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The effect of diagenesis on carbon isotope values of fossil wood

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ABSTRACT

The carbon isotope ($\delta^{13}C$) value of modern and fossil wood is widely used as a proxy for environmental and climatic change. Many researchers who study stable carbon isotopes in modern and recently deceased trees chemically extract cellulose ($\delta^{13}C_{cell}$) rather than analyzing whole wood ($\delta^{13}C_{wood}$) due to concerns that molecular variability across tree rings could influence $\delta^{13}C_{wood}$ values, and that diagenesis may preferentially degrade cellulose over lignin. However, the majority of deep-time researchers analyze $\delta^{13}C_{wood}$ without correcting for possible diagenetic effects due to cellulose loss. We measured $\delta^{13}C_{cell}$, $\delta^{13}C_{wood}$, and cellulose content of 38 wood fossils that span ~50 m.y. in age from early Eocene to late Miocene, using variability across such a large range of geologic ages and settings as a natural laboratory in diagenesis. For comparison with our measurements, we produced a literature compilation of 1210 paired $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ values made on fossil and modern trees. We report that, on average, the apparent enrichment factor (ε) between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ ($\varepsilon = \delta^{13}C_{cell} - \delta^{13}C_{wood}$) is 1.4‰ ± 0.4‰ larger in deep-time samples than Holocene wood, and this can be explained by loss of cellulose during degradation, independent of atmospheric chemistry or climate conditions during growth. A strong linear correlation exists between $\delta^{13}C_{wood}$ and $\delta^{13}C_{cell}$ in both deep-time ($r^2 = 0.92$) and Holocene ($r^2 = 0.87$) samples, suggesting that either substrate can provide a reliable record of environmental conditions during growth. However, diagenetic effects must be corrected if $\delta^{13}C_{wood}$ values are compared to extant trees or across long time scales, where cellulose content may vary.

INTRODUCTION

The stable carbon isotope composition ($\delta^{13}C$) of terrestrial plants is one of the primary means for tracking changes in Earth's carbon cycle and climate before the instrument record (Nordt et al., 2016; Strauss and Peters-Kottig, 2003). Diagenetic alteration of organic substrates presents a fundamental limitation for interpreting $\delta^{13}C$ signals from deep-time (i.e., pre-Quaternary) records (Jones, 1994; Tu et al., 2004; Baczynski et al., 2016). This challenge has been mitigated through the measurement of compound-specific isotope ratios using biomolecular substrates selected for their recalcitrance to diagenetic modification (e.g., Goni et al., 2000; Ververis et al., 2004). In the past 30 yr, at least 229 $\delta^{13}C$ records have been developed for reconstructing past climate using annual growth rings in modern trees; 83% of these measured $\delta^{13}C$ of cellulose ($\delta^{13}C_{cell}$), a polysaccharide that can be chemically extracted from whole wood (Table DR1 in the GSA Data Repository[1]). However, for deep-time applications that utilized fossil wood across a wide range of preservation states (e.g., lignified [Bechtel et al., 2003] to mummified [Jahren and Sternberg, 2002]), only 23% of studies measured $\delta^{13}C_{cell}$, compared to 77% that reported $\delta^{13}C$ values of whole wood ($\delta^{13}C_{wood}$; Table DR1).

Despite clear differences in the use of whole wood versus compound-specific analyses, measurement of $\delta^{13}C$ values of living, buried, and fossilized trees is routinely used to discern past hydroclimate (Livingston and Spittlehouse, 1996; Barber et al., 2000; Edvardsson et al., 2014), precipitation patterns (Schubert et al., 2012; Schubert and Timmermann, 2015; Schubert et al., 2017), plant life strategy and taxonomy (Bechtel et al., 2007; Jahren and Sternberg, 2008), and atmospheric chemistry (Hesselbo et al., 2000; Schubert and Jahren, 2013). As yet, the effect of decomposition on $\delta^{13}C$ value is poorly constrained, but it is necessary for the quantification of atmospheric and climatic change within the deep-time geologic record. For example, recent work linking organic matter $\delta^{13}C$ values to changes in atmospheric pCO_2 have the potential to greatly increase the resolution of paleoclimate and paleoatmospheric reconstructions (Schubert and Jahren, 2012; Cui and Schubert, 2018). Correction of $\delta^{13}C$ values for diagenesis will better constrain the nature and magnitude of pCO_2 change and help to reduce uncertainty in $\delta^{13}C$-based paleoclimatic and paleoenvironmental proxies.

Wood offers a unique opportunity to study diagenetic alteration of organic matter, because it is primarily composed of two compounds: lignin (25%–35%) and cellulose (40%–50%), with lesser amounts of hemicellulose and extractives (Parham and Gray, 1984; Pettersen, 1984; Scott, 2009). Lignin is more recalcitrant than cellulose; therefore, the preservation state of wood can be modeled using these two end members (Loader et al., 2003), where the $\delta^{13}C$ value of lignin is typically 0.5‰–2‰ lower than that of cellulose (Harlow et al., 2006). Several researchers have concluded that as cellulose preferentially degrades in fossil wood, $\delta^{13}C_{wood}$ will trend toward the $\delta^{13}C$ value of lignin and result in up to 2‰ lower values (Benner et al., 1987; Spiker and Hatcher, 1987; Schleser et al., 1999; van Bergen and Poole, 2002). Consequently, the apparent enrichment (ε) between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ (i.e., $\varepsilon = \delta^{13}C_{cell} - \delta^{13}C_{wood}$) should show a negative correlation with cellulose content of wood. In contrast, incubation experiments (Schleser et al., 1999) and some deep-time fossil wood assemblages (Bechtel et al., 2007) possibly indicate that higher ε values may result from enrichment of ^{13}C during cellulose degradation.

Numerous studies have reported a 1:1 correlation between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ for living and exceptionally well-preserved, subfossil trees (Schleser, 1990; Leavitt and Long, 1991; Livingston and Spittlehouse, 1996; Borella and

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[1]GSA Data Repository item 2019354, descriptions of fossil wood localities and analytical methods, Figures DR1–DR3, and Tables DR1 and DR2, is available online at http://www.geosociety.org/datarepository/2019/, or on request from editing@geosociety.org.

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Leuenberger, 1998; Macfarlane et al., 1999; Loader et al., 2003; Edvardsson et al., 2014). Testing of this correlation for deep-time wood samples has been inhibited by the paucity of well-preserved wood in the stratigraphic record relative to Quaternary strata, and by differences in analytical approaches between Quaternary and deep-time workers. Whereas $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ are widely measured on living and recently felled trees (see review in McCarroll and Loader, 2004), only $\delta^{13}C_{wood}$ is routinely measured on deep-time wood fossils (e.g., Gröcke et al., 1999; Hesselbo et al., 2000, 2002, 2003, 2007; Pearce et al., 2005; Yans et al., 2010; Table DR1). We sought to rectify this discrepancy and quantify the effects of diagenesis on $\delta^{13}C$ values by measuring $\delta^{13}C_{cell}$, $\delta^{13}C_{wood}$, and cellulose content on 38 fossil wood specimens that ranged in age from early Eocene to late Miocene. We supplemented these analyses with a new compilation of published paired $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ values from modern trees and deep-time wood fossils to test the following hypotheses: (1) $\delta^{13}C_{wood}$ correlates with $\delta^{13}C_{cell}$ regardless of geologic age, and (2) deep-time wood fossils that have lost cellulose will have greater ε values.

METHODS

The fossil wood samples analyzed in this study were recovered from deltaic and lacustrine deposits in the Eureka Sound Formation on Banks Island, Northwest Territories, Canada; the Yongning Formation in Nanning, China; the Xiaolongtan Formation in Yunnan Province, China; and the Khapchansky locality in northeast Siberia (Fig. 1; Table DR1). Descriptions of these localities and details of laboratory sampling and analytical methods are provided in the Data Repository.

Typically, $\delta^{13}C$ values of tree-ring tissue are corrected for changes in the $\delta^{13}C$ value of atmospheric CO_2 and pCO_2 prior to interpretation of climatic signals (McCarroll et al., 2009; Treydte et al., 2009; Wang et al., 2011; Schubert and Timmermann, 2015; Trahan and Schubert, 2016). Biosynthetic fractionation between different plant substrates, however, is not affected by atmospheric chemistry (e.g., Loader et al., 2003; Schubert and Jahren, 2012; Diefendorf et al., 2015); therefore, determination of net carbon isotope discrimination was unnecessary for interpretation of the carbon isotopic difference between cellulose and whole wood.

RESULTS AND DISCUSSION

Effect of Diagenesis on Fossil Wood $\delta^{13}C$ Values

Our new analyses extend the age range and more than double the number of reported deep-time fossil wood $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ pairs. The $\delta^{13}C_{wood}$ values of the 38 fossil samples ranged from −31.8‰ to −22.6‰ ($\delta^{13}C_{cell}$ = −30.2‰ to − 19.8‰), consistent with the wide range of environments, taxa, climates, and atmospheric compositions represented by these fossils. The $\delta^{13}C$ values of paired wood and cellulose samples were highly correlated between substrates (Spearman's ρ = 0.97), and $\delta^{13}C_{cell}$ values were higher than $\delta^{13}C_{wood}$ values in every pair (Fig. DR2). Cellulose content ranged from 0.4% to 44.5%.

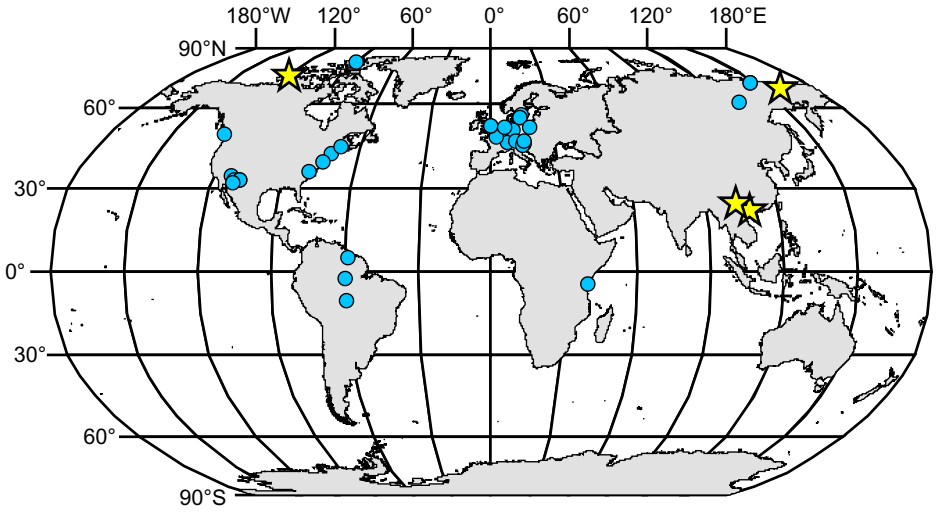

Figure 1. Locations of fossil wood samples analyzed in this study (yellow stars) and locations associated with published $\delta^{13}C_{cell}$ (cell—cellulose) and $\delta^{13}C_{wood}$ (wood—whole wood) pairs from living, recently felled, and fossilized wood (blue circles; Table DR2 [see text footnote 1]).

Calculated ε values were negatively correlated with cellulose content (Pearson's $r = -0.49$, $p = 0.003$; Fig. 2). A linear regression model estimated that pure cellulose (i.e., $\delta^{13}C_{wood} = \delta^{13}C_{cell}$) would have an ε value ($\delta^{13}C_{cell} - \delta^{13}C_{wood}$) within error of zero (−0.4‰ ± 0.4‰). The difference in ε between a sample that has 45% cellulose—a typical value for living trees—and one that has no cellulose is 1.4‰ ± 0.4‰. Cellulose content broadly corresponds to geologic age, with older wood fossils tending to have less cellulose remaining (Fig. 2B). However, individual deposits (e.g., the Oligocene Nanning Lagerstätte; Table DR2) can contain a large range of cellulose content among fossil samples. These findings indicate that diagenetic alteration of wood, which preferentially removes cellulose, can significantly bias deep-time $\delta^{13}C_{wood}$ values.

Comparison of the $\delta^{13}C$ Value of Whole Wood Versus Cellulose

We augmented our data set ($n = 38$) with paired $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ data from 18 published studies, yielding a total of 1248 pairs (Table DR2). This comprehensive data set was stratified into three age categories: post-industrial Holocene (post–1850 C.E.), pre-industrial Holocene (1850 C.E.–12 ka), and

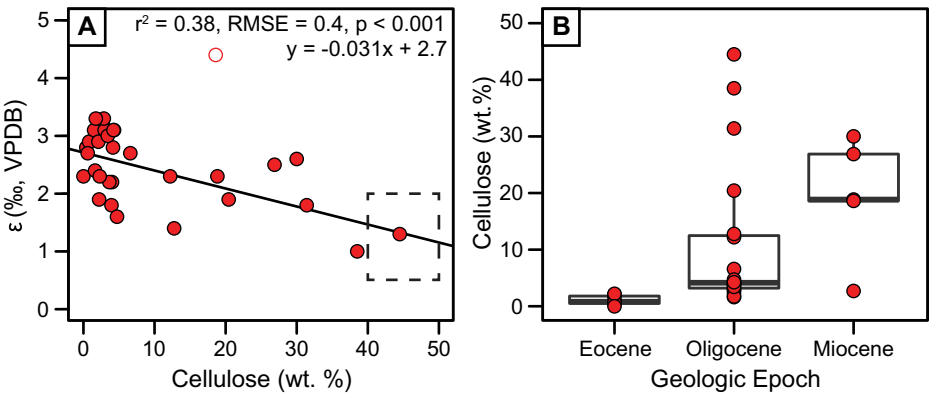

Figure 2. Results of fossil wood $\delta^{13}C$ analysis and cellulose extraction. (A) ε (calculated as $\delta^{13}C_{cell} - \delta^{13}C_{wood}$; cell—cellulose, wood—whole wood) plotted against cellulose content. In order to avoid bias in our linear regression model, one outlier (open circle) was omitted prior to analysis. Dashed box shows the range of cellulose content and apparent enrichment, ε, typical in living trees. (B) Cellulose content binned by epoch, shown as box-and-whisker plots. Boxes span the first to third quartiles, with bold lines indicating median (second quartile) values. Whiskers extend to values that are within the envelope of the interquartile range multiplied by 1.5. VPDB—Vienna Peedee belemnite; RMSE—root mean square error.

deep-time (pre-Quaternary). Together, this data set includes paired $\delta^{13}C$ values from both field and herbarium collections and includes at least 56 genera sampled across 80 degrees of latitude. Deep-time fossil samples are represented from across the Cenozoic (early Eocene, middle Eocene, Oligocene, early Miocene, middle Miocene, late Miocene, and Pliocene).

We report a strong linear correlation between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ ($p \leq 0.001$) for Holocene ($r^2 = 0.87$, $m = 0.94$) and deep-time samples ($r^2 = 0.92$, $m = 1.08$; Fig. 3A). The median ε values between cellulose and whole wood for post-industrial (ε = 1.3‰) and pre-industrial (ε = 1.2‰) Holocene samples are within analytical uncertainty of each other, but the value is significantly larger (paired Wilcoxon rank-sum test, $p < 0.001$) for deep-time samples (ε = 2.9‰; Fig. 3B), consistent with lower cellulose content in the deep-time samples compared with modern trees.

Although deep-time samples have, on average, larger ε values than Holocene trees, ε values do not systematically vary across deep-time age bins (Fig. 4). For example, the Oligocene Nanning, China, locality contained 19 samples recovered from a single stratum with ε = 1.0‰–3.3‰, which spans the 23rd to 90th percentiles

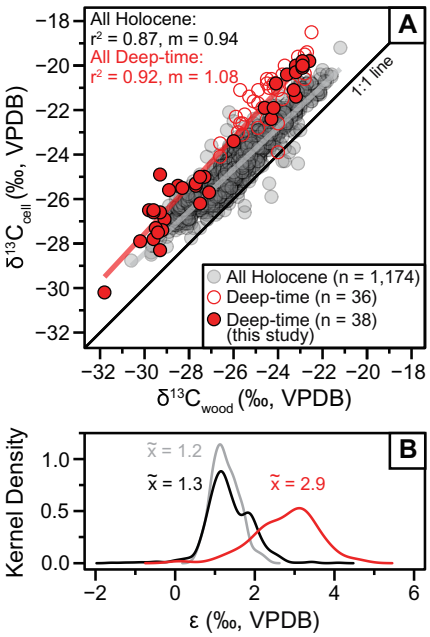

Figure 3. (A) Cross-plot of $\delta^{13}C_{cell}$ versus $\delta^{13}C_{wood}$ (cell—cellulose, wood—whole wood); all Holocene data (12 ka to present) are grouped together. Deviation from the 1:1 line indicates apparent enrichment (ε) between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$. Regression coefficient of determination (r^2) and slope (m) are shown for Holocene and deep-time data. (B) Kernel density functions for ε, grouped by Holocene (post–1850 C.E., black line; pre–1850 C.E., gray line) and deep-time (red line). Median ($\tilde{x}$) ε values are shown. VPDB—Vienna Peedee belemnite.

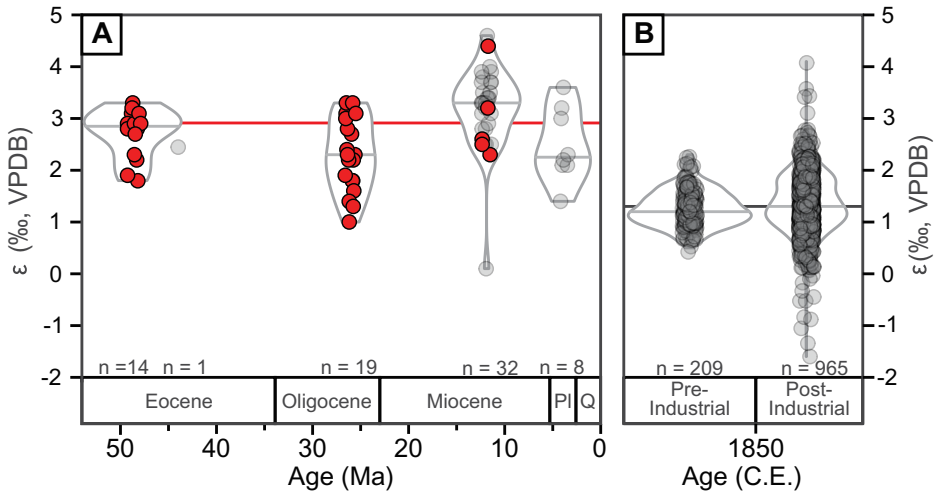

Figure 4. Violin plots of apparent enrichment, ε, grouped by geologic epoch for new analyses (red circles) and isotope pairs compiled from literature (gray circles; Table DR2 [see footnote 1]). Each "violin" represents the probability distribution of ε values in each group normalized to the same area, with cross-bar indicating median value. Note: All Miocene data were combined. Red line—median of deep-time ε values. Black line—median of post–1850 C.E. Holocene ε values; VPDB—Vienna Peedee belemnite; Pl—Pliocene; Q—Quaternary.

of post-industrial Holocene ε values. These samples also have a large range of cellulose contents that vary between extremely low values (1.6%) and those similar to living trees (44.5%). The large ranges in ε values and cellulose content across 19 samples of the same age support our finding that cellulose content—rather than age—is a better predictor of ε in fossil wood.

These results have two significant implications. First, the correlation between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ values in modern and well-preserved, subfossil Holocene wood indicates that isotopic signals are similarly represented by both substrates, and whole wood can therefore be analyzed rather than cellulose when higher sample throughput is desired. Researchers who previously reported a lack of correlation between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ were observing samples from a limited isotopic range, across which the strong correlation between substrates was not evident (e.g., Schleser et al., 2015). In rare cases, *in situ* decay of standing trees can lead to moderate cellulose loss and consequent bias in $\delta^{13}C_{wood}$ values, which suggests a need for analysis of $\delta^{13}C_{cell}$ for some species (e.g., *Populus deltoides*, eastern cottonwood; Friedman et al., 2019).

The second implication of our findings is that the pervasive analysis of $\delta^{13}C_{wood}$ in deep-time geologic archives has, in many cases, included a negative bias in $\delta^{13}C$ values due to cellulose loss. We note that the presence of exquisitely preserved fossil wood is itself a rarity in the geologic record. Due to substantial taphonomic bias against wood preservation, we do not consider geologic age to be a predictive variable for estimating fossil wood cellulose content, even though our older samples tended to have less average cellulose content (Fig. 3).

Unifying Relationship to Explain ε in the Fossil Record

The difference in median ε value between deep-time and post-industrial Holocene samples in the comprehensive data set is 1.6‰, which is similar to the value of 1.4‰ predicted by cellulose degradation in our fossil wood samples (Fig. 2). These values are also similar to the value of 1.3‰ found in artificial aging of wood via carbonization experiments (Turney et al., 2006). From this, we conclude that the $\delta^{13}C_{wood}$ value of deep-time fossil trees is, on average, biased toward lower values. We note that the opposite trend is observed in soil organic matter, which experiences an increase in $\delta^{13}C$ value of 1‰–8‰ during diagenesis (Wynn, 2007), caused by respiration of ^{12}C and fixation of ^{13}C by microbes.

These data serve as an empirical confirmation that the $\delta^{13}C_{wood}$ value of fossil specimens varies as a function of cellulose content, which is in turn an indicator of preservation state. The empirical relationship between ε and cellulose content from our fossil wood samples (Fig. 2A) can be used as a correction for comparing $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ values among fossil wood samples in various preservation states:

$$\delta^{13}C_{wood} = \delta^{13}C_{cell} + 0.031x - 2.7, \quad (1)$$

where x is cellulose content in weight percent, and the root mean square error is 0.4‰. However, direct analysis of $\delta^{13}C_{cell}$ is likely more reliable for interpreting paleoclimatic and paleoenvironmental change from wood across myriad preservation states.

According to Equation 1, fossil wood $\delta^{13}C_{wood}$ values can be biased by up to 1.4‰ as a result of cellulose loss during diagenesis

(i.e., 45% vs. 0% cellulose). If unaccounted for, this would lead to the erroneous interpretation of climatic and environmental change. A 1.4‰ decrease in $\delta^{13}C$ value due to diagenesis may be incorrectly interpreted as a large increase in precipitation (Kohn, 2010) or pCO_2 (Schubert and Jahren, 2012), or it may lead to misinterpretation of plant taxa when using $\delta^{13}C_{wood}$ values as a chemotaxonomic tool (Bechtel et al., 2007). We illustrate the importance of accounting for diagenetic alteration through calculation of pCO_2 using the methods described in Schubert and Jahren (2015) for a published $\delta^{13}C_{wood}$ record across the Early Jurassic (Toarcian) carbon isotope excursion (CIE; Hesselbo et al., 2007). We found that using uncorrected $\delta^{13}C_{wood}$ values results in an overestimation of peak pCO_2 at the CIE by ~100% (i.e., 2154 vs. 1039 ppm; see the Data Repository). The pCO_2 estimate of 1039 ppm at the CIE calculated after correcting for cellulose loss overlaps with an estimate of 1200 ± 400 ppm based on fossil leaf stomatal frequency (McElwain et al., 2005).

CONCLUSION

Our laboratory analyses and literature compilation demonstrate that apparent enrichment between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ is consistent across a wide range of environments, climates, and taxonomic groups. The 1:1 correlation between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ in modern and Holocene trees should unburden researchers in these areas from performing time- and resource-intensive cellulose extraction procedures. Further, the correlation between $\delta^{13}C_{cell}$ and $\delta^{13}C_{wood}$ across deep-time samples demonstrates that each substrate provides similar paleoenvironmental information, but it can only be used for detecting relative changes in $\delta^{13}C$ value. The increased ε values determined for deep-time samples relative to modern trees suggests a need for workers to correct $\delta^{13}C_{wood}$ values based on cellulose content when comparing modern and fossil $\delta^{13}C_{wood}$ values.

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