Constraints on Late Jurassic and Cretaceous atmospheric pCO_2 and primary productivity from triple oxygen isotopes in dinosaur eggshells

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Thanks to: **Beverly Johnson**

Background

Triple Oxygen isotope system

^{16}O (99.762%), ^{17}O (0.038%), ^{18}O (0.200%)

Mass Dependent Fractionation (MDF)

$$\delta^{17}O \approx 0.52\ \delta^{18}O$$

Mass Independent Fractionation (MIF)

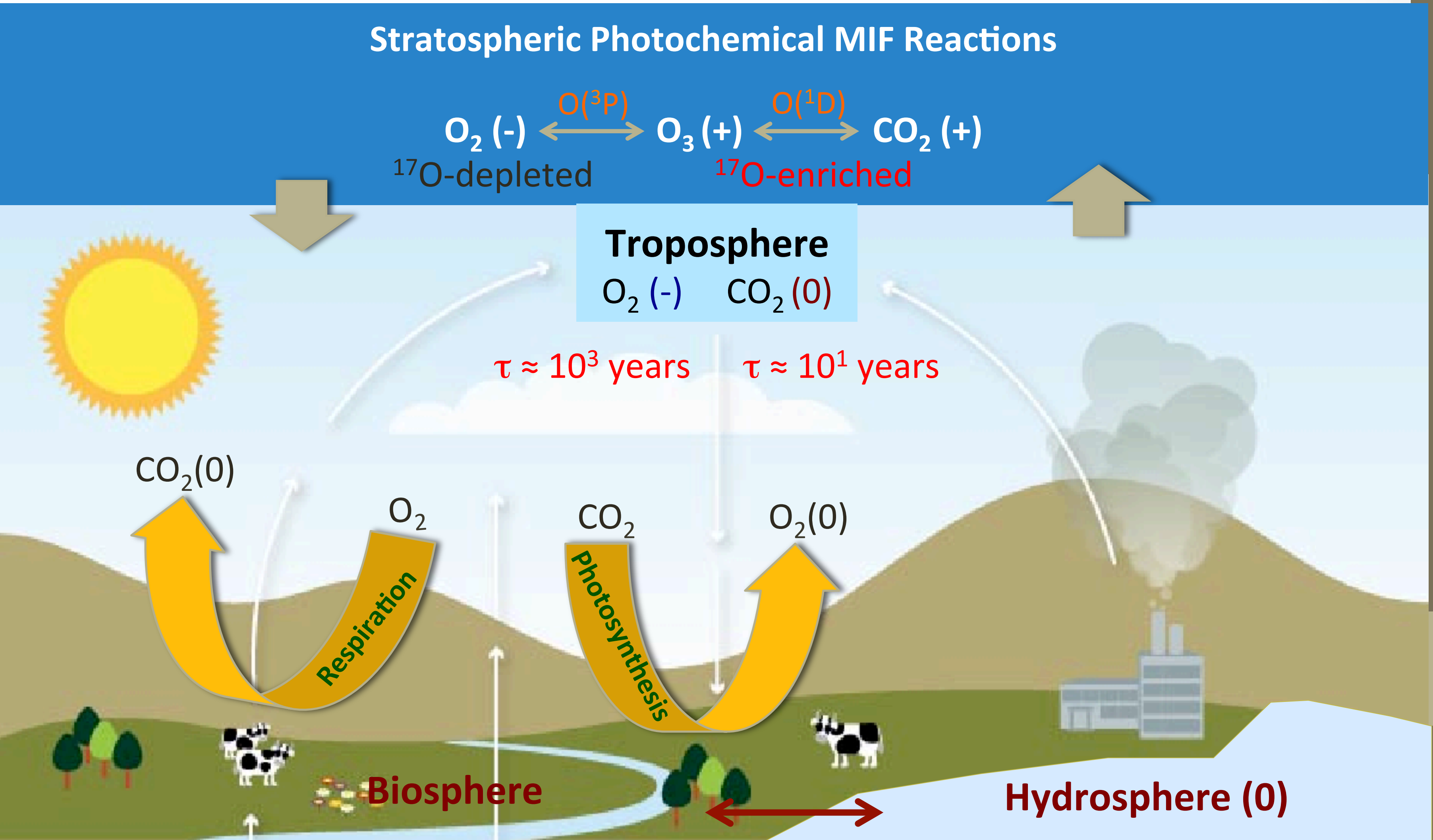
$$\delta^{17}O = C \bullet \delta^{18}O, \text{ where C is} \approx 1$$

^{17}O anomaly ($\Delta^{17}O$)

$$\Delta^{17}O = \delta^{17}O - \lambda \cdot \delta^{18}O \ (\lambda = 0.528)$$

$\Delta^{17}O$ (O_2) Budget Model

pCO_2-$\Delta^{17}O$ relationship



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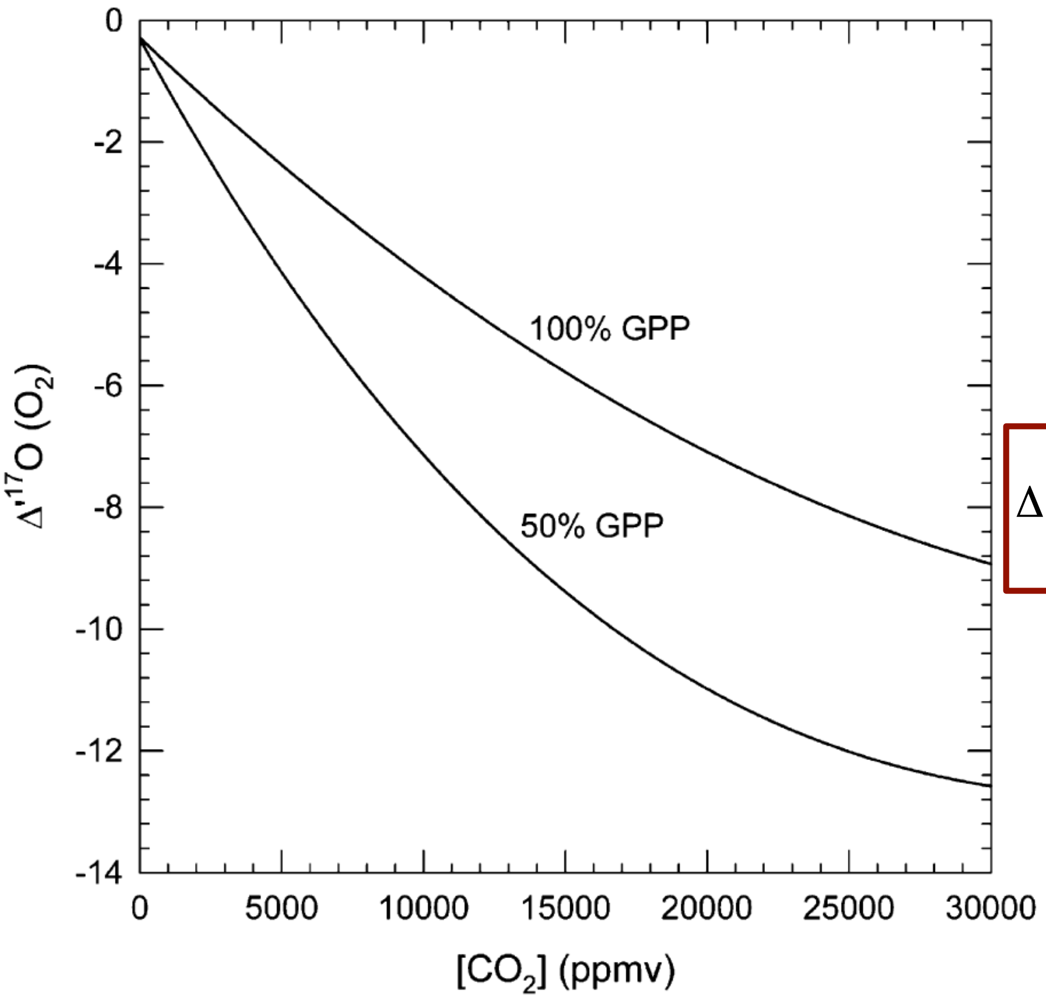


Young et al., 2014

$\Delta^{17}O$ (O_2) ~ pCO_2/GPP

$$\Delta^{17}O(O_2) = -0.2876 - 0.00058 \bullet \left[pCO_2 / \frac{GPP_t}{GPP_0} \right]$$

(Bao et al., 2008)

Body water isotope model

Respiration:

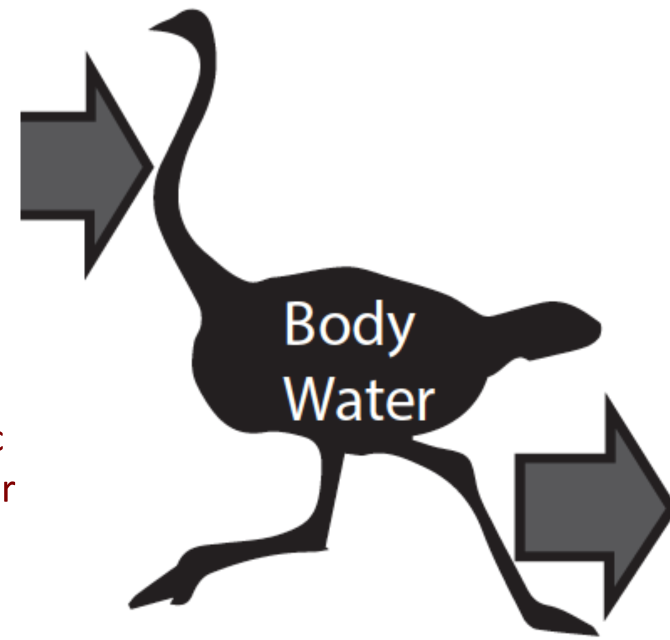
food

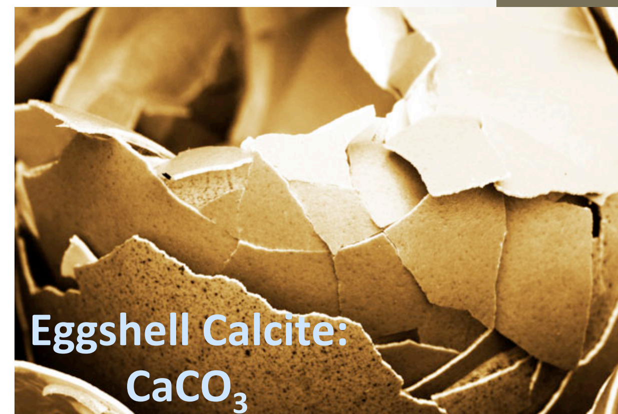
DIC

$CH_2O + O_2 \rightarrow CO_2 + H_2O$

Atm.O_2

metabolic body water





$$^{18}\alpha_{CaCO_3-H_2O} = 1.0380 \pm 0.0008 (1\sigma, n=7)$$

$$\lambda_{CaCO_3-H_2O} = 0.5245 \pm 0.0003 (1\sigma, n=7)$$

Body water isotope model

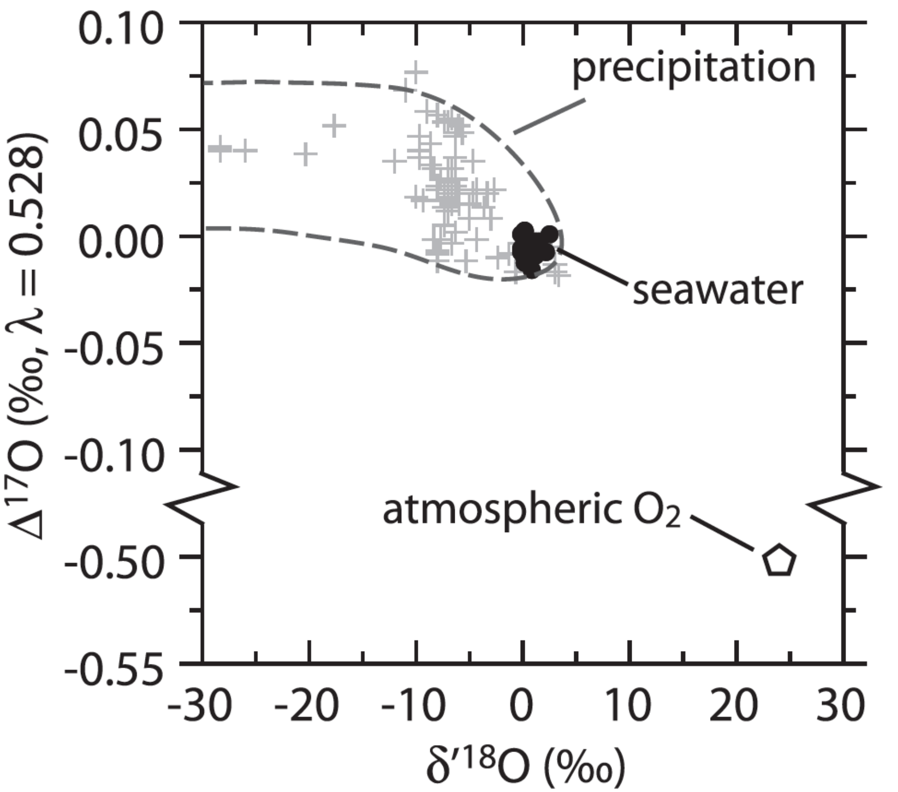
Oxygen Isotope Mass Balance

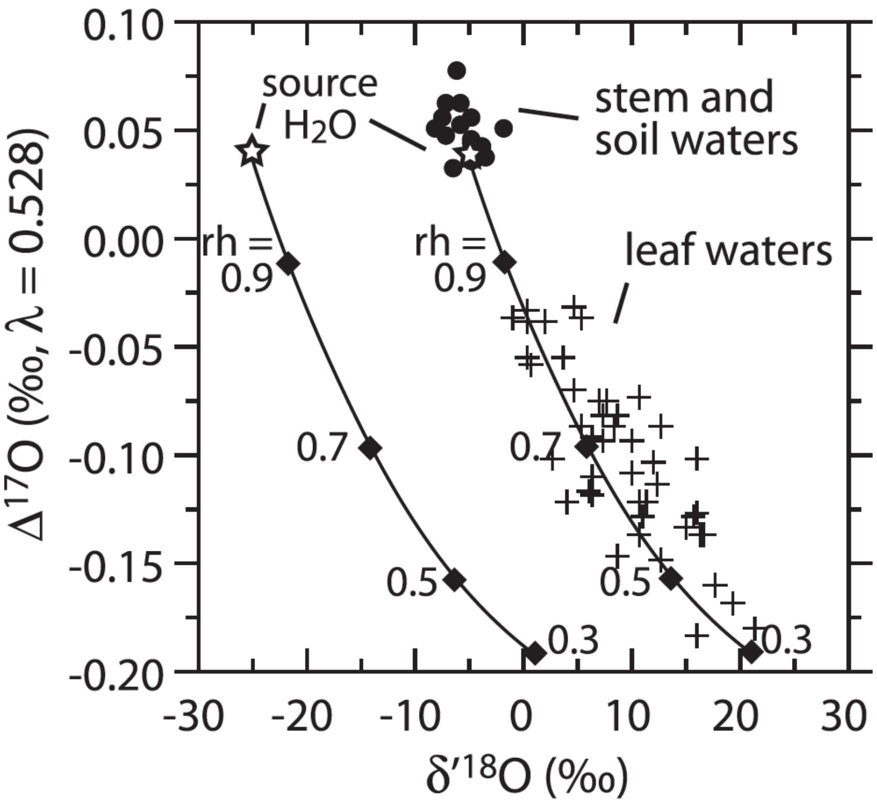
$$\sum_{a} R_{MW} \cdot f_{in,\alpha} \cdot \alpha_{\alpha-MW} + \boxed{R_{O_2} \cdot f_{O_2} \cdot \alpha_{lung-O_2}} = \sum_{\beta} R_{BW} \cdot f_{out,\beta} \cdot \alpha_{\beta-BW}$$

^{17}O-enabled version of the Kohn (1996, GCA) body water model

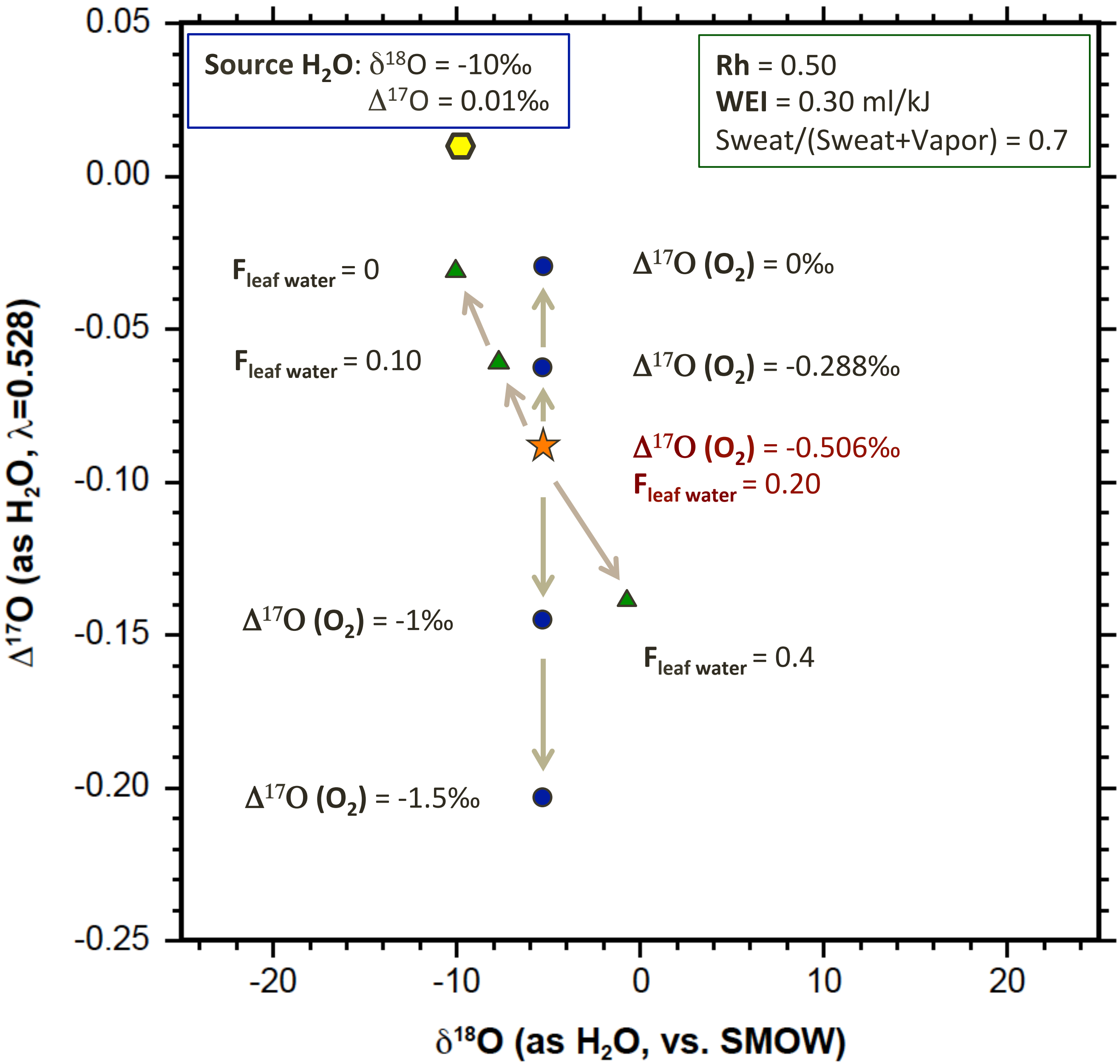
Important Model Parameters	
Humidity	meteoric water/leaf water composition
Animal Physiology	e.g..: Sweat/Vapor ratio; WEI: amount of water used per unit energy metabolized: (ml / kJ)
Fraction of Leaf Water	Fraction of evaporated leaf water relative to whole food water intake
Atmospheric O_2	Atmospheric O_2 composition ($\Delta^{17}O$)

Oxygen Input Space

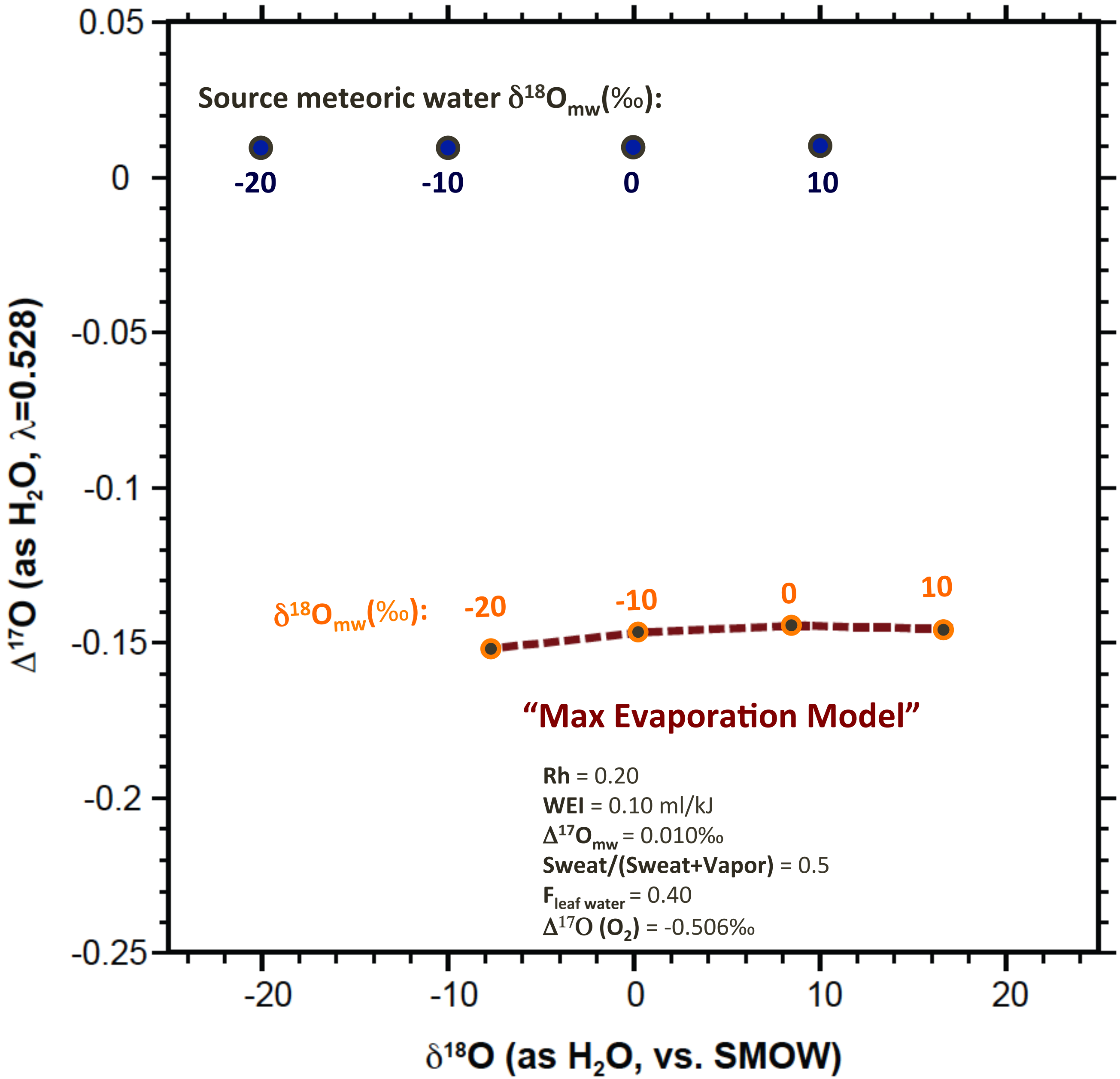




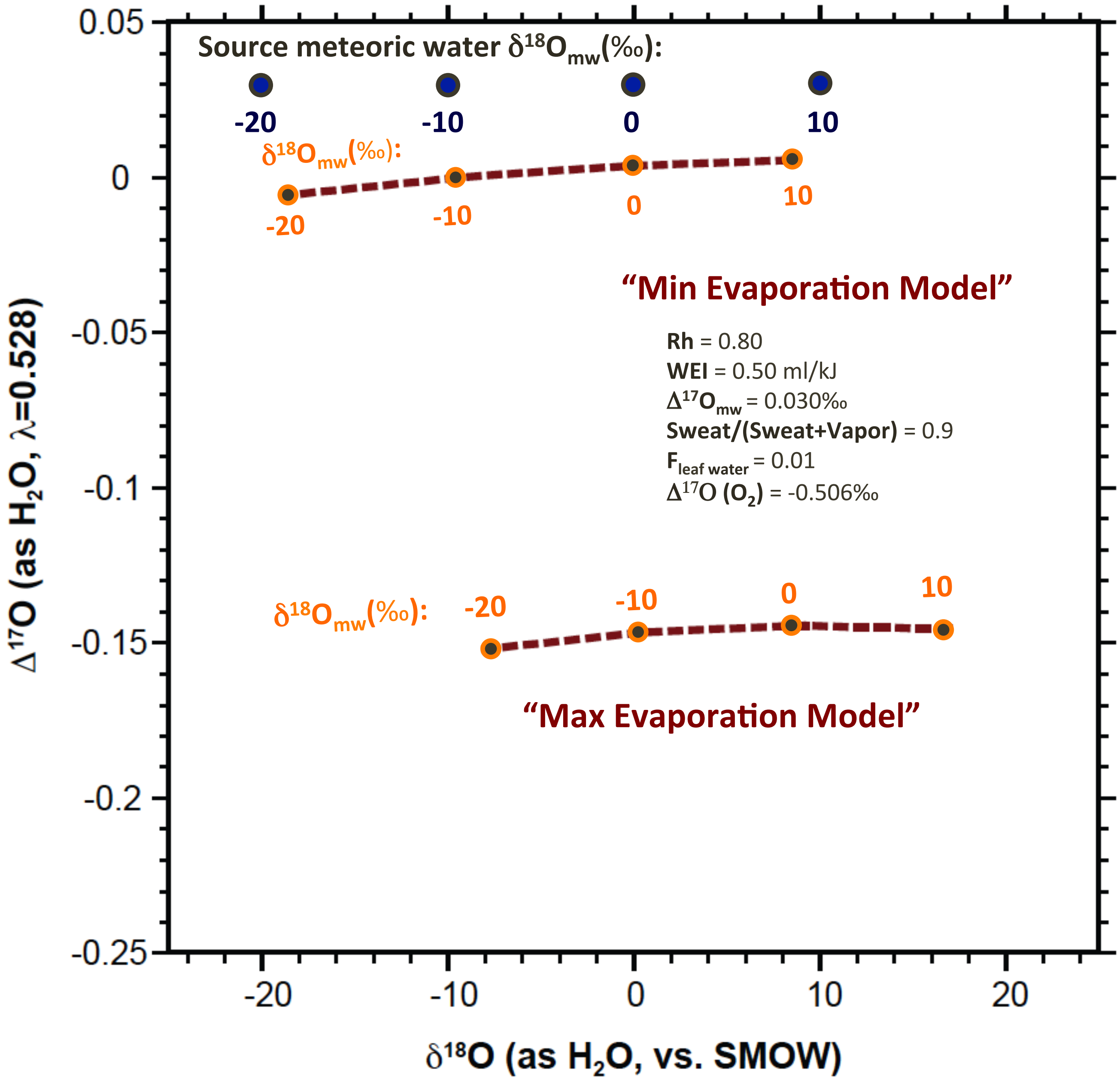
Model Sensitivity



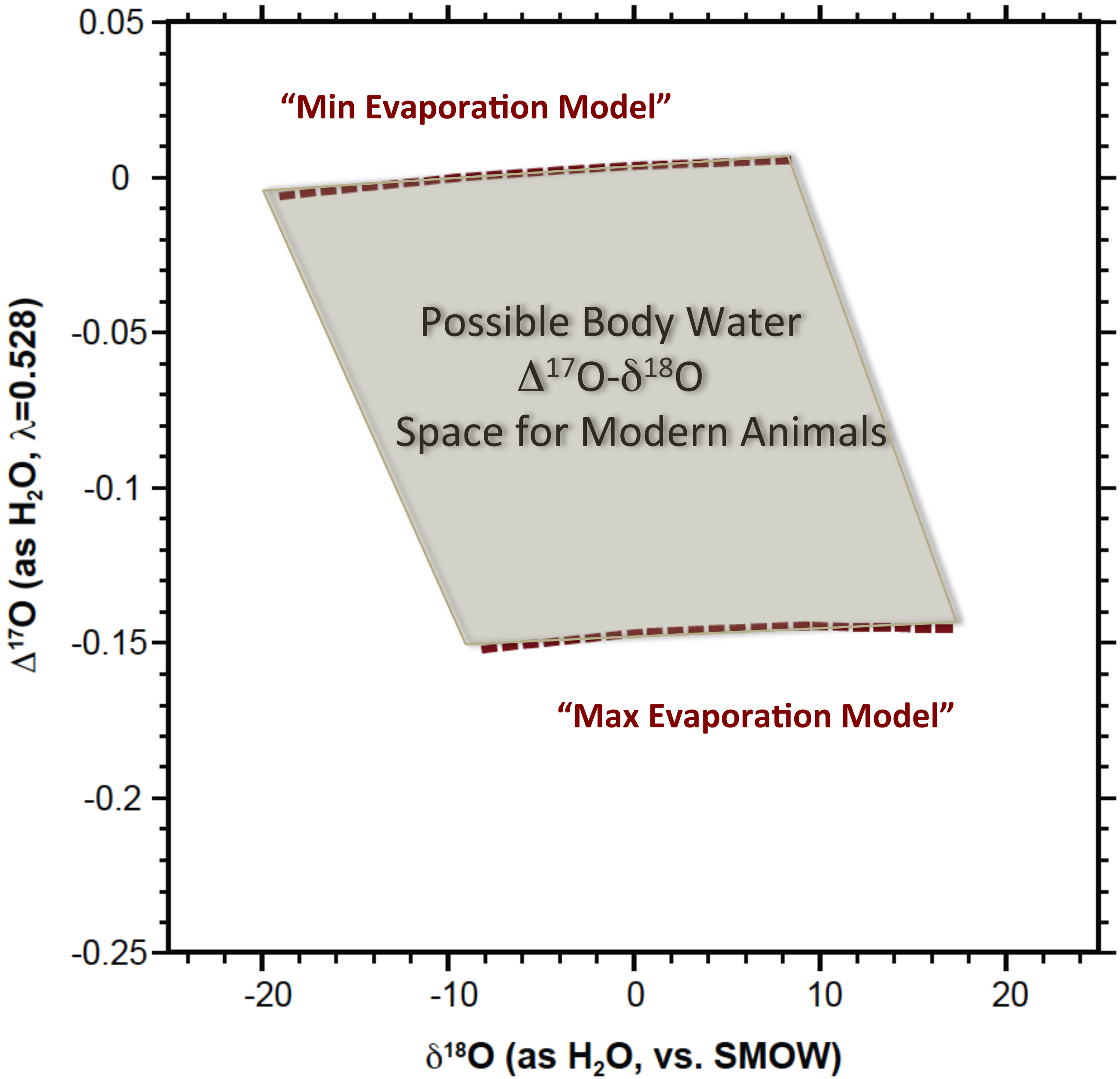
Modeled Endmembers (Max Evap.)



Modeled Endmembers (Min Evap.)



Body Water Model



Triple oxygen isotopes in biogenic and sedimentary carbonates

Benjamin H. Passey[a,*], Huanting Hu[a], Haoyuan Ji[a], Shaena Montanari[b], Shuning Li[a], Gregory A. Henkes[a], Naomi E. Levin[a]

[a] Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, MD 21218, USA
[b] American Museum of Natural History, Sackler Institute for Comparative Genomics, New York, NY 10024, USA

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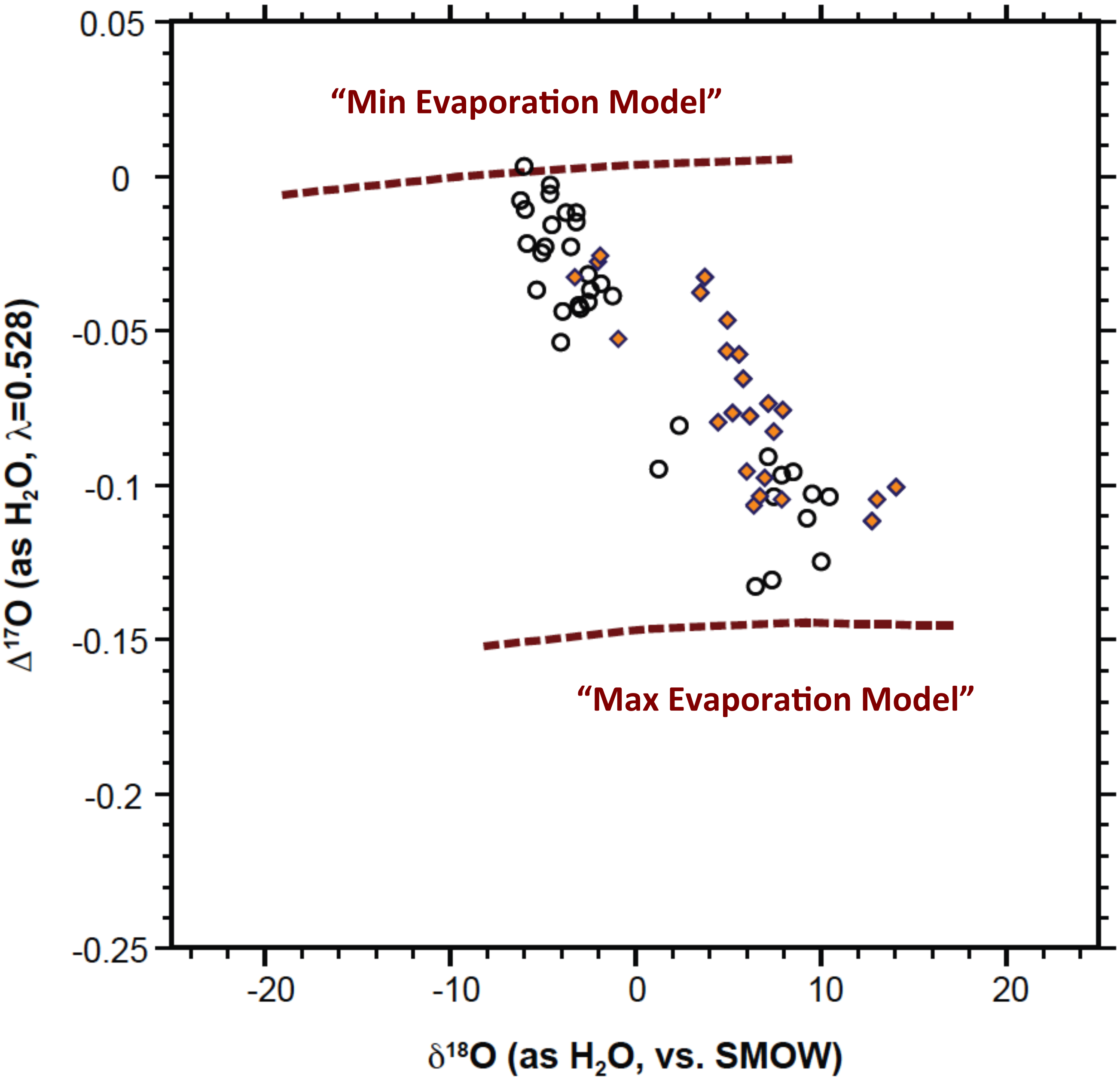
- Modern Samples

Sample Type	Species	N	Location
Wild Birds	Ostrich	3	Ethiopia, South Africa
	Starling	1	Baltimore
Captive Birds	Chicken	6	Baltimore, New Jersey, China, Japan,
	Ostrich	2	China
	Duck	1	New Jersey
	Emu	1	New Jersey

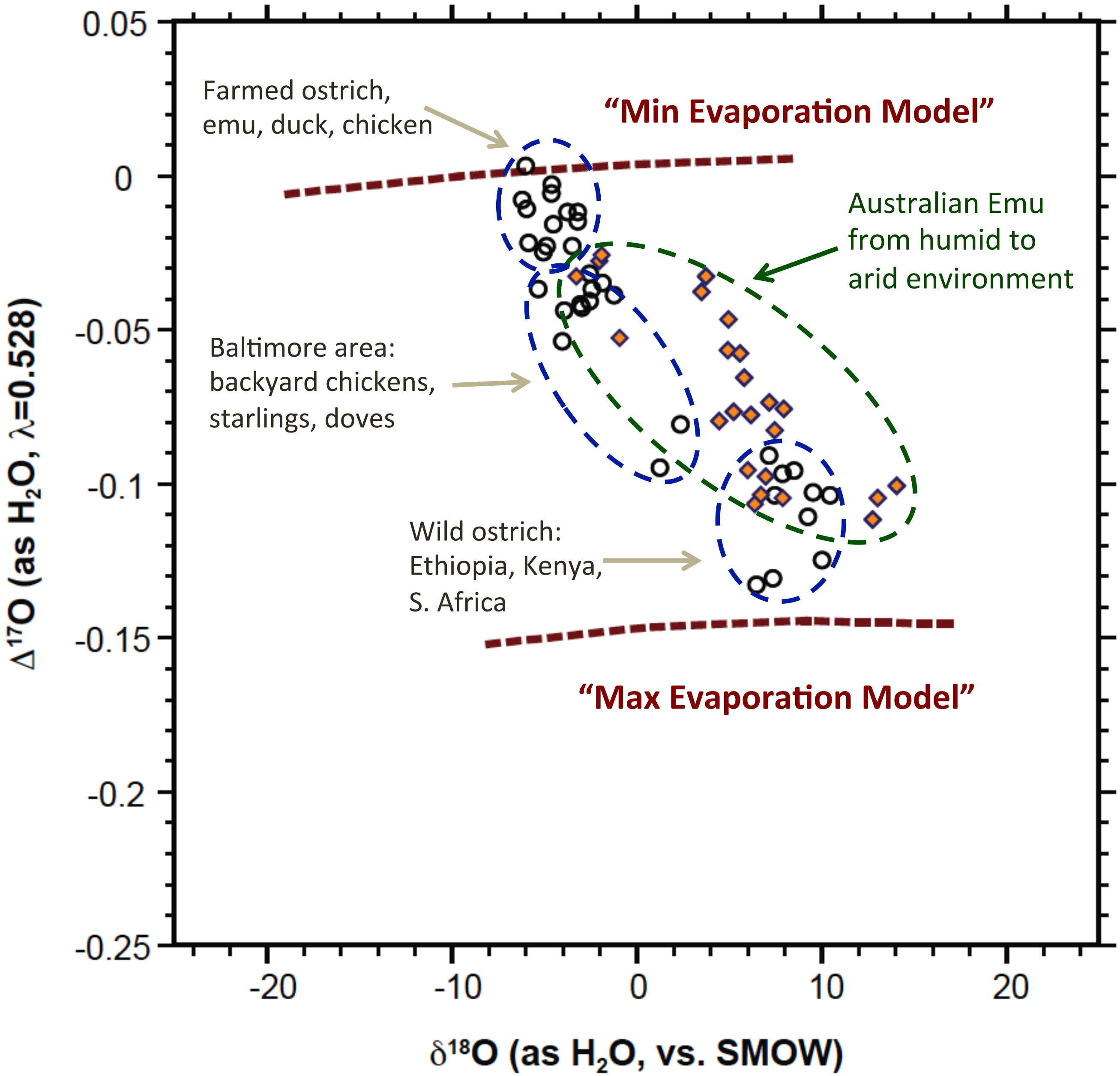
- Fossil Dinosaur Eggshells

Location	Species	N	Time Period	Age
Bugin Tsav	Oviraptorid	5	Late Cretaceous	Camp. /Mass.
Bayn Dzak	Oviraptorid, Protoceratops (?)	3	Late Cretaceous	Campanian
Ukhaa Tolgod	Oviraptorid	4	Late Cretaceous	Campanian
Two Medicine Fm.	Hadrosaur, Troodon	5	Late Cretaceous	Campanian
Cedar Mountain Fm.	Dinosaurid	3	Early Cretaceous	Albian
Morrison Fm.	Dinosaurid	11	Late Jurassic	Oxfordian

Modern Birds



Modern Birds



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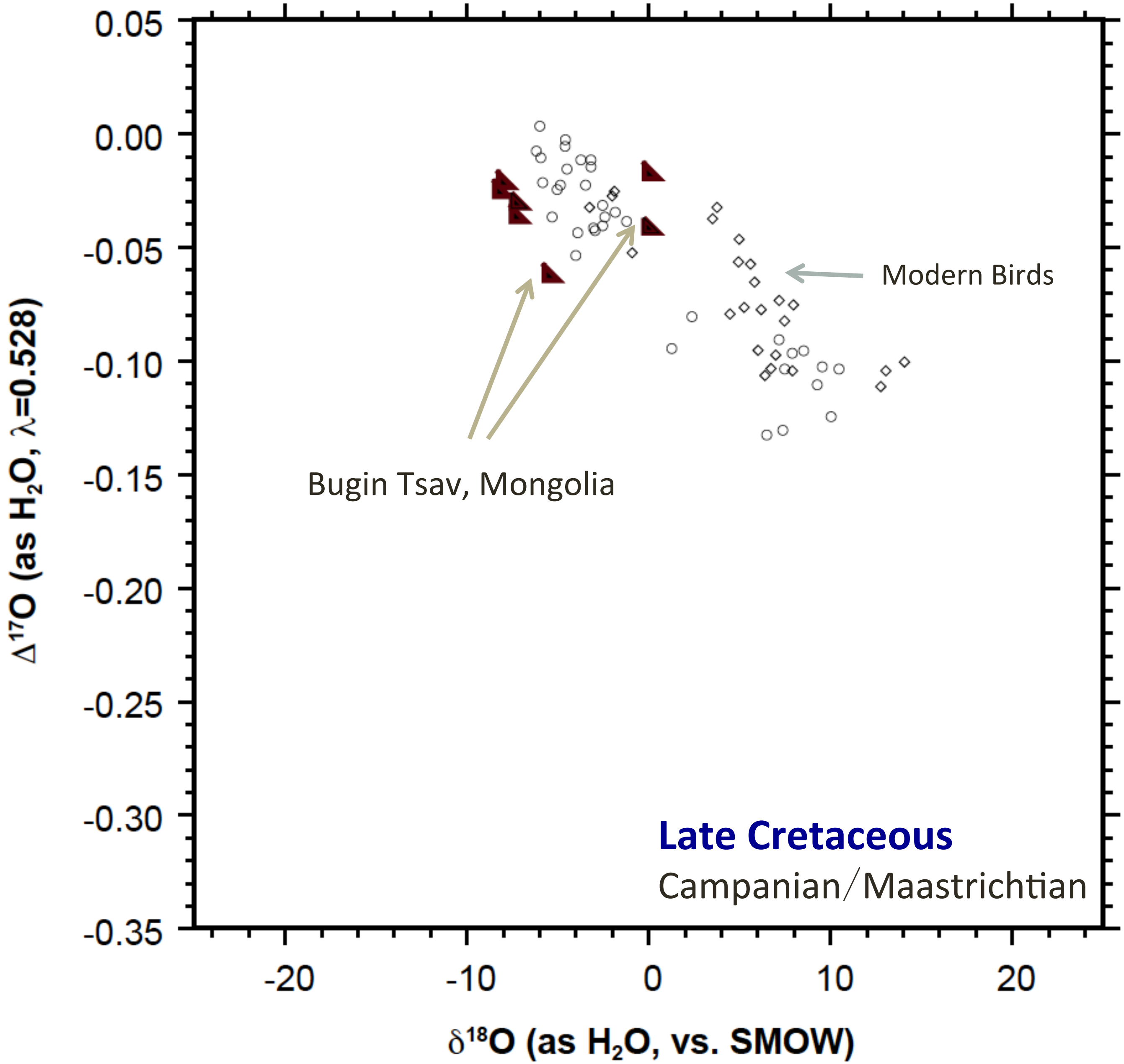
Dinosaurs



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-0.30
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-20
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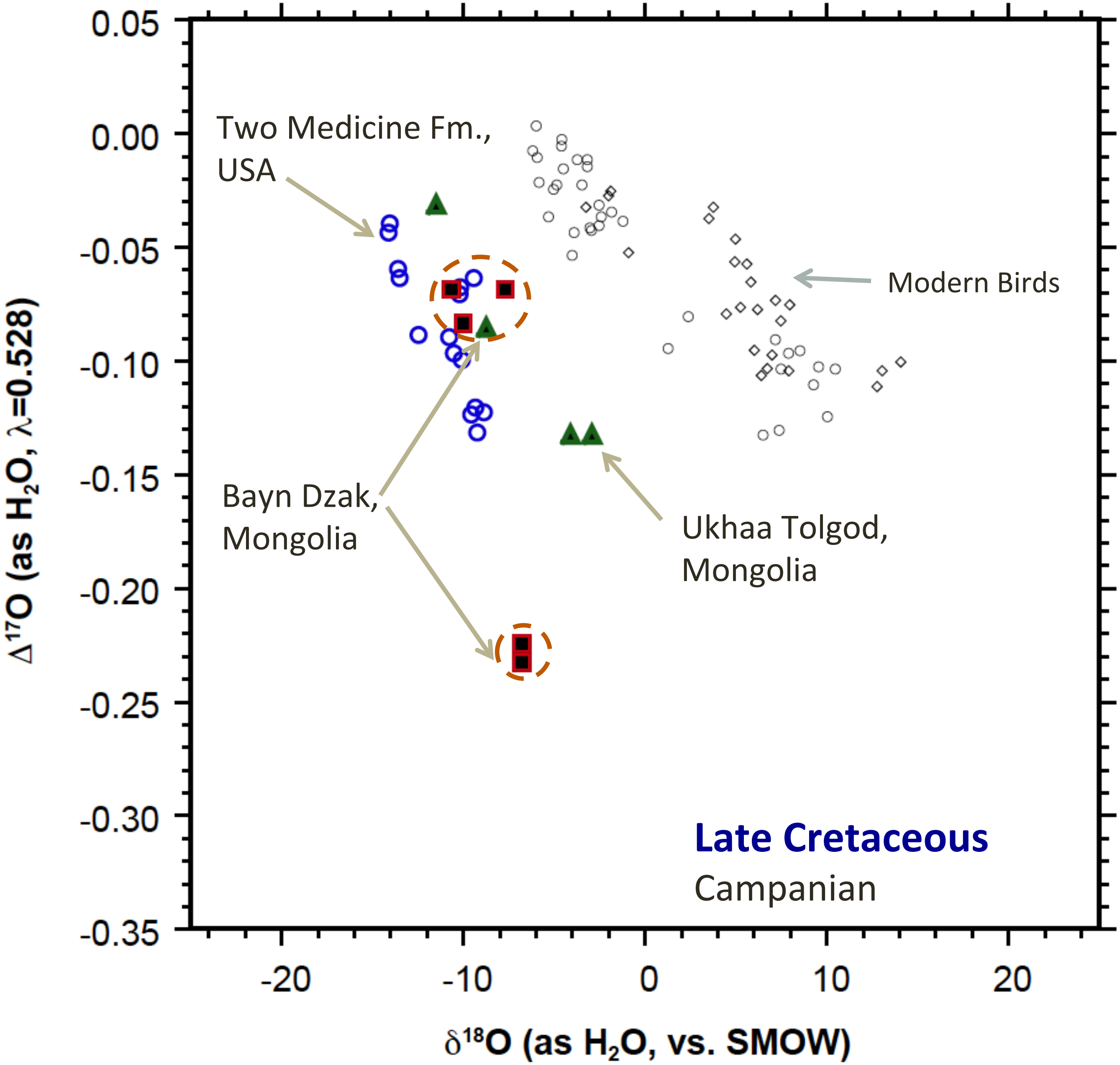
20
Δ17O (as H2O, λ=0.528)
δ18O (as H2O, vs. SMOW)
Modern Birds
Bugin Tsav, Mongolia
Late Cretaceous
Campanian/Maastrichtian

Dinosaurs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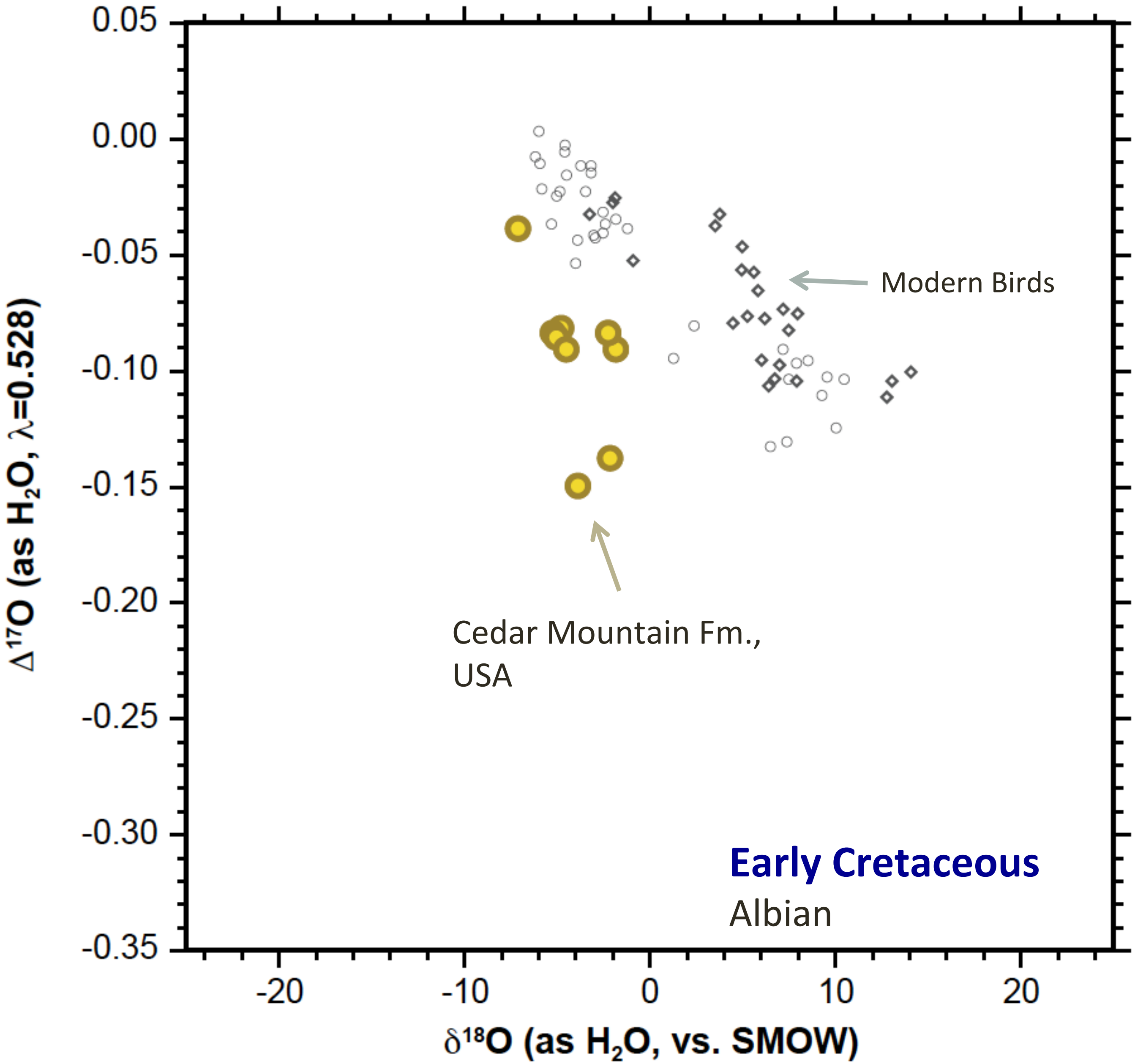
$\Delta^{17}O$ (as H_2O, λ=0.528)
Two Medicine Fm., USA
Modern Birds
Bayn Dzak, Mongolia
Ukhaa Tolgod, Mongolia
Late Cretaceous
Campanian
-20
-10
0
10
20
$\delta^{18}O$ (as H_2O, vs. SMOW)

Dinosaurs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$\Delta^{17}O$ (as H_2O, λ=0.528)
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Modern Birds
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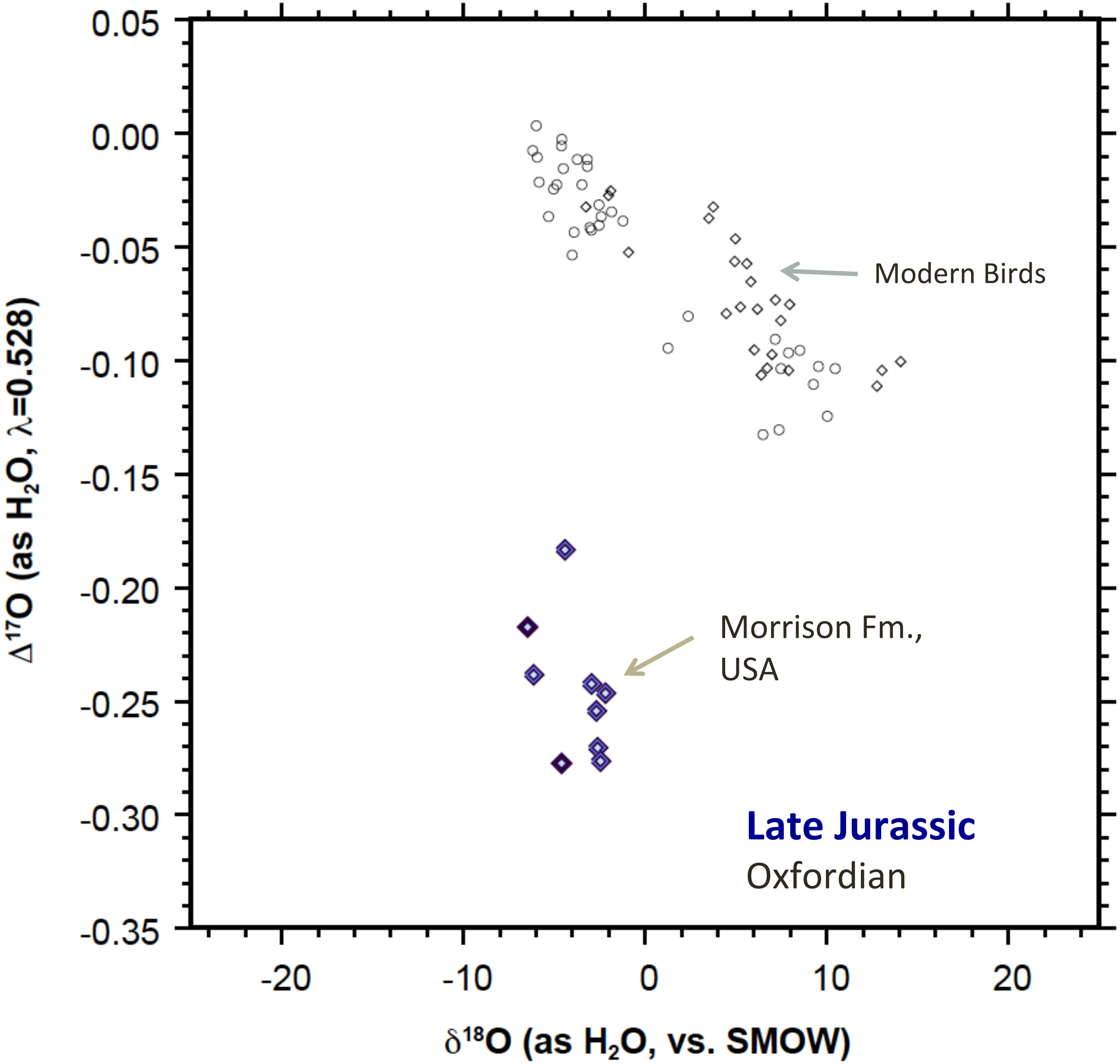
Dinosaurs



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Δ17O (as H2O, λ=0.528)
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Modern Birds
Morrison Fm., USA
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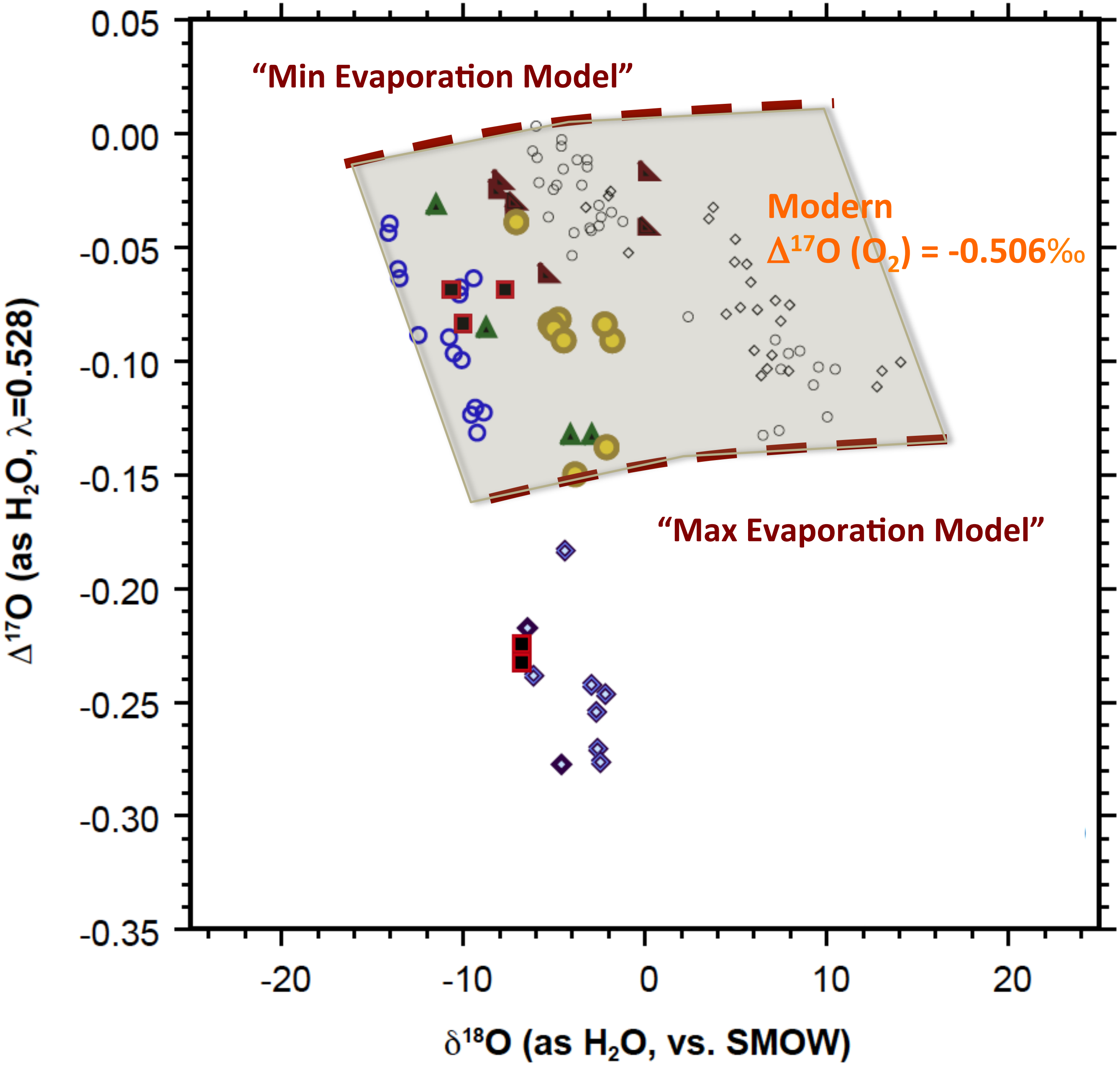
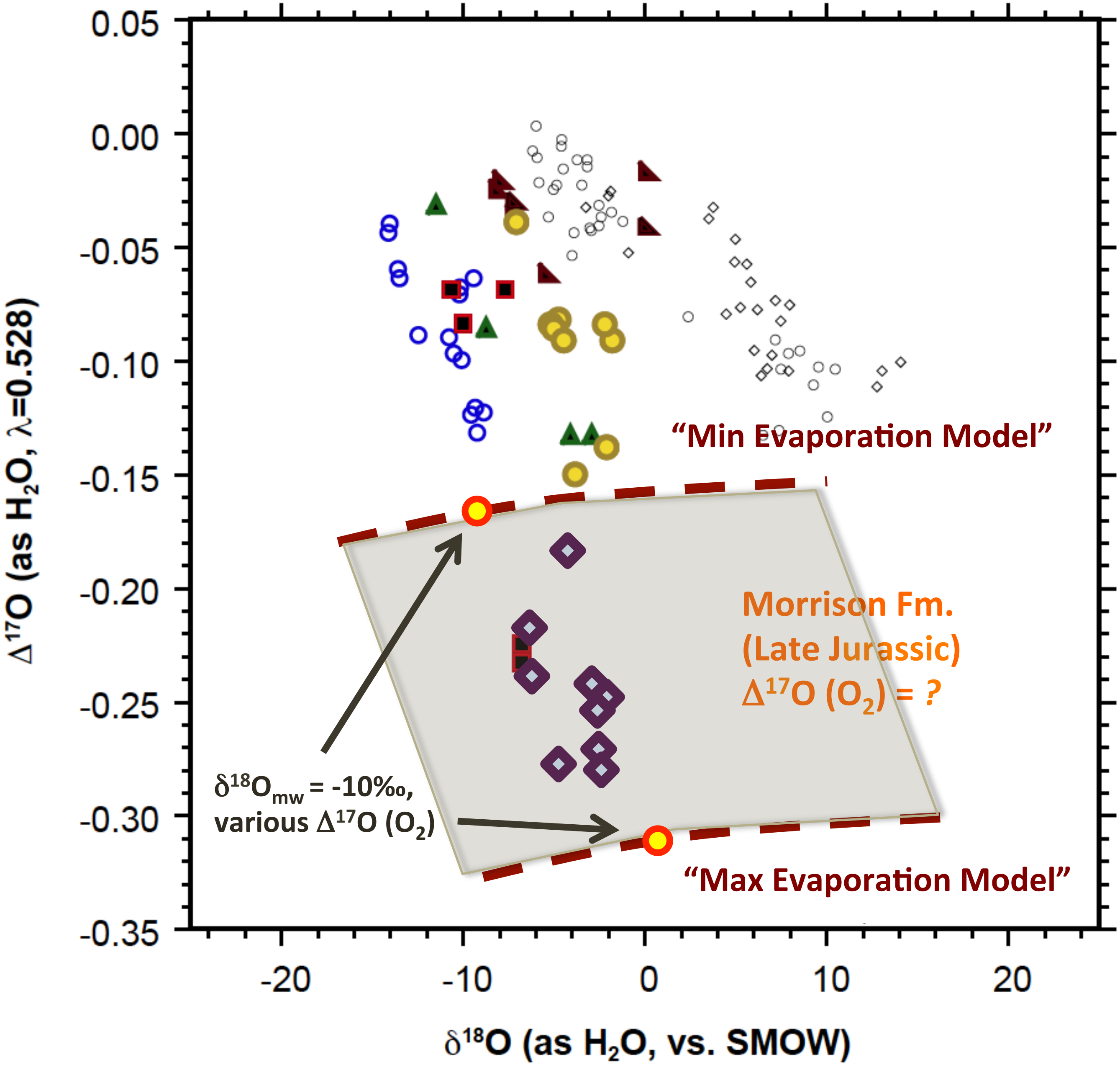
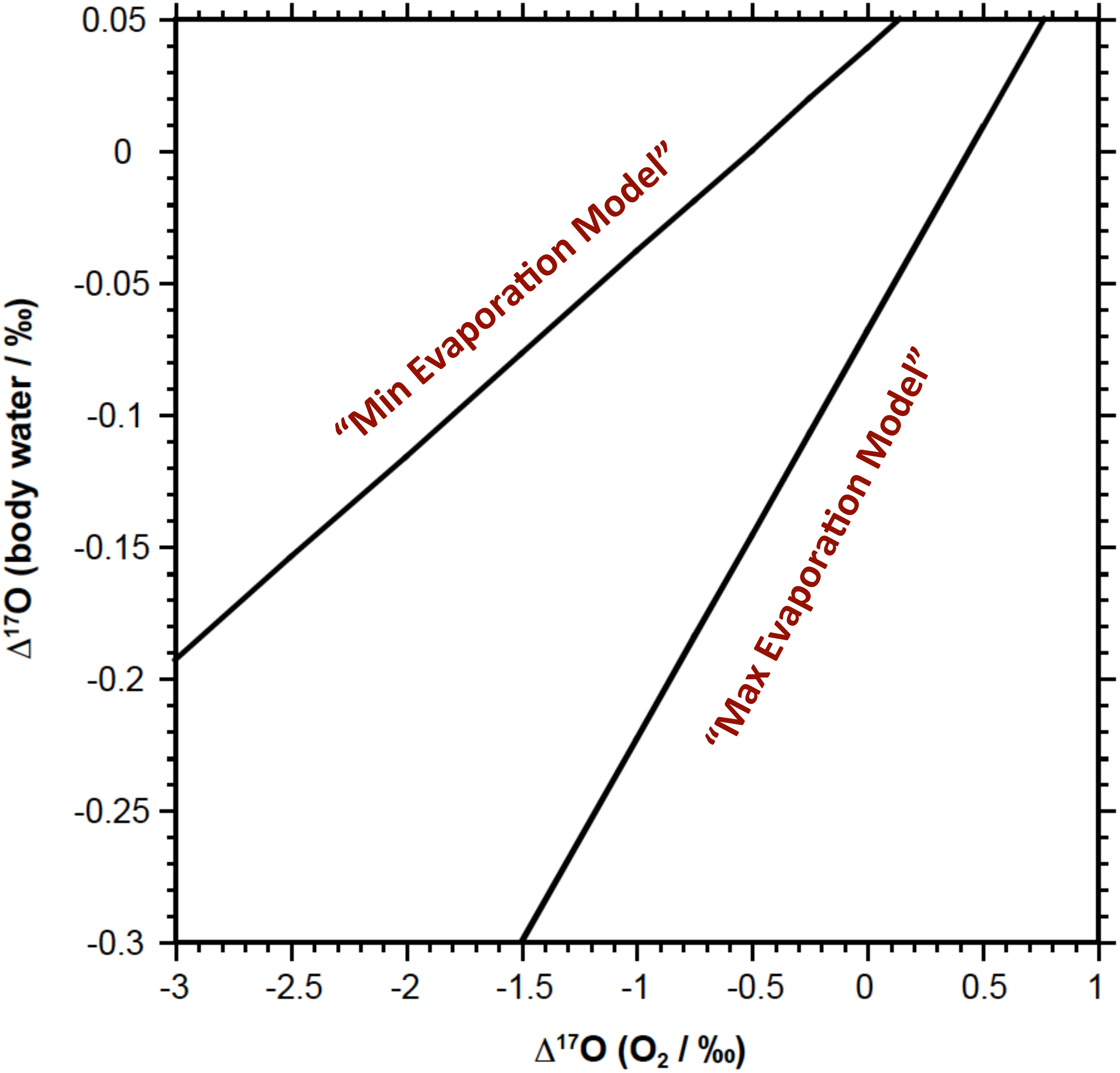
Models for Dinosaurs



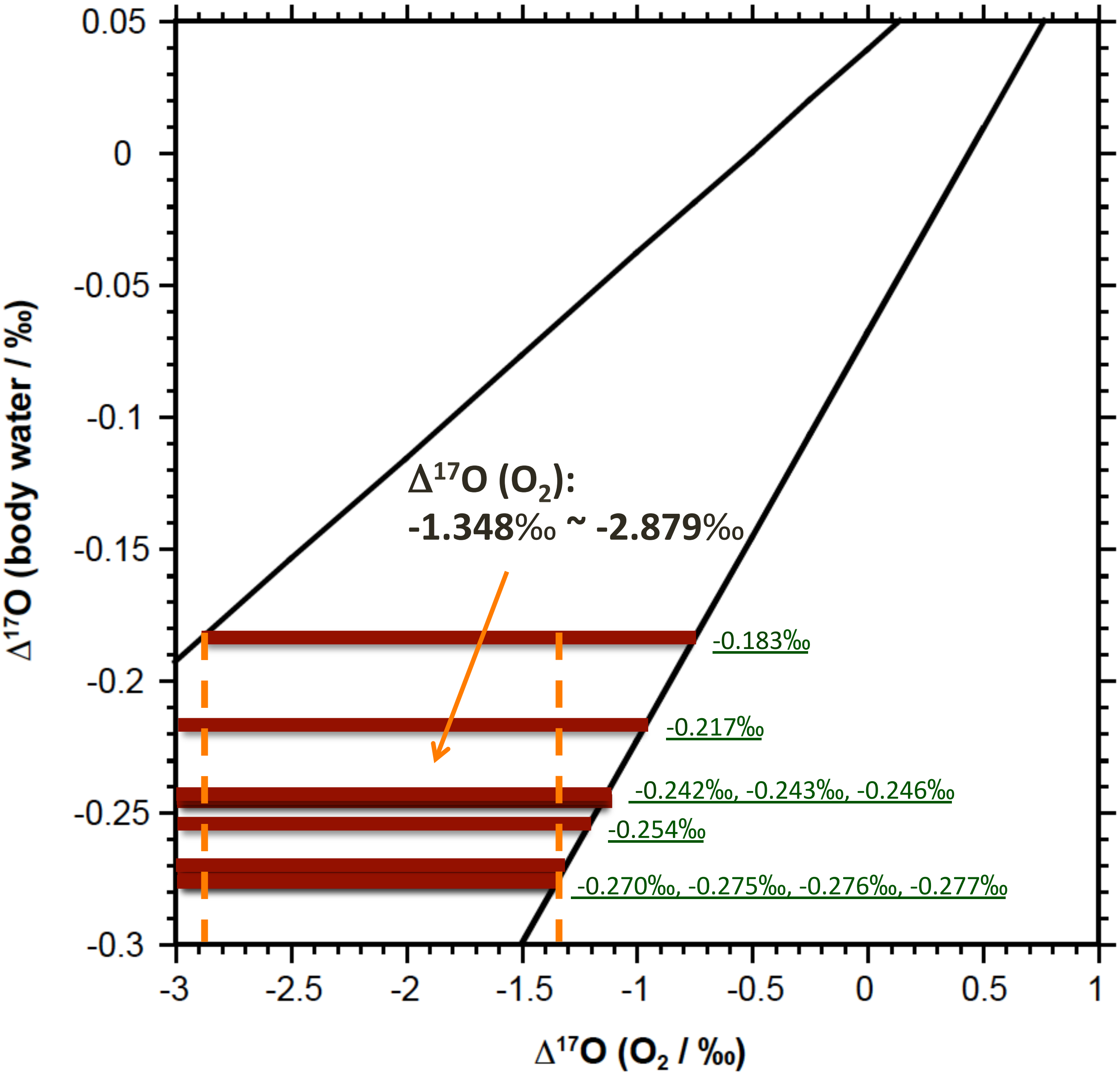
Models for Dinosaurs



$\Delta^{17}O_{bw}$-$\Delta^{17}O$ (O_2) response Curves



Morrison Formation Results



Estimates of $\Delta^{17}O(O_2)$

Time	Location	Min (‰)	Max (‰)
Modern	Various	- 0.450	- 0.405
Maastrichtian/ Campanian	Bugin Tsav	- 0.717	- 0.288
Campanian	Bayn Dzak	- 1.380	- 1.058
Campanian	Ukhaa Tolgod	- 0.908	- 0.412
Campanian	Two Medicine Fm.	- 1.004	- 0.401
Albian	Cedar Mountain Fm.	- 0.999	- 0.524
Oxfordian	Morrison Fm.	- 2.879	- 1.348

$$\Delta^{17}O(O_2) = -0.2876 - 0.00058 \bullet \left[pCO_2 / \frac{GPP_t}{GPP_0} \right]$$

pCO_2 at GPP_t=GPP_0

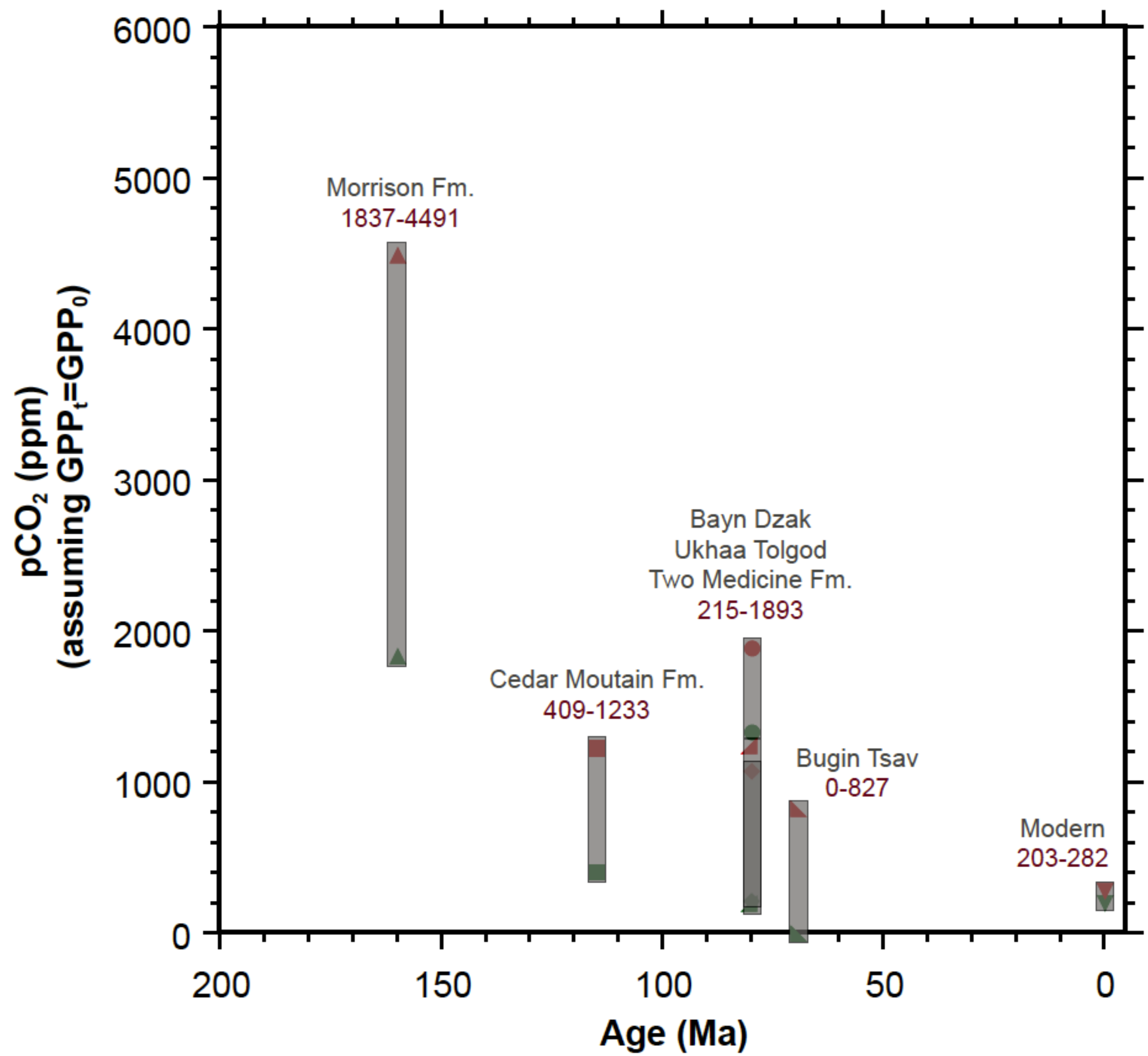
Time	Location	Min (ppm)	Max (ppm)
Modern	Various	203	282
Maastrichtian /Campanian	Bugin Tsav	0	827
Campanian	Bayn Dzak	1335	1893
Campanian	Ukhaa Tolgod	215	1075
Campanian	Two Medicine Fm.	197	1241
Albian	Cedar Mountain Fm.	409	1233
Oxfordian	Morrison Fm.	1837	4491

$$\Delta^{17}O(O_2) = -0.2876 - 0.00058 \bullet \left[pCO_2 / \frac{GPP_t}{GPP_0} \right]$$

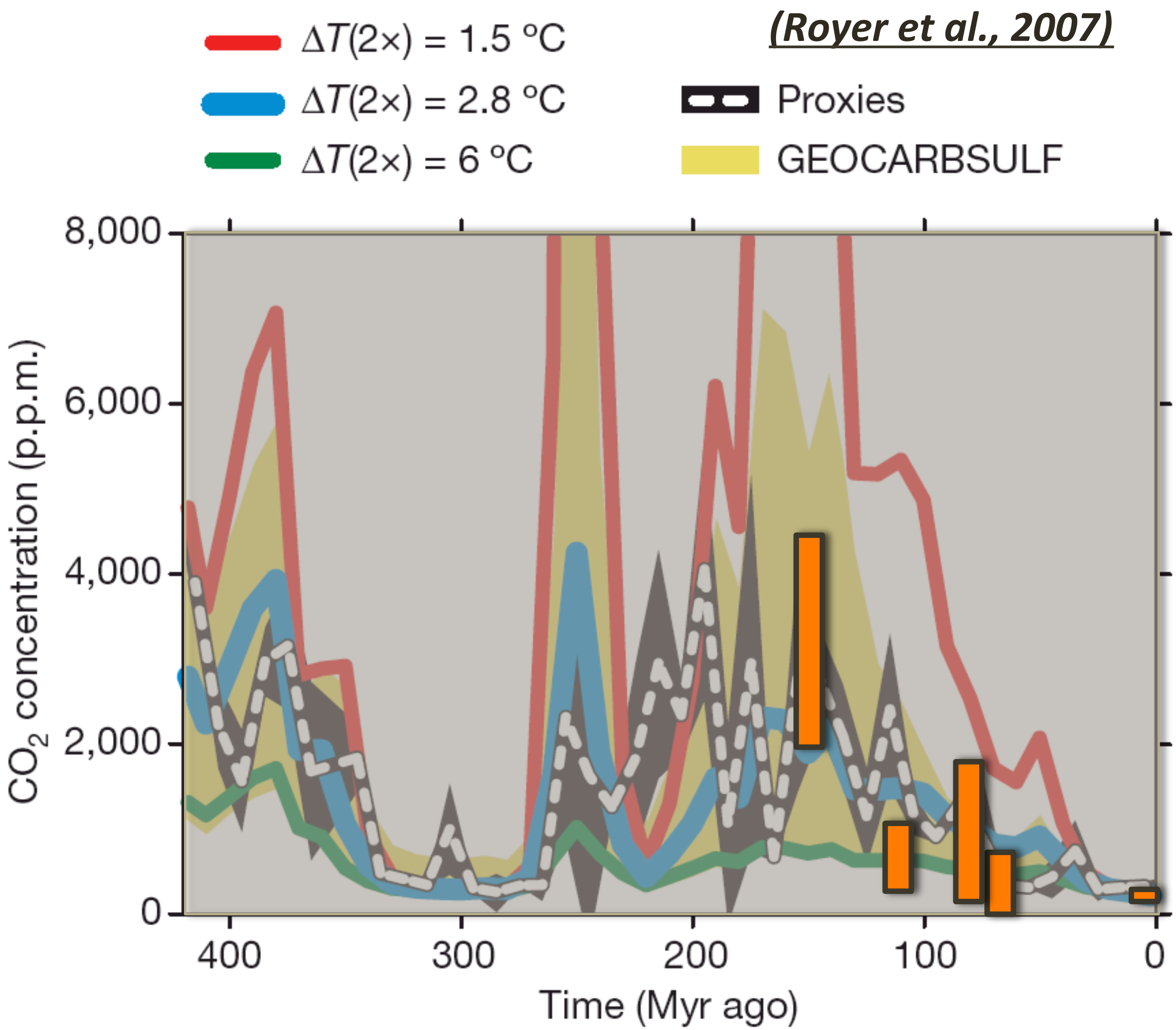
Assuming GPP_t=GPP_0

Inferring the paleo-pCO_2

pCO_2 at GPP_t=GPP_0



Comparison with other studies



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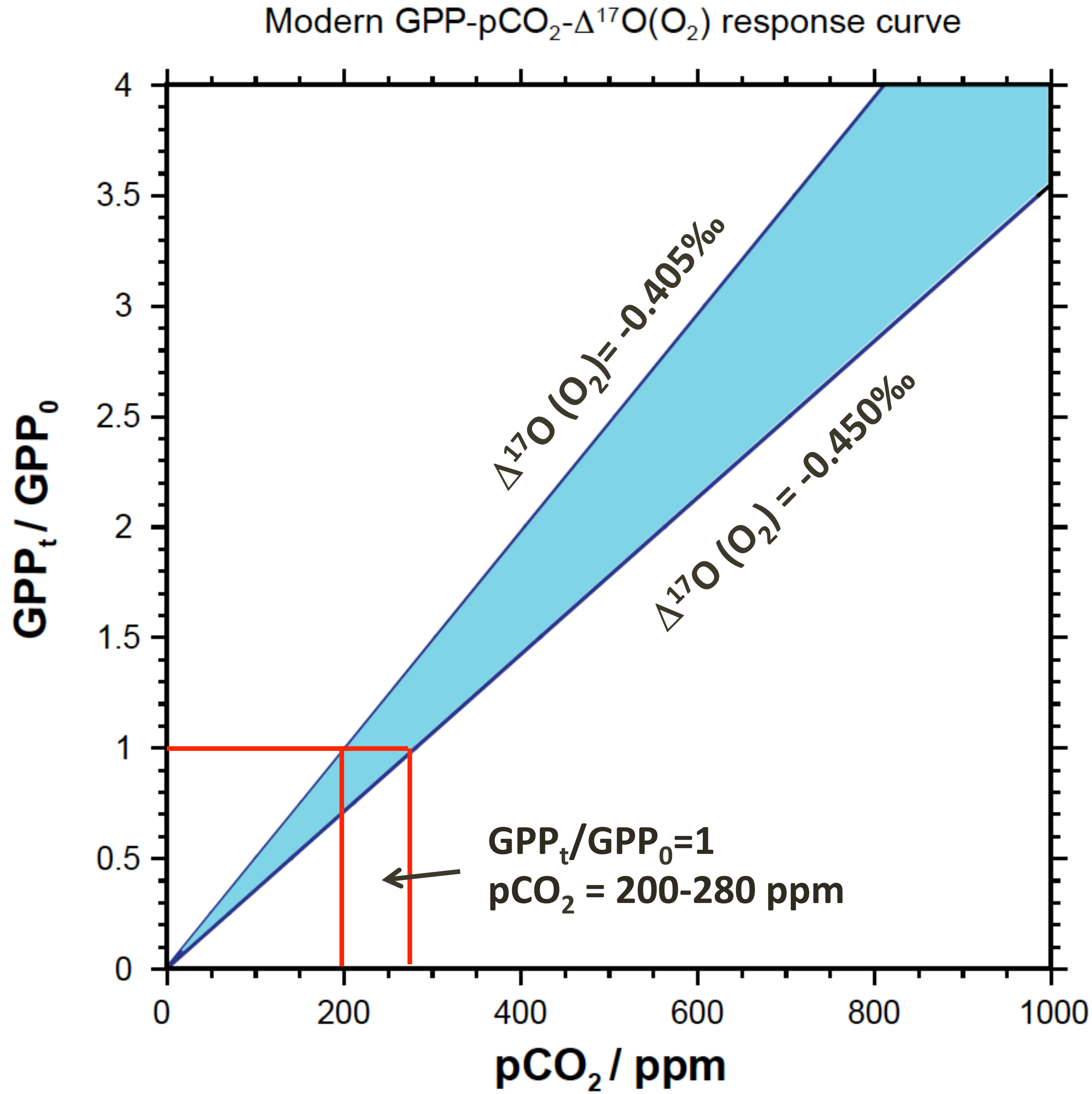
Inferring $\Delta^{17}O(O_2)$-pCO_2-GPP



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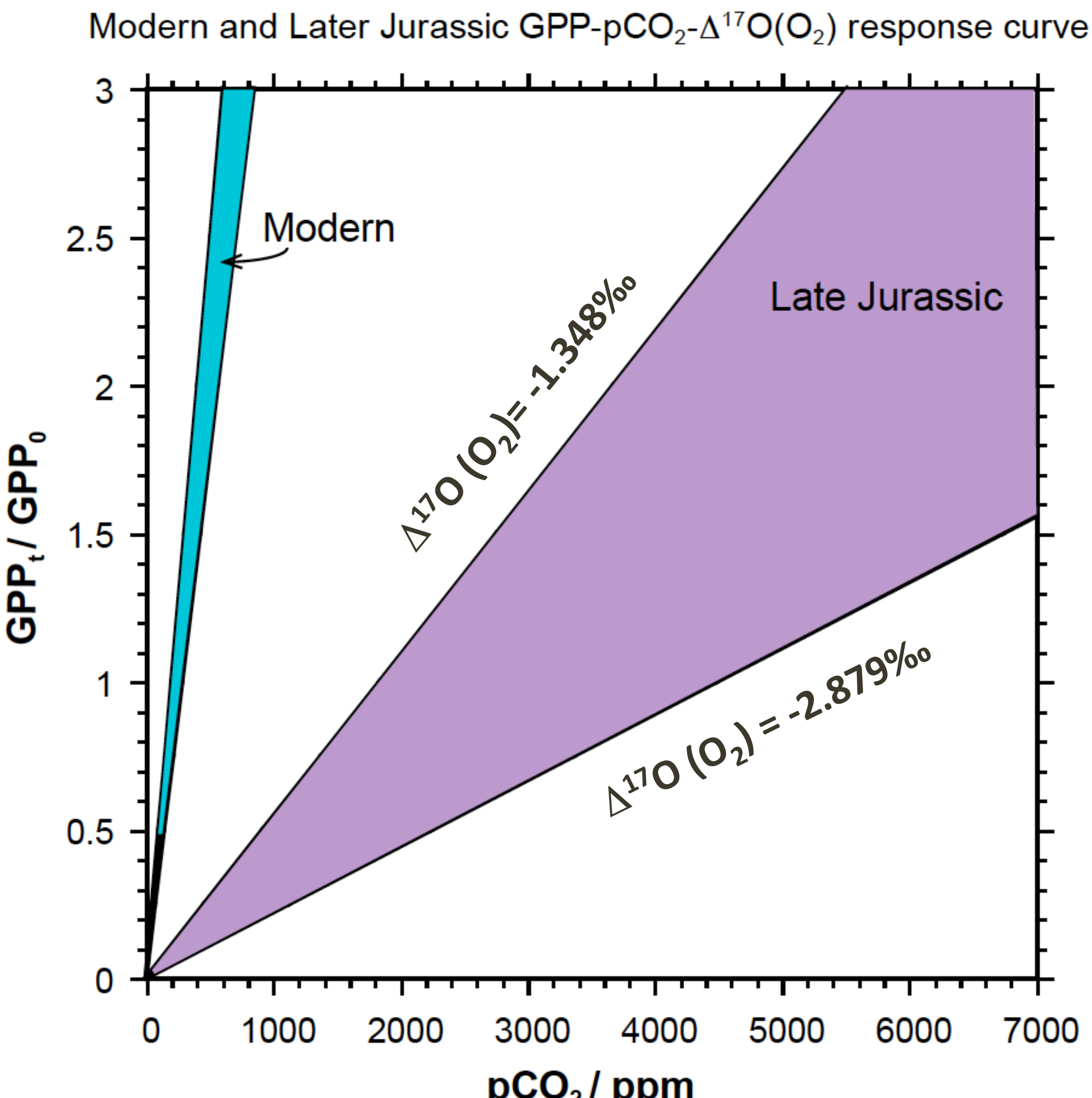

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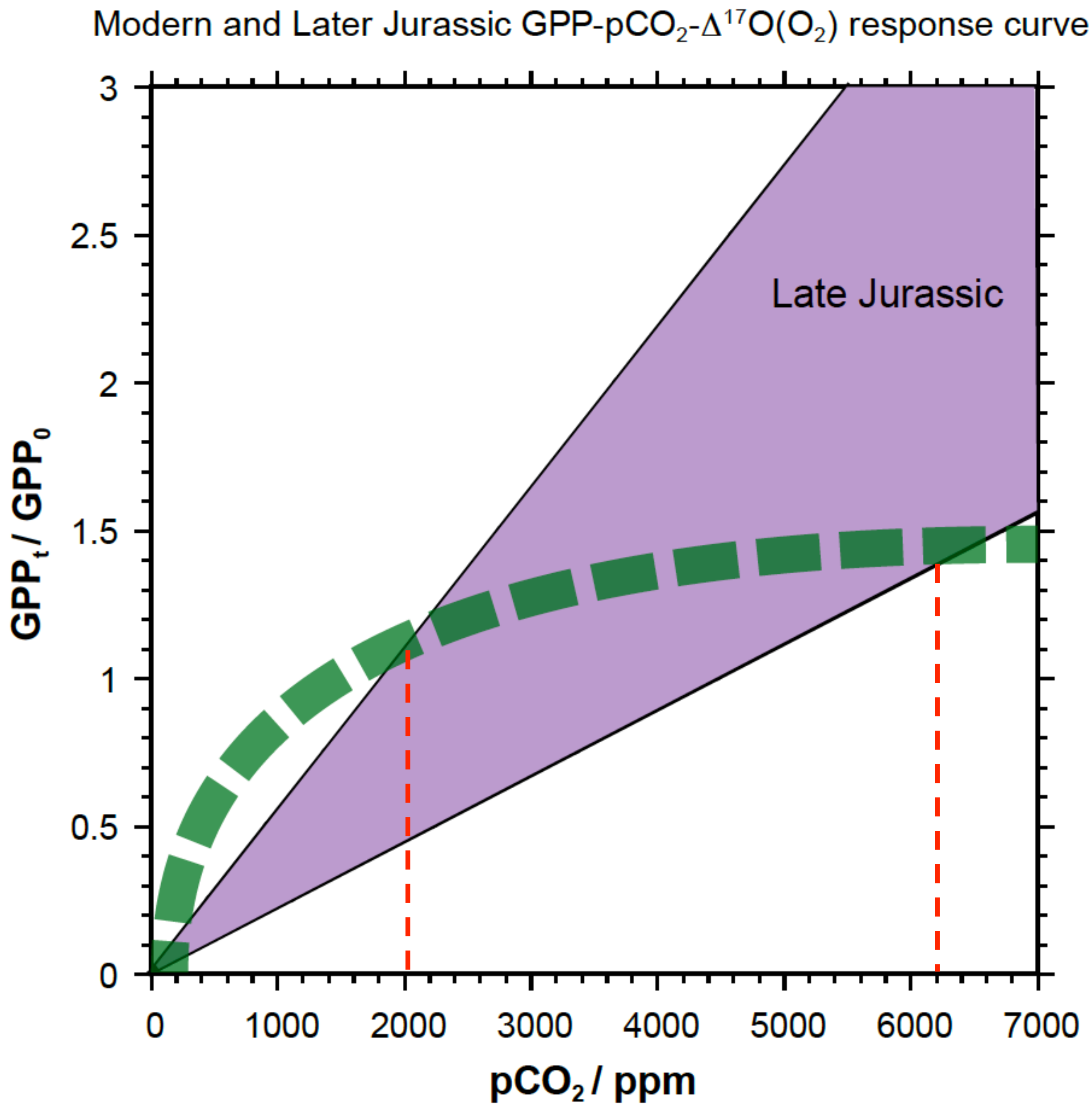

Conclusions and Future Work

- **Conclusions**
  - The $\Delta^{17}O$ (O_2) in troposphere is an indicator for the ratio of pCO_2 and GPP
  - The ^{17}O-body water model enables the predictions for $\Delta^{17}O$ (O_2).
  - Fossil biocarbonates carry the $\Delta^{17}O$ (O_2) signal and can be used to reconstruct pCO_2/GPP and we have observed anomalous $\Delta^{17}O$ signals compared to modern samples. This proxy is based on entirely different mechanisms than existing pCO_2/GPP proxies.
  - The triple oxygen isotope approach, while unable to uniquely constrain pCO_2 or GPP, shows promise for identifying distinctive modes of the carbon cycle in the geological past.

- **Future Work**
  - Combing our model with accurate GPP models to find out the best fit of pCO_2 and GPP for each time period.
  - Fine tuning the body water model by investigating more details into the animal physiology.
  - More work in determining the environment conditions for these samples to constrain the predicted $\Delta^{17}O$ (O_2) range.

Acknowledgements

- We thank **Michael Bender** and **Kate Dennis** for bringing to our attention the potential use of animal $\Delta^{17}O$ to reconstruct past CO_2 levels, and for many useful discussions since.
- We thank **John Southon** for showing us the use of H_2 and Fe catalyst to convert oxygen from CO_2 to H_2O.
- We thank **Matt Kohn** for sharing his body water $^{18}O/^{16}O$ model spreadsheet.
- Thank **Scott Pitz, Sara Rivero, Naomi Levin, Greg Henkes**, and **Sophie Lehmann** for providing chicken and wild bird eggshells.
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