Review


Guaciara M. Santos a, *, Anne Alexandre b, Christine A. Prior c

a Earth System Science, University of California, Irvine, B321 Croul Hall, Irvine CA 92697-3100, USA
b CEREGE, UMR7330, CNRS-Aix-Marseille Université, Aix En Provence, France
c Rafter Radiocarbon Lab, National Isotope Centre, GNS Science, Lower Hutt, New Zealand

ABSTRACT

The paper “Phytolith Radiocarbon Dating in Archaeological and Paleoeocological Research: A Case Study of Phytoliths from Modern Neotropical Plants and a Review of the Previous Dating Evidence” by Dolores R. Piperno presents radiocarbon analysis of phytoliths from modern Neotropical plants collected between 1964 and 2013. The analyses presented were intended to rebut the emerging hypothesis that invokes root-plant uptake, transport and reallocation of soil organic carbon into phytoliths that has been recently put forward as an explanation for the anomalous radiocarbon (14C) ages (of hundreds to thousands of years old) reported for modern grass phytoliths in Santos et al. (2010a, 2012a). We believe that the results presented in Piperno (2015) lack methodological rigor, mostly due to the absence of any procedural blank assessment, and that the attempts to disprove the hypothesis of uptake of soil organic matter (SOM) by phytoliths in Santos et al. (2012a) are not supported by a careful analysis. Rather than supporting the position that 100% of the carbon in phytoliths is of photosynthetic origin, which allows the use of phytolith carbon (or phytC) as a dating tool, the analysis of 14C in phytoliths from modern Neotropical plants presented in the study shows that the 14C ages are strongly affected by other sources of carbon. In this comment, we carefully reassess the 14C results in phytoliths from modern Neotropical plants presented in Piperno (2015) in the context of the 14C bomb-pulse methodology, SOM ages and turnover rates, and offer an alternative interpretation of the experimental results.

© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).

Contents

1. Introduction ........................................................................................................ 37
2. Radiocarbon bomb-pulse dating ........................................................................ 37
3. Comment on methods and the need for an experimental control ....................... 37
4. Comment on phytolith 14C data analysis and interpretation ................................ 38
5. Difference between SOM turnover time and ages — implications for phytC ...... 40
6. Interpretations of fossil and present phytC 14C data .......................................... 40
7. Conclusions ........................................................................................................ 41
Acknowledgments .................................................................................................. 42
References ................................................................................................................ 42

* Corresponding author.
E-mail address: gdoasant@uci.edu (G.M. Santos).

http://dx.doi.org/10.1016/j.jas.2015.11.012
0305-4403/© 2015 The Authors. Published by Elsevier Ltd. This is an open access article under the CC BY-NC-ND license (http://creativecommons.org/licenses/by-nc-nd/4.0/).
1. Introduction

It is generally assumed that the source of phytC is atmospheric CO2 fixed by the plant via photosynthesis (Wilding, 1967; Kelly et al., 1991; Raven, 2003; Carter, 2009; Piperno, 2006). It follows from this assumption that its 14C signature can be used as a dating tool. However intuitively appealing this assumption might be, it cannot be accepted as scientific fact without adequate testing. Before asserting that phytolith ages from archaeological contexts are coeval with their sedimentary context (or expected ages), the assumption of a 100% photosynthetic source for the phytC must be validated by testing known-year post bomb specimens.

Piperno (2015) recently addressed anomalously old 14C ages obtained for the carbon occluded in phytoliths extracted from living vegetation reported in Santos et al. (2010a, 2012a). Similar discrepancies have been reported previously in a scientific report to the Australian Institute of Nuclear Science and Engineering (e.g., Sullivan et al., 2008). In Santos et al. (2010a), the 14C-AMS results were obtained from phytolith concentrates extracted from plants of known age harvested at two sites in USA and France, using an extraction protocol (Kelly et al. 1991) similar to that performed in several labs. Lab contaminants were systematically evaluated and a procedural blank obtained for each of them. In Sullivan et al. (2008) 14C signatures were obtained from phytoliths extracted from harvested leaves of bamboo and the underlying litter layers, with the intention of reproducing the 14C bomb-peak. Harvested leaves produced an age of 3.5 ka yrs BP, recently senesced leaves 1.9 ka yrs BP, and the litter 14C results averaged ~100 pMC (percent Modern Carbon) — significantly lower than the values expected from a bomb-peak signature. This dataset was published in Sullivan and Parr (2013) and discussed in an interactive comment by Santos et al. (2012b). Other researchers (Yin et al., 2014) have also reported unexpected low 14C values, when trying to reproduce bomb 14C signatures in phytoliths extracted from rice and millet harvested in 2011 and 2012.

In Piperno (2015), it is asserted that the anomalies reported in the direct 14C dating of phytC are relatively recent and limited to extra-tropical regions. In order to refute the hypothesis proposed in Santos et al. (2010a, 2012a), 14C signatures obtained from phytoliths extracted from modern Neotropical plants collected between 1964 and 2013 were reported. Since all but one of the 14C ages exhibited a post-bomb 14C signature (e.g., after 1955) it was claimed that no extraneous carbon biased the phytolith 14C ages. Here, we present several reasons why this claim cannot be supported. The primary goal of this comment is to demonstrate how the 14C bomb pulse methodology should be interpreted with respect to 14C analysis of phytoliths. A secondary goal is to use that interpretation in order to draw attention to the implications and consequences of using phytC as a proxy of total plant carbon and in environmental reconstructions.

2. Radiocarbon bomb-pulse dating

Although there is abundant literature on the use of bomb-pulse dating, we briefly summarize the methodology below in order to clarify some common misperceptions.

Radiocarbon is a naturally occurring radioisotope produced in the atmosphere by cosmic rays. Radiocarbon is oxidized to carbon dioxide (CO2) and enters the food chain through photosynthesis. Consequently all living organisms contain 14C and continue to take in 14C as long as they are alive. Once an organism dies or its parts (tree rings, for example) stop assimilating 14C, the time-specific isotopic ratio of atmospheric 14CO2 during the year of tissue formation is preserved. Atmospheric nuclear weapons testing in the late 1950s and early 1960s almost doubled the amount of atmospheric 14C. After the banning of atmospheric nuclear testing in 1963, subsequent 14C exchange with the ocean and land reservoirs, and dilution by fossil fuel emissions (Suess, 1955; Levin, 1997) caused the excess of atmospheric 14C to gradually decrease. The penetration of atmospheric 14C into terrestrial ecosystems has also led to a non-uniform labeling of soil profiles (Trumbore, 2000; Torn et al., 2009), with a reversal towards older pre-bomb ages below 10, 20 or >50 cm depth (Telles et al., 2003).

Almost 60 years of high resolution atmospheric 14CO2 observations of the spike and subsequent decline at multiple locations in both the northern and southern hemispheres (Currie et al., 2011; Levin et al., 2013; Huan et al., 2013), have allowed researchers to use bomb 14C as a very precise tracer. The 14C content of terrestrial organic materials can be compared to the 14C content of the atmospheric 14CO2 bomb pulse as a way to: a) reveal modern forgeries (Caforio et al., 2014); b) identify poaching (Uno et al., 2013); c) validate the annual growth patterns in tropical tree species (Westbrook et al., 2008; Andreu-Hayles et al., 2015); d) determine birth- and/or death-age of subjects in forensic cases (Wild et al., 2000; Lyennerup et al., 2010); as well as e) verify sources of 14C in organic materials (such as phytC).

Whether expressed as Fraction modern Carbon (FMC) or percent Modern Carbon (pMC) = FMC × 100 − the carbon content of materials with 14C signatures similar to those of atmospheric 14C after 1955 is generally referred as “modern” for simplicity. However, the usage of the term can create confusion. The mismatch between post-bomb or “modern” 14C results for materials of known single calendar ages and the atmospheric 14C content for that year can imply that the material measured contains a mixture of 14C of different atmospheric calendar ages from the pre- and post-bomb periods. While pre-bomb 14C values range from 0 to ~99 pMC (equivalent to >50 ka yrs BP to 1955 calendar year, respectively), the 60 last years of the bomb-period also show large variations from 100 to approximately 180 pMC. As a result, small offsets in pMC within the bomb peak period are extremely significant and permit the identification of 14C from different sources within organic materials. Similarly, when 14C offsets between the true and measured ages occur during the pre-bomb period they also correspond to chronological offsets. For example, for each 1% of 14C-free added, the expected age would be skewed by 80 14C years towards older values, regardless of the true age of the sample (Aitken, 1990; Wood, 2015).

3. Comment on methods and the need for an experimental control

In order to compare the efficiency of different oxidizing agents for phytolith extraction, sulfuric acid (H2SO4) and a nitric acid/potassium chloride mixture (HNO3/KClO3) were used in Piperno’s work on duplicates. To ensure that all organic material was removed from phytolith surfaces, a second treatment was performed for additional hours. For 14C analyses the phytolith extracts were combusted with tin to elevate the combustion temperature to 1400–1500 °C and therefore ensure phytolith melting. This is described as a necessary step according in Piperno and Stothert (2003), although this step has been shown to be unnecessary by other investigations (Table 2 in Santos et al., 2010a) who have shown that phytoliths combusted at 900 °C could be recovered and combusted to verify combustion efficiency as well as background levels. The absence of CO2 during recombustion confirmed that the combustion of phytoliths at 900 °C without the addition of tin reached completion without the addition of unnecessary catalysts, which can be potential sources of carbon contaminates (Ramsey and Humm, 2000). Whether or not higher combustion temperatures can be shown to improve combustion efficiency, the rest of
the protocol described in Piperno (2015) requires more detailed documentation in order to assess its robustness. For example.

a) No evidence of the purity of phytolith concentrates, either by light microscope or SEM-EDX (Santos et al., 2012a; Corbineau et al., 2013) was provided. This is necessary to check that all organic matter from the living tissue was removed and that extraneous carbon was not added.

b) The absorptive properties of pure phytoliths with regard to atmospheric CO₂ were also not assessed (Mintz et al., 2009; Hatté et al., 2010; Santos et al., 2010a). Trapped atmospheric CO₂ on the surfaces of phytolith extracts can be removed by use of a low temperature combustion step. The absorptive properties of phytoliths with regard to the use of solvents were also not considered. Santos et al. (2010a) demonstrated that solvent treatments applied to phytoliths bias their ¹⁴C values (UCAMS# 39672 and −45447; Table 2 in Santos et al., 2010a). Nevertheless, Piperno (2015) suggests its use (first paragraph of Results section) without any evaluation of the effects on phytoliths concentrates, and consequently phytC ¹⁴C.

c) No information is provided on phytolith concentrations by mass, amounts combusted, or yields from combustion and graphitization, all of which are necessary to assess the efficiency of the phytolith extraction protocol and ¹⁴C sample processing. This is especially relevant, considering that the amount of C within pure phytoliths is on the order of 0.1–0.3% (Santos et al., 2010a). Several hundreds of mg of phytoliths have to be combusted in order to produce graphite samples of >=0.1 mgC for a measurement. A consequence of such small samples is that special attention must be applied to handle the small targets processed, the spectrometer measurements and inherent uncertainties. Greater uncertainties are generally linked to the combination of lower statistics (associated with low ion beam currents during spectrometer measurements, see Santos et al., 2007a,b) and background corrections from the addition of exogenous carbon during full sample processing (which should be determined by measuring a procedural blank, Santos et al., 2010b).

d) Most importantly, no procedural blank has been reported for any of the chemical extractions described above, and not for the carbon added during Accelerator Mass Spectrometry (AMS) sample processing. High chemical blanks (relative to sample size) might become a major contributor to the inaccuracy in the ¹⁴C ages obtained and to overall uncertainties. To illustrate the importance of this issue, we note that dedicated research and explicit information on producing and measuring quality sub-milligram targets for ¹⁴C-AMS measurements has been published by a number of authors (Santos et al., 2007a,b, 2010a,b; De Rooij et al., 2010; Fahrm et al., 2010; Wacker et al., 2013; Ruff et al., 2007; among others). Neither this research nor any of these factors were discussed by Piperno (2015).

4. Comment on phytolith ¹⁴C data analysis and interpretation

In Fig. 1, we reproduce the Neotropical phytC ¹⁴C values reported in Piperno (2015) plotted against the ¹⁴C bomb curve, except for the anomalous result associated with the 1964 calendar year (Tables 1 and 2 of Piperno, 2015). Although Panama and Ecuador are located across the Inter Tropical Convergence Zone and are therefore within North Hemisphere zones 2 and 3 (NH Zone 2 and 3 — according Hua et al., 2013), after 1980 both the ¹⁴C timescale curves overlap so just one ¹⁴C calibration curve (NH Zone 2) is plotted together with the Neotropical phytC ¹⁴C values. Regardless of the species tested, all pMC values appear depleted by ~3–12 pMC, except the duplicate values associated with phytolith concentrates from material collected near Santo Domingo Ecuador (Table 1 in this comment) for which ¹⁴C is enriched by >2 pMC. Assuming that these offsets are not a product of laboratory contamination, they are abnormal in a ¹⁴C bomb–pulse dating perspective where ¹⁴C annual signatures in each of the last 60 years can be separated, especially if they are from C pools expected to be 100% photosynthetic.

It was explained in Piperno (2015) that the bomb curve was not used to directly compare phytC pMC results with the calendar years of plant collection because local environmental variabilities can cause significant deviations from available bomb curve databases (details in small print under Table 2). However, such offsets have not been observed in Panamanian tree species Hymenaea Courbaril measured by Westbrook et al. (2006) that were obtained from an urbanized area near the city of David, Panama (8° 26’ N, 82° 26’ W).

Even when carbonaceous resinous compounds from previous years were incompletely removed from the tree rings by chemical pretreatment, only the consecutive ¹⁴C signals recorded in the tree rings between 1955 and 1964 were affected, while the rings between 1965 and 1997 were in complete agreement with the Northern Hemisphere ¹⁴C atmospheric time scale. We regard the explanation of local environmental variability provided by the author to account for the pMC offset to be inadequate as it implies local CO₂ variations that are much larger than expected.

a) Anthropogenic CO₂ contributions due to the burning of fossil fuels (coal, petroleum and natural gas) can indeed significantly deplete atmospheric ¹⁴C CO₂. Consequently, regional-scale ¹⁴C fossil fuel maps have been generated to show spikes around the globe, or to monitor CO₂ emissions mitigation efforts. However, even close to large urban areas in the USA, biomass samples are ¹⁴C depleted by only a few decades (Hsueh et al., 2007). In Los Angeles, one of the largest urbanized areas in Southern California, USA, the depletions in

![Fig. 1. Changes in atmospheric ¹⁴C with time since 1950 are shown in the upper panel (solid lines). In this panel the time-scale calibration curves are split into zones, according to the conventions shown in Hua et al. (2013) to illustrate that most of the differences within the ¹⁴C timescale curves across the northern and southern hemispheres falls between 1950 and 1980, while after 1980 all curves overlap. The phytC ¹⁴C values of Piperno (2015) (red circles) are plotted in the lower panel against the Northern Hemisphere Zone 2 (NH Zone 2), except for the phyt: ¹⁴C value associated with the 1964 calendar year (discussed in the text). The uncertainties, as error bars, are smaller than the symbols in most cases. Radiocarbon values are expressed as percent Modern Carbon (pMC). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)](image-url)
The amount of 14C added and the age offset in years is also provided. The age offset was calculated based on the 1%14C-free to 80yrs relationship as per Aitken (1990) and Wood (2011).

### Table 1

Reproduction of the dataset in Piperno (2015). The averaged values for the pMC expected for each calendar year, the pMC offset between measured and expected, the estimated amount of %C added and the age offset in years is also provided. The age offset was calculated based on the 1%14C-free to 80yrs relationship as per Aitken (1990) and Wood (2011).

<table>
<thead>
<tr>
<th>Plant Source</th>
<th>Processing method</th>
<th>Calendar year</th>
<th>pMC 14C-AMS</th>
<th>Beta lab#</th>
<th>pMC expected</th>
<th>pMC offset</th>
<th>Amount of %C added</th>
<th>Age offset (yrs)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Zea mays</strong></td>
<td>Nitric acid</td>
<td>1990–91</td>
<td>103.3</td>
<td>360361</td>
<td>115.2</td>
<td>11.9</td>
<td>10.3</td>
<td>825</td>
</tr>
<tr>
<td><strong>Zea mays</strong></td>
<td>Sulphuric acid</td>
<td>1990–91</td>
<td>106.7</td>
<td>360362</td>
<td>115.2</td>
<td>8.5</td>
<td>7.4</td>
<td>589</td>
</tr>
<tr>
<td><strong>Cucurbita ecuadorensis</strong></td>
<td>Nitric acid</td>
<td>1995</td>
<td>114.2</td>
<td>360359</td>
<td>112.0</td>
<td>2.2</td>
<td>2.0</td>
<td>157</td>
</tr>
<tr>
<td><strong>Cucurbita ecuadorensis</strong></td>
<td>Sulphuric acid</td>
<td>1995</td>
<td>114.4</td>
<td>360682</td>
<td>112.0</td>
<td>–2.4</td>
<td>2.1</td>
<td>171</td>
</tr>
<tr>
<td><strong>Cucurbita ficifolia</strong></td>
<td>Nitric acid</td>
<td>1995</td>
<td>101.8</td>
<td>360819</td>
<td>112.0</td>
<td>10.2</td>
<td>9.1</td>
<td>729</td>
</tr>
<tr>
<td><strong>Hirtella americana</strong></td>
<td>Nitric acid</td>
<td>1964</td>
<td>81.5a</td>
<td>360360</td>
<td>180.0</td>
<td>98.5</td>
<td>54.7</td>
<td>4376</td>
</tr>
<tr>
<td><strong>Hirtella americana</strong></td>
<td>Nitric acid</td>
<td>2013</td>
<td>100.1</td>
<td>368020</td>
<td>104.0</td>
<td>3.9</td>
<td>3.8</td>
<td>300</td>
</tr>
<tr>
<td><strong>Socratea durissima</strong></td>
<td>Nitric acid</td>
<td>1981</td>
<td>123.1</td>
<td>368023</td>
<td>125.9</td>
<td>2.8</td>
<td>2.2</td>
<td>180</td>
</tr>
</tbody>
</table>

* pMC 14C-AMS was determined based on the 14C age of 1640 ± 30 yr BP, as seen in Table 2 in Piperno (2015).

In summary, all 14C results for the post-bomb Neotropical samples with known year of collection reported in Piperno (2015) differ by >2 to ~12 pMC from the expected 14C atmospheric signatures. The Hirtella americana #1 phytoliths sample shows an even greater difference. Its 14C signature is offset by 9.5 pMC, since a plant growing in 1964 should measure ~180 pMC. Such differences represent significant deviations from the expected 14C values even when the combined uncertainties are taken into account (Fig. 1). They are also in significant disagreement with the 14C time-scales obtained from a Panamanian tree ring 14C-AMS dataset reported in Westbrook et al. (2006), which should have recorded the effects of some of the local atmospheric CO2 anomalies invoked by Piperno (2015). In an effort to reconcile the discrepancies, Piperno speculates that CO2 fixed from both fossil fuel emissions and fires must be present in plant tissue, or in the case of the anomalous result of phtC 14C Hirtella americana #1, contamination by pesticide. Unfortunately, no proof that any of these events has occurred has been provided, such as measuring the corresponding bulk plant tissue by 14C-AMS. We find
it interesting that the offset range reported in Piperno (2015), excluding the H. americana #1, is similar to the one reported in Yin et al. (2014). They report offsets of ~3–13 pMC (see detailed information in supplementary material provided by the authors) that have been acknowledged as anomalous (see statements in the introduction and discussion of Piperno, 2015).

We suggest two explanations for these anomalous values. First, they are inaccurate because some unexpected source of exogenous carbon (old and/or young) was added during sample processing which was not accounted for due to the lack of processing blank(s) during phytolith extractions and AMS sample processing. In Table 1, we calculate the amounts of %C needed to skew the 14C signatures and the associated 14C ages offsets. If these were due to the addition of 14C-free carbon, such contributions would translate to 14C age offsets between 157 and 4376 yrs. A second explanation could be that the plants took in small amounts of soil carbon through the roots (including post-bomb signatures), which were later allocated within phytoliths (the Santos et al., 2012a hypothesis). Santos et al., 2012a also point out the possible effects of incomplete digestion. If miniscule amounts of weathered-resistant SOM are already stored in plant tissue, upon digestion this oxidation-resistant OM tends to illustrate that the phytC 14C result falls on a miniscule array of organic compounds comprising the SOM pool (Torn et al., 2009).

Fig. 2. pM 14C signatures from the Northern Hemisphere atmospheric 14C timescale series (NH zone 2 and 3; Hua et al., 2013) and hypothetical SOM turnover times from a single/steady C pool reservoir. The phytC 14C ages of Cucurbita ecuadorensis and Cucurbita ficifolia (red circle in Piperno (2015) are also shown. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

5. Difference between SOM turnover time and ages — implications for phytC

A careful reading of Piperno (2015) seems to present a sequence of contradictory statements with regard to SOM age and turnover rates. In the first paragraph of the discussion Section 4.1, it is stated that 14C dates of 1250 BP→2000 BP for soil depths between 12 and 20 cm have been found in Brazil, Peru, and Ecuador supporting the carbon persistence of plant remains in the tropics. Much later in the same section, it is also stated that “…the most resistant soil carbon fraction in northeast Brazilian soil was only 100 years old, one-tenth that of temperate soils (Chao and Holm, 1997)”, and “…that tropical soils typically have faster SOM turnover rates than those in temperate biomes (e.g., Trumbore 1993)” in order to reinforce the idea that old SOM uptake by plant roots in the tropics is unlikely. We would suggest that first of all, SOM fractions are highly heterogeneous among ecosystems and their vertical 14C ages vary widely between locations, even in the tropics. For instance, in Telles et al. (2003) shows several 14C SOM profiles for a large array of Amazonian tropical forest soils, some with an uneven dispersal of bomb atmospheric 14C with reversing patterns towards older pre-bomb ages reaching as much as 9.6 ka yrs at 200 cm in depth. Second, SOM turnover rates are generally defined as the carbon fluxes in and out of the C pool. Consequently, the mean residence time (MRT) of carbon in soils can be quite different than the individual 14C ages of the large array of organic compounds comprising the SOM pool (Torn et al., 2009).

In Fig. 2, we show the predicted values of 14C for a homogenous, steady state reservoir with different turnover times. To illustrate that the phytC 14C ages can reflect those of a mixture of atmospheric 14CO2 and SOM, we also plotted the 1995 calendar age samples of Cucurbita ecuadorensis (Beta-360359 and –306082) and the Cucurbita ficifolia (Beta-368020). Although we do not have the 14C age of the SOM or refractory fractions of the soils where those plants (and consequently phytC’s) came from for a more precise comparison, it is quite likely that the carbon taken up by roots and reallocated into phytoliths of Santo Domingo (Cucurbita ecuador-ensis; Beta-360359 and –306082) came from a faster turnover-time SOM pool with many carbon fractions bearing post-bomb 14C-enriched signatures (e.g. from previous decades). For the Chirique site (Cucurbita ficifolia; Beta-368020) the phytC 14C result falls on a plot of 300 yrs turnover time. This possibly implies that this site contains a much slower time scale (millennia) SOM pool (Torn et al., 2009), which would potentially negatively affect the phytC 14C ages towards older values. Although the accuracy of these estimates cannot be evaluated without a thorough investigation of the soil pools and their multiply-aged compounds, a SOM-derived C contribution to phytC still can be inferred from the 14C results for post-bomb Neotropical Plants reported in Piperno (2015). Moreover, because the C in phytC may be from mixtures of labile to recalcitrant C pools with different chemical resistances to oxidation, its 14C signature might be affected by the method used to extract the phytoliths (Santos et al., 2010a, Yin et al., 2014). The duplicate C ecuadorensis (Beta-360359 and -306082) specimens processed in sulfuric and nitric yielded the same phytC 14C pMC signatures within uncertainties, while those of Z. mays did not by ~3 pMC (Beta-360361 and –360362; Table 1 of this comment). If a sample comes from a C pool that is 100% homogeneous, measurements from different fractions should always yield similar 14C values, independent of the method used during sample processing. This is demonstrated in Fernandez et al. (2015).

6. Interpretations of fossil and present phytC 14C data

In Piperno (2015) it is stated that most attempts at phytolith dating and comparisons with independent dating techniques have been successful. The statement is supported by a series of references previously discussed in Santos et al. (2010a). To assert that at least some of these examples describing acceptable phytolith studies have been misinterpreted, we reproduce below the passages and datasets of some references cited in Piperno (2015).

The first reference is Wilding (1967). This paper reported the first attempt to directly date phytC by 14C methodology and a date of 13,300 ± 450 years BP was obtained (I-2277). Unfortunately, in Wilding’s words “… it was anticipated that the radiocarbon age of
opal isolated from Warsaw soil would be between 1000 and 1500 years before the present … “ He later states that “additional work is underway to understand the apparent anomaly between the anticipated and obtained carbon dates … ” Wilding suggested that the 10 times greater than expected age was due to preferential oxidation of younger phytoliths and added: “Upon oxidation, such a phenomenon would favor preservation of older carbon occlusions at the expense of younger ones, and thus may account in part for the older carbon date obtained”. Thus, “Preferential oxidation would not affect the validity of the date as an estimate of the minimum age of the valley train sediments. It would, however, preclude the use of such dates to reconstruct ecologically the major period of grass vegetation at a particular site.” Note the importance of the last sentence. For this reason, we conclude that the work of Wilding (1967) cannot correctly be cited as a successful application of the radiocarbon dating of phytoliths, as further analyses were still pending.

Piperno also cites research by Rieser et al. (2007) as producing credible phytC 14C results that match expected ages. In Table 2 of the present comment, phytolith 14C results and Optically Stimulated Luminescence (OSL) ages of the associated Kawakawa tephra (New Zealand) produced by Rieser et al. (2007) in their poster, are presented. The first batch of phytoliths extracted at Victoria University and analyzed at the Rafter Radiocarbon laboratory returned unexpectedly young ages. After a more rigorous oxidation was applied, the phytC 14C ages became older by at least 8 ka yrs BP, and consequently older than the associated OSL ages (Table 2). While further OSL analyses on materials associated with the Kawakawa tephra from different sites (e.g. Schermer et al., 2008) suggested that the tephra could possibly be younger than previously reported, these revised phytC 14C ages were still significantly younger than the accepted radiocarbon age of the Kawakawa tephra (25,360 ± 160 cal yr BP, Vandergoes et al., 2013). Because the phytC 14C dates matched neither the OSL ages nor previously published radiocarbon ages for the tephra, the data from this study were never formally published as a paper, while further testing of phytolith extraction methods and dating continued. Regardless of the true age of the Kawakawa tephra, it is clear that the phytolith ages of the revised extractions reported in Rieser et al. (2007) are several thousand years older than the OSL ages of the surrounding sediments, contrary to what is implied in Piperno (2015).

Although Piperno (2015) acknowledges the abnormality of the phyt14C ages of 3510 and 1865 yrs BP for living and recently senesced bamboo leaves in Sullivan et al. (2008), the “modern” phyt14C ages extracted from the leaf litter were presented as evidence that the phytoliths did not take up old SOM. Santos et al. (2012b) reanalyzed the Sullivan et al. (2008); Sullivan and Parr (2013) dataset using a corrected post bomb-pulse methodology and found age anomalies of at least 400 years towards older values. As highlighted in Section 2, and in Table 1 (this comment) “modern” or post-bomb pMC does not automatically imply correct 14C ages. In Piperno (2015) it was also suggested that Santos et al. (2010a, 2012a) assumed that all phytoliths found in the uppermost few cm of soils should be of modern age. This is incorrect, as the investigators were certainly aware that there is always a mixture of old and new phytoliths even in the uppermost layers of soils (Alexandre et al., 1997, 2011). Santos et al. (2010a) pointed out large differences in the 14C ages of SOM and phytC from the same soil layer (e.g. McClaran and Umlauf, 2000) and that these differences would have been even larger had a high purity extraction methodology been used. Other references cited by Piperno (2015) that echo similar problems have been extensively discussed in Santos et al. (2010a, 2012a,b), and although it is tempting to challenge them one by one again, these refutations will not be repeated here.

Attempts to resolve some of the difficulties with direct 14C dating of phytoliths have prompted researchers to investigate other independent phytolith repositories. A post-bomb Nothofagus truncata phytolith extract yielded an anomalous 14C age of 2152 ± 60 yrs BP (July 2007 NZA-28219, R29539, measurement performed by Dr. Prior at Rafter). In parallel, phytoliths from upper soil layers from the Sahelian zone, Senegal, Africa (April 2008 UCIAMS47170, S.27, measurement performed by Dr. Santos at UCI) returned a 14C age of 3750 ± 15 yrs BP. In this last example, inconsistency is found not just in the remarkably older age of the phytC topsoil layer, but also in the fact that the phytolith assemblage from S.27 mirrors modern vegetation, whereas 4000 years ago the vegetation in the same area was quite different (e.g. Alexandre et al., 1997). Because these phytC 14C dates were clearly anomalous and failed to support the 100% photosynthetic carbon signal in phytC, they were also never formally published. However, they clearly highlight our concerns regarding the assessment of paleoenvironmental and paleodiet reconstructions based on geochemical analyses of phytC.

7. Conclusions

In our view, the post bomb results newly presented in Piperno (2015) were misinterpreted, as were most of the reinterpretations on the discussions in Santos et al. (2010a, 2012a,b), both of which support the systematic offset in 14C signature of phytC and probable extraneous soil carbon contribution to phytC.

We clarify the points raised by the author regarding her reinterpretations of 14C phytolith dating in the literature, and reassess the 14C results for phytoliths from modern Neotropical plants in the context of a standard 14C bomb-pulse methodology. However, the lack of comparison between the 14C signatures of phytC and the 14C signatures of the plant of origin prevents further assessment of the hypothetical explanations provided by Piperno (2015) for the reported anomalous depleted and enriched phytC 14C values. Moreover, since the quality of the presented 14C results cannot be properly evaluated due to the lack of important information on phytolith purity, phytolith carbon recovery, and procedural blank assessment, an exogenous source of C cannot be completely dismissed.

If the 14C results presented in Piperno (2015) are correct, and are...
correctly interpreted, they add to the long list of phytoliths from modern plants with unexpectedly anomalous $^{14}C$ ages. They show $^{14}C$ signature offsets equivalent to 157–4376 pre-bomb years. This may imply that previous pre-bomb phytC $^{14}C$ from Neotropical regions of the world might be affected by SOM contributions to phytC, and therefore should be carefully and rigorously re-appraised. Considering that $^{14}C$ analysis are more accessible than ever, phytC, and therefore should be carefully and rigorously reappraised. We hope that this comment will help future scholars to be more critical and careful when examining radiocarbon data.

Acknowledgments

The authors gratefully acknowledge the support of the U.S. National Science Foundation (DEB-1144888 to GMS). We wish to thank Gergana Mouteva and Yuje He for helping with the soil turnover time age model. Dr. E. Taylor (Professor of the Department of Anthropology, University of California, Riverside) and Dr. John Southon (Co-director of the KCCAMS Facility at University of California, Irvine) provided some suggestions on early drafts of this comment. The views expressed here remain those of the authors. The authors also wish to extend their thanks to the anonymous reviewer and the Editor Thilo Rehren.

References


Wharekauhau fault system, North Island, New Zealand: implications for an unstable linkage between active strike-slip and thrust faults. Tectonics 28 (6).


Wharekauhau fault system, North Island, New Zealand: implications for an unstable linkage between active strike-slip and thrust faults. Tectonics 28 (6).


