

How does carbonate $\Delta^{17}\text{O}$ relate to source waters? Examples from biogenic and abiogenic minerals

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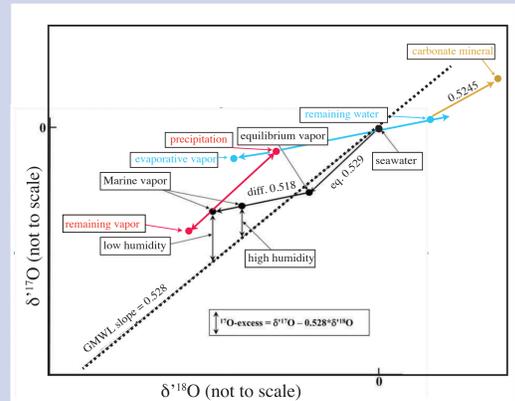
Abstract

The ^{17}O excess ($\Delta^{17}\text{O}$) of surface waters can largely be explained by Rayleigh fractionation and evaporation where:

$$\Delta^{17}\text{O} = \ln(\delta^{17}\text{O}+1) - 0.528 \ln(\delta^{18}\text{O}+1)$$

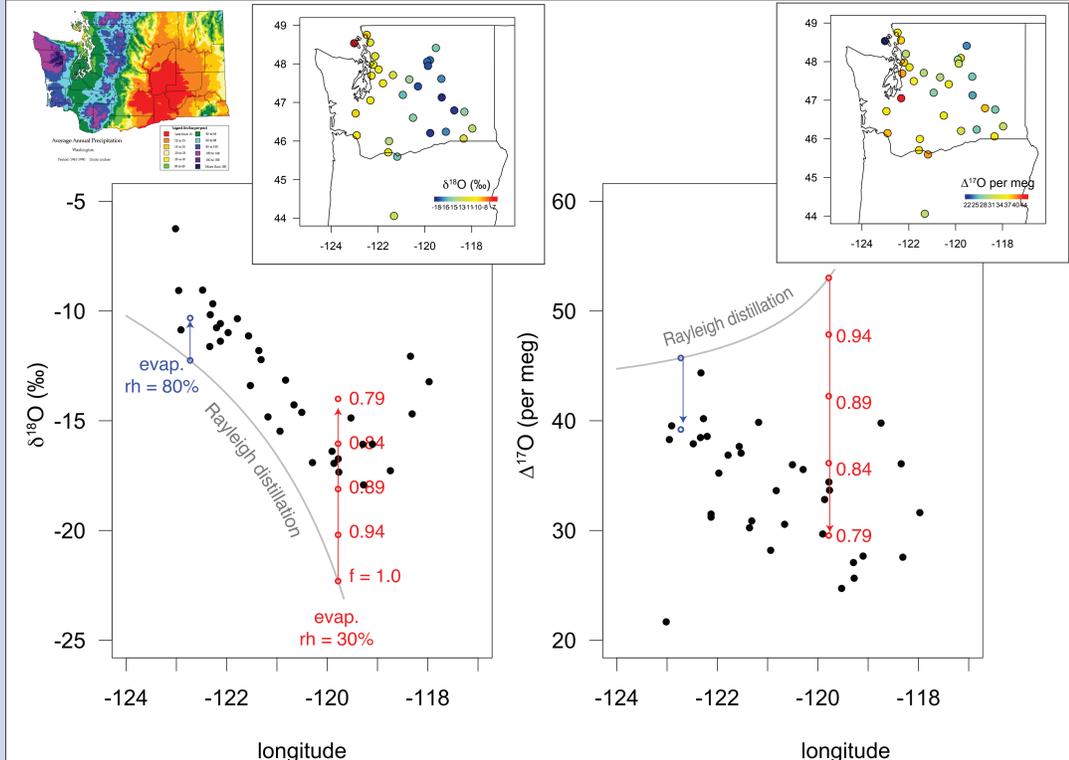
- Carbonate $\Delta^{17}\text{O}$ is a potential proxy for past variations in these hydrological variables.
- Passey et al. (2014) present a method to calculate $\Delta^{17}\text{O}$ of parent waters from carbonate $\Delta^{17}\text{O}$, but could not evaluate if it was unique to their analytical protocol
- We demonstrate the efficacy of the Passey et al. approach using a distinct preparatory approach
- The precision with which $\Delta^{17}\text{O}$ can be measured will be the major limitation of $\Delta^{17}\text{O}$ paleohydrology for the foreseeable future

Motivation: $\Delta^{17}\text{O}$ variations along a natural hydrologic gradient



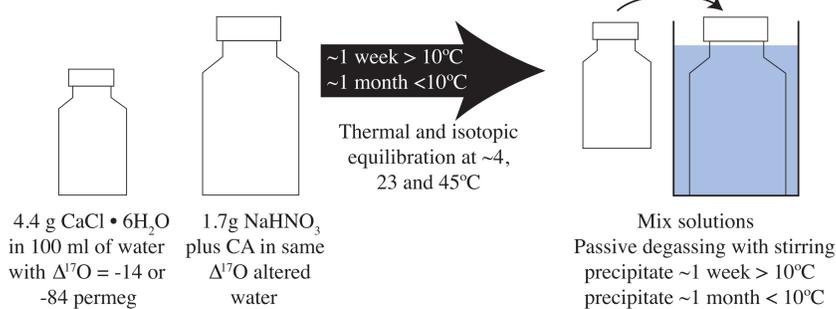
- An ideal natural laboratory with sharp hydrologic gradients
- Tap water approximates annual average precipitation $\delta^{18}\text{O}$ (Bowen et al. 2007)
- Evaluate the primary controls of $\Delta^{17}\text{O}$
- 34 waters measured via fluorination/IRMS (Schoenemann et al., 2013) and CRDS (Steig et al., 2014)

$$\Delta^{17}\text{O} \sim f(\text{Rayleigh, evaporation}) + \epsilon$$



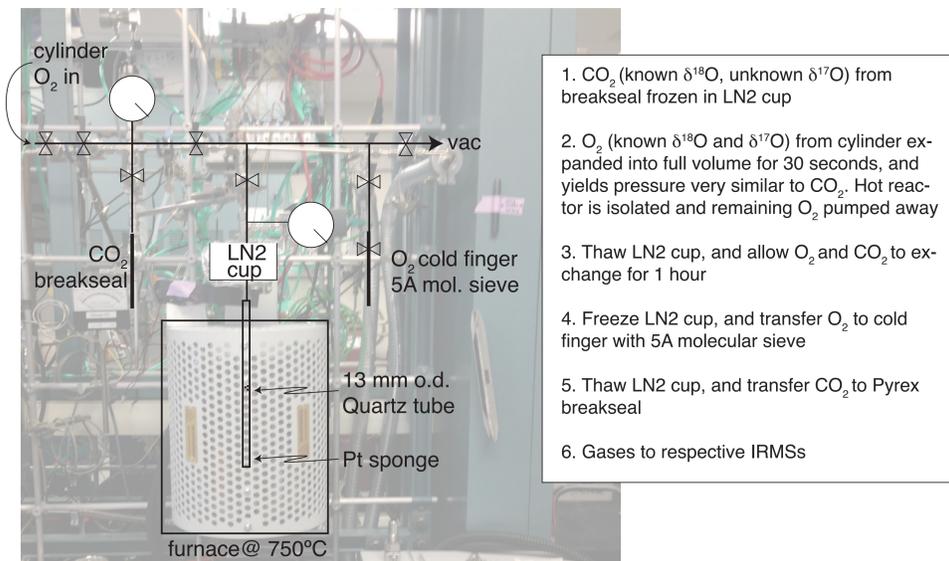
Methods

Abiogenic precipitation from fluids evaporatively altered $\Delta^{17}\text{O}$



Preparatory

- ~8 mg calcite digested in 90°C phosphoric acid to produce CO_2
- CO_2 - O_2 isotope exchange at 750°C, catalyzed by platinum (Mahata et al., 2013; Barkan et al., 2015)



- “Pump” bellows when introducing O_2 to the IRMS: 9 x [3 x (100%, 3 sec, 25%, 3 sec); 180 sec] (Laurence Yeung, personal comm.)

Calculation of initial CO_2 $\delta^{17}\text{O}$ following Barkan et al. (2015)

$$\delta^{17}\text{O}_{\text{in}}(\text{CO}_2) = \frac{1}{\beta} [(\delta^{17}\text{O}_{\text{f}}(\text{O}_2) + 1)(1 + ^{17}\alpha\beta) - (\delta^{17}\text{O}_{\text{in}}(\text{O}_2) + 1)] - 1$$

where beta is molar CO_2/O_2 ratio

$$\beta = \frac{\delta^{18}\text{O}_{\text{in}}(\text{O}_2) - \delta^{18}\text{O}_{\text{f}}(\text{O}_2)}{\delta^{18}\text{O}_{\text{f}}(\text{CO}_2) - \delta^{18}\text{O}_{\text{in}}(\text{CO}_2)}$$

and $\theta_{\text{ss}} = \frac{\ln^{17}\alpha_{\text{CO}_2/\text{O}_2}}{\ln^{18}\alpha_{\text{CO}_2/\text{O}_2}}$ is assumed to be 0.5964 (Barkan et al., 2015)

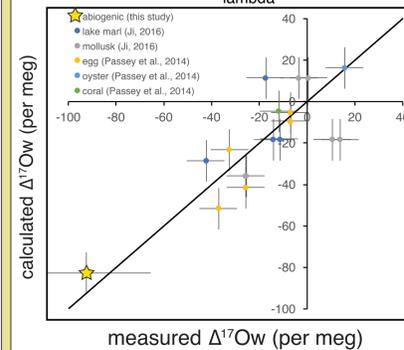
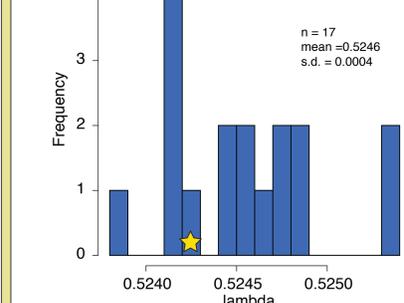
Preliminary results, and comparison with previous work

	$\text{O}_2\text{-i}$	$\text{O}_2\text{-f}$	$\text{CO}_2\text{-i}$	$\text{CO}_2\text{-f}$	$\text{CO}_2\text{-i}$	beta	$\Delta^{17}\text{O}$	$\Delta^{17}\text{O}$ (permeg)		
	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$					
17OB245_20170806	11.66	22.88	18.89	36.76	49.67	38.31	25.71	1.22	-0.0002066	-207
17OB245_20170808	11.66	22.88	19.67	38.16	49.67	39.20	25.77	1.46	-0.0001553	-155
										average = -181 ± 36

Calculation of parent water $\Delta^{17}\text{O}$ (Passey et al., 2014)

$$\Delta^{17}\text{O}_{\text{H}_2\text{O}} = \Delta^{17}\text{O}_{(\text{O}_2/\text{CaCO}_3)} + 10^3 \ln \alpha_{(\text{O}_2/\text{CaCO}_3) - (\text{O}_2/\text{H}_2\text{O})} \times [0.528 - \lambda_{(\text{O}_2/\text{CaCO}_3) - (\text{O}_2/\text{H}_2\text{O})}]$$

$$= \ln(^{17}\alpha_{\text{O}_2/\text{CaCO}_3 - \text{H}_2\text{O}}) / \ln(^{17}\alpha_{\text{O}_2/\text{CaCO}_3 - \text{H}_2\text{O}})$$



- λ combines many fractionations and has been suggested to vary with:
 - CO_2 - O_2 conversion method
 - temperature
- We calculate 0.5242 at 45°C (star), which is very similar to previous values at lower T using a different protocol (blue; Passey et al., 2014; Ji, 2016)
- No obvious λ T-dependence
- Reconstructed parent water $\Delta^{17}\text{O}$ generally within error of measured
- We extend the demonstrated accuracy range of the method by ~40 permeg
- No obvious difference between abiogenic and biogenic carbonates

Conclusions, challenges and future work

- Tap waters spanning large gradients in humidity and precipitation amount can be sufficiently explained by Rayleigh distillation of precipitation and subsequent evaporation
- The University of Washington now has carbonate $\Delta^{17}\text{O}$ capabilities with the potential to facilitate paleohydrological reconstructions from geological archives, although improved precision and interlaboratory comparison is warranted.
- The $\Delta^{17}\text{O}$ of abiogenic calcite precipitated from fluid of known $\Delta^{17}\text{O}$ shows the same λ as lake marls and biogenic carbonates despite being generated using a different preparatory approach.
- This suggests a range of carbonates may be promising targets for paleo-proxy work, limited primarily by $\Delta^{17}\text{O}$ analytical error, and secondarily by $10^3 \ln \alpha$ estimation

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