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^{17}O -excess of grass leaf phytoliths across the North American prairies records late-growing season daytime relative humidity

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A B S T R A C T

Because it is an important climate parameter, an accurate proxy is required for the reconstruction of past Relative Humidity (RH). Triple oxygen isotopes of grass-leaf phytoliths have a high potential for this purpose. A strong correlation between RH and ^{17}O -excess of grass leaf phytoliths has been previously demonstrated from calibration experiments in growth chambers and at natural Sub-Saharan African and Mediterranean sites. Here we focus on the potential of ^{17}O -excess of grass leaf phytoliths as a proxy of RH across the North American Great Plains. We tested the relationship between the ^{17}O -excess of naturally grown *Calamovilfa longifolia* phytoliths and RH for different periods of the grass growing season. The results show that ^{17}O -excess of leaf phytoliths has a strong correlation with late-growing season (July–August) daytime RH, which varies from 29 to 72 % across North America. The correlation can be expressed as: $^{17}\text{O}\text{-excess}_{\text{leaf phytoliths}} = 4.14(\pm 0.47) \times \text{RH} (\%) - 497(\pm 26)$ ($R^2 = 0.85$, $p\text{-value} < 0.0001$). To use the ^{17}O -excess of bulk phytoliths buried in soils and sediments as a quantitative proxy of past RH, future calibration studies on soil phytoliths are needed to evaluate the contribution of non-transpiring phytoliths. The ^{17}O -excess of stem water, which was determined by ^{17}O -excess of stem phytoliths, shows similar values to the ^{17}O -excess of precipitation in North America without evaporation, which therefore does not affect the ^{17}O -excess of leaf phytoliths in North America. These results demonstrate that the ^{17}O -excess of phytoliths is a promising proxy for regional growing season RH.

1. Introduction

Relative humidity (RH) is the percentage of water vapor in the air relative to the saturation state at the same air temperature. RH is a key climate parameter driving transpiration and the productivity of ecosystems (López et al., 2021; Grossiord et al., 2020), and the accurate reconstruction of past RH is needed to predict modern ecosystem responses to climate change (Tierney et al., 2020). Thus, there is a need for a quantitative indicator of past continental RH, applicable to different climatic regimes and suitable for model-data comparisons.

RH controls the isotopic composition of leaf water, because during plant transpiration, the magnitude of fractionation in oxygen isotopes between the leaf water and the atmospheric water vapor is inversely related to RH (Craig and Gordon, 1965; Cernusak et al., 2016). Mineral compounds formed during plant growth, such as phytoliths, that contain oxygen derived from plant water, have the potential to indicate ancient

RH from their oxygen-isotope compositions (Alexandre et al., 2018; Outrequin et al., 2021; Voigt et al., 2023). Phytoliths are amorphous silica microparticles ($\text{SiO}_2 \cdot n\text{H}_2\text{O}$) formed after dissolved silica (silicic acid) in soil water is absorbed by roots and translocated to plant tissues via the transpiration stream. Their polymerization in or between cells can be either metabolically controlled or a result of passive silica saturation (Hayward and Parry, 1975; Motomura et al., 2004; Kumar et al., 2017, 2020; Markovich et al., 2019). In grasses, phytoliths are abundant in the mature cells of leaf epidermis and to a lesser extent of stem epidermis (Webb and Longstaffe, 2000, 2002; Ma and Yamaji, 2006; Alexandre et al., 2018). After the death of plants and organic matter mineralization, phytoliths can be preserved in soils and sediments for thousands to millions of years under favorable conditions. When extracted from buried soils and sediments, phytoliths can be used as an indicator of past vegetation and climate.

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The morphology of phytoliths found in soil and sediments has been used to reconstruct past vegetation of the Northern American great plains (Fredlund and Tieszen, 1994; Strömberg, 2004; Cordova et al., 2011; Woodburn et al., 2017; Strömberg et al., 2018). By comparing the phytolith contents of grasses grown in different RH conditions, Webb and Longstaffe (2002) showed that grass leaf phytolith content is negatively correlated with RH across North America. Moreover, as phytoliths precipitate in isotopic equilibrium with the plant water, their oxygen-isotope composition has potential for ancient climate reconstruction (Shahack-Gross et al., 1996; Webb and Longstaffe, 2000, 2002, 2003, 2006). The difference in $\delta^{18}\text{O}$ between leaf and stem phytoliths, $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytolith}}$, was shown to be strongly related to late-growing season RH (Webb and Longstaffe, 2002). However, the current impossibility of separating leaf and stem phytoliths with similar morphology from soils made $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytolith}}$ unsuitable as an indicator of past RH. The $\delta^{18}\text{O}$ of leaf phytoliths alone cannot be used as an indicator for RH either, as it is controlled by phytolith forming temperature, RH, and $\delta^{18}\text{O}$ of water absorbed by roots. The triple oxygen-isotope composition and in particular, the ^{17}O -excess (also expressed as $\Delta^{17}\text{O}$ in triple oxygen isotope studies) of phytoliths is much more promising and can be expressed as:

$$^{17}\text{O-excess} = \delta^{17}\text{O} - 0.528 \times \delta^{18}\text{O} \quad (1)$$

Unlike the d-excess ($\text{d-excess} = \delta^2\text{H} - 8.0 \times \delta^{18}\text{O}$), the ^{17}O -excess of water is not significantly impacted by water phase changes and Rayleigh distillation (Uemura et al., 2010). It is therefore ideally suited for the study of evaporation processes in the water cycle, as shown by the growing number of recent studies on the subject (Uemura et al., 2010; Surma et al., 2018, 2021; Voigt et al., 2021; Aron et al., 2021, 2023; Xia et al., 2023). In grasses, isotope fractionation of water in non-transpiring tissues (like roots and stems) is weak, so the oxygen-isotope composition of stem water is close to that of soil water (Allison et al., 1984; Webb and Longstaffe, 2000, 2002, 2003). In leaves, stomata opening allows plant water to transpire, which translates into leaf water evaporation. The proportion of evaporated water increases from the base to the tip of the grass leaf, which leads to progressive increases of $\delta^{17}\text{O}$, $\delta^{18}\text{O}$, and $\delta^2\text{H}$, and decreases of d-excess and ^{17}O -excess in the leaf water (Gan et al., 2002; Farquhar and Gan, 2003; Webb and Longstaffe, 2000, 2003; Cernusak et al., 2016; Alexandre et al., 2019). Despite this variation in ^{17}O -excess of the water along the leaf, the average ^{17}O -excess of bulk leaf water is independent of the leaf length and controlled by RH (Landais et al., 2006; Li et al., 2017; Alexandre et al., 2019). Calibration experiments in growth chambers showed that this RH-dependency is recorded in the ^{17}O -excess of leaf phytoliths ($^{17}\text{O-excess}_{\text{leaf phytolith}}$) (Alexandre et al., 2018; Outrequin et al., 2021; Voigt et al., 2023), regardless of the $\delta^{18}\text{O}$ of soil water, atmospheric temperature and CO_2 concentration (Outrequin et al., 2021). The growth chamber calibration line (GCCL) is expressed as (Alexandre et al., 2018; Outrequin et al., 2021):

$$^{17}\text{O-excess}_{\text{leaf phytolith}} = 4.4 (\pm 0.5) \times \text{RH} - 510 (\pm 33) \quad (2)$$

The RH signal imprinted in $^{17}\text{O-excess}_{\text{leaf phytolith}}$ depends on the timing of transpiration and silica polymerization (Voigt et al., 2023). For example, for a natural Mediterranean climate, where stomatal conductance is low at night, $^{17}\text{O-excess}_{\text{leaf phytolith}}$ is reflective of the average daytime RH throughout the growing season.

These studies demonstrate that the ^{17}O -excess of leaf phytoliths has a high potential to be an independent quantitative proxy of RH. It is necessary to test the applicability of the GCCL (Eq. 2) to different climates and ecosystems. In this study, the relationship between ^{17}O -excess of modern grass phytoliths and RH is examined across the spectrum of North American prairies and steppes, where average late-growing season daytime atmospheric temperature and RH range from 15 to 26 °C and from 29 to 75 %, respectively. We further assessed which RH (diurnal or daily, and seasonal) is recorded by the ^{17}O -excess of leaf phytoliths.

2. Fractionation expression in the triple oxygen isotope system

The fractionation factor α between a and b follows: $\alpha^{17}\text{O}_{a-b} = \alpha^{18}\text{O}_{a-b}^{\text{eq}}$, which can also be expressed as $\theta_{a-b} = \ln \alpha^{17}\text{O}_{a-b} / \ln \alpha^{18}\text{O}_{a-b}$. The equilibrium fractionation between liquid water and vapor is defined by $\theta_{\text{eq}} = 0.529$ (Luz and Barkan, 2005), and the θ of vapor diffusion into air (θ_{diff}) is 0.518 (Luz and Barkan, 2009; Landais et al., 2006). θ_{eq} and θ_{diff} are not significantly changed by temperature in the 11.4 to 41.5 °C range (Luz and Barkan, 2005). In contrast to θ_{a-b} which is linked to a particular physical process (equilibrium or kinetic), λ_{a-b} is empirically measured between two groups of materials and is not related to a well understood single process (Pack and Herwartz, 2014). λ_{a-b} is expressed as $(\delta^{17}\text{O}_a - \delta^{17}\text{O}_b) / (\delta^{18}\text{O}_a - \delta^{18}\text{O}_b)$ in the $\delta^{18}\text{O}$ vs $\delta^{17}\text{O}$ space, where $\delta^*\text{O} = \ln(\delta^*\text{O} + 1)$ and $*$ is the isotope mass, e.g. ^{17}O or ^{18}O .

Because the ^{17}O -excess is defined as the small deviation in $\delta^{17}\text{O}$ from the Global Meteoric Water Line (GMWL), with a reference slope $\lambda_{\text{ref}} = 0.528$ (Barkan and Luz, 2007; Terzer-Wassmuth et al., 2023), which is close to θ_{eq} of 0.529, it does not vary much during equilibrium fractionation but is very convenient to trace diffusion during evaporation.

The fractionation between phytolith and plant water, defined as $\lambda_{\text{Phyto-water}}$, systematically obtained in previous calibration studies is 0.522 ± 0.001 (Alexandre et al., 2018, 2019; Outrequin et al., 2021; Voigt et al., 2023). It is slightly lower than the theoretical fractionation, $\theta_{\text{SiO}_2\text{-water}}$, of 0.524 calculated for the 5–30 °C temperature range (Cao and Liu, 2011; Sharp et al., 2016).

3. Materials and methods

3.1. Sample collection and treatment

Calamovilfa longifolia was collected at the end of the growing season in 1995 and 1996 at seventeen locations across North America between 38°51'N and 53°00'N (Webb and Longstaffe, 2002). Sample locations are listed in Table 1. As shown in Fig. 1, the sampling sites are mainly located in warm-summer humid continental climate and cold semi-arid climate zones. The warm-summer humid continental climate is characterized by a minimum monthly mean temperature below −3 °C with at least 4 months with a mean temperature above 10 °C, and no significant difference in precipitation between seasons. The cold semi-arid climate zone has an average annual temperature of less than 18 °C. Annual precipitation is low but higher than in desert climates, and typically occurs seasonally (Kottek et al., 2006). A few samples were collected from the humid subtropical climate zone, hot-summer humid continental climate zone, and monsoon-influenced hot-summer humid continental climate zone (Köppen climate classification; Kottek et al., 2006). Data for the $\delta^{17}\text{O}$ in precipitation is not available for our study area, but the ^{17}O -excess of tap water, that can be used as a proxy for precipitation for our U.S. sample locations, ranges from −6 to +43 permeg (Li et al. 2015; Fig. 2C). *C. longifolia* is a native, perennial, warm-season C4 grass with long rhizomes and roots adapted to sandy soils. It is drought-tolerant thus widely distributed over different climates with wide range of precipitation amounts (Weaver, 1958). *C. longifolia* reproduces by seeds and rhizomes, and it grows from the beginning of May to the early fall in North America (Maun, 1985; Hendrickson et al., 2000).

Grass samples were separated into stems and leaves, hand-washed and dried (Webb and Longstaffe, 2002). Phytoliths were extracted by wet ashing technique, and the purity of each phytolith sample was assured by X-ray diffraction (Webb and Longstaffe, 2002).

3.2. Climate data and growing season

Climate data (RH and atmospheric temperature measured at ground-level) were extracted from the WFDE5 dataset, which comprises bias-adjusted ERA5 reanalysis data (an interpolation of spatial observations with a coupled surface-atmosphere model from the European Centre for

Table 1

Relative humidity (RH) and atmospheric temperature (T) extracted for the 1995–1996 grass growing season from the WFDE5 dataset for the 17 sites where *C. longifolia* was collected across the North American steppes and prairies.

Site	Location	Latitude	Longitude	Estimated Growing Season ^a	Whole-growing season T (°C)		Late-growing season ^b T (°C)		Whole-growing season RH (%)		Late-growing season ^b RH (%)	
					Whole day	Daytime	Whole day	Daytime	Whole day	Daytime	Whole day	Daytime
1	Pinery, ON, CAN	43°19'N	81°45'W	May 5-Sep 13, 1995	19	21	21	23	74	72	75	72
2	Colorado Springs, CO, USA	38°51'N	104°45'W	May 6-Aug 23, 1996	20	22	22	24	58	50	59	51
3	Havanna, IL, USA	40°18'N	90°03'W	April 30-Aug 20, 1996	21	22	23	25	74	70	71	66
4	Kellogg, MN, USA	44°18'N	91°59'W	May 2-Aug 27, 1995	20	22	23	24	70	66	75	70
5	Aroya, CO, USA	38°51'N	103°07'W	May 21-Aug 23, 1996	22	24	22	25	62	55	68	60
6	Quinter, KS, USA	39°04'N	100°13'W	May 15-Aug 22, 1996	22	24	23	25	67	61	70	64
7	Thedford, NE, USA	42°02'N	100°49'W	May 22-Sep 6, 1995	21	23	23	25	66	60	62	57
8	Bonner, NE, USA	41°56'N	103°01'W	May 25-Sep 6, 1995	21	24	24	26	59	53	52	46
9	Fertile, MN, USA	47°32'N	96°16'W	May 12-Aug 28, 1995	19	21	21	22	68	64	73	68
10	Cheyenne, WY, USA	41°20'N	104°34'W	May 23-Sep 5, 1995	18	21	21	24	55	48	46	38
11	Onefour, AB, CAN	49°07'N	110°28'W	May 30-Sep 3, 1995	17	19	18	20	59	53	55	49
12	Dundurn, SA, CAN	51°49'N	106°30'W	June 1-Aug 31, 1995	17	19	17	19	66	62	69	64
13	Sprucewoods, MA, CAN	49°52'N	99°22'W	May 26-Aug 30, 1995	19	21	19	21	70	66	71	66
14	Rawlins, WY, USA	42°03'N	106°56'W	June 5-Sep 5, 1995	18	21	21	23	43	37	34	29
15	Broadus, MT, USA	46°24'N	106°16'W	May 18-Sep 4, 1995	21	22	23	25	53	48	48	42
16	Kinsella, AB, CAN	53°00'N	111°32'W	May 25-Sep 1, 1995	15	17	15	16	67	62	70	65
17	Kortes Dam, WY, USA	42°03'N	106°56'W	June 5-Sep 5, 1995	18	21	21	23	43	37	34	29

^a The start date of the growing season of each location was estimated based on the consideration of: 1. When the calculated NDVI is larger than 0.3, and NDVI of the sampling year is calculated by $NDVI = (NIR - R) / (NIR + R)$ via QGIS, where the NIR is near-infrared band and R is visible red band from satellite images. 2. When the NDVI is larger than 0.3, and on a rising trend (from a web-based platform: ONESOL, data from 2017 to 2022). 3. Landsat satellite images of the sampling year. The end date of the growing season is the sample collection date of each location.

^b Late-growing season is set as the second half of the entire growing season.

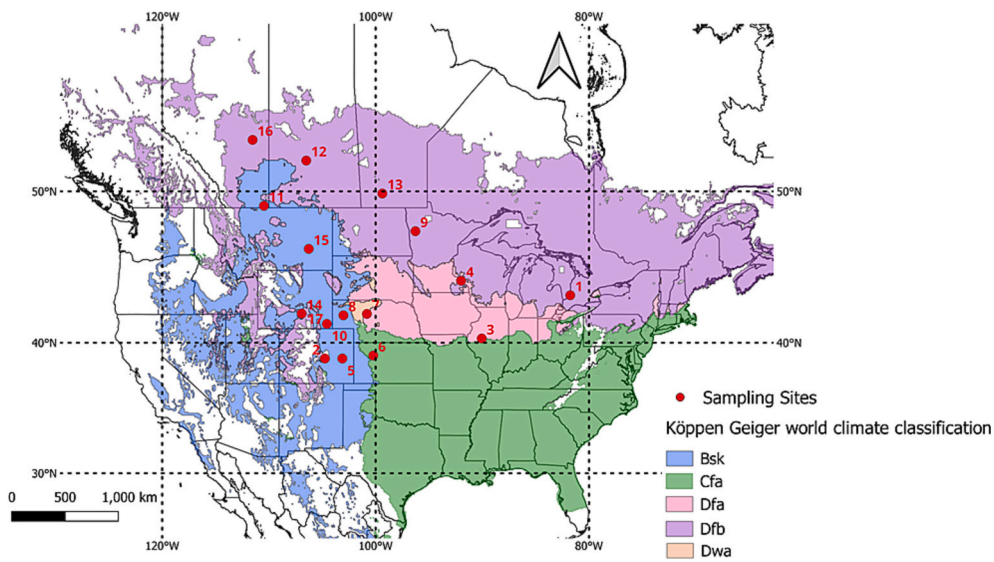


Fig. 1. Sample locations shown on the map of Köppen climate classification (Kottek et al., 2006). In the legend, Bsk represents cold semi-arid climate, Cfa represents humid subtropical climate, Dfa represents hot-summer humid continental climate, Dfb represents warm-summer humid continental climate, and Dwa represents monsoon-influenced hot-summer humid continental climate. See also Table 1 for more details (site #17 in Table 1 is close to site #14, so it is expressed as the same location as site #14 on Fig. 1).

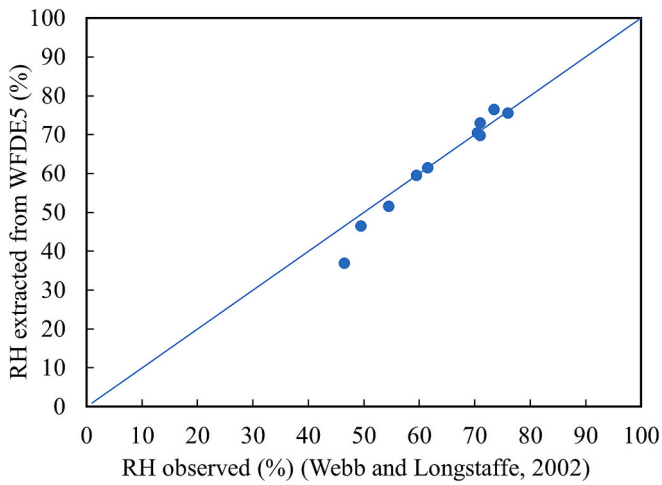


Fig. 2. The comparison between July to August daily average whole day RH measured at 10 meteorological stations in 1995 and 1996 in the North American plains (Webb and Longstaffe, 2002) and RH extracted from WFDE5 associated cell for the same period.

Medium Range Weather Forecast) (Cucchi et al., 2020). The resolution of the WFDE5 dataset is 0.5° in space and 1 h in time, over the period 1979–2018. It has a high correlation with meteorological observations, which minimises observational uncertainties and model errors (Cucchi et al., 2020). For this study, we extracted atmospheric temperature, RH, and downward shortwave radiation flux for the WFDE5 grid cells (about 40×55 km in the study area) containing each sampling location displayed on Fig. 1 and Table 1.

For each of the 17 sampling sites, the grass growing season was estimated using satellite Landsat 4–5 images and the Normalized Difference Vegetation Index (NDVI) for the sampling year (shown in Table 1). The average whole-growing season ranges from mid-May to the end of August, and the late-growing season is July and August at the studied North American sampling sites. This is consistent with the productivity data of *C. longifolia* in North America which shows that stem elongation rate and tiller numbers reach maximum in July and August (Madakadze et al., 1998). The daily averages of RH and T were computed from the WFDE5 dataset for four growth periods (Table 1): 1) whole-growing season whole day (24-h period); 2) whole-growing season daytime (average over diurnal periods, defined as the period of the day during which the incoming short wave radiation is higher than zero; 3) late-growing season whole day, and 4) late-growing season daytime.

3.3. Isotopic analysis

For this study, prior to analysis, all phytolith samples were dehydrated using the inert gas flow dehydration method (iGFD) under a continuous flow of N_2 gas to remove exchangeable oxygen from the phytoliths (Chaplin et al., 2010; Prentice and Webb, 2016). The isotopic analyses were conducted at Laboratory for Stable Isotope Science (LSIS) at Western University. The dehydrated phytolith samples were weighed to 1.5–2 mg, loaded into nickel reaction tubes, and pre-heated overnight at $100^\circ C$ under vacuum to remove any adsorbed moisture from their surfaces. Oxygen in the phytoliths was extracted by reaction with BrF_5 at $600^\circ C$ (Clayton and Mayeda, 1963) for at least 14 h by the reaction: $SiO_2 + BrF_5 \rightarrow SiF_4 + O_2 + BrF_3$. The released oxygen was purified by KBr, cryogenic traps, and a slurry at $-114^\circ C$ to remove possible NF contamination that interferes with mass-33 oxygen gas. The purified oxygen was collected in a sample tube with only one pellet of $13\times$ molecular sieve to avoid potential fractionation during passage through multiple molecular sieves (Abe, 2008). The sample tube was delivered to the dual-inlet stable isotope ratio mass spectrometer (Thermo Scientific MAT 253), and the sample gas was transmitted to the

sample bellows with the heater on at $120^\circ C$ for 1–2 min to allow full expansion of oxygen into the mass spectrometer without fractionation prior to analysis.

All samples and standards in this study were measured using the MAT 253, and the results are expressed as $\delta^{17}O$ and $\delta^{18}O$. Values for ^{17}O -excess were calculated using Eq.1. The oxygen-isotope composition of standard oxygen (reference gas) used throughout this research remains the same. Each oxygen gas sample was analyzed at least twice with the MAT 253 (8 acquisitions per analysis) until the standard deviation (s.d.) of the mean ^{17}O -excess from any two analyses was smaller than ± 15 per meg. The average of all s.d. for two analyses of the same sample gas is: ^{17}O -excess: ± 6 per meg and $\delta^{17}O$ and $\delta^{18}O$: ± 0.01 ‰.

Raw $\delta^{17}O$ and $\delta^{18}O$ were calibrated to the VSMOW-SLAP scale using quartz standard (NBS-28) and phytolith standard (MSG 60), which were analyzed on the same day as the phytolith samples at LSIS. MSG 60 is the working standard of the isotope laboratory at CEREGE, where triple oxygen-isotope compositions of phytoliths were measured in previous calibration studies. For data comparability, triple oxygen isotopic composition of phytoliths measured at LSIS in this study were normalized using the long-term calibrated values obtained at CEREGE for NBS-28 and MSG60. For NBS-28: $\delta^{17}O = +4.997$ ‰, $\delta^{18}O = +9.581$ ‰/VSMOW-SLAP ($n = 4$), and for MSG 60: $\delta^{17}O = +18.931$ ‰, $\delta^{18}O = +36.583$ ‰/VSMOW-SLAP ($n = 12$). Most of the phytolith samples have $\delta^{18}O$ within the range of these two standards. In addition to analysing each gas at least twice (as described above), oxygen gas was extracted separately from different aliquots of each phytolith sample for replicate analyses until the s.d. of the mean ^{17}O -excess of any two replicates was smaller than ± 15 per meg. The average s.d. of all replicates ($n = 31$ pairs) is: ^{17}O -excess: ± 5 per meg, $\delta^{17}O$: ± 0.30 ‰, $\delta^{18}O$: ± 0.57 ‰. The high s.d. for $\delta^{18}O$ is probably due to the heterogeneity of the phytolith samples.

Other quartz and phytolith standards (not used in the calibration) were analyzed to test measurement accuracy. The laboratory phytolith standard “G95–25-CL leaves” was measured 10 times: $\delta^{18}O = +36.48 \pm 1.22$ ‰/VSMOW-SLAP, $\delta^{17}O = +18.77 \pm 0.61$ ‰/VSMOW-SLAP, ^{17}O -excess: -319 ± 26 per meg, which shows consistency with $\delta^{18}O_{G95-25-CL \text{ leaves}} = +36.3$ ‰ measured by Webb and Longstaffe (2002) and the inter-laboratory comparison study: $\delta^{18}O_{G95-25-CL \text{ leaves}} = +36.6$ ‰ (Chaplin et al., 2011). Two other standards were also measured: Boulange: $\delta^{18}O = +15.57 \pm 1.10$ ‰/VSMOW-SLAP, ^{17}O -excess: -75 ± 2 per meg ($n = 2$), and P4–40: $\delta^{18}O = +49.46$ ‰/VSMOW-SLAP, ^{17}O -excess: -331 per meg ($n = 1$), which are close to the values obtained in CEREGE: Boulange: $\delta^{18}O = +16.25$ ‰, ^{17}O -excess: -88 per meg, and P4–40: $\delta^{18}O = +48.95$ ‰, ^{17}O -excess: -347 per meg (Outrequin et al., 2021).

4. Results

4.1. Climate information and the growing seasons of seventeen sampling locations

To evaluate the accuracy of late-growing season RH in 1995 and 1996 extracted from the WFDE5 dataset, they are compared to July–August whole day RH obtained from ten meteorological stations located in the same cell (Webb and Longstaffe, 2002), as shown in Fig. 2. The data are distributed around the 1:1 line. Differences between observed RH and RH extracted from WFDE5 reach 10 % at one meteorological station, while the differences among the other nine meteorological stations range from 0 % to 3 %, which confirms the accuracy of the RH extracted from WFDE5.

For each sampling site, RH and atmospheric temperature were extracted from the WFDE5 dataset for the four growth periods previously defined (Table 1). Daytime RH is lower than whole day RH, both for the whole-growing season (difference of 5 ± 1 %) and the late-growing season (difference of 6 ± 1 %) at all sampling sites. On average, the late-growing season RH is similar to the whole-growing season RH, both for the whole day RH (difference of 1 ± 5 %) and

daytime RH (difference of $2 \pm 5\%$) at most of sampling sites.

4.2. Triple oxygen-isotope compositions of leaf and stem phytoliths of at seventeen sampling locations

Table 2 lists the triple oxygen-isotope compositions of stem and leaf phytoliths of *C. longifolia* measured in this study, which is also shown in Fig. 3. Leaf phytoliths from all locations have higher $\delta^{18}\text{O}$ (+28.7 to +40.9 ‰) and lower ^{17}O -excess (−412 to −170 per meg) than stem phytoliths ($\delta^{18}\text{O}$: +22.0 to +28.7 ‰, ^{17}O -excess: −127 to −191 per meg) due to water evaporation in leaves during transpiration. The standard deviation of all ^{17}O -excess_{stem phytoliths} measured (average = −161 ± 19 per meg, $n = 15$) is close to measurement precision (±15 per meg) and much smaller than the variation of ^{17}O -excess_{leaf phytoliths} across the sampled area (^{17}O -excess_{leaf phytoliths}: −272 ± 64 per meg, $n = 16$). The $\Delta^{17}\text{O}$ -excess_{leaf-stem phytolith} is the difference in ^{17}O -excess between leaf and stem phytoliths. $\lambda_{\text{leaf-stem phytolith}}$ is the slope observed between leaf and stem phytoliths from each location in $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ space, and the average is 0.5149 ± 0.0033 among all locations.

5. Discussion

Plant phytoliths are assumed to form in oxygen-isotope equilibrium with plant water during polymerization. The $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ of leaf phytoliths are determined by the oxygen-isotope composition of leaf water, which is controlled by RH averaged over the silica polymerization period. Secondary parameters, like the oxygen-isotope compositions of precipitation and evaporation of soil water that also influence the oxygen-isotope composition of leaf water, plant growth/phytolith forming period, and temperature of polymerization of phytoliths can potentially influence the relationship between ^{17}O -excess_{leaf phytoliths} and RH. The ^{17}O -excess of phytoliths deposited in soils and sediments (^{17}O -excess_{bulk phytoliths}) is derived from a mixture of phytoliths from transpiring and non-transpiring tissues.

5.1. Estimations of the triple oxygen isotope composition of plant water

The average isotopic composition of plant water from which phy-

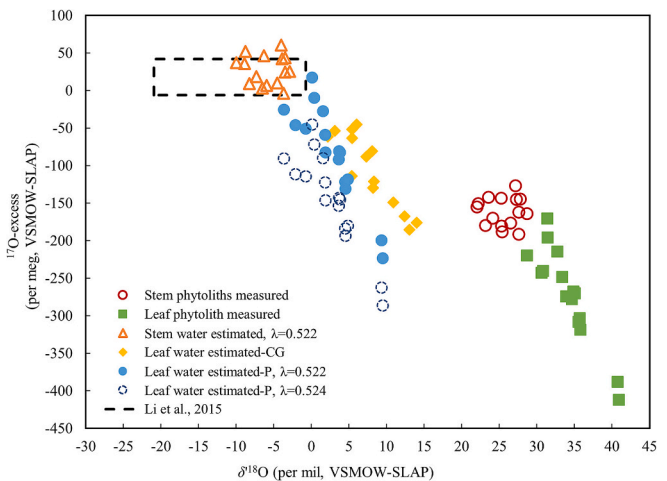


Fig. 3. $\delta^{18}\text{O}$ versus ^{17}O -excess of stem and leaf phytoliths (measured), stem and leaf water estimated from phytolith isotopic composition (P) and from the Craig-Gordon model combined with a mixing eq. (CG). Average s.d. of all sample replicates of measured phytoliths is smaller than the markers. The dashed line box represents the range of $\delta^{18}\text{O}$ versus ^{17}O -excess of tap water (the proxy of precipitation) measured across North America by Li et al. (2015).

toliths precipitate provides clues on the dynamics of silicification. The triple oxygen isotopic composition of plant water can be estimated in two ways. In the first method, the $\delta^{18}\text{O}$ of plant water can be calculated from the $\delta^{18}\text{O}$ of phytoliths using the biogenic silica-water thermo-dependent relationship (Dodd and Sharp, 2010), expressed by:

$$1000 \ln^{18}\alpha_{\text{silica-water}} = 2.39 \times 10^6 T^{-2} + 4.23 \quad (3)$$

The $\delta^{17}\text{O}$ of plant water can be calculated using $\lambda_{\text{Phyto-water}}$ (0.522 as defined in section 2). The second method is to use the Craig-Gordon model (Craig and Gordon, 1965) to calculate the isotopic enrichment of leaf water during steady-state conditions of transpiration (Dongmann et al., 1974; Flanagan et al., 1991; Farquhar and Lloyd, 1993; Farquhar et al., 2007; Cernusak et al., 2016; Voigt et al., 2022). The Craig-Gordon

Table 2
Triple oxygen isotope composition of stem phytoliths (SP) and leaf phytoliths (LP) from *C. longifolia* sampled at 17 locations across the North American plains. The number of replicate analyses is 2 for each sample.

Site #	Location	Stem Phytoliths						Leaf Phytoliths						$\Delta^{17}\text{O}$ -excess _{LP-SP} (per meg)	$\lambda_{\text{LP-SP}}$
		$\delta^{17}\text{O}$ (‰)	s.d.	$\delta^{18}\text{O}$ (‰)	s.d.	^{17}O -excess (per meg)	s.d.	$\delta^{17}\text{O}$ (‰)	s.d.	$\delta^{18}\text{O}$ (‰)	s.d.	^{17}O -excess (per meg)	s.d.		
1	Pinery, ON, CAN	+15.1	±0.1	+29.1	±0.2	−164	±1	+17.5	±0.1	+33.9	±0.2	−248	±2	−84	0.5100
2	Colorado Springs, CO, USA	+14.5	±0.6	+27.9	±1.1	−191	±4	+18.4	±0.4	+35.7	±0.8	−270	±2	−79	0.5175
3	Havanna, IL, USA	+14.3	±1.0	+27.5	±2.0	−127	±14	+17.2	±0.8	+33.3	±1.5	−215	±0	−88	0.5122
4	Kellogg, MN, USA	+14.6	±0.3	+28.1	±0.5	−144	±5	+16.5	±0.2	+31.9	±0.3	−170	±4	−26	0.5208
5	Aroya, CO, USA	+14.4	±0.2	+27.6	±0.4	−145	±13	+18.3	±0.1	+35.5	±0.3	−268	±10	−123	0.5118
6	Quinter, KS, USA	+14.5	±0.4	+28.0	±0.7	−162	±3	+16.5	±0.2	+31.9	±0.4	−196	±4	−34	0.5191
7	Thedford, NE, USA	+13.9	±0.0	+26.8	±0.0	−176	±0	+18.2	±0.1	+35.3	±0.2	−278	±8	−101	0.5156
8	Bonner, NE, USA							+18.7	±1.0	+36.3	±1.9	−303	±9		
9	Fertile, MN, USA	+13.3	±0.1	+25.6	±0.2	−143	±1	+16.2	±0.2	+31.3	±0.3	−240	±6	−97	0.5106
10	Cheyenne, WY, USA	+13.3	±0.5	+25.6	±0.9	−180	±3	+18.7	±0.4	+36.4	±0.7	−318	±5	−138	0.5150
11	Onefour, AB, CAN	+11.5	±0.2	+22.3	±0.5	−155	±9	+17.8	±0.6	+34.5	±1.2	−274	±5	−119	0.5179
12	Dundurn, SA, CAN	+12.4	±0.4	+23.8	±0.7	−142	±0	+15.0	±0.5	+29.1	±0.9	−220	±2	−78	0.5129
13	Sprucewoods, MA, CAN	+13.3	±0.1	+25.7	±0.2	−188	±4								
14	Rawlins, WY, USA	+12.6	±0.2	+24.4	±0.4	−170	±6	+21.4	±0.0	+41.8	±0.0	−412	±12	−242	0.5136
15	Broadus, MT, USA	+11.6	±0.0	+22.4	±0.0	−150	±6	+18.6	±0.3	+36.2	±0.5	−308	±2	−158	0.5162
16	Kinsella, AB, CAN							+16.1	±0.2	+31.1	±0.4	−243	±13		
17	Kortes Dam, WY, USA	+12.1	±0.1	+23.4	±0.2	−179	±8	+21.4	±0.1	+41.6	±0.3	−388	±9	−209	0.5161

model includes four components: 1) the isotopic composition of source water (δ^*O_s) in stems before transpiration; 2) the equilibrium fractionation factor between leaf water and water vapor within the boundary layer (ϵ_{eq}), where RH is 100 %; 3) the diffusion of water vapor through the leaf stomata and boundary layer to air, which is affected by the kinetic diffusion fractionation factor (ϵ_{diff}) and h , which is the ratio between actual atmospheric vapor pressure and saturation vapor pressure at leaf temperature (T_l). If T_l is not equal to air temperature (T_a), h is different from RH. Voigt et al. (2022) showed for a natural Mediterranean climate that the average daytime T difference between air and leaf ($\Delta T_{a-l} < 1.1^\circ\text{C}$) introduced only a small bias in the estimation of RH by assuming $T_l = T_a$. Because T_l is not available in this study, h is assumed to be equal to RH. 4) back diffusion of water vapor into the leaf (affected by RH and the difference between the isotope values of vapor and source water ($\Delta\delta^*O_{v-s}$)). Overall, the isotopic evaporative enrichment $\Delta\delta^*O_{e-s}$ of plant water is calculated as follow:

$$\Delta\delta^*O_{e-s} = \left\{ \left(1 + \epsilon^*O_{eq(e-s)}/1000 \right) \left[\left(1 + \epsilon^*O_{k(e-s)}/1000 \right) (1 - RH/100) + RH/100 (1 + \Delta\delta^*O_{v-s}/1000) \right] - 1 \right\} \times 1000 \quad (4)$$

where $\Delta\delta^*O_{a-b} = (\delta^*O_a - \delta^*O_b) / (1 + \delta^*O_b/1000)$, $\epsilon^* = 1000(\alpha^* - 1)$, $\epsilon^*O_{eq(e-s)}$ is the equilibrium enrichment factor, $\epsilon^*O_{k(e-s)}$ is the kinetic enrichment factor, $\Delta\delta^*O_{v-s}$ is the isotope difference between water vapor and source water, subscripts e, s, v are leaf water remaining at the sites of evaporation, source water, and atmosphere water vapor respectively.

Because the bulk leaf water ($\delta^*O_{\text{leaf water}}$) consists of a mixture of an evaporated pool (δ^*O_e) and an unevaporated pool circulating in the veins (source water: δ^*O_s) (Leaney et al., 1985; Yakir et al., 1994; Cerinusak et al., 2016; Outrequin et al., 2021; Voigt et al., 2022), a mixing equation is added to the Craig-Gordon model:

$$\delta^*O_{\text{leaf water}} = (1 - f) \delta^*O_e + f \delta^*O_s \quad (5)$$

where δ^*O_e and δ^*O_s are the oxygen-isotope compositions of leaf water remaining at the sites of evaporation and source water, and f is the fraction of unevaporated leaf water pool.

Fig. 3 and Table 3 show: 1) ^{17}O -excess and $\delta^{18}\text{O}$ of stem and leaf

water calculated from the isotopic composition of phytoliths using Eq. 3 assuming a T_l value identical to the average late-growing season daytime atmospheric temperature and a $\lambda_{\text{Phyto-water}}$ of 0.522, and 2) ^{17}O -excess and $\delta^{18}\text{O}$ of leaf water calculated from the Craig-Gordon model and mixing equation (Eqs. 4 and 5) in which the source water is considered to be estimated stem water. Average late-growing season daytime RH was used, and the contribution of unevaporated water was set at 0.2 (Alexandre et al., 2019). More detail on the calculations, assumptions, and their validation for each parameter in Eqs. 4 and 5 is given in Supplementary material.

For stem water, ^{17}O -excess estimated from stem phytoliths ranges from -4 to $+60$ per meg, with an average of $+27 \pm 20$ per meg (as shown in Table 3). This average is close to the isotopic composition of tap water in the U.S. (average: $+17 \pm 11$ per meg) and similar to the $+25$ per meg reported for tap water in the northwestern U.S. (Li et al., 2015; Fig. 3) that is used as a proxy of average pluri-annual precipitation. It is also close to the ^{17}O -excess of summer precipitation across United States reported in Aron et al. (2023): $+18 \pm 18$ per meg, and the average value of ^{17}O -excess of global precipitation (average = $+37 \pm 4$ per meg; Luz and Barkan, 2010). There is no significant dependency of the ^{17}O -excess of stem water reconstructed from stem phytoliths with growing season RH (p -values > 0.05). These results suggest that the ^{17}O -excess of stem water, and therefore stem phytoliths, reflects average ^{17}O -excess of precipitation across the study area. Post-precipitation processes, such as evaporation and mixing, that may occur in soils do not imprint significantly on the ^{17}O -excess of stem phytoliths and stem water.

For leaf water calculated with the Craig-Gordon model, the average $\lambda_{\text{Phyto-water}}$ is 0.5218 ± 0.0011 in this study, which is consistent with the $\lambda_{\text{Phyto-water}}$ value: 0.522 ± 0.001 obtained in previous phytolith studies (Alexandre et al., 2018; Outrequin et al., 2021; Voigt et al., 2022) but inconsistent with $\theta_{\text{SiO}_2\text{-water}} = 0.524$ expected for silica-water equilibrium (Sharp et al., 2016). When using the triple oxygen isotopic value of measured leaf phytoliths, Eq. 3, and a $\lambda_{\text{Phyto-water}}$ value of 0.522, the $\delta^{17}\text{O}$, $\delta^{18}\text{O}$ and ^{17}O -excess estimates for leaf water are close to those reconstructed using the Craig-Gordon model and the average late-growing season daytime atmospheric temperature and RH, but ^{17}O -excess values are on average 23 per meg higher (Fig. 3). When using a

Table 3

$\delta^{18}\text{O}$ and ^{17}O -excess of stem phytoliths and leaf phytoliths measured, stem water and leaf water estimated from phytolith isotopic composition (Eq. 3), and leaf water estimated from the Craig-Gordon model combined with a mixing equation (Eqs. 4 and 5). $\lambda_{\text{Phyto-water}}$ is calculated by $\lambda_{\text{Phyto-water}} = (\delta^{17}\text{O}_{\text{leaf phytoliths}} - \delta^{17}\text{O}_{\text{leaf water estimated by Craig-Gordon model}}) / (\delta^{18}\text{O}_{\text{leaf phytoliths}} - \delta^{18}\text{O}_{\text{leaf water estimated by Craig-Gordon model}})$.

Site#	Sample location	T^a	RH ^b	Stem phytoliths		Stem water estimated by stem phytoliths		Leaf water estimated by Craig-Gordon model		Leaf phytoliths		$\lambda_{\text{Phyto-water}}$	Leaf water estimated by leaf phytoliths	
				$\delta^{18}\text{O}$	^{17}O -excess	$\delta^{18}\text{O}$	^{17}O -excess	$\delta^{18}\text{O}$	^{17}O -excess	$\delta^{18}\text{O}$	^{17}O -excess		$\delta^{18}\text{O}$	^{17}O -excess
Unit		$^\circ\text{C}$	%	‰	per meg	‰	per meg	‰	per meg	‰	per meg		‰	per meg
1	Pinery	23	72	28.7	-164	-2.9	25	5.4	-64	33.3	-248	0.5214	1.8	-59
2	Colorado Springs	24	51	27.6	-191	-3.7	-4	10.9	-149	35.1	-270	0.5230	3.8	-83
3	Havanna	25	66	27.1	-127	-4.0	60	6.0	-45	32.7	-215	0.5217	1.6	-28
4	Kellogg	24	70	27.8	-144	-3.5	43	5.4	-52	31.4	-170	0.5234	0.1	+17
5	Aroya	25	60	27.3	-145	-3.9	42	8.1	-81	34.9	-268	0.5210	3.7	-81
6	Quinter	25	64	27.6	-162	-3.5	25	7.3	-88	31.4	-196	0.5235	0.4	-10
7	Thedford	25	57	26.5	-176	-4.5	10	8.3	-121	34.7	-278	0.5221	3.6	-92
8	Bonner	26	46							35.7	-303		4.8	-118
9	Fertile	22	68	25.2	-143	-6.3	46	3.1	-54	30.8	-240	0.5213	-0.8	-51
10	Cheyenne	24	38	25.3	-180	-6.0	7	12.4	-168	35.8	-318	0.5216	4.5	-131
11	Onefour	20	49	22.0	-155	-10.0	37	5.4	-114	33.9	-274	0.5224	1.9	-82
12	Dundurn	19	64	23.5	-142	-8.8	52	2.2	-61	28.7	-220	0.5220	-3.6	-26
13	Sprucewoods	21	66	25.3	-188	-6.5	3							
14	Rawlins	23	29	24.1	-170	-7.3	19	14.0	-176	40.9	-412	0.5192	9.5	-223
15	Broadus	25	42	22.2	-150	-8.9	36	8.2	-130	35.5	-308	0.5215	4.5	-122
16	Kinsella	16	65							30.6	-243		-2.1	-46
17	Kortes Dam	23	29	23.2	-179	-8.3	9	13.0	-186	40.8	-388	0.5207	9.3	-199
	Average	23	55	25.6	-161	-5.9	27	7.8	-106	34.1	-272	0.5218	2.7	-83
	s.d.	3	14	2.2	19	2.4	20	3.6	49	3.4	64	0.0011	3.6	65

^a The late-growing season daytime T.

^b The late-growing season daytime RH.

$\lambda_{\text{Phyto-water}}$ value of 0.524 with Eq.3, the estimates of ^{17}O -excess in leaf water are on average 40 per meg lower than leaf water ^{17}O -excess values determined using the Craig-Gordon model. The difference between a $\lambda_{\text{Phyto-water}}$ of 0.522 ± 0.001 , systematically obtained for phytolith studies, and a $\theta_{\text{Silica-water}}$ value of 0.524 was explained by the contribution of phytoliths formed in epidermal short cells at the beginning of the grass growth before transpiration occurs (Alexandre et al., 2019; Outrequin et al., 2021). To explore whether the lower $\lambda_{\text{Phyto-water}}$ value is the result of a kinetic effect, the calculated values for $\lambda_{\text{Phyto-water}}$ (Table 3) were plotted against late-growing season daytime RH and a weak positive relationship was observed ($R^2 = 0.3$; p-value = 0.5), which could suggest a dependency. However, additional high-resolution $\lambda_{\text{Phyto-water}}$ data is necessary to robustly assess whether $\lambda_{\text{Phyto-water}}$ can change with RH.

Although the ^{17}O -excess of leaf water reconstructed from phytoliths using a $\lambda_{\text{Phyto-water}}$ of 0.522 is close to the Craig-Gordon model estimates, the range is larger with the highest and lowest values respectively higher and lower (Fig. 3 and Table 3). Discrepancies between Craig-Gordon model isotopic estimates and observed data have been seen in other studies (Alexandre et al., 2018; Outrequin et al., 2021; Voigt et al., 2023). Inaccurate parameterization of the model, in particular large underestimation of the temperature difference between the leaf and the atmosphere, or misestimation of the isotopic composition of source water and water vapor can explain the observed gaps. In the mixing equation (Eq. 5), misestimation of the contribution of non-evaporated water to the bulk water, i.e. underestimated at high RH and overestimated at low RH, can also explain these discrepancies.

5.2. The triple oxygen isotopic composition of grass phytoliths and its relationship with RH

The oxygen-isotope composition of leaf water evolves from that of stem water and is dependant on the extent of evaporation in the leaf epidermis during transpiration. The extent of evaporation fluctuates temporally (both daily and seasonally) at each site and spatially across the study area.

5.2.1. The relationship of $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}}$ with RH

Fig. 4 shows the relationships between the late-growing season, whole day/daytime RH and $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}}$ from the fourteen sampling locations that have $\delta^{18}\text{O}$ data for both leaf and stem phytoliths. $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}}$ increases when the RH decreases, as expected for increasing fractionation of leaf water and subsequently leaf phytoliths when transpiration increases. The comparison of the relationships between $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}}$ and RH in this study to the previous study (Webb and Longstaffe, 2002), which measured $\delta^{18}\text{O}$ of the same phytolith samples and used late-growing season whole day meteorological station data, is shown in Fig. 4. Using late-growing season whole day RH, the relationship between $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}}$ and RH in this study is close to Webb and Longstaffe (2002). Supplementary material compares the $\delta^{18}\text{O}$ of the same samples analyzed in this study and Webb and Longstaffe (2002).

5.2.2. ^{17}O -excess of leaf phytoliths is a good proxy for late-growing season daytime RH across North America

There is no relationship between ^{17}O -excess_{leaf phytoliths} of *C. longifolia* and atmospheric temperature across all locations. In contrast, there are strong relationships between ^{17}O -excess_{leaf phytoliths} and daytime and whole day RH averages calculated for the whole and late growth periods (Fig. 5). Regardless of the RH period considered, ^{17}O -excess_{leaf phytoliths} decreases when RH decreases, as a result of a larger evaporation fractionation associated with more intense leaf water transpiration. The relationship is stronger when the late-growing season RH is considered ($R^2 = 0.87$ and 0.85 for whole day RH and daytime RH, respectively) in agreement with the hypothesis that most leaf phytoliths precipitate in the late-growing season when the plant reaches maturity

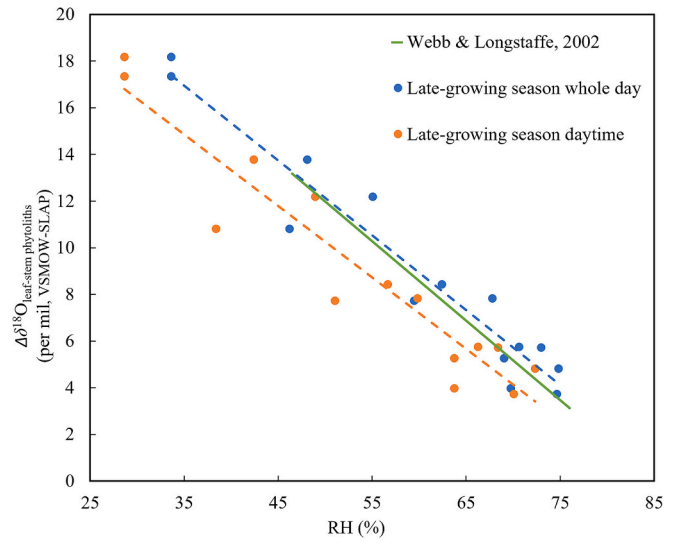


Fig. 4. The relationship between measured $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}}$ and the late-growing season whole day RH obtained for *C. longifolia* from sampling locations in the North American plains. This study: $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}} = -0.32 \times \text{RH} + 28.2$, $R^2 = 0.93$ (blue line); Webb and Longstaffe (2002): $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}} = -0.34 \times \text{RH} + 29.0$, $R^2 = 0.82$ (green line). The relationship of $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}}$ from this study with late-growing season daytime RH is also shown: $\Delta\delta^{18}\text{O}_{\text{leaf-stem phytoliths}} = -0.31 \times \text{RH} + 25.6$, $R^2 = 0.90$ (orange line). (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

(Shahack-Gross et al., 1996; Webb and Longstaffe, 2002; Alexandre et al., 2018).

The relationship between late-growing season daytime RH and ^{17}O -excess_{leaf phytoliths} is the closest to the GCCL (Eq. 2). Both RH and stomatal conductance vary diurnally, which controls the transpiration rate and passive formation of phytoliths. Based on the $\delta^{18}\text{O}$ of leaf water, Webb and Longstaffe (2003) suggested that in Ontario, Canada, the leaves of *C. longifolia* do not transpire during nighttime for most of the growth period. In agreement with this hypothesis, our results show that the RH recorded by the ^{17}O -excess_{leaf phytoliths} reflects the daytime RH of the late-growing season, during which the majority of phytoliths are forming.

From these data, a North American Leaf Phytolith Line (NALPL) can be defined by Eq. 6:

$$\begin{aligned} ^{17}\text{O-excess}_{\text{leaf phytoliths}} &= 4.14 (\pm 0.47) \times \text{RH} - 497 (\pm 26) (R^2 \\ &= 0.85 \text{ } p\text{-value} < 0.0001) \end{aligned} \quad (6)$$

The NALPL is statistically similar to GCCL (as shown in Supplementary material). The effective RH range for the GCCL is 40–80 % while NALPL has an effective RH range of 29–72 %, which extends the lower RH range of the calibration line. For every 1 % difference in RH, a 4 per meg difference in ^{17}O -excess_{leaf phytoliths} can be recorded. The maximum uncertainty on the measurement of ^{17}O -excess_{leaf phytoliths} is ± 15 per meg, which introduces an uncertainty of ± 4 % RH. This uncertainty is greater than the mean difference between late-growing season vs. whole-growing season RH. The shaded area in Fig. 5 shows the ± 15 per meg analytical precision on the NALPL, which overlaps with the linear relationships for ^{17}O -excess_{leaf phytoliths} versus whole growing season daytime RH, especially in the RH range from 50 to 75 %. Overall, ^{17}O -excess_{leaf phytoliths} in the NALPL better represents late-growing season daytime RH but does not differentiate between late-growing season vs. whole-growing season RH when measurement precision is considered. As *C. longifolia* is a naturally grown warm season grass, ^{17}O -excess_{leaf phytoliths} in different grasses such as naturally grown cool season grasses, might record RH of a different growth period.

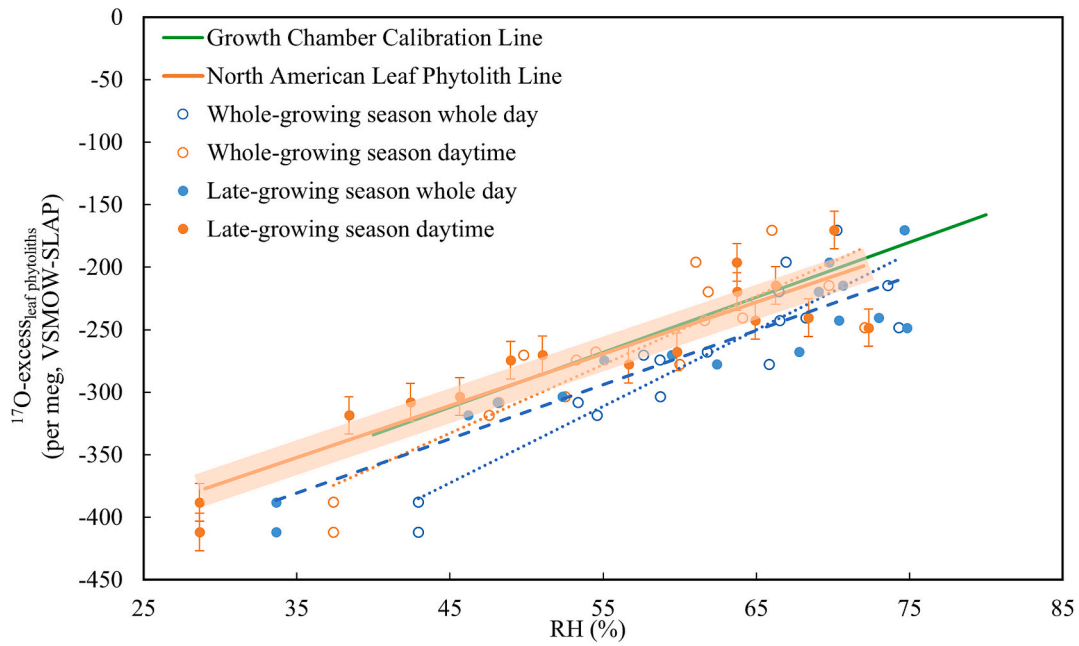


Fig. 5. The measured $^{17}\text{O-excess}_{\text{leaf phytoliths}}$ versus RH, obtained for *C. longifolia*, calculated for four periods: (1) blue dotted line: the whole-growing season whole day RH, $^{17}\text{O-excess}_{\text{leaf phytoliths}} = 6.1 \times \text{RH} - 648$, $R^2 = 0.82$; (2) orange dotted line: the whole-growing season daytime RH, $^{17}\text{O-excess}_{\text{leaf phytoliths}} = 5.5 \times \text{RH} - 579$, $R^2 = 0.78$; (3) blue dashed line: the late-growing season whole day RH, $^{17}\text{O-excess}_{\text{leaf phytoliths}} = 4.3 \times \text{RH} - 533$, $R^2 = 0.87$; (4) orange line: the late-growing season daytime RH, or NALPL, $^{17}\text{O-excess}_{\text{leaf phytoliths}} = 4.1 \times \text{RH} - 497$, $R^2 = 0.85$, with all p -values < 0.0001 . The orange shaded area shows the ± 15 per meg analytical precision on the NALPL; and (5) the calibration line (green line) from growth chambers study under controlled RH, (GCCL): $^{17}\text{O-excess}_{\text{leaf phytoliths}} = 4.4 \times \text{RH} - 510$, $R^2 = 0.92$ (Alexandre et al., 2018; Outrequin et al., 2021). The error bars represent measurement precision (± 15 per meg). Error bars shown only for “ $^{17}\text{O-excess}_{\text{leaf phytoliths}}$ ” data for the late-growing season daytime RH” to reduce clutter. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

5.2.3. Assessment of the proxy limitations

Variable $^{17}\text{O-excess}$ in the source water feeding the grass leaves (i.e., precipitation, soil water or stem water) could cause variations in the $^{17}\text{O-excess}$ of leaf water and leaf phytoliths unrelated to transpiration, which would bias the regional dependency of the $^{17}\text{O-excess}$ of grass leaf phytoliths to RH. To bypass variations in the isotopic composition of the source water, the difference in $^{17}\text{O-excess}$ between leaf and stem phytoliths, defined as $\Delta^{17}\text{O-excess}_{\text{leaf-stem phytoliths}}$, was calculated and plotted versus late-growing season daytime RH (Fig. 6). The relationship ($R^2 = 0.76$, p -value < 0.0001) is not as strong as the one obtained for the NALPL ($R^2 = 0.85$, p -value < 0.0001), but the two lines have the same slope. This result shows that the $^{17}\text{O-excess}$ variations in precipitation, soil water, and stem water add noise to the NALPL but do not change the trend of 4 per meg decrease in $^{17}\text{O-excess}_{\text{leaf phytoliths}}$ for 1 % decrease in RH.

Phytoliths can form in roots, stems, sheaths, leaves, and inflorescence of grasses. Webb and Longstaffe (2002) measured the silica content of the same *C. longifolia* samples as the ones studied here and estimated based on proportion of tissue mass that non-transpiring organs (including roots, stems, and sheaths) would contribute 59 % of the grass phytoliths to underlying soils, producing a bulk phytolith sample. By assuming phytoliths from non-transpiring tissues (59 %) have the same $\delta^{18}\text{O}$ and $^{17}\text{O-excess}$ as stem phytoliths and phytoliths from transpiring tissues (41 %) have the same $\delta^{18}\text{O}$ and $^{17}\text{O-excess}$ as leaf phytoliths, the oxygen-isotope compositions of a *C. longifolia* bulk phytolith sample can be estimated. Fig. 7 shows the relationships of estimated $\delta^{18}\text{O}_{\text{bulk phytoliths}}$ and $^{17}\text{O-excess}_{\text{bulk phytoliths}}$ with late-growing season daytime RH. $\delta^{18}\text{O}_{\text{bulk phytoliths}}$ is invariable with RH. In contrast, $^{17}\text{O-excess}_{\text{bulk phytoliths}}$ strongly depends on RH but the slope of the relationship is lower than the slope of the NALPL. The lower slope is a result of the isotopic difference between phytoliths from transpiring and non-transpiring tissues, which is greater when the evaporative isotopic fractionation is greater under low RH conditions. This comparison highlights that the contribution of non-transpiring phytoliths to the bulk

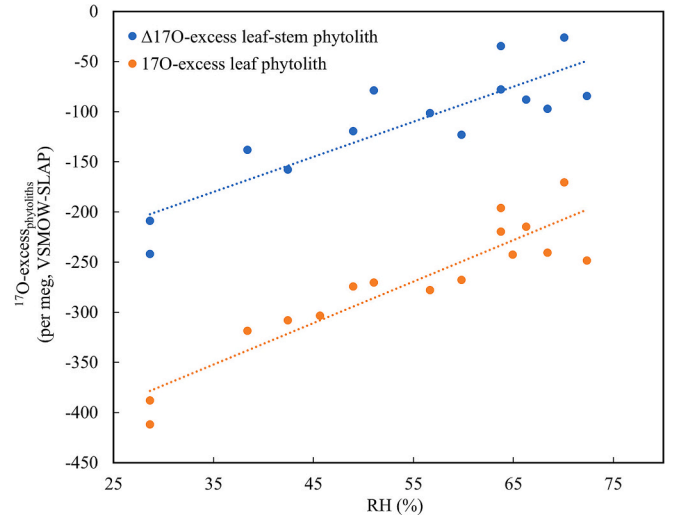


Fig. 6. Comparison of the relationships between late-growing season daytime RH and $\Delta^{17}\text{O-excess}_{\text{leaf-stem phytoliths}}$ ($\Delta^{17}\text{O-excess}_{\text{leaf-stem phytoliths}} = 3.5 \times \text{RH} - 302$, $R^2 = 0.76$) and $^{17}\text{O-excess}_{\text{leaf phytoliths}}$ ($^{17}\text{O-excess}_{\text{leaf phytoliths}} = 4.1 \times \text{RH} - 497$, $R^2 = 0.85$). p -values are < 0.0001 .

phytolith assemblages extracted from soils or sediments used for paleoclimate reconstructions, can decrease the regional dependency of the $^{17}\text{O-excess}$ of grass leaf phytoliths to RH obtained for the NALPL.

Indeed, belowground biomass are abundant in *C. longifolia* samples studied. The root mass fraction of *C. longifolia* (68.8 %; Webb and Longstaffe, 2002; Maun, 1985) is in the range of observed for temperate grasslands but is significantly higher than the root biomass observed for tropical grasslands (Ma et al., 2021). Roots do not regrow each year,

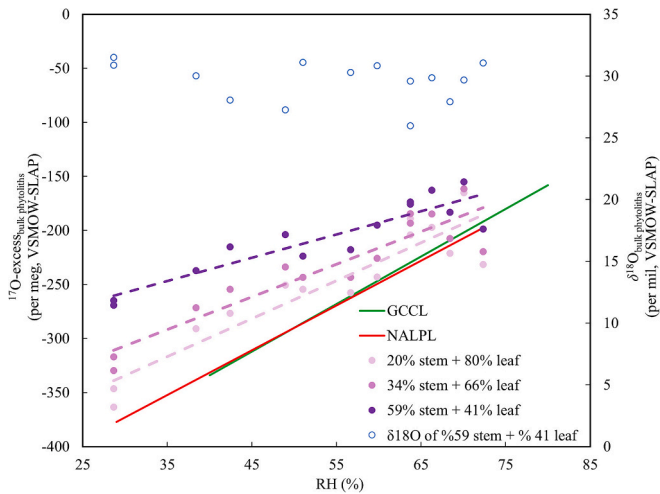


Fig. 7. ^{17}O excess of hypothetical bulk phytolith assemblages versus daytime late growing season RH: (1) Green line: Growth chamber calibration line (GCCL); (2) Red line: North American Leaf Phytolith Line (NALPL); (3) pale pink line: 20 % of non-transpiring phytoliths + 80 % of transpiring phytoliths: $^{17}\text{O-excess}_{\text{bulk phytoliths}} = 3.5 \times \text{RH} - 440$ ($R^2 = 0.85$, $p\text{-value} < 0.0001$); (4) dark pink line: 34 % of non-transpiring phytoliths + 66 % of transpiring phytoliths: $^{17}\text{O-excess}_{\text{bulk phytoliths}} = 3.0 \times \text{RH} - 397$ ($R^2 = 0.85$, $p\text{-value} < 0.0001$); (5) purple line: 59 % of non-transpiring phytoliths + 41 % of transpiring phytoliths: $^{17}\text{O-excess}_{\text{bulk phytoliths}} = 2.1 \times \text{RH} - 322$ ($R^2 = 0.82$, $p\text{-value} < 0.0001$); (6) The $\delta^{18}\text{O}_{\text{bulk phytoliths}}$ (59 % of non-transpiring phytoliths + 41 % of transpiring phytoliths) and RH has no statistically significant correlation. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

unlike leaves, which should reduce the relative contribution of non-transpiring phytoliths to bulk phytolith assemblages. Furthermore, although sheaths are categorized as non-transpiring organs, stomata in the sheaths are few but present (Chaffey, 1985). Sheath water is enriched in $\delta^{18}\text{O}$ compared to stem water (Webb and Longstaffe, 2003), and Alexandre et al. (2019) found that the sheaths contain about 60 % evaporated water. The proportion of phytoliths forming in non-transpiring organs will be less than 59 % if the sheath is counted as or partly counted as transpiring tissue. In light of this, Fig. 7 also shows the relationships of estimated ^{17}O -excess bulk phytoliths with late-growing season daytime RH using the proportion of phytoliths in non-transpiring organs as 20 % if the sheath is counted as transpiring tissue, and the proportion non-transpiring phytoliths as 34 % if 60 % of sheath phytoliths behave as if formed in transpiring tissue. The greater the proportion of phytoliths from transpiring tissues to total phytoliths, the closer the relationship of bulk phytolith and RH is to NALPL (Fig. 7). When mixed with non-transpiring phytoliths, the $^{17}\text{O-excess}_{\text{bulk phytoliths}}$ is still sensitive to RH, but without knowing the % of non-transpiring phytoliths, it is difficult to estimate RH. For example, a $^{17}\text{O-excess}_{\text{bulk phytoliths}}$ of -250 per meg could mean a RH of 54 % if there are 20 % of non-transpiring phytoliths, a RH of 49 % if there are 34 % of non-transpiring phytoliths, or a RH of 34 % if there are 59 % of non-transpiring phytoliths.

Bias might also be introduced by differences in phytolith morphologies, which likely favours preservation of phytoliths with more compact shapes (Strömberg et al., 2018), so examination of selective dissolution of phytoliths in litter and soil is necessary. Phytolith productivity in transpiring and non-transpiring tissues and preservation bias need to be evaluated in future soil phytoliths (especially in low RH climates) before using phytoliths from soil and sediment to reconstruct paleo-RH in different ecosystems. To produce a relationship that can be used for paleoclimatic reconstructions, a calibration must now be carried out between bulk phytolith assemblages from soils and surface sediments of the North American Plains and RH.

6. Conclusions

This study shows that the ^{17}O -excess of stem phytoliths of *C. longifolia*, a naturally grown warm-season grass widespread in the North American plains (161 ± 19 per meg), can be used to calculate the ^{17}O -excess of stem water (27 ± 20 per meg) that reflects the average, ^{17}O -excess of tap water (17 ± 11 per meg) (Li et al., 2015) considered as a proxy of the ^{17}O -excess of mean annual precipitation. Because the annual average of ^{17}O -excess in precipitation varies little from one location to another (Terzer-Wassmuth et al., 2023), the ^{17}O -excess of grass leaf phytoliths is dependant on the degree of leaf water evaporation and can be used as a direct proxy of RH.

In North America, warm-season grass leaf phytoliths record daytime RH of the late growing season, i.e. July–August, according to a 4 per meg decrease in ^{17}O -excess for a 1 % decrease in RH. This relationship can be expressed as: $^{17}\text{O-excess}_{\text{leaf phytolith}} = 4.14 \times \text{RH} (\%) - 497$ ($R^2 = 0.85$), which is statistically equivalent to the calibration line previously obtained from growth chamber experiments (Alexandre et al., 2018; Outrequin et al., 2021). This result also confirms that the growth chamber calibrations apply to the grass leaf phytoliths from the North American plain area where daytime RH and atmospheric temperature of the late growing season range from 29 to 72 % and 15 to 26 °C, respectively.

We further show that before using the ^{17}O -excess of bulk phytoliths deposited in soils and sediments as a quantitative proxy of past RH in the North American plains an additional calibration step is required: the contribution of non-transpiring phytoliths to bulk phytolith assemblages must be estimated, taking taphonomic processes into account, or a calibration must be performed between bulk phytolith assemblages from soils and surface sediments and RH.

CRedit authorship contribution statement

Minger Guo: Writing – review & editing, Writing – original draft, Visualization, Validation, Project administration, Methodology, Investigation, Conceptualization. **Anne Alexandre:** Writing – review & editing, Methodology, Conceptualization. **Fred J. Longstaffe:** Writing – review & editing, Resources, Formal analysis. **Christophe Peugeot:** Writing – review & editing, Resources. **Elizabeth A. Webb:** Writing – review & editing, Supervision, Resources, Project administration, Methodology, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

Data can be retrieved directly from the current paper or requested from the corresponding author.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at <https://doi.org/10.1016/j.chemgeo.2024.122484>.

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