Guerriero G (2017) Silicon and Plants: Current Knowledge and Technological Perspectives. Front. Plant Sci. 8:411. doi: 10.3389/fpls.2017.00411. https://doi.org/10.3389/fpls.2017.00411

Ma JF, Takahashi E (2002) Soil, fertilizer, and plant silicon research in Japan. Elsevier, Amsterdam, 296p.

Ma JF, Yamaji N, Mitani N, Xu XY, Su YH, McGrath SP, Zhao FJ (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. Proceeding National Academy of Sciences 105, 9931-9935. https://doi.org/10.1073/pnas.0802361105

Ma Y, Yang X, Huan X, Wang W, Ma Z, Li Z, Sun G, Jiang L, Zhuang Y, Lu H (2016) Rice bulliform phytoliths reveal the process of rice domestication in the Neolithic lower Yangtze River region. Quaternary Int. 426, 126-132, http://dx.doi.org/10.1016/j.quaint.2016.02.030.

Markovich O, Steiner E, Kouril S, Tarkowski P, Aharoni A, Elbaum R (2017) Silicon promotes cytokinin biosynthesis and delays senescence in Arabidopsis and sorghum. Plant, Cell & Environment 40: 1189–1196. https://doi.org/10.1111/pce.12913

Masson P, Dauthieu M, Trolard F, Denaix (2007) Application of direct solid analysis of plant samples by electrothermal vaporization-inductively coupled plasma atomic emission spectrometry: Determination of Cd and Si for environmental purposes. Spectrochimica Acta Part B 62, 224–230. doi:10.1016/j.sab.2007.01.004

Matichenkov VV, Bocharnikova EA, Pakhnenko EP, Khomoakov DM (2017) Effect of Si-rich substances on phosphorus adsorption by sandy soils. Environ Sci Pollut Res 24, 24311-24317. https://doi.org/10.1007/s11356-017-0051-x

Meunier JD, Keller C, Guntzer F, Riotte J, Braun JJ, Anupama K (2014) Assessment of the 1%NaCO3 technique to quantify the phytolith pool. Geoderma 216, 30-35. https://doi.org/10.1016/j.geoderma.2013.10.014

Meunier JD, Barboni D, Anwar-ul-Haq M, Levard C, Chaurand P, Vidal V, Grauby O, Huc R, Laffont-Schwob I, Rabier J, Keller C (2017) Effect of phytoliths for mitigating water stress in durum wheat. New Phytologist 215, 229-239. 71. https://doi.org/10.1111/nph.14554

Meunier JD, Sandhya K, Prakash NB, Borschneck D, Dussouillez P (2018) pH as a proxy for estimating plant-available Si? A case study in rice fields in Karnataka (South India). Plant and Soil 432, 143-155. https://doi.org/10.1007/s11104-018-3758-7

Millenium Ecosystem Assessment (2005) Ecosystems and Human Well-being: Synthesis. Island Press, Washington, DC.

Monger HC, Kelly EF (2001) Silica minerals In Soil mineralogy with Environmental applications. Dixon JB, Schulze GD, eds. SSA Book Series No.7, 611-636.

Neaman A, Chorover J, Brantley SL (2006) Effects of organic ligands on granite dissolution in batch experiments at pH 6. Am J of Science 306, 451-473. https://doi.org/10.2475/06.2006.03

Neu S, Schaller J, Dudel EG (2017) Silicon availability modifies nutrient use efficiency and content, C:N:P stoichiometry, and productivity of winter wheat (*Triticum aestivum* L.). Sci Rep 7:40829. https://doi.org/10.1038/srep40829

Nguyen MN (2021) Potential use of silica-rich biochar for the formulation of adaptively controlled release. Journal of Cleaner Production. doi.org/10.1016/j.jclepro.2021.127188

Nguyen MN, Picardal F, Dultz S, Dam TTN, Nguyen AV, Nguyen KM (2017) Silicic acid as a dispersibility enhancer in a Fe-oxide-rich kaolinitic soil clay. Geoderma 286, 8–14. https://doi.org/10.1016/j.geoderma.2016.10029

Novello A, Barboni D, Sylvestre F, Lebatard AE, Paillès C, Bourlès DL, Likius A, Mackaye HT, Vignaud P, Brunet M (2017) Phytoliths indicate significant arboreal cover at Sahelanthropus type locality TM266 in northern Chad and a decrease in later sites. Journal of Human Evolution 106, 66-83. https://doi.org/10.1016/j.jhevol.2017.01.009

Obihara CH, Russell EW (1972) Specific adsorption of silicate and phosphate by soils. J Soil Sci 23:105–117. https://doi.org/10.1111/j.1365-2389.1972.tb01646.x

Parr JF (2002) A comparison of heavy liquid floatation and microwave digestion techniques for the extraction of fossil phytoliths from sediments. Review of Palaeobotany and Palynology 120, 315-336. https://doi.org/10.1016/S0034-6667(01)00138-5

Parr JF, Lentfer CJ, Boyd WE (2001) A comparative analysis of wet and dry ashing techniques for the extraction of phytoliths from plant material. Journal of Archaeological Science 28, 875–886. doi:10.1006/jasc.2000.0623

Parr JF, Sullivan LA (2005) Soil sequestration in phytoliths. Soil Biology and Biochemistry 37, 117-124. https://doi.org/10.1016/j.soilbio.2004.06.013

Piperno DR (2006) Phytoliths: A Comprehensive Guide for Archaeologists and Paleoecologists. Rowman Altamira.

Piperno DR (2009) « Identifying crop plants with phytoliths (and starch grains) in Central and South America: A review and an update of the evidence ». Quaternary International 193,146-59. https://doi.org/10.1016/j.quaint.2007.11.011.

Prabha S, Durgalakshmi D, Rajendran S, Lichtfouse E (2021) Plant-derived silica nanoparticles and composites for biosensors, bioimaging, drug delivery and supercapacitors: a review. Environ Chem Lett 19, 1667–1691. https://doi.org/10.1007/s10311-020-01123-5

Puppe D, Kaczorek D, Schaller J, Barkusky, Sommer M (2021) Crop straw recycling prevents anthropogenic desilication of agricultural soil–plant systems in the temperate zone – Results from a long-term field experiment in NE Germany. Geoderma 403 (2021) 115187. doi.org/10.1016/j.geoderma.2021.115187

Puppe D, Sommer, M (2018) Chapter One - Experiments, Uptake Mechanisms, and Functioning of Silicon Foliar Fertilization—A Review Focusing on Maize, Rice, and Wheat. Advances in Agronomy Vol. 152,1-49. https://doi.org/10.1016/bs.agron.2018.07.003

Radomski KU, Neumann K (2011) Grasses and grinding stones: inflorescence phytoliths from modern West African Poaceae and archaeological stone artefacts. In: Fahmy AG, Kahlheber S, D'Andrea AC, editors. Windows on the African past. Current approaches to African archaeobotany. Frankfurt: Africa Magna Verlag. pp. 153–166.

Ranere AJ, Piperno DR, Holst I, Dickau R, Iriarte J (2009) The cultural and chronological context of early Holocene maize and squash domestication in the Central Balsas River Valley, Mexico. Proceedings National Academy Sciences 106, 5014–5018. https://doi.org/10.1073/pnas.0812590106

Reiniger S, Ramsey M, Hartley (2012) Rapid and accurate analyses of silicon and phosphorus in plants using a portable X-ray fluorescence spectrometer. New Phytologist 195, 699-706. doi: 10.1111/j.1469-8137.2012.04179.x

Rhodes C, Bingham A, Heard AM, Hewitt J, Lynch J, Waite R, Bell MD (2017) Diatoms to human uses: linking nitrogen deposition, aquatic eutrophication, and ecosystem services. Ecosphere 8(7):e01858. 10.1002/ecs2.1858

Roberts N, Rosen A (2009) Diversity and complexity in early farming communities of southwest Asia: new insights into the economic and environmental basis of Neolithic Çatalhöyük . Current Anthropology 50, no 3, 393-402. DOI:10.1086/598606

Rodriguez FA, Datnoff LE (2015) Silicon and plant diseases. Springer International Publishing Switzerland.

Rosen A, Weiner S (1994) Identifying ancient irrigation: a new method using opaline phytoliths from emmer wheat. Journal of Archaeological Science 21, 125-32. DOI:10.1006/JASC.1994.1013

Rounsevell MDA, Evans SP, Bullock P (1999) Climate change and agricultural soils: impacts and adaptation. Clim Change 43(4): 683–709

Riotte J, Sandhya K, Prakash NB, Audry S, Zambardi T, Chmelef J, Buvaneshwari S, Meunier JD (2018) Origin of silica in rice plants and contribution of diatom Earth fertilization:

insights from isotopic Si mass balance in a paddy field. Plant and Soil, 423, 481–501. https://doi.org/10.1007/s11104-017-3535-z

Rizwan M, Meunier JD, Davidian JC, Pokrovsky OS, Bovet N, Keller C (2016) Effects of silicon on growth and physiology of wheat seedlings (*Triticum turgidum* L. cv. Claudio) under Cd stress: a hydroponic study, Environ Sci Pollut Res, 23, 1414-1427. https://doi.org/10.1007/s11356-015-5351-4

Saccone L, Conley DJ, Koning E, Sauer D, Sommer M, Kaczorek D, Blecker SW, Kelly EF (2007) Assessing the extraction and quantification of amorphous silica in soils of forest and grassland ecosystems. Eur. J. Soil Sci. 58, 1446–1459. DOI: 10.1111/j.1365-2389.2007.00949.x

Sachs J (1865) Handbuch der experimental physiologie des pflanzen. Leipzig: Verlag von Wilhelm Engelmann, p. 150.

Saito K, Yamamoto A, Sa T, Saigusa M (2005) Rapid, micro-methods to estimate plant silicon content by dilute hydrofluoric acid extraction and spectrometric molybdenum method. I. Silicon in rice plants and molybdenum yellow method. Soil Sci. Plant Nutr 51, 29-36. DOI: 10.1111/j.1747-0765.2005.tb00003.x

Sandhya K, Prakash NB, Meunier JD (2018) Diatomaceous earth as source of silicon on the growth and yield of rice in contrasted soils of Southern India. Journal of Soil Sci and Plant Nutr. 18, 344-360. http://dx.doi.org/10.4067/S0718-95162018005001201

Santos GM, Alexandre A (2017) The phytolith carbon sequestration concept: fact or Fiction? A comment on "Occurrence, turnover and carbon sequestration potential of phytoliths in terrestrial ecosystems by Song et al.. Earth-Science Rev 164, 251-255. doi: 10.1016/j.earscirev.2016.04.007

Schaller J, Brackhage C, Gessner MO, Bäuker E, Gert Dudel E (2012) Silicon supply modifies C:N:P stoichiometry and growth of Phragmites australis. Plant Biol 14:392–396. https://doi.org/10.1111/j.1438-8677.2011.00537.x

Schaller J, Faucherre S, Joss H, Obst M, Goeckede M, Planer-Friedrich B, Peiffer S, Gilfedder B, Elberling B (2019) Silicon increases the phosphorus availability of arctic soils. Scientific Report 9: 449. https://doi.org/10.1038/s41598-018-37104-6

Schaller J, Cramer A, Carminati A, Mohsen Z (2020) Biogenic amorphous silica as main driver for plant available water in soils. Scientific Reports 10:2424. https://doi.org/10.1038/s41598-020-59437-x

Schaller J, Puppe D, Kaczorek D, Ellerbrock R, Sommer M (2021) Silicon Cycling in Soils Revisited. Plants 10, 295. https://doi.org/10.3390/plants10020295

Sigg L, Stumm W (1980) The interaction of anions and weak acids with the hydrous goethite (a-FeOOH) surface. Colloids and Surfaces, 2, 101-117. https://doi.org/10.1016/0166-6622(81)80001-7

Silverman MP, Munoz EF (1970) Fungal attack on rock: solubilization and altered infrared spectra. Science 169, 585-587. https://doi.org/10.1126/science.169.3949.985

Sheng XF, Zhao F, He LY, Qiu G, Chen L (2008) Isolation and characterization of silicate mineral-solubilizing Bacillus globisporus Q12 from the surfaces of weathered felspar. Can. J. Microbiol. 54, 1064-1068. https://doi.org/10.1139/W08-089

Sommer M, Kaczorek D, Kuzyakov Y, Breuer J (2006) Silicon pools and fluxes in soils and landscape-a review. J. Plant Nutr. Soil Sci 169, 310-329. https://doi.org/10.1002/jpln.200521981

Sommer M Jochheim H, Höhn A, Breuer, Zagorski JZ, Busse J, Barkusky D, Meier K, Puppe D (2013) Si cycling in a forest biogeosystem – the importance of transient state biogenic Si pools. Biogeosciences, 10, 4991–5007. https://doi.org/10.5194/bg-10-4991-2013

Song A, Li Z, Liao Y, Liang Y, Wang, E, Wang, S, Li X, Bi J, Si, Z, Lu Y, Nie J, Fan F (2021) Soil bacteria communities interact with silicon fraction transformation and promote

rice yield after long-term straw return. Soil Ecol. Lett. https://doi.org/10.1007/s42832-021-0076-4

Struyf E, Smis A, Van Damme S, Meire P, Conley DJ (2009) The global biogeochemical silicon cycle. Silicon 1, 207-213. https://doi.org/10.1007/s12633-010-9035-x

Tréguer PJ, De La Rocha C (2013) The world ocean silicon cycle. Annu. Rev. Mar. Sci. 5, 477-501. https://doi.org/10.1146/annurev-marine-121211-172346

Tréguer P, Nelson DM, van Bennekom AJ, DeMaster DJ, Leynaert A, Que guiner B. (1995) The balance of silica in the world ocean: a re-estimate. Science 268:375–79. doi: 10.1126/science.268.5209.375

Tubana BS, Heckman JR (2015) Silicon in soils and plants. In Rodriguez FA, Datnoff LE eds. Silicon and plant diseases. P. 7-51. https://doi.ordeg/10.1007/978-3-319-22930-0_2

Vandevenne F, Struyf E, Clymans W, Meire P (2011) Agricultural silica harvest: have humans created a new loop in the global cycle? Front Ecol Environm doi:10.1890/110046

Vandevenne F, Barão L, Schoelynck J, Smis A, Ryken N, Van Damme S, Meire P, Struyf E (2013) Grazers: Bio-catalysts of terrestrial silica cycling. Proc. Roy. Sci. B 280, 20132083. https://doi.org/10.1098/rspb.2013.2083

Vandevenne F, Barao L, Ronchi B, Govers G, Meire P, Kelly EF, Struyf E (2015) Silicon pools in human impacted soils of temperate zones, Global Biogeochem. Cycles, 29, doi:10.1002/2014GB005049

Van Hees PAW, Jones DL, Jentschke G, Godbold DL (2004) Mobilization of aluminium, iron and silicon by *Picea abies* and ectromycorrhizas in a forest soil. Eur. J Soil Science 55, 101-111. https://doi.org/10.1046/j.1365-2389.2003.00581.x

Viera Filho LO, Monteiro FA (2020) Silicon modulates copper absorption and increases yield of Tanzania guinea grass under copper toxicity. Env. Sci. Poll. Res. 27, 31221-31232. https://doi.org/10.1007/s11356-020-09337-4

Wang S, Wang F, Gao S (2015) Foliar application with nano-silicon alleviates Cd toxicity in rice seedlings. Environ. Sci. Pollut. Control Ser. 22, 2837-2845. https://doi.org/10.1007/s11356-014-3525-0

Wang JJ, Dodla SK, Henderson RE (2004) Soil silicon extractability with seven selected extractants in relation to colorimetric and ICP determination. Soil Science 169, 861-870. DOI:10.1097/01.ss.0000149362.88935.8d

Wang M, Gao L, Dong S, Sun Y, Shen Q, Guo S (2017) Role of Silicon on Plant– Pathogen Interactions. Front. Plant Sci. 8:701. https://doi.org/10.3389/fpls.2017.00701

WoldeGabriel, G, Stanley H. Ambrose SH, Barboni D, Bonnefille R, Bremond L, Currie B, DeGusta D, Hart WK, Murray AM, Renne PR, Jolly-Saad MC, Stewart KM, White (2009) The geological, isotopic, botanical, invertebrate, and lower vertebrate surroundings of Ardipithecus ramidus. Science 326, no 5949 (2009). https://doi.org/10.1126/science.1175817

Yang X, Song Z, Van Zwieten L, Sun X, Yu C, Wang W, Liu C, Wang H (2021) Spatial distribution of plant-available silicon and its controlling factors in paddy fields of China. Geoderma 401,115215. https://doi.org/10.1016/j.geoderma.2021.115215

Yang JL, Zhang GL (2018) Silicon cycling by plant and its effects on soil Si translocation in a typical subtropical area. Geoderma 310, 89-98. https://doi.org/10.1016/j.geoderma.2017.08.014

Zini Q, Buldini PL, Morettini L (1985) Rapid determination of dissolved silica in natural waters. Microchemical Journal 32, 148-152. https://doi.org/10.1016/0026-265X(85)90070-0

Figure and table captions

Figure 1. The main pools and fluxes in the terrestrial Si cycle. Adapted from Monger and Kelly, 2001; Sommer et al. 2006; Cornelis and Delvaux 2016; Tubana and Heckman, 2015, Schaller et al, 2021. (¹) Mineral e.g. slag, diatomite and organic e.g. compost, biochar; (²) BSi: biogenic silicon; (³) SRO: short ranged-order aluminosilicates; (⁴) SSB: silicate solubilizing bacteria).

Figure 2. The Si terrestrial ecosystem service framework

Figure 3. Scanning electron microscopy micrographs of phytoliths and diatoms from paleosols with high cultural values. Phytolith ELONGATE SINUOUS, common to many plant taxa, (a) and diatom frustule (b) from the silica-rich sediments of the Toros Menalla paleoanthropological locality TM 266 in Chad, which yielded the cranial remains and teeth of *Sahelanthropus tchadensis*, the oldest hominin known so far, dated ca. 7 million years. Phytolith SPHEROID DECORATED, common to many woody plants, from the paleoanthropological locality of Koro Toro in Chad, which yielded the lower jaw and teeth of *Australopithecus bahrelghazali* dated ca 3.6 million years.

Table 1. Procedures for measuring the forms of Si in terrestrial ecosystems. (¹) ICP-AES: Inductively Coupled Plasma-Atomic Emission Spectroscopy; (²) XRF: X-Ray Fluorescence; (³) ICP-MS: Inductively Coupled Plasma-Mass Spectrometry; (⁴) MIRS: Microwave Integrated Retrieval System.





Figure 2





Table 1

Forms of Si	Procedures	References
Tatal (aal: 4)	1	Corrections (1004)
Total (solid)	ICP-AES ¹ after alkaline fusion	Germanique (1994)
	XRF ² after alkaline fusion	Aureli et al. (2020)
	ICP-MS ³ after HF digestion	Landré et al. (2018)
	MDc ⁴	Liang et al. (2015)
	MIRS	
Amorphous (solid)	Spectrophotometry after NaOH extraction	Barao et al. (2015)
	Spectrophotometry after Na ₂ CO ₃	Saccone et al. (2007); Meunier et al.
	extraction	(2014)
	Tiron extraction	Kendrick and Graham (2004)
Plant available, adsorbed (dry soil)	CaCl ₂ extraction	Haysom and Chapman (1975)
	Acetate-acetic acid	Korndorfer et al. (2001)
	Others	Liang et al. (2015); Tubana and Haskman (2015)
Dissolved Si	Spectrophotometry (monosilicic	$\operatorname{Teck}(2013)$ Zini et al. (1985): Wang et al. (2004)
	acid)	
	ICP-AES ¹ (total DSi)	Wang et al. (2004)
Plant	Alkaline extraction	Elliott and Snider (1991); Meunier et al. (2014)
	Tiron extraction	Guntzer et al. (2010)
	HF extraction	Saito et al. (2005)
	Electrothermal vaporization	Masson et al. (2007)
	combined with ICP-AES ¹	De Souza et al. (2013)
	Laser-induced breakdown	
	spectroscopy	Reidinger et al. (2012)
	Portable X-ray fluorescence	g (=)
Extraction of phytoliths	Plant: wet or dry ashing	Parr et al. (2001): Corbineau et al
and other biogenic	i mate wet of all ashing	(2013) ; Kamenik et al. (2013)
silica particles	Soil and sediments: heavy liquid	Lentfer & Boyd (1998)
<u>^</u>	flotation	
	Microwave digestion	Parr (2002)