

Oxygen isotopes in cellulose identify source water for archaeological maize in the American Southwest

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Abstract

Maize (*Zea mays*) was a primary food crop for aboriginal societies of the arid American Southwest. Water used for maize production in these arid zones could have come from precipitation and runoff during the summer monsoon, from perennial streams and springs, or from stored soil water fed by snowmelt. The oxygen stable isotope ratio ($\delta^{18}\text{O}$) of summer and winter precipitation on the Colorado Plateau naturally differ by more than 10‰ providing a powerful tool for distinguishing winter- from summer-derived water sources used in cultivation of maize. We investigated whether variation in $\delta^{18}\text{O}$ of potential source waters is preserved in the $\delta^{18}\text{O}$ of cellulose ($\delta^{18}\text{O}_{\text{cellulose}}$) of maize cobs by growing four aboriginal and one modern maize variety in pots irrigated with water of known $\delta^{18}\text{O}$ composition. The $\delta^{18}\text{O}_{\text{cellulose}}$ values of cobs ranged from 26.8 to 36.4‰ (averaged within varieties) and were highly correlated with $\delta^{18}\text{O}$ values of the source irrigation water (−15.8 to −8.2‰). Cob $\delta^{18}\text{O}_{\text{cellulose}}$ from five archaeological sites on the Colorado Plateau in southeastern Utah ranged from 27.3 to 34.6‰, closely matching the range of values observed in experimental plants. A $\delta^{18}\text{O}_{\text{cellulose}}$ model developed originally for tree rings was parameterized and applied to the archaeological maize cobs. The model indicated that monsoonal precipitation accounted for 0–20% of the moisture for archaeological cob samples from a site adjacent to a perennial stream and 43–98% for samples from an upland site, more distant from a perennial water source. These results reveal the potential for using $\delta^{18}\text{O}_{\text{cellulose}}$ to investigate prehistoric irrigation practices and source water used for maize production in the American Southwest.

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1. Introduction

Maize (*Zea mays*) was the primary food crop for aboriginal economies on the Colorado Plateau in the arid American Southwest from as early as 2000 B.P. [24]. Maize is a summer crop and requires substantial inputs of growing season rainfall or irrigation for

successful production. However, direct moisture inputs from growing season rainfall during the annual summer monsoon in this region were often too low to support production of maize. Maize production in this environment required irrigation. Water not supplied directly by summer precipitation came either from runoff generated by intense convective storms during the summer monsoon or from perennial streams, springs and stored soil water fed by winter snowmelt. Consequently, climatic fluctuations leading to changes in storm runoff over the past two millennia may have had substantial economic and social impact on aboriginal settlements of

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the region if perennial snowmelt-fed streams were not available.

Agricultural practices used for maize production, and particularly the sources of water used for irrigation, are key aspects of cultural adaptation in the arid American Southwest [25]. Maize cobs are plentiful in the archaeological record throughout this region and easily can be dated. Such samples hold isotopic information on the origin of maize cobs [1] and potentially the source(s) of water used for maize production. Isotope information from archaeological cobs is likely to provide valuable insight into the spatial and temporal record of irrigation practices used in pre-historic agriculture.

We analyzed the oxygen isotope ratio ($\delta^{18}\text{O}$) of potted maize grown with water of known isotopic composition to monitor the relationship between source water and the $\delta^{18}\text{O}$ value of maize cob cellulose, employing a parameterized mechanistic model that relates source water $\delta^{18}\text{O}$ to that of cellulose [21]. We then analyzed the $\delta^{18}\text{O}$ value from cellulose of maize cobs recovered from archaeological sites on the northern Colorado Plateau to estimate moisture inputs from summer monsoon precipitation versus winter snowmelt. Our goals were to determine whether variation in the $\delta^{18}\text{O}$ value of source water is preserved in maize cob $\delta^{18}\text{O}_{\text{cellulose}}$ and to test the usefulness of the ^{18}O -cellulose model of Roden et al. [21] for interpretation of $\delta^{18}\text{O}_{\text{cellulose}}$ in archaeological maize.

The oxygen isotope ratio ($\delta^{18}\text{O}$) of summer precipitation differs from that of winter precipitation on the northern Colorado Plateau owing to highly seasonal air temperature and continental rain out effects. Summer monsoon precipitation in this region has a $\delta^{18}\text{O}$ value ($\approx 6\text{‰}$) that is easily distinguished from moisture derived from winter snowmelt ($\approx 16\text{‰}$). Plants generally do not fractionate the stable isotopes of oxygen (^{16}O , ^{18}O) in water during uptake from soil or transport through root and stem tissues [5,15]. However, evaporation causes leaf water to be enriched in ^{18}O compared to water taken up by roots [9]. Water is the source of oxygen in biochemical constituents of a plant. Therefore, the $\delta^{18}\text{O}$ value of maize cob cellulose preserved in archaeological samples potentially records information about the $\delta^{18}\text{O}$ value of the source water used by the plant during cob formation.

1.1. Archaeological maize cobs

Three uncharred maize cobs from each of four sites in southeastern Utah and one cob from the Uintah Basin in northeastern Utah (Fig. 1) were obtained from the Utah Museum of Natural History. These samples represent collections from Fremont (ca. AD 400–1350) [3,16] and Puebloan [4] sites described below, located either near a perennial water source or in an

upland area where rain-fed maize production would be likely (Table 1). Several charred maize cobs also were obtained from the Utah Museum of Natural History to investigate the feasibility of extracting cellulose and analyzing and interpreting $\delta^{18}\text{O}$ values from such altered samples.

Located in the Uintah Basin of northeastern Utah, site 42Un118 is a badly vandalized but deeply-stratified, south-facing rock shelter near the mouth of Wagon Hound Canyon 0.3 km from the modern White River Bridge. Remaining evidence for occasional use by Fremont groups included maize cobs and husks, fragments of matting, worked flint, fire-cracked rock and burned bone. 42Gr176, in the pinyon-juniper zone of the LaSal Mountains east of Moab, Utah, is a Fremont residential site recorded by Hunt [13] in the early 1950s. Features and artifacts included the remains of six circular stone foundations for residential dwellings, a well-built granary, lithic materials, and gray, black and black-on-white pottery.

The remaining three sites are thought to be Puebloan in derivation. Site 42Sa1477, a south facing rock alcove ca. 60 m above the floor of an unnamed alluvial canyon east of the Colorado River in southeastern Utah, was attributed to the “Mesa Verde” culture when recorded in 1965. The site consisted of ten structures with dry-stacked residential dwellings, wet-laid storage cists and a fully subterranean kiva with a cribbed roof of cedar logs. Numerous bedrock metates were present as well as black-on-white and corrugated pottery, maize cobs and lithic debitage. Site 42Ka178 is a north facing dry cave 15–20 m above the floor of 25 Mile Gulch, also east of the Colorado along an Escalante River tributary. The site is not well reported but contained five or six structures identified as storage cists or dwellings. Finally, Bernheimer Alcove, 42Sa736, is a well-studied rock shelter 12.5 m above the mouth of Moqui Canyon, Utah, east of the Colorado River [10,23]. A Basket-maker II occupation is overlain by a surface Pueblo III component. The latter included two structural groupings, a well-built wet-laid cluster of residential dwellings, storage cists and a kiva at the north end of the alcove, and a poorly built dry-stacked grouping at the south end. A large assemblage of artifacts consisting of various Puebloan pottery types, chipped and ground stone, worked bone and shell, basketry, matting, maize cobs, sandals, hides, cordage and faunal bone was recovered.

1.2. The ^{18}O -cellulose model

Roden et al. [21] present a mechanistic model relating the $\delta^{18}\text{O}$ value of plant source water to that of tree-ring cellulose. The model describes fractionation processes influencing the $\delta^{18}\text{O}$ of leaf water and biochemical

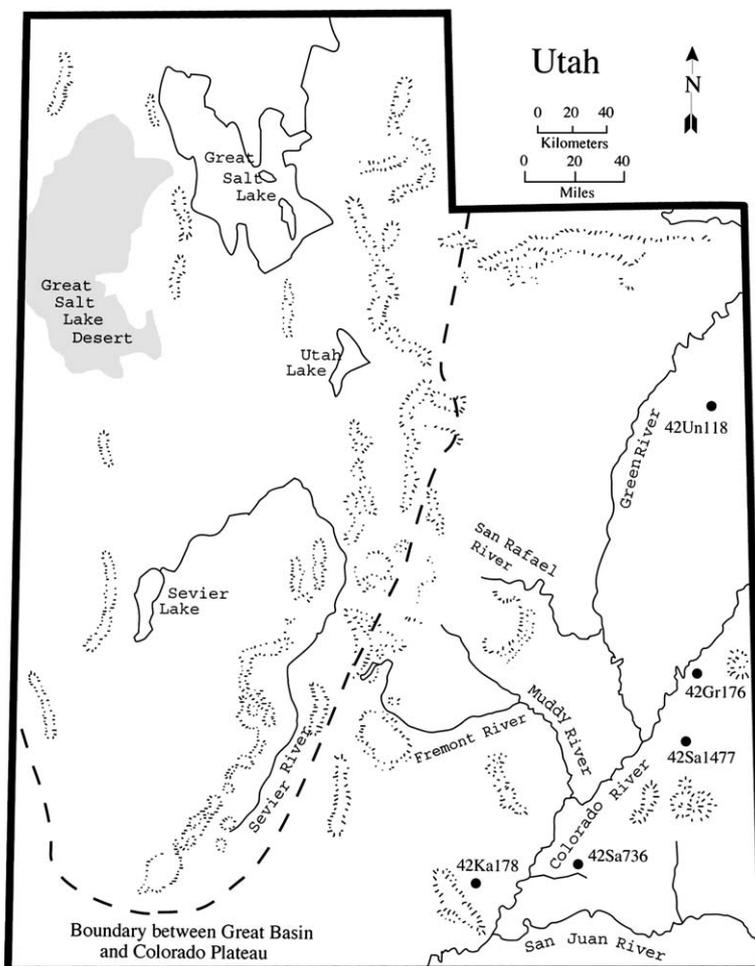


Fig. 1. Map showing the location of sites where archaeological maize cobs used in this study were collected.

fractionations associated with the formation of photosynthetic sugars and cellulose synthesis. The cellulose oxygen isotope ratio ($\delta^{18}\text{O}_{\text{cellulose}}$) is calculated as:

$$\delta^{18}\text{O}_{\text{cellulose}} = f_{\text{O}}(\delta^{18}\text{O}_{\text{wx}} + \varepsilon) + (1 - f_{\text{O}})(\delta^{18}\text{O}_{\text{wl}} + \varepsilon) \quad (1)$$

where $\delta^{18}\text{O}_{\text{wx}}$ is the oxygen isotope value of water at the site of cellulose formation, $\delta^{18}\text{O}_{\text{wl}}$ is that of the water at the site of photosynthetic carbon dioxide assimilation in the leaf, ε ($=27\text{‰}$) is the biosynthetic fractionation associated with cellulose and sugar synthesis, and f_{O} (≈ 0.42) is the fraction of carbon-bound oxygen in

photosynthetic sugars that undergoes exchange with medium water during cellulose formation [8,21]. The oxygen isotope value of leaf water at the site of sugar formation is influenced by equilibrium and kinetic fractionations associated with evaporation [9], but is determined also by the isotopic value of source water. Roden et al. [21] provide convincing evidence that the oxygen isotope composition of cellulose is affected not only by the oxygen isotope composition of medium water at the sites of cellulose formation, but also the oxygen isotope composition of water at sites of photosynthate production in leaves that carries a strong

Table 1

Brief description of sites in southeastern Utah, USA, sampled for uncharred archaeological maize cobs analyzed for cellulose $\delta^{18}\text{O}$ in this study

Site	Utah County	Location (lat, long)	Physiographic Setting/Elevation
42Gr176	Grand	38° 33', 109° 31'	Residential site, north fork Mill Creek, ca. 1500 m elevation
42Ka178	Kane	37° 35', 111° 10'	Dry cave 17 m above floor of 25 Mile Gulch 8 km from Escalante River, 1460 m elevation
42Sa736	San Juan	37° 35', 110° 30'	Bernheimer Alcove 12.5 m above mouth of Moqui Canyon, 1400 m elevation
42Sa1477	San Juan	38° 11', 109° 32'	Unnamed alcove on tributary of Horse Canyon, Canyonlands Nat'l Park, elevation unknown
42Un118	Uinta	39° 59', 109° 11'	Rock shelter, mouth of canyon near White River, 1550 m elevation

humidity signal. Thus, simpler models based only on oxygen isotope composition of medium water at sites of cellulose formation are inappropriate.

2. Methods

2.1. Experimental studies with potted maize plants

We conducted two controlled experiments with maize plants grown in pots using source water with known $\delta^{18}\text{O}$ values. The objective of these controlled studies was to determine whether the tree-ring ^{18}O -cellulose model accurately predicted maize cob ^{18}O -cellulose variations. Experiments using one modern and four aboriginal maize cultivars were conducted in Salt Lake City, Utah, USA and Tucson, Arizona, USA to capture variation in environmental growing conditions and genetically determined attributes of maize that potentially could influence patterns of cob $\delta^{18}\text{O}_{\text{cellulose}}$. Potted plants grown outdoors during summer months were irrigated with water of known and constant $\delta^{18}\text{O}$ value and grown to maturity. Three cultivars were grown in Salt Lake City: modern ‘Hybrid Sweet’, and two aboriginal cultivars ‘Acoma Mix’ and ‘Tarahumara Maiz Rojo’. Two additional aboriginal cultivars (‘Yuman Yellow’ and ‘Hopi Red’) were grown in Tucson. The aboriginal cultivars (Table 2) were obtained from Native Seeds/SEARCH (Tucson, Arizona, USA).

Seeds for each experiment were planted in 19 liter plastic pots filled with standard greenhouse potting mix. Plants were grown with ample water and nutrients and were thinned to one plant per pot shortly after emergence. The upper portion of each pot was sealed with thick opaque plastic sheeting to prevent isotopic enrichment of soil moisture by evaporation and contamination from rain water. The plastic was fitted tightly around the base of the young growing maize plant in each pot.

Plants grown in Salt Lake City were hand watered daily from two 2200 liter sealed water containers. One container was filled with water collected from a well in central New Mexico ($\delta^{18}\text{O} = -8.2\text{‰}$) and the other with Salt Lake City municipal tap water ($\delta^{18}\text{O} = -15.8\text{‰}$).

Table 2

Aboriginal maize cultivars obtained from Native Seeds/SEARCH used in experimental pot studies

Cultivar name	Accession	Origin of accession ^a
Tarahumara Maiz Rojo	ZF55	Creel, Chihuahua, Mexico
Acoma Mix	ZF141	Acoma Pueblo, New Mexico
Yuman Yellow	ZS112	Sonoran Desert along the lower Colorado River
Hopi Red	ZS200	Hopi Reservation, Arizona

^a Personal communication, Suzanne Nelson, Director of Conservation, Native Seeds/SEARCH, Tucson, Arizona.

Half ($n = 5$ for aboriginal cultivars; $n = 10$ for modern sweet corn) of the plants were irrigated with the isotopically heavy New Mexico water and the other half received the isotopically light Salt Lake City water for the duration of plant growth through maturation of cobs. Plants grown in Salt Lake City were started in early June 1995 and cobs were harvested August 8 (sweet corn) and August 22 (aboriginal cultivars). The uppermost cob on each plant was collected. The core of each cob was excised, placed in a large coin envelope and dried at 70 °C for 48 h in a convection oven at the University of Utah.

Plants grown in Tucson ($n = 3$ for each of the two aboriginal cultivars ‘Yuman Yellow’ and ‘Hopi Red’) were drip-irrigated with Tucson municipal tap water ($\delta^{18}\text{O} = -8.6\text{‰}$). Plants were started from seed on April 22, 2002, and mature cobs, leaf and basal stem tissue were harvested at midday (12:00 to 13:00 h) on July 2. Micro-meteorological sensors installed at 1.5 m above ground next to the growing maize plants recorded average air temperature and relative humidity at 10-minute intervals for the duration of the experiment.

Cob, leaf and basal stem samples from maize plants grown in Tucson were collected so that $\delta^{18}\text{O}$ measurements could be made on tissue water. The fresh core of each harvested cob was excised and placed individually into glass vials. Glass vials were tightly sealed with screw-on caps and parafilm and stored in a freezer at the University of Arizona. Fresh leaf and basal stem tissue was collected in the same fashion from each plant. Tissue without mid-rib from the youngest, fully expanded leaf blade was collected 30 and 60 cm distal from the leaf collar. In addition to plant tissue, atmospheric water vapor was sampled on the date of harvest. Water vapor from near the leaf canopy of the plants was cryogenically collected in Pyrex glass traps (modified from Ref. [12]) over a 1-h period (12:00 to 13:00 h). Air was drawn through low-absorption plastic tubing at 300 mL/min into the glass trap, which was immersed in an ethanol/dry ice slurry (~ 78 °C). The water vapor sample was sealed with a rubber stopper and parafilm and stored in a refrigerator until analysis for $\delta^{18}\text{O}$.

2.2. Stable isotope analysis

Water from fresh maize tissue samples (e.g., cob, leaf blade and basal stem) collected in the Tucson pot experiment was quantitatively extracted by cryogenic vacuum distillation [7]. The waters were analyzed for ^{18}O composition using an automated $\text{CO}_2\text{-H}_2\text{O}$ equilibration device attached to a dual-inlet isotope ratio mass spectrometer (Delta S, Finnigan MAT, San Jose, CA., USA) at the Laboratory for Isotope Geochemistry at the University of Arizona. Analytical precision of an internal lab reference water (GSDI; Gould Simpson building deionized water) was 0.14‰. GSDI reference

water was calibrated directly against the international standards VSMOW, GISP and SLAP obtained from IAEA. The $\delta^{18}\text{O}$ values for tissue water and atmospheric vapor are reported relative to VSMOW.

Cob samples obtained from both pot experiments and archaeological collections were prepared for cellulose extraction and ^{18}O analysis first by drying at 70 °C and then grinding to pass a #40-mesh screen. The $\delta^{18}\text{O}$ of cellulose was obtained by on-line pyrolysis [22] of α -cellulose extracted from ground cob tissue using methods described by Leavitt and Danzer [14]. Analyses were conducted on a continuous flow isotope ratio mass spectrometer (Delta-plus XL). Measurement precision at the Laboratory for Isotope Geochemistry, University of Arizona, for $\delta^{18}\text{O}$ of a benzoic acid internal working standard analyzed with maize samples from the Tucson pot experiment was 0.22‰. Samples from archaeological maize and from the Salt Lake City pot experiment were extracted and analyzed at the Stable Isotope Ratio Facility for Environmental Research (SIRFER) at the University of Utah. Precision for these analyses was 0.3‰. The $\delta^{18}\text{O}$ values for α -cellulose for all samples are reported relative to VSMOW.

2.3. Tree-ring ^{18}O -cellulose model simulations

The tree-ring ^{18}O -cellulose spreadsheet model [H_&_O_model_ver_5.xls; ftp://ecophys.biology.utah.edu/Tree_Ring/, 21] was parameterized to predict the $\delta^{18}\text{O}$ of α -cellulose in maize cobs. The model includes components that describe 1) oxygen isotope effects associated with leaf water enrichment during transpiration, 2) incorporation of leaf water ^{18}O values into photosynthetic carbohydrates that are transported to the developing tree ring (in this case, the growing cob), 3) a partial exchange of oxygen isotopes in carbohydrates with medium water (i.e., cob water) at sites of cellulose synthesis, and 4) a biochemical fractionation associated with cellulose synthesis.

Parameters for the biochemical fractionation model are in the description for Eq. (1) above [21]. The leaf water enrichment part of the model from Flanagan et al. [9] is an expanded form of the Craig-Gordon evaporation enrichment model for open waters, but modified to include kinetic fractionations associated with water vapor diffusion through stomata and the turbulent boundary layer around the leaf. Helliker and Ehleringer [11] found that grasses possessing leaf blades with parallel venation may have leaf water that is more enriched isotopically than is predicted by the Flanagan et al. [9] model. The deviation from predicted values depended on the ratio of leaf length to interveinal distance. Maize leaf blades collected from the Tucson pot experiment had fairly low ratios of leaf length to interveinal distances, averaging 569 (SE = 35) to 659 (SE = 58) for Hopi Red and Yuman Yellow, respectively.

These maize leaf structural characteristics would have caused deviations in leaf water $\delta^{18}\text{O}$ values of less than 2‰ from values predicted from the leaf water enrichment model [11].

Inputs for the leaf water enrichment model to estimate $\delta^{18}\text{O}_{\text{wl}}$ in Eq. (1) include $\delta^{18}\text{O}$ of source water, $\delta^{18}\text{O}$ of atmospheric humidity, relative humidity, leaf temperature, barometric pressure, leaf stomatal conductance to water vapor, and leaf boundary layer conductance to water vapor. Source water $\delta^{18}\text{O}$ was known for the pot studies in Salt Lake City and Tucson. Air temperature was obtained from NOAA meteorological records from Salt Lake City airport and air temperature and relative humidity were recorded with the micro-meteorological station at the Tucson research site. We assumed that leaf temperature was equivalent to air temperature. The $\delta^{18}\text{O}$ of atmospheric humidity was assumed to be in isotopic equilibrium with source water at each site. This was verified at the Tucson site with atmospheric vapor collected on the day of harvest. The leaf water enrichment model is most sensitive to the isotopic composition of atmospheric vapor when relative humidity is high, which is rarely the case in the arid southwestern US. Thus, if a slight error exists in estimation of atmospheric water vapor $\delta^{18}\text{O}$ it will not produce a substantial error in estimation of leaf water and cob cellulose $\delta^{18}\text{O}$ values.

We varied the value leaf stomatal conductance between 0.1 (low stomatal conductance; stressed condition) and 1.0 mol m⁻² s⁻¹ (high stomatal conductance; favorable condition) in model simulations. These stomatal conductance values for maize were obtained from the literature [18,19]. Leaf boundary layer conductance was assumed to be 0.7 mol m⁻² s⁻¹ in all cases. This value is calculated for a leaf blade with a width of 0.1 m and wind speed of 1 m s⁻¹ [2]. Because the model is sensitive to humidity, we varied this parameter from 10 to 30% in simulations with plants grown at Salt Lake City as we were unable to obtain hourly relative humidity values at this site. This range is typical for minimum daily values when monsoonal air is absent or present, respectively. Barometric pressure was estimated from elevation [20].

3. Results

The oxygen isotope values of cob α -cellulose ($\delta^{18}\text{O}_{\text{cellulose}}$) for aboriginal and modern maize cultivars grown in Salt Lake City and Tucson reflected differences in the $\delta^{18}\text{O}$ of irrigation source water (Table 3). The Mean $\delta^{18}\text{O}_{\text{cellulose}}$ values of cobs in these controlled studies ranged from 27.4‰ (SE = 0.4‰) in the aboriginal cultivar Acoma Mix, grown with isotopically depleted ($\delta^{18}\text{O} = -15.6$ ‰) water, to 36.0‰ (SE = 0.2‰) in the modern cultivar Hybrid Sweet grown with

Table 3
 $\delta^{18}\text{O}$ values of cob α -cellulose and source water for cultivars of potted maize grown in Salt Lake City and Tucson

	Source water $\delta^{18}\text{O}$ (‰)	<i>n</i>	Mean (1 SE) $\delta^{18}\text{O}_{\text{cellulose}}$ (‰)
Salt Lake City			
Hybrid Sweet	−8.2	10	36.0 (0.2)
	−15.8	10	30.2 (0.2)
Tarahumara Maiz Rojo	−8.2	5	33.6 (0.3)
	−15.8	5	27.6 (1.2)
Acoma Mix	−8.2	5	33.8 (0.2)
	−15.8	4	27.4 (0.4)
Tucson			
Yuman Yellow	−8.6	3	35.9 (0.9)
Hopi Red	−8.6	3	35.8 (1.1)

isotopically enriched ($\delta^{18}\text{O} = -8.2\text{‰}$) water. The two aboriginal cultivars grown in Salt Lake City had mean $\delta^{18}\text{O}_{\text{cellulose}}$ values up to 2.8‰ lower than mean values observed in Hybrid Sweet from the same pot study. Mean cob $\delta^{18}\text{O}_{\text{cellulose}}$ values for the two aboriginal cultivars grown in Tucson with isotopically enriched ($\delta^{18}\text{O} = -8.6\text{‰}$) water differed by only 0.1‰ and were very similar to values observed in Hybrid Sweet grown in Salt Lake City with enriched water.

The $\delta^{18}\text{O}$ value of water in the Tucson-grown plants revealed little evaporative enrichment from basal portions of the main stem up to the leaf, but isotopic enrichment in the expanded leaf blades (Table 4). Cob water, which is the medium water participating in ^{18}O isotopic exchange during cellulose synthesis, was only 0.9 and 1.0‰ more positive than source water. As expected, leaf blade water was highly enriched above source water due to evaporation. There was a slight tendency for leaf water to show progressive enrichment along the long axis of the blade from 30 to 60 cm distal from the leaf collar. This progressive enrichment was more pronounced in Hopi Red than in Yuman Yellow. Hopi Red also had slightly higher leaf water $\delta^{18}\text{O}$ values than that observed in Yuman Yellow. The water vapor $\delta^{18}\text{O}$ value at the Tucson site was -19.5‰ , which was 10.9‰ lighter than the source water (-8.6‰) obtained from Tucson municipal tap water. This depletion is equivalent to vapor in equilibrium with source water at $\sim 10\text{ °C}$ [17], but likely reflects a disequilibrium between atmospheric water vapor and groundwater.

For simulations using the tree-ring ^{18}O -cellulose model, we applied a 1‰ enrichment of $\delta^{18}\text{O}$ to source water to account for the observed enrichment in cob water. Further, we assumed that the $\delta^{18}\text{O}$ value of atmospheric water vapor at Salt Lake City and at other locations where archaeological maize samples were collected were in isotopic equilibrium with local source water. The value of leaf water $\delta^{18}\text{O}$ is moderately sensitive to variations in humidity and stomatal conductance. Both these parameters were varied to predict the relationship

Table 4
 $\delta^{18}\text{O}$ values of tissue water extracted from stem, cob and leaf blades in potted plants of two aboriginal maize cultivars grown in Tucson

	Yuman Yellow	Hopi Red
$\delta^{18}\text{O}$ of stem water (‰)	−8.9 (0.8)	−8.7 (0.1)
$\delta^{18}\text{O}$ of cob water (‰)	−7.7 (0.1)	−7.6 (0.1)
$\delta^{18}\text{O}$ of leaf water (‰)		
30 cm from collar	20.3 (0.3)	23.1 (1.5)
60 cm from collar	22.0 (1.4)	27.8 (2.7)

Plant tissue samples were collected at midday on the date that cob tissue was sampled for the $\delta^{18}\text{O}$ value of α -cellulose. The source water value was -8.6‰ . Data are means with one standard error in parentheses.

between cob $\delta^{18}\text{O}_{\text{cellulose}}$ and the $\delta^{18}\text{O}$ of source water (Fig. 2). The measured values of cob $\delta^{18}\text{O}_{\text{cellulose}}$ at Salt Lake City were within the range of predicted values bounded by realistic variation in stomatal conductance and relative humidity. Differences in the observed values of cob $\delta^{18}\text{O}_{\text{cellulose}}$ between aboriginal and modern maize cultivars could be accounted for by differences in humidity, stomatal conductance, or both. The aboriginal cultivars matured and were collected two weeks later than the modern cultivar Hybrid Sweet in the Salt Lake City study. Thus it is possible that cobs of the aboriginal cultivars developed under a humidity regime different than that of the modern cultivar.

For model simulations at the Tucson site, we used measured daytime mean relative humidity (15.7%) for the 15-d period preceding cob harvest. Observed values of cob $\delta^{18}\text{O}_{\text{cellulose}}$ were within the range predicted by the tree-ring ^{18}O -cellulose model. All else held constant, a stomatal conductance value of $0.25\text{ mol m}^{-2}\text{ s}^{-1}$ best fit the observed cob $\delta^{18}\text{O}_{\text{cellulose}}$ values for Tucson-grown plants. The leaf water enrichment component of the model predicted a leaf water $\delta^{18}\text{O}$ value of 20.6‰, which was very close to the observed value in Yuman Yellow, but underestimated values for Hopi Red (Table 4).

Values of $\delta^{18}\text{O}_{\text{cellulose}}$ from archaeological cobs ranged from 27.3 to 33.9 ‰ (Table 5). The former is virtually identical to the mean value for potted aboriginal maize watered with winter snowmelt, in Salt Lake City, while the latter is equally similar to experimentally grown maize watered with summer monsoonal moisture (Table 3). The three charred samples analyzed had an average $\delta^{18}\text{O}_{\text{cellulose}}$ value of 12.2‰ (SE = 0.3‰), more than 15‰ more depleted isotopically than the uncharred samples. We used inverse modeling with the tree-ring ^{18}O -cellulose model to predict the $\delta^{18}\text{O}$ value of source water used during growth of the uncharred archaeological maize cobs (Fig. 3). The value for stomatal conductance was set at $0.25\text{ mol m}^{-2}\text{ s}^{-1}$ and relative humidity was varied between 10 and 30% to establish boundary conditions for the simulation. Values for other parameters of the

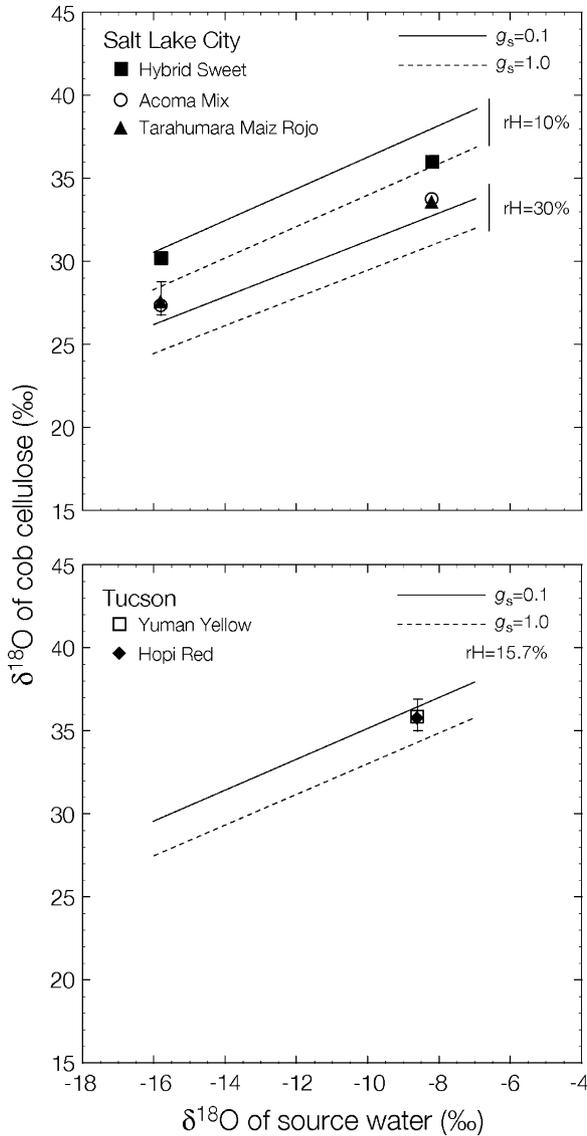


Fig. 2. Relationship between the oxygen isotope composition of source water and the measured values (symbols) of cob α -cellulose for cultivars of maize grown in Salt Lake City (upper panel) and Tucson (lower panel). Shown also are model simulations (lines) of this relationship with relative humidity set at either 10 or 30% (at Salt Lake City) and stomatal conductance set at either 0.1 or 1.0 mol m⁻² s⁻¹. Relative humidity for Tucson grown plants was 15.7%, which was the average measured value at the Tucson site over 15 days prior to cob harvest. Values for other model parameters are described in the text.

Table 5
 $\delta^{18}\text{O}$ values of α -cellulose extracted from uncharred archaeological maize cobs collected in southeastern Utah

Collection ID	n	Mean (SE) of $\delta^{18}\text{O}_{\text{cellulose}}$ (‰)
42Gr176	3	27.3 (0.9)
42Ka178	3	33.9 (1.0)
42Sa736	3	29.8 (0.9)
42Sa1477	3	32.8 (0.9)
42Un118	1	30.6 (—)

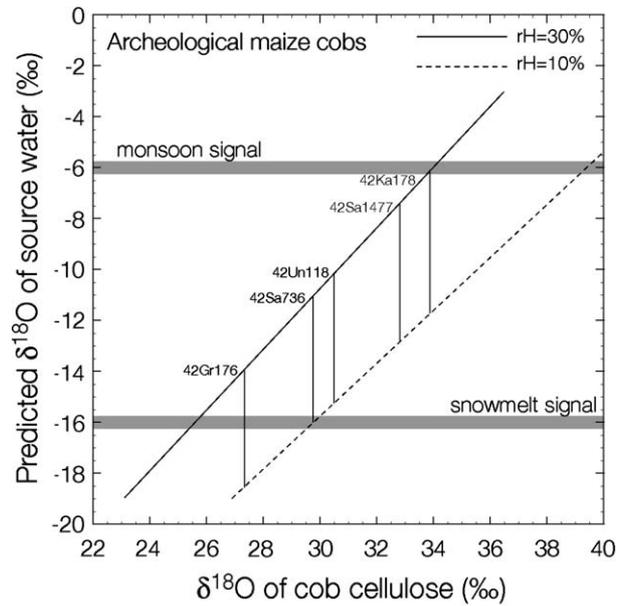


Fig. 3. Predicted values of source water $\delta^{18}\text{O}$ using cob cellulose $\delta^{18}\text{O}$ values as a model input. The model was run with humidity values of 10 and 30%. Other model parameters used are described in the text. Also shown as horizontal bars are the $\delta^{18}\text{O}$ values of monsoon precipitation and snow melt runoff from the Colorado River near Moab, UT (Jim Ehleringer, unpublished data). Vertical bars show the range of predicted source water $\delta^{18}\text{O}$ values for archaeological maize cobs collected in southeastern Utah (see Table 1) based on their measured cob $\delta^{18}\text{O}_{\text{cellulose}}$ values.

model were identical to those used to predict cob $\delta^{18}\text{O}_{\text{cellulose}}$ for potted plants with the following exceptions: the $\delta^{18}\text{O}$ value of atmospheric vapor was assumed to be in equilibrium with local groundwater (Ehleringer, unpublished data) in the Four Corners region; air temperature was assumed to be 32 °C, and barometric pressure was 84.5 kPa. Based on this analysis, we estimate that the $\delta^{18}\text{O}_{\text{cellulose}}$ values of archaeological maize correspond to a range of source water $\delta^{18}\text{O}$ values from -18.6 to -14.0‰ for cobs from site 42Gr176 and from -6.2 to -11.7‰ for cobs from site 42Ka178 (Fig. 3). The $\delta^{18}\text{O}$ values of cobs from other sites fall within this range. Simple linear mixing between seasonal precipitation end members (-16 to -6‰) indicates that monsoonal precipitation contributed between 0 to 20% of the moisture for production of cobs from site 42Gr176 and 43 to 98% of the moisture for those from site 42Ka178. The model yielded a range of source water input estimates because relative humidity was varied from 10 to 30% to simulate boundary conditions.

4. Discussion

Prehistoric Fremont and Puebloan cultures on the northern Colorado Plateau of the American Southwest,

like other farming cultures of Meso- and North America, relied on maize as a dietary staple. But due to low and highly variable precipitation, the region was marginal for maize production [6]. Remains of various irrigation structures imply that water used to grow crops was scarce [25]. Here we show that the stable isotope composition of oxygen in α -cellulose ($\delta^{18}\text{O}_{\text{cellulose}}$) from maize cobs provides information about the sources of irrigation water used for maize production. The $\delta^{18}\text{O}_{\text{cellulose}}$ values of uncharred maize cobs collected from archaeological sites were very similar to those collected from potted maize plants grown experimentally in Salt Lake City and Tucson. The range of variability in $\delta^{18}\text{O}_{\text{cellulose}}$ values from archaeological samples mirrored that of cobs from experimental plants grown with isotopically enriched (monsoon) and depleted (winter snowmelt) irrigation source waters. The mechanistic model describing ^{18}O fractionation during the synthesis of cellulose [21] indicated that a substantial amount of the variation in archaeological maize $\delta^{18}\text{O}_{\text{cellulose}}$ values was due to variation in the $\delta^{18}\text{O}$ values of source water. Conversely, charred samples of archaeological maize cobs are apparently unsuitable for $\delta^{18}\text{O}_{\text{cellulose}}$ analysis. Charred samples had $\delta^{18}\text{O}_{\text{cellulose}}$ values more than 15‰ lower than those of uncharred samples, a difference that can not arise from natural variation in the $\delta^{18}\text{O}$ values of source water or other environmental factors during growth and cob development.

Although our estimates are coarse, it is possible to derive site specific comparative data on the input of summer monsoonal versus winter moisture from the $\delta^{18}\text{O}_{\text{cellulose}}$ of aboriginal maize cobs. Maize recovered at site 42Gr176 apparently received the least moisture input from monsoonal precipitation (0–20%) while 42Ka178 received the most among the samples analyzed (43–98%). 42Gr176 [13] was a Fremont residential site in the pinyon-juniper zone of the LaSal Mountains; maize may have been irrigated with snow melt from adjacent Mill Creek, while monsoonal moisture provided the bulk of source water for maize recovered from 42Ka178, further south and west near the Kaiparowits Plateau. In the absence of better temporal control and paleoclimatic data on relative humidity, it is not possible to derive further inferences about variation in farming practices and/or the strength of the summer monsoon system with this data set; however with improved paleoclimatic reconstructions and a larger, directly dated collection of maize cobs we may be able to monitor spatio-temporal variation in parameters that structured aboriginal farming practices in the arid Southwest. Further, we are not certain of the average $\delta^{18}\text{O}$ values of summer and winter precipitation for the Colorado Plateau region during pre-historic times. Greater certainty for these values will develop as other proxy records are validated.

The modeled source water $\delta^{18}\text{O}$ values for uncharred archaeological cobs ranged from close to that of winter snowmelt ($\approx 16\text{‰}$) to values apparently originating from summer monsoon precipitation ($\approx 6\text{‰}$). Pre-Columbian farmers of the northern Colorado Plateau were opportunistic with respect to irrigation of maize. Consequently, changes in the North American Monsoon climate system would have greatly impacted maize agriculture, but this impact would have been mitigated by the availability of perennial water sources. The $\delta^{18}\text{O}$ value of cob cellulose provides insight into these irrigation practices and thus may help elucidate the impact of climate fluctuations and hydrologic changes on prehistoric agriculture in the American Southwest.

The ^{18}O -cellulose model requires a number of parameter inputs for estimation of leaf water enrichment and ^{18}O exchange of photosynthates with medium water during cellulose formation (Eq. (1)). The leaf water enrichment part of the model is highly sensitive to variations in relative humidity and stomatal conductance. However, the model accurately predicted $\delta^{18}\text{O}_{\text{cellulose}}$ values in experimentally grown maize cobs using realistic or measured values for these two parameters. Improved paleoclimate reconstructions for the northern Colorado Plateau would help reduce the uncertainty in estimates of humidity, which in turn would greatly enhance the applicability of our approach to understanding prehistoric maize agriculture. Variation in humidity between 10 and 30% resulted in variation of the estimate for source water $\delta^{18}\text{O}$ of up to 5.5‰, which is large considering that summer monsoon and winter snowmelt sources differ by only about 10‰. Regardless, our approach distinguished cobs that clearly were grown with little if any input from monsoonal moisture from those grown with substantial inputs of monsoonal water. Such information, even at this relatively coarse scale, is valuable for understanding the impact of climate change on aboriginal maize cultivation in the arid American Southwest.

The biochemical pathway of cellulose formation is the same for all parts of a plant. The difference isotopically between cellulose synthesis in leaves and other parts of the plant is that medium water at the site of cellulose formation where precursors are allowed to exchange oxygen isotopes differs and the “*f*” value, which is the fraction of O atoms in the photosynthate that re-equilibrate with medium water before cellulose formation (Eq. (1)). The Roden et al. model was developed for tree rings, but is applicable to cellulose formation in any part of the plant. We demonstrate in Table 4 that cob medium water is very similar to plant source water, but very different than leaf water, so a simple model using leaf water $\delta^{18}\text{O}$ values for isotopic exchange in cobs would be inappropriate. In fact, a very simple model based on leaf water $\delta^{18}\text{O}$ values and assuming no post synthesis exchange of ^{18}O in

photosynthates prior to cob cellulose formation over estimates cob $\delta^{18}\text{O}_{\text{cellulose}}$ by 10 to 20‰.

The “*f*” value in the model (Eq. (1)) is assumed in our study to be 0.42, which was reported by Roden et al. [21]. Theoretically, this value could range between 0.2 and 0.6 depending on the fraction of sucrose molecules transported from leaves that are converted to triose phosphate prior to incorporation into cellulose. Complete conversion of hexose phosphate to triose phosphate leading to cellulose synthesis would equate to an *f* value of 0.6. Farquhar et al. [8] show that 40 to 50% of sucrose is converted to triose phosphate prior to synthesis of cellulose, which would match closely an *f* value of 0.42. Variation in the fractional exchange of O isotopes with medium water due to variation in triose phosphate recycling should be investigated further with maize to improve the usefulness of cellulose oxygen stable isotopes in maize source water determinations.

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