## Title

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Discussion

# 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. doi: 10.1016/j.earscirev.2016.04.007”

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ABSTRACT

In their review, Song et al. (2016) overstate the validity of the atmospheric carbon sequestration potential of phytoliths as they misrepresent recent literature on the topic and omit any evidence that calls into question this concept. Here, we evaluate and present the full range of the misrepresented and omitted literature, and question the representativeness of their original assumptions. We also address Song et al.'s concerns regarding isotopic fractionation and/or the negative effects of over-rigorous oxidation on the isotopic analysis of phytoliths. Finally, we call for further data acquisition to properly quantify all the fluxes involved in the phytolith carbon cycle.

## 1. Introduction

A recent article published in Earth Science Reviews by Song et al. (2016) made some stunning conclusions regarding the accumulation rates of phytoliths in soils and the usefulness of phytoliths for atmospheric carbon dioxide ($CO_2$) biosequestration. In our view, this review article contains serious errors in its presentation of facts and serious omissions of competing evidence, resulting in a false impression that carbon (C) sequestration in phytoliths is a well-established process that should be exploited to mitigate present-day $CO_2$ emissions.

The phytolith carbon sequestration concept (Parr and Sullivan, 2005; Parr et al., 2010; Song et al., 2013; Song et al., 2014; Song et al., 2016) is based on the following hypotheses, mostly from Parr and Sullivan (2005): i) in phytoliths, the C (termed phytOC or phytC) concentration is high; ii) once the C is encapsulated in the phytolith structure (cavities) it is protected from mineralization; and iii) most phytoliths do not dissolve in soils (for hundreds to thousands of years). We would like to note here that each of these hypotheses has been challenged (Santos et al., 2010, 2012a, 2012b; Corbineau et al., 2013; Alexandre et al., 2015, 2016; Reyerson et al., 2016), although this was not properly reported in Song et al. (2016). Our discussion will focus on Song et al.'s omissions regarding the state of knowledge of phytC concentration, and the distribution and accessibility of phytC in phytolith structures. Then we will propose a framework for the phytC cycle at the soil/plant/atmosphere interface and highlight the phytC fluxes that must be quantified to accurately estimate the flux of atmospheric $CO_2$ sequestered by soil phytoliths. We will also comment on the effects of isotopic fractionation on $^{14}C$ data and the possibility of that C isotopic phytoliths are altered through over-vigorous oxidization raised originally by Sullivan and Parr (2013) and referenced in Song et al. (2016) to undermine the evidence showing that phytC is not uniquely constituted of photosynthetic C, and is thus ineffective as a dating tool.

## 2. Carbon concentrations in phytoliths

In the review by Song et al. (2016), the phytC concentration in phytoliths is assumed to be 3 ± 1% of the dry weight based on a selected set of data (Parr et al., 2010; Zuo and Lü, 2011; Li et al., 2013; Song et al., 2013). Other datasets, however, showed C concentrations on the order of 0.1–0.5% of the dry weight (Santos et al., 2010; Yin et al., 2014; Reyerson et al., 2016; Alexandre et al., 2015, 2016). Song et al. (2016) argued that in these cases the concentrations were underestimated as high purity phytolith extraction led to partial oxidation of phytC. Partial oxidation of phytC was effectively shown by Reyerson et al. (2016) but the reverse can also occur: the phytC concentration can be overestimated if the purity of phytolith concentrates is not properly checked using scanning electron microscopy-energy-dispersive X-ray spectroscopy (SEM-EDS) analyses (Santos et al., 2012a; Corbineau et al., 2013; Reyerson et al., 2016). Organic remains that may not be distinguishable under light microscopy can be

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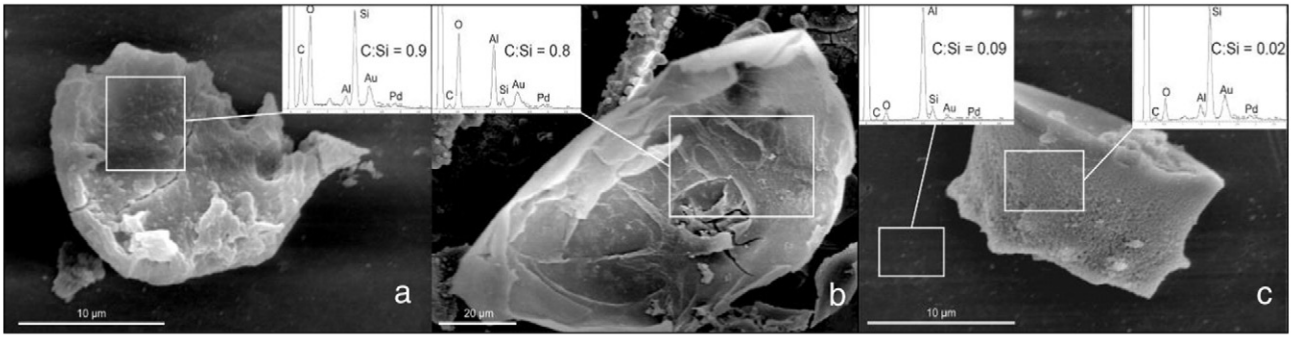

**Fig. 1.** Example of SEM images and EDS spectra obtained after the screening of phytolith concentrates extracted from grasses. It shows that organic remains (a and b) with high C:Si % mass ratios can be distinguished from phytoliths (c) with lower C:Si % mass ratios (adapted from Santos et al., 2012a).

clearly identified from their high C:Si % mass ratios (Fig. 1). This quality check for phytolith purity is imperative as it can reveal small C particulate contamination that may considerably bias quantitative (and isotopic) analyses of phytC (Santos et al., 2012a; Corbineau et al., 2013). For this reason, we suggest that the high uncertainty on measurements of phytC concentration in phytoliths should be properly acknowledged when attempting to quantify phytC fluxes.

## 3. Fate of carbon encapsulated in the phytolith structure

For decades, phytolith opaque spots visible in optical-microscopy analysis have been interpreted as carbon occlusions. In Song et al. (2016) the pictures and conceptual diagrams of Carter (2007, 2009) and Parr and Sullivan (2014) are cited as evidence for differentiated forms of organic carbon (OC), protected from dissolution within the silica structure, although no elemental analyses supported this claim. Alexandre et al. (2015) demonstrated using optical microscope analysis, three-dimensional X-ray microscopy and Nanoscale secondary ion mass spectrometry (NanoSIMS) that the cavities within the silica are often empty-pockets that at certain angles can mimic dark spots and thus be mistakenly identified as C occlusions (Fig. 2).

These cavities may be originally delineated by cell organic compounds during the cell silicification. However, this phytC should be rapidly oxidized when phytoliths start to dissolve and when cavities become open, after phytolith deposition in litter, soil or sediment (Fig. 3). In this case, the phytC in phytolith cavities would participate only to a limited extent in long-term atmospheric $CO_2$ sequestration. NanoSIMS analyses have provided evidence of another pool of phytC continuously distributed in the silica structure (Alexandre et al., 2015) that may be less prone to oxidation. However, for a reliable assessment of the significance of phytC fluxes in soils, comprehensive elemental analyses direct in soil phytoliths (prone to weathering - Oleschko et al., 2004; Borrelli et al., 2010) must be undertaken.

## 4. The phytC cycle at the soil/plant/atmosphere interface: involved fluxes

In order to properly estimate the flux of atmospheric $CO_2$ sequestered by soil phytoliths, the steady-state cycle of phytC has to be quantified at ecosystem spatial scales (Fig. 3). Several of the fluxes involved in the cycle have never been estimated or are subject to considerable uncertainty. They are detailed below.

From the atmosphere to plant phytoliths, the flux of C (phytC production from photosynthesis in Fig. 3) equals the net primary productivity (NPP) times [total phytC minus phytC from soil origin]. Although ecosystem NPP data is easily found in the literature, estimates of total phytC are subject to large uncertainties, and the phytC soil fraction is even harder to quantify. Although the contribution of soil-C to phytC has been recently demonstrated from over 200 isotopic measurements involving phytoliths, plant tissues, atmospheric $CO_2$, soil organic matter (SOM) and soil amendments (Reyerson et al., 2016), the soil-C contribution under natural conditions still remains to be quantified (Alexandre et al., 2016), even though it has been reported as negligible in Song et al. (2016).

From plant to soil, the flux of phytC (phytC input to the soil in Fig. 3) equals the flux of C from atmosphere to phytoliths plus the flux of phytC from eolian inputs minus the flux of phytC exportation from the ecosystem due to erosion (e.g. Cary et al., 2005; Alexandre et al., 2011; Zuo et al., 2014) and straw exportation (e.g. Keller et al., 2012). The order of magnitude of these fluxes can be estimated from bibliographic data. However, none of these fluxes are taken into account in the calculations presented in Song et al. (2016).

In soils, phytC may be mineralized (phytC mineralization) or stabilized (phytC sequestration). A soil phytolith stability factor of 0.8 to 1.0 is quoted in Song et al. (2016). While this range of values has been used in several studies from the same group of authors (Song et al., 2016 and references therein), the original references are given as Parr

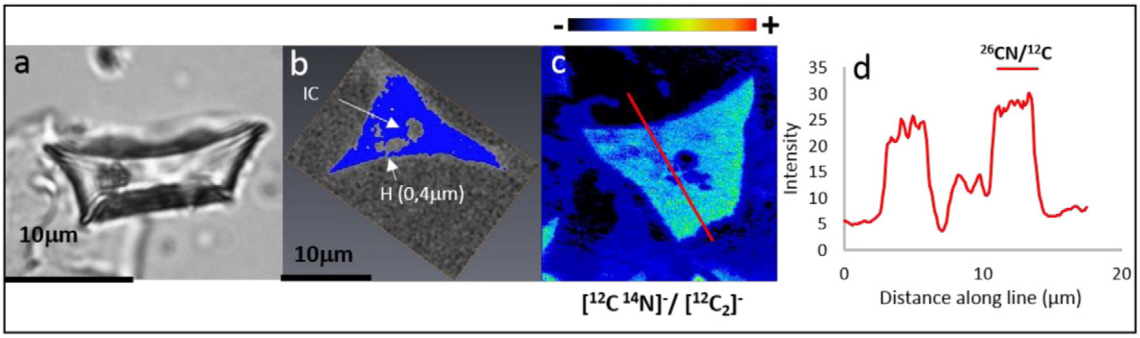

**Fig. 2.** Light microscopy image of an opaque area in a grass short cell (GSC) phytolith (a); 3D-X-ray microscopy image showing the inner internal cavity (IC) and its connection to the surface, forming holes (H) (b); NanoSIMS image of $[^{12}C^{14}N]^-/[^{12}C_2]^-$ distribution (c) and secondary ion intensity along line scan (red line) showing C in the silica structure (d). Adapted from Alexandre et al., 2015.

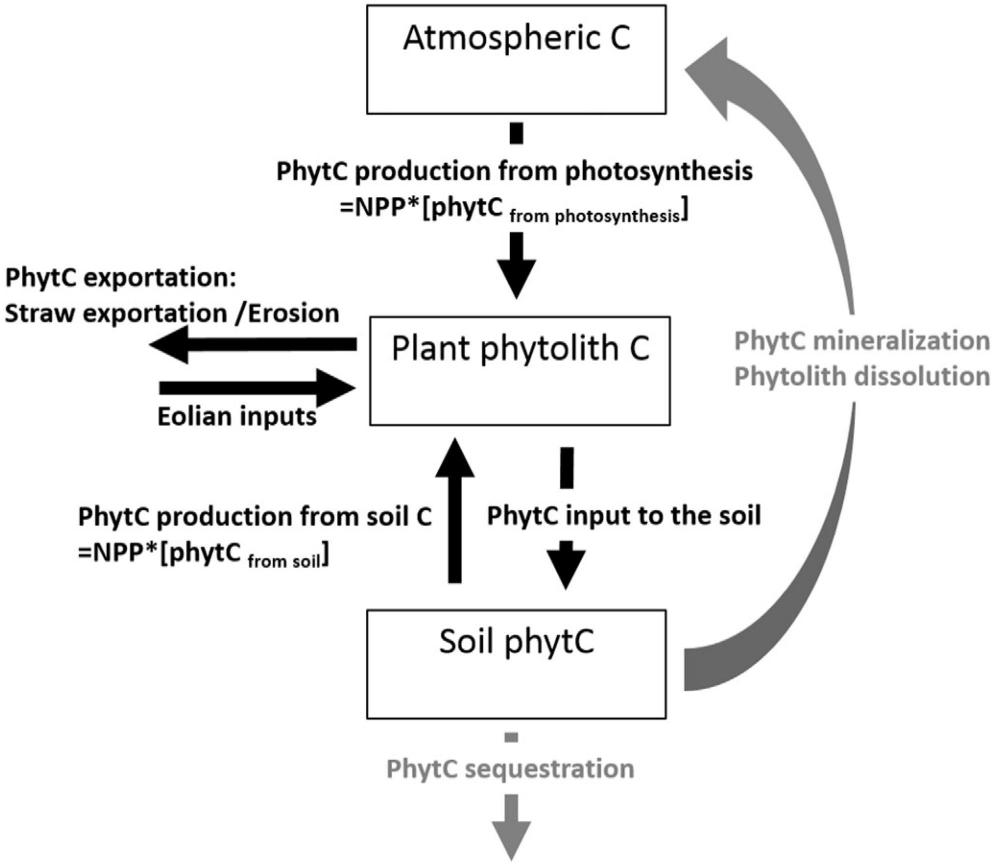

**Fig. 3.** Stocks and flows in the phytC cycle at steady state. To date, data is lacking to quantify the phytC sequestration and phytC mineralization fluxes (in gray) on global and ecosystem scales.

and Sullivan (2005) and Parr et al. (2010). However, these latter studies do not present the data necessary to calculate a stability factor (i.e. phytC flux to the soil minus phytC flux due to mineralization). The phytolith biosequestration hypothesis is put forward solely based on the estimation that phytC may represent up to 43% of soil organic carbon (SOC) of buried soils in volcanic ash deposits (Parr and Sullivan, 2005). The raw data in the study (i.e. phytC concentration in phytoliths and phytolith concentration in soils) are not presented. Furthermore, it is unclear if the presence of volcanic glasses, which are hard to separate from phytoliths, may have led to an overestimation of soil phytolith concentration and *in fine* of soil phytC concentration. Nevertheless, such high phytC concentrations should not be extrapolated or generalized to all soils, when phytoliths can account for less than 1% of the dry matter (Alexandre et al., 2011).

To establish the stability of phytoliths on scales of hundreds to thousands of years in soil horizons, Parr and Sullivan (2005) use direct phytolith $^{14}C$ measurements. However, several failed attempts to reproduce bomb-pulse period $^{14}C$ ages with phytC (Santos et al., 2010, 2012a, 2012b; Yin et al., 2014; Piperno, 2015, 2016), including the work of Sullivan et al. (2008), suggest that phytC is not homogeneous in origin. Recently Reyerson et al. (2016) showed that a portion of phytC is from old soil-C mobilized by roots, questioning the usefulness of phytoliths as a dating tool. Indeed, any amount of ancient soil-C can significantly bias the $^{14}C$ ages of phytoliths and estimates of phytolith residence time in soils (Santos et al., 2012a). Finally, the phytolith stability factor of 0.8 to 1.0 used in Song et al. (2016) for forests, grasslands and croplands appears devoid of any serious scientific foundation.

The silicon cycle has been estimated for tropical savanna and humid forest based on a ferruginous and a ferralitic soil, respectively (Alexandre et al., 2011). From the quantification of the involved fluxes and assuming a bi-compartmental distribution of phytoliths in soil (i.e. a stable and a labile pool), it was calculated that less than 10–20% of phytoliths produced annually by the vegetation was preserved in soils for extended periods. These proportions would reasonably depend on environmental conditions such as the activity of a number of elements (such as Si, Al, Fe, HC) in soil solution, the morphology of phytoliths (and thus vegetation type), and elemental concentration of phytoliths (and thus soil type). Song et al. (2016) rejected the soil phytolith bi-compartmental distribution approach arguing that changes in porosity with depth were not taken into account and that the stable pool of phytoliths was consequently underestimated. However, changes in bulk density were actually taken into account for the ferralitic soil (e.g. from 1.7 at the soil top to 1.64 t $m^{-3}$ at the bottom; Alexandre et al., 1997). The argument is thus not relevant. Nonetheless, further field data are necessary to quantify the extent of phytolith preservation/dissolution on an ecosystem scale.

As an exercise, taking the highest phytC yield measured in Reyerson et al. (2016) (0.3% of phytoliths) coupled with the 20% phytolith stability factor estimated from Alexandre et al. (2011), the global grassland phytC sink ($8.2 \times 10^{-2}$ Tg C $yr^{-1}$) would be more than three orders of magnitude lower than the $4 \times 10^{2}$ Tg C $yr^{-1}$ global mean long-term soil C accumulation rate (Schlesinger, 1990). The value mistakenly cited by Song et al. (2016) as a world grassland sequestration rate (41.4 Tg $CO_2$ $yr^{-1}$; Song et al., 2012) is in fact the phytC production rate (Fig. 3) of world grassland, using a phytC concentration in phytoliths of 1.5%. Song et al. (2016) wrongly assume that all the phytC produced in plants enters the soil and is preserved in soils, neglecting most of the phytC input and output fluxes involved in the phytC cycle (Fig. 3).

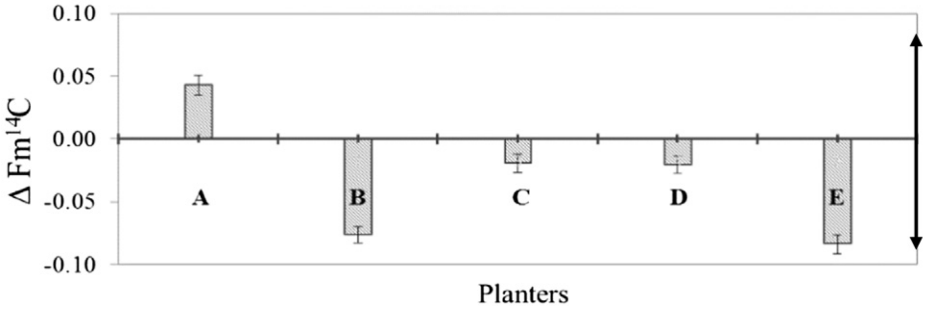

**Fig. 4.** Radiocarbon offsets between phytC and *Sorghum bicolor* plants grown under similar conditions, except that the soil amendments had different $^{14}$C signatures. Phytoliths were extracted using a wet-digestion protocol (termed 1a in Reyerson et al. (2016)). Offset values were correlated to the $^{14}$C signatures of the amendments. The Planter A amendment was composed of rich bulk-complex organic C imprinted with $^{14}$C post-bomb values (or Fm$^{14}$C signatures higher than present-day values), while the Planter E amendment received a solution of fossil organic C (Fm$^{14}$C = 0; $^{14}$C age close to 43 kyr BP). On the right, the positive and negative offsets are represented by arrows.

## 5. Assessing the source of phytC and its use as a dating tool: effect of isotopic fractionation or excessive oxidation on phytC $^{14}$C data

Song et al. (2016) explained in their review that the recently identified anomalous $^{14}$C ages of phytoliths from contemporary plants (Santos et al., 2010; Santos et al., 2012a, 2012b; Reyerson et al., 2016; Santos et al., 2016) could be due to "artificial effects of $^{14}$C dating of phytoliths" and cited Sullivan and Parr (2013), and Yin et al. (2014) without further explanation. Later, Song et al. (2016) also criticized the evidence for an old soil C contribution to phytC (Reyerson et al., 2016) on the grounds of "both incomplete and over-vigorous extractions of phytoliths" that "can have significant adverse consequences on carbon isotope fractionation", and once again cite Sullivan and Parr (2013) and Yin et al. (2014). However, it is unclear if the authors are discussing carbon isotopic fractionation (the relative abundance among isotopes), or carbon partitioning (the pattern, distribution and allocation of different carbon pools).

Natural and processing mass-dependent fractionation (also termed "isotopic fractionation" for simplicity) must be taken in account when normalizing $^{14}$C ages (Stuiver and Polach, 1977). Thus, as has been extensively explained in Santos et al. (2012b), and demonstrated in Reyerson et al. (2016), the mass-dependent fractionation effects on $^{14}$C results are automatically canceled by the direct measurement of $\delta^{13}$C of graphite targets at the accelerator mass spectrometer. Moreover, the $\delta^{13}$C associated with the chemical phytolith extractions obtained by Santos et al. (2010), Sullivan and Parr (2013), Yin et al. (2014), Piperno (2015) and Reyerson et al. (2016) have been reported alongside of $^{14}$C data, and the mass-dependent fractionations they trace are insufficient to explain the anomalous $^{14}$C values reported. Thus mass-dependent fractionation cannot be invoked as an explanation for anomalous phytC ages.

The alteration of the natural isotopic signatures of phytC by over-vigorous or excessive oxidative phytolith extraction protocols have been also invoked by Sullivan and Parr (2013). No evidence or reasoning has been provided to support this explanation reproduced in Parr and Sullivan (2014), Piperno (2015), Hodson (2016), and Song et al. (2016). If by over-vigorous, the authors imply carbon partitioning, then the following should be considered. Radiocarbon analyses of C pools from the same origin always yield the same $^{14}$C values, regardless of the C fraction analyzed (labile vs. recalcitrant), or the extraction procedure applied. Different $^{14}$C values can be obtained only from a mixture of C pools of different ages, once those are partitioned by chemical or thermal processes (Yin et al., 2014; Reyerson et al., 2016).

In Reyerson et al. (2016), it is shown that even when a single grass species is grown under the same conditions (except that the substrates have different and well-characterized bulk carbon $^{14}$C values), the phytC $^{14}$C signatures vary according to the $^{14}$C value of the organic matter in the substrates from positive (post-bomb) to negative (pre-bomb) values (Fig. 4). Note that for this small subset of plants and phytC $^{14}$C results just one phytolith extraction protocol has been used. These results also illustrate that the "selectively old" criticism by Song et al. (2016) is an oversimplification, and that the emphases should be on the fact that plants can make use of belowground C of multiple ages and compositions, including transporting and embedding them into phytoliths (Alexandre et al., 2016). The belowground C conditions in the Reyerson et al. (2016) experiment showed not only the modified $^{14}$C signatures of the selected soil-C incorporated into phytoliths, but also the transformation of their molecular makeup (as evidenced in Gallagher et al., 2015). Finally the argument of artificial $^{14}$C alteration through either isotopic fractionation or over vigorous-oxidation brought by Song et al. (2016) to refute the evidence for an old soil C contribution to phytC (Santos et al., 2010; Santos et al., 2012a, 2012b; Santos et al., 2016; Reyerson et al., 2016) appears to be not relevant.

The hypothesis of an old soil C contribution to phytC, presented in Santos et al. (2012a) and validated in Reyerson et al. (2016), is supported by recent soil paradigm-shifts showing that old carbon can be accessed by microbes (Schmidt et al., 2011; Dungait et al., 2012; Marín-Spiotta et al., 2014), and that roots and plants can actively exchange as much as 40% of non-structural carbon among themselves (Klein et al., 2016). The fact that phytC is not uniquely constituted of photosynthetic C limits its usefulness as a dating tool. Reports of anomalous $^{14}$C dates between phytC and plants are now widespread among independent researchers, locations, species, laboratories and types of phytolith extractions (Sullivan and Parr, 2013, Sullivan et al., 2008, Sullivan and Parr, 2013; Yin et al., 2014; Piperno, 2015, 2016). A critical reappraisal of those papers and the phytolith $^{14}$C dating evidence in the literature was also previously presented in Santos et al. (2012b, 2016), but is ignored in Song et al. (2016) review.

## 6. Final remarks

If Song et al. (2016) wish to unequivocally establish that C encapsulation in phytoliths should be considered as a viable mechanism for atmospheric $CO_2$ sequestration, they should have properly acknowledged and explained any findings that did not support their hypothesis. Furthermore, in order to present reliable values of phytC sequestration fluxes on ecosystem scales, we call for further data acquisition (rather than reviews of reviews) to quantify the fluxes involved in the phytC cycle at steady state. Currently, the data available do not suggest any significant phytC biosequestration fluxes, contrary to what is claimed in Song et al. (2016).

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