

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

Casey Saenger^{1,2}, csaenger@uw.edu

Andrew Schauer², Julia Kelson², Keith Hodson², Katharine Huntington², Eric Steig², Anne Gothmann^{1,3}, Karen Valladares¹

1. Joint Institute for the Study of the Atmosphere and Ocean, University of Washington 2. Department of Earth and Space Sciences, University of Washington 3. University of Washington School of Oceanography

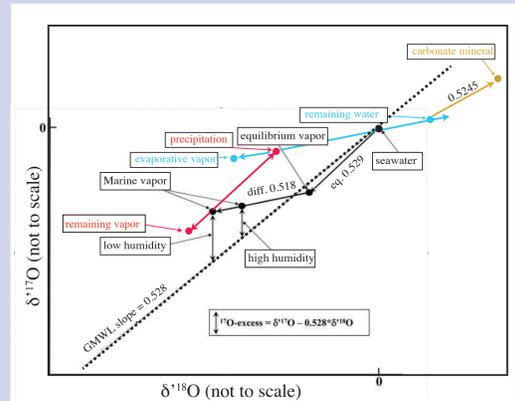
Abstract

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

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

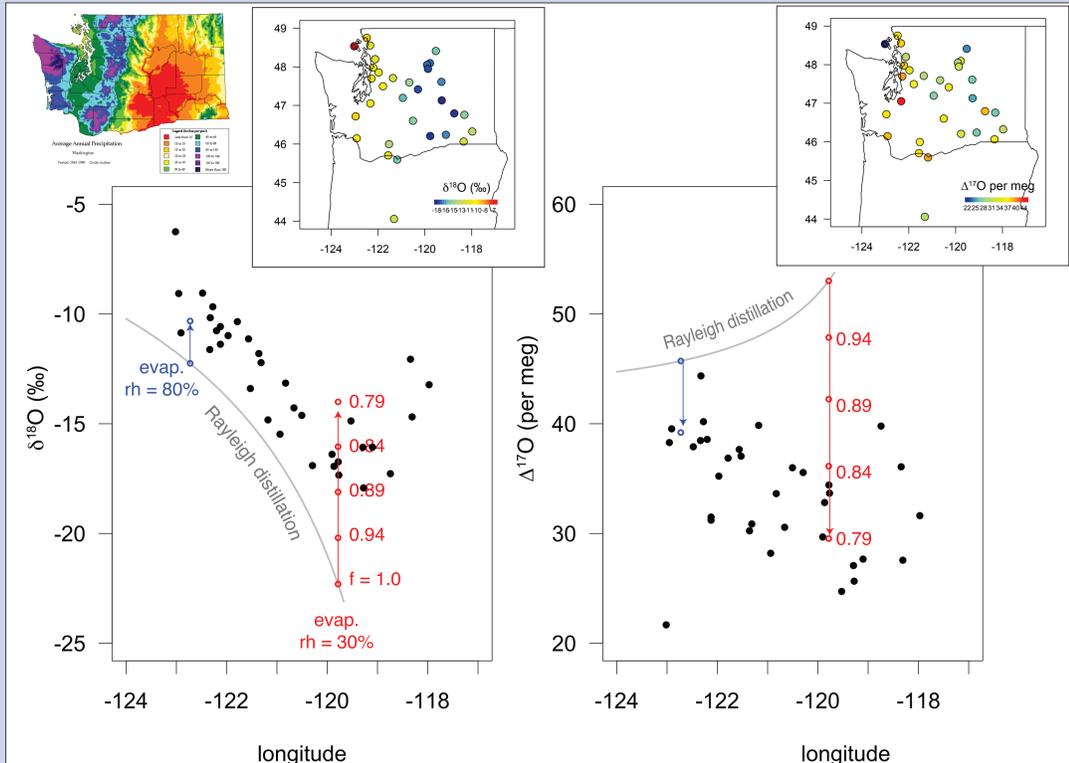
- Carbonate $\Delta^{17}\text{O}$ is a potential proxy for past variations in these hydrological variables.
- Passey et al. (2014) present a method to calculate $\Delta^{17}\text{O}$ of parent waters from carbonate $\Delta^{17}\text{O}$, but could not evaluate if it was unique to their analytical protocol
- 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



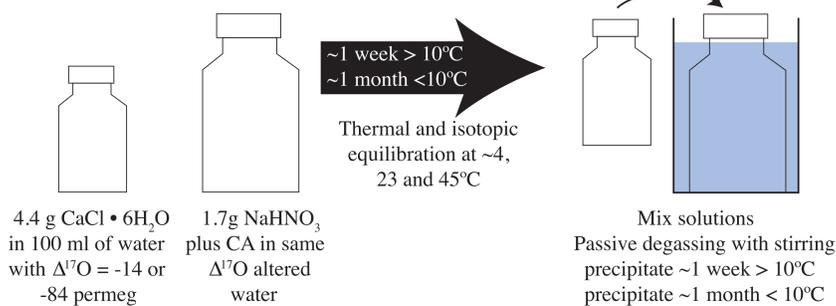
- An ideal natural laboratory with sharp hydrologic gradients
- Tap water approximates annual average precipitation $\delta^{18}\text{O}$ (Bowen et al. 2007)
- Evaluate the primary controls of $\Delta^{17}\text{O}$
- 34 waters measured via fluorination/IRMS (Schoenemann et al., 2013) and CRDS (Steig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

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



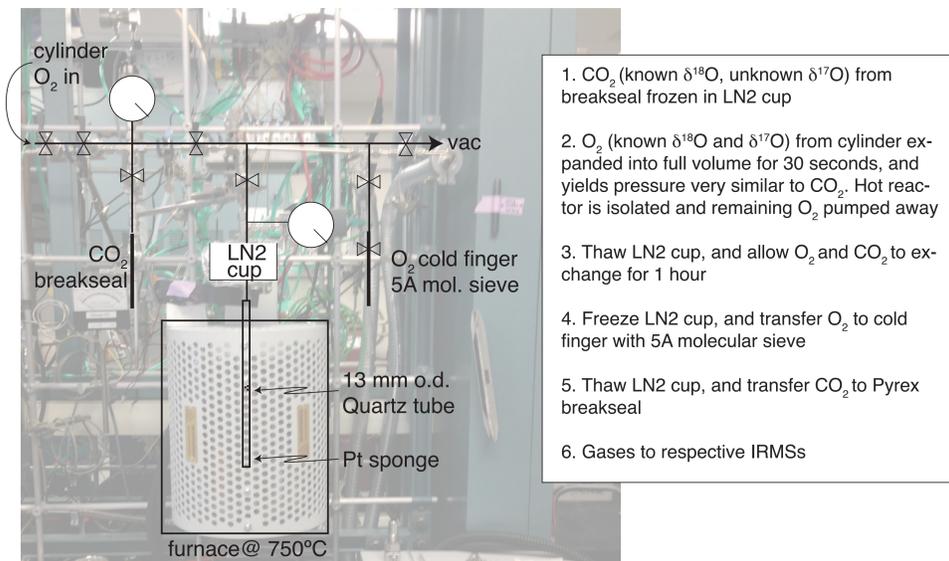
Methods

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

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

$$\text{and } \theta_{\text{ss}} = \frac{\ln^{17}\alpha_{\text{CO}_2/\text{O}_2}}{\ln^{18}\alpha_{\text{CO}_2/\text{O}_2}}$$

is assumed to be 0.5964 (Barkan et al., 2015)

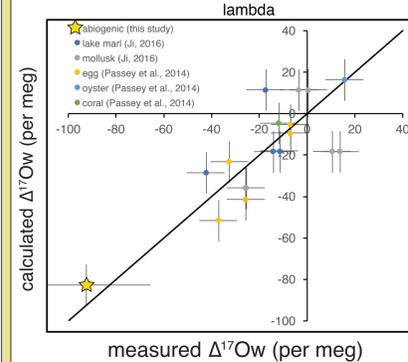
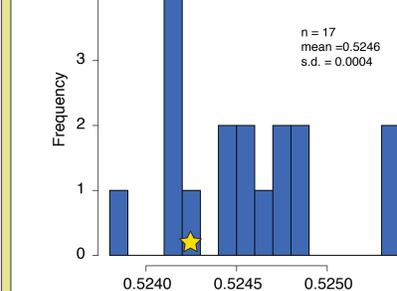
Preliminary results, and comparison with previous work

	$\text{O}_2\text{-i}$	$\text{O}_2\text{-f}$	$\text{CO}_2\text{-i}$	$\text{CO}_2\text{-f}$	$\text{CO}_2\text{-i}$	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

Acknowledgements: We are indebted to Eugeni Barkan, Boaz Luz and Ben Passey for their continued openness, advice and patience in support of this project

References:
 Barkan et al., 2015. High-precision measurements of $\delta^{17}\text{O}$ and ^{17}O excess of NBS19 and NBS18. RCMS. doi: 10.1002/rcm.7378
 Luz and Barkan, 2010. Variations of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ in meteoric waters. GCA. doi: 10.1016/j.gca.2010.08.016
 Ji, 2016. Triple oxygen isotopes in lake waters, lacustrine carbonates and pedogenic carbonates: An indicator for evaporation. JHU Ph.D thesis
 Mahata et al., 2013. Oxygen isotope exchange between O_2 and CO_2 over hot platinum: An innovative technique for measuring $\Delta^{17}\text{O}$ in CO_2 . Analytical chemistry. doi: 10.1021/acs.1011777
 Mahata et al., 2016. An improved method of high-precision determination of $\Delta^{17}\text{O}$ of CO_2 by catalyzed exchange with O_2 using hot platinum. RCMS. doi: 10.1002/rcm.7423
 Passey et al., 2014. Triple oxygen isotopes in biogenic and sedimentary carbonates. GCA. doi: 10.1016/j.gca.2014.06.006
 Schoenemann et al., 2013. Measurement of SLAP2 and GISP $\delta^{17}\text{O}$ and proposed VSMOW-SLAP normalization for $\delta^{17}\text{O}$ and ^{17}O excess. RCMS. doi: 10.1002/rcm.6486
 Steig et al., 2014. Calibrated high-precision ^{17}O -excess measurements using cavity ring-down spectroscopy with laser-current-tuned cavity resonance. Atmospheric Measurement Techniques. doi: 10.5194/amt-7-2421-2014