Using Oxygen Isotope Analysis of Modified Cellulose to Investigate Salt Water Intrusion and Paleotemperatures

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INTRODUCTION- Organic Oxygen Isotopes

- ^{18}O vs. ^{16}O
  - .2% of oxygen atoms vs. 99.76% of oxygen atoms
- Factors affecting the ^{18}O content of organic matter
  - Variation in the source water $\delta^{18}O$
  - Leaf water evaporative $\delta^{18}O$ enrichment
  - Water mixing within the plant (stem/leaves)
  - Isotope exchange between water and organic oxygen

INTRODUCTION- Source Water $\delta^{18}O$

- $\delta^{18}O_{rainfall} = 0.52T - 0.006T^2 + 2.42P - 1.43P^2 - (0.046Elv^{1/2}) - 13.0$
  - T = temperature, P = precipitation, E = elevation
  - Higher temperatures = higher $\delta^{18}O$ values
  - More precipitation = lower $\delta^{18}O$ values
  - Higher elevations = lower $\delta^{18}O$ values
  - Barbour et. al (2001), based on data from IAEA (1992)
- Because of the relationship to temperature, δ18O values of cellulose have been proposed as "isotopic thermometers"
  - Libby et. al 1976
- Groundwater vs. Precipitation
  - Different $\delta^{18}O$ signatures, Clark and Fritz, 1997.

INTRODUCTION- Leaf water $\delta^{18}O$

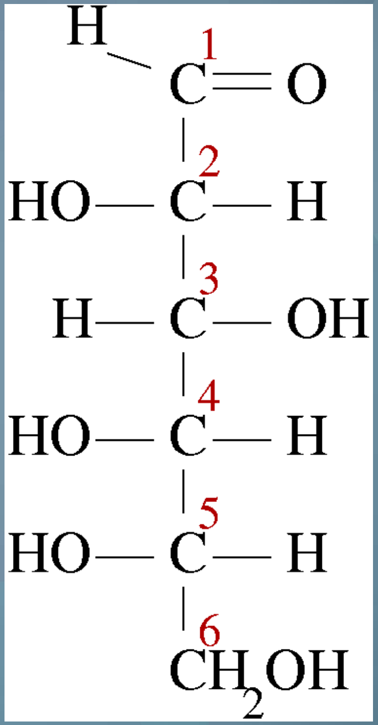
- Because ^{16}O atoms evaporate more readily, leaf water gets enriched according to the Craig-Gordon equation (1965):
  - $\delta^{18}O_E = \delta^{18}O_s + \varepsilon^* + \varepsilon_k + e_a/e_i\ (\delta^{18}O_A - \delta^{18}O_s - \varepsilon_k)$
    - $\delta^{18}O_s$ = isotopic composition of the stem water
    - ε^* and ε_k =
    - e_a = ambient vapor pressure/e_i = intercellular vapor pressure
      - e_a/e_i = relative humidity, leaf is usually saturated
    - $\delta^{18}O_A$ = isotopic composition of atmospheric water vapor
- Transpiration reduces leaf water evaporative enrichment by drawing stem water into the leaf.
  - Péclet Effect equation: $\rho = (TL)/(CD)$
    - T is transpiration rate, L is the mixing length of the leaf
    - C and D are constants.
- Combined equation predicts bulk leaf water enrichment.
  - $\Delta^{18}O_l = [(1-\alpha)\delta^{18}O_s] + [\alpha\delta^{18}O_E]$
    - $\alpha = (1- (1/e^{\rho}))/\rho$

INTRODUCTION- Mix of Source and Leaf Water

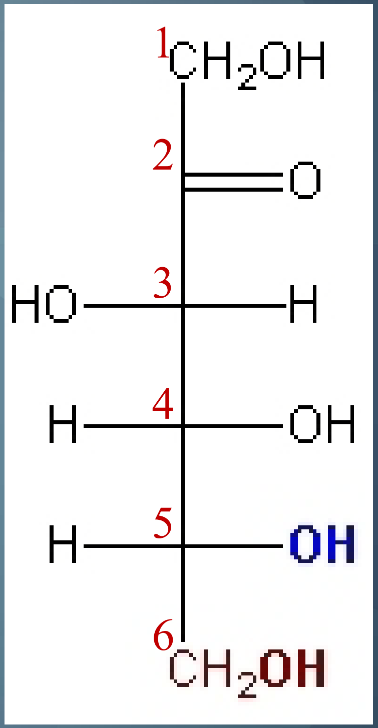
- Phloem transports sugar and water from the leaves to growing cells.
  - Slightly less enriched than leaf water, because it equilibrates with source water in the xylem
  - Bret-Harte and Silk, 1994
- The two water sources mix; how they mix effects the $\delta^{18}O$ of the cellulose.

INTRODUCTION- Biochemical fractionation

- To make cellulose, sucrose breaks into glucose and fructose.
  - Sucrose has $\delta^{18}O$ of leaf water (Barbour, 1999)
- Glucose and fructose exchange in equilibrium.
- The oxygen atom on the carbonyl group (C=O) exchanges with the oxygen in the water.



Glucose



Fructose

INTRODUCTION- Biochemical noise

- Some fructose molecules are used by the plant to make other, non-cellulose compounds . Lighter fructose molecules with ^{16}O on the second carbon are used first, changing the isotopic ratio.
  - Example: manitol
- Phenolglucosazone removes the oxygen from the first and second carbons, eliminating the oxygen isotope changes caused by fructose use.
  - Sternberg et. al., 2006
- Even without considering that particular biochemical factor, $\delta^{18}O$ ratios are affected by many different variables and can be difficult to interpret correctly.

INTRODUTION- *Conocarpus erectus*

- aka Buttonwood
- Survive at up to 1,000 ppm NaCl
- Salinity vs. $\delta^{18}O$
  - More salt – more ^{18}O
  - Sternberg et. al, 1991
- Hypothesis- Buttonwood samples collected from freshwater areas will have lower cellulose and PG $\delta^{18}O$ values than those collected from saltwater areas.
- Application- Buttonwoods could provide a record of salt-water intrusion

INTRODUCTION- *Sphagnum*

- aka peat moss
- *Sphagnum* genus of bryophyte
  - Leafy stem topped with capitulum, stem decays while plant keeps growing
- Slow decay rate preserves organic matter
  - acidic conditions, phenolic compounds, dry/cold conditions
- Hypothesis- The $\delta^{18}O$ values of derived phenolglucosazone will be more strongly correlated with estimated paleotemperatures than the $\delta^{18}O$ of peat cellulose.
- Application- Peat cores are often used to establish paleoclimate conditions, including temperatures.

METHODS

- Sample Collection
  - Buttonwood samples collected from University of Miami, SW 62nd Avenue, Matheson Hammock, Sugar Loaf Key
  - Peat cellulose samples sent by Elise G. Pendall, U of Wyoming
- Cellulose Extraction
  - to isolate cellulose from bulk dry plant matter
  - Leavitt and Danzer, 1993
- NaOH wash
  - to isolate α-cellulose, eliminate hemi-celluloses
- Hydrolysis
  - to break up cellulose chains into glucose monomers
  - Fengel and Wegener, 1979
- Derivation
  - to form phenolglucosazone from glucose
  - Oikawa, 1998
- Isotope Ratio Mass Spectrometer (IRMS)

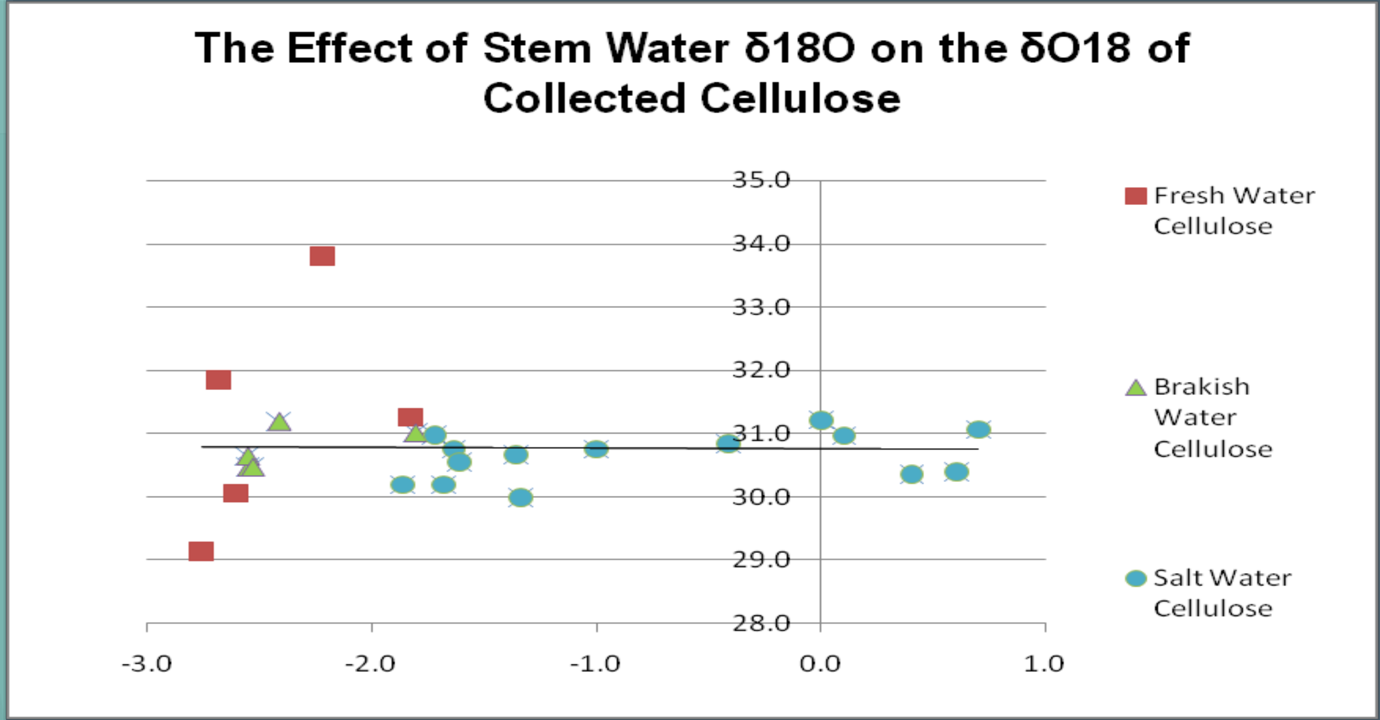
RESULTS

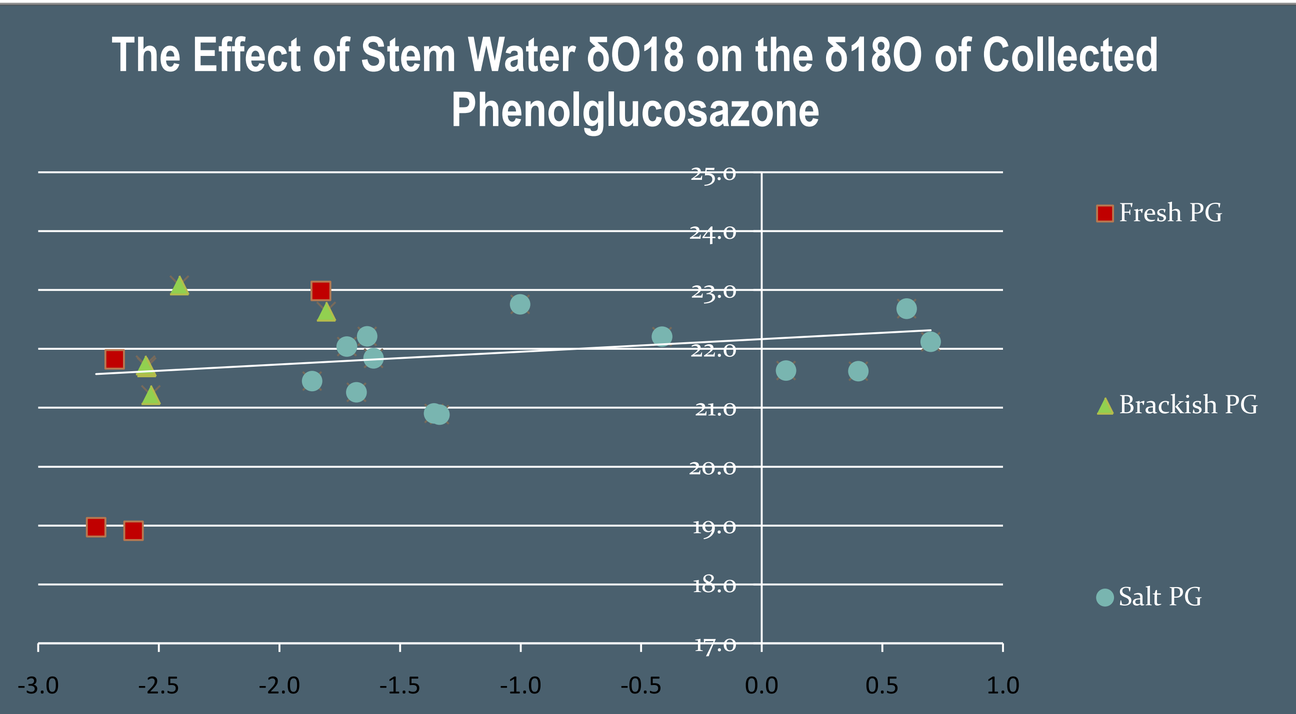
- Cellulose
- $y = -.0076x + 30.767$
- $R^2 = .0001$
- (no relationship)

- Phenolglucosazone
- $y = .2151x + 22.168$
- $R^2 = .0306$
- (no relationship)

Neither cellulose nor phenolglucosazone does a very good job of predicting stem water $\delta^{18}O$.

Neither result is statistically significant.





DISCUSSION

Conocarpus erectus	*Sphagnum*/Peat

• $\delta^{18}O$ of cellulose unrelated to $\delta^{18}O$ of stem water, same for phenolglucosazone
• $\delta^{18}O$ of cellulose almost constant
  ◦ Difficult to use for study of salt-water intrusion
	• Peat Samples did not produce phenolglucosazone.
	• Fresh Sphagnum moss did produce phenolglucosazone.
	  ◦ Low yield
	• Possible presence of molecules in peat strongly bonded to cellulose which may interfere with phenolglucosazation.
	  ◦ lignin?

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