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**

\[ ^{16}\text{O} (99.762\%), \quad ^{17}\text{O} (0.038\%), \quad ^{18}\text{O} (0.200\%) \]

- **Mass Dependent Fractionation (MDF)**
  \[ \delta^{17}\text{O} \approx 0.52 \delta^{18}\text{O} \]

- **Mass Independent Fractionation (MIF)**
  \[ \delta^{17}\text{O} = C \cdot \delta^{18}\text{O}, \text{ where } C \approx 1 \]

- **\(^{17}\text{O}\) anomaly (\(\Delta^{17}\text{O}\))**
  \[ \Delta^{17}\text{O} = \delta^{17}\text{O} - \lambda \cdot \delta^{18}\text{O} \quad (\lambda = 0.528) \]
\[ \Delta^{17}\text{O} \left( \text{O}_2 \right) \text{ Budget Model} \]

\[ \text{pCO}_2 - \Delta^{17}\text{O} \text{ relationship} \]

**Stratospheric Photochemical MIF Reactions**

\[ \text{O}_2 (-) \xleftrightarrow{} \text{O}^{(3\text{P})} \xleftrightarrow{} \text{O}_3 (+) \xleftrightarrow{} \text{CO}_2 (+) \]

17O-depleted \hspace{2cm} 17O-enriched

**Troposphere**

\[ \text{O}_2 (-) \quad \text{CO}_2 (0) \]

\[ \tau \approx 10^3 \text{ years} \quad \tau \approx 10^1 \text{ years} \]

\[ \text{Respiration} \quad \text{Photosynthesis} \quad \text{Hydrosphere} (0) \]

\[ \text{Biosphere} \]
$\Delta^{17}\text{O} (\text{O}_2)$ Budget Model

$\Delta^{17}\text{O} (\text{O}_2) \sim p\text{CO}_2 / \text{GPP}$

$\Delta^{17}O(O_2) = -0.2876 - 0.00058 \cdot \left[ \frac{p\text{CO}_2}{\text{GPP} / \text{GPP}_0} \right]$

(Bao et al., 2008)

Young et al., 2014
Respiration:

\[ \text{food} \rightarrow \text{Atm.}O_2 \rightarrow \text{DIC} \rightarrow \text{CH}_2\text{O} + O_2 \rightarrow \text{CO}_2 + \text{H}_2\text{O} \]

Body water isotope model

Eggshell Calcite: \( \text{CaCO}_3 \)

Tooth enamel apatite: \( \text{Ca}_5(\text{PO}_4,\text{CO}_3)_3(\text{OH},\text{CO}_3) \)

\[ ^{18}\alpha_{\text{CaCO}_3-\text{H}_2\text{O}} = 1.0380 \pm 0.0008 \quad (1\sigma, n = 7) \]

\[ \lambda_{\text{CaCO}_3-\text{H}_2\text{O}} = 0.5245 \pm 0.0003 \quad (1\sigma, n = 7) \]
Body water isotope model

Oxygen Isotope Mass Balance

\[ \sum_a R_{MW} \cdot f_{in,a} \cdot \alpha_{\alpha-MW} + R_{O_2} \cdot f_{O_2} \cdot \alpha_{\text{lung-O}_2} = \sum_{\beta} R_{BW} \cdot f_{out,\beta} \cdot \alpha_{\beta-BW} \]

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

Important Model Parameters

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Humidity</td>
<td>meteoric water/leaf water composition</td>
</tr>
<tr>
<td>Animal Physiology</td>
<td>e.g.: Sweat/Vapor ratio; WEI: amount of water used per unit energy metabolized: (ml / kJ)</td>
</tr>
<tr>
<td>Fraction of Leaf Water</td>
<td>Fraction of evaporated leaf water relative to whole food water intake</td>
</tr>
<tr>
<td>Atmospheric O₂</td>
<td>Atmospheric O₂ composition ($\Delta^{17}$O)</td>
</tr>
</tbody>
</table>
Oxygen Input Space
Model Sensitivity

Source H$_2$O: $\delta^{18}$O = -10‰
$\Delta^{17}$O = 0.01‰

$\Delta^{17}$O (O$_2$) = 0‰
$\Delta^{17}$O (O$_2$) = -0.288‰
$\Delta^{17}$O (O$_2$) = -0.506‰
$\Delta^{17}$O (O$_2$) = -1‰

$F_{\text{leaf water}} = 0$
$F_{\text{leaf water}} = 0.10$
$F_{\text{leaf water}} = 0.20$
$F_{\text{leaf water}} = 0.4$

Rh = 0.50
WEI = 0.30 ml/kJ
Sweat/(Sweat+Vapor) = 0.7
Modeled Endmembers (Max Evap.)

Source meteoric water $\delta^{18}O_{mw}$(%o):

-20, -10, 0, 10

$\Delta^{17}O$ (%):

-20, -10, 0, 10

$\delta^{18}O_{mw}$(%o): $\lambda = 0.528$

$\delta^{18}O$ (as H$_2$O, vs. SMOW):

-0.25 to 0.05

$\Delta^{17}O$ (O$_2$) = -0.506‰

Rh = 0.20
WEI = 0.10 ml/kJ
$\Delta^{17}O_{mw}$ = 0.010‰
Sweat/(Sweat+Vapor) = 0.5
$F_{leaf\ water}$ = 0.40

"Max Evaporation Model"
Modeled Endmembers (Min Evap.)

“Min Evaporation Model”

\[ \text{Rh} = 0.80 \]
\[ \text{WEI} = 0.50 \text{ ml/kJ} \]
\[ \Delta^{17}\text{O}_{\text{mw}} = 0.030\% \]
\[ \text{Sweat/(Sweat+Vapor)} = 0.9 \]
\[ F_{\text{leaf water}} = 0.01 \]
\[ \Delta^{17}\text{O} (\text{O}_2) = -0.506\% \]

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Body Water Model

"Min Evaporation Model"

Possible Body Water
\(\Delta^{17}O - \delta^{18}O\)
Space for Modern Animals

"Max Evaporation Model"

\[ \Delta^{17}O \text{ (as H}_2\text{O, } \lambda=0.528) \]

\[ \delta^{18}O \text{ (as H}_2\text{O, vs. SMOW) \} }\]
Modern Samples

<table>
<thead>
<tr>
<th>Sample Type</th>
<th>Species</th>
<th>N</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wild Birds</td>
<td>Ostrich</td>
<td>3</td>
<td>Ethiopia, South Africa</td>
</tr>
<tr>
<td></td>
<td>Starling</td>
<td>1</td>
<td>Baltimore</td>
</tr>
<tr>
<td>Captive Birds</td>
<td>Chicken</td>
<td>6</td>
<td>Baltimore, New Jersey, China, Japan,</td>
</tr>
<tr>
<td></td>
<td>Ostrich</td>
<td>2</td>
<td>China</td>
</tr>
<tr>
<td></td>
<td>Duck</td>
<td>1</td>
<td>New Jersey</td>
</tr>
<tr>
<td></td>
<td>Emu</td>
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Fossil Dinosaur Eggshells

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<tr>
<th>Location</th>
<th>Species</th>
<th>N</th>
<th>Time Period</th>
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<tr>
<td>Bugin Tsav</td>
<td>Oviraptorid</td>
<td>5</td>
<td>Late Cretaceous</td>
<td>Camp. /Mass.</td>
</tr>
<tr>
<td>Bayn Dzak</td>
<td>Oviraptorid, Protoceratops (?)</td>
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<td>Late Cretaceous</td>
<td>Campanian</td>
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<tr>
<td>Ukhaa Tolgod</td>
<td>Oviraptorid</td>
<td>4</td>
<td>Late Cretaceous</td>
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</tr>
<tr>
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<td>Hadrosaur, Troodon</td>
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<td>Dinosaurid</td>
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<td>Albian</td>
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<tr>
<td>Morrison Fm.</td>
<td>Dinosaurid</td>
<td>11</td>
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<td>Oxfordian</td>
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Modern Birds

\[ \Delta^{17}O \text{ (as } H_2O, \lambda=0.528) \]

vs.

\[ \delta^{18}O \text{ (as } H_2O, \text{ vs. SMOW}) \]

“Min Evaporation Model”

“Max Evaporation Model”
Modern Birds

- Farmed ostrich, emu, duck, chicken
- Australian Emu from humid to arid environment
- Baltimore area: backyard chickens, starlings, doves
- Wild ostrich: Ethiopia, Kenya, S. Africa

"Min Evaporation Model"

"Max Evaporation Model"
Modern Samples

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Modern Birds

Bugin Tsav, Mongolia

Late Cretaceous Campanian/Maastrichtian

Dinosaurs
Late Cretaceous
Campanian

Two Medicine Fm., USA

Bayn Dzak, Mongolia

Ukhaa Tolgod, Mongolia

Modern Birds

Dinosaurs

$\Delta^{17}O$ (as $H_2O, \lambda = 0.528$)

$\delta^{18}O$ (as $H_2O$, vs. SMOW)
Dinosaurs

Early Cretaceous
Albian

Cedar Mountain Fm., USA

Modern Birds

$\Delta^{17}\text{O} \text{ (as H}_2\text{O, } \lambda = 0.528)$

$\delta^{18}\text{O} \text{ (as H}_2\text{O, vs. SMOW)}$
Late Jurassic Oxfordian Morrison Fm., USA

Modern Birds

Morrison Fm., USA

Late Jurassic Oxfordian

\[ \Delta^{17}O \text{ (as H}_2\text{O, } \lambda = 0.528) \]

\[ \delta^{18}O \text{ (as H}_2\text{O, vs. SMOW)} \]
Modern $\Delta^{17}\text{O (O}_2) = -0.506\%$
Models for Dinosaurs

Min Evaporation Model

Max Evaporation Model

Morrison Fm. (Late Jurassic)

$\Delta^{17}O (O_2) = ?$

$\Delta^{17}O (as \text{H}_2\text{O, } \lambda = 0.528) = \ ?$

$\delta^{18}O_{mw} = -10\%$

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

$\Delta^{17}O (O_2)$:
-1.348‰ ~ -2.879‰
<table>
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<tr>
<th>Time</th>
<th>Location</th>
<th>Min (‰)</th>
<th>Max (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern</td>
<td>Various</td>
<td>-0.450</td>
<td>-0.405</td>
</tr>
<tr>
<td>Maastrichtian/</td>
<td>Bugin Tsav</td>
<td>-0.717</td>
<td>-0.288</td>
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<td>Bayn Dzak</td>
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$\Delta^{17}O(O_2) = -0.2876 - 0.00058 \left( \frac{pCO_2}{GPP_i \over GPP_0} \right)$
<table>
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<th>Time</th>
<th>Location</th>
<th>Min (ppm)</th>
<th>Max (ppm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Modern</td>
<td>Various</td>
<td>203</td>
<td>282</td>
</tr>
<tr>
<td>Maastrichtian/Campanian</td>
<td>Bugin Tsav</td>
<td>0</td>
<td>827</td>
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<td>Campanian</td>
<td>Bayn Dzak</td>
<td>1335</td>
<td>1893</td>
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<tr>
<td>Campanian</td>
<td>Ukhaa Tolgod</td>
<td>215</td>
<td>1075</td>
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<tr>
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<td>197</td>
<td>1241</td>
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<td>409</td>
<td>1233</td>
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<tr>
<td>Oxfordian</td>
<td>Morrison Fm.</td>
<td>1837</td>
<td>4491</td>
</tr>
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</table>

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

Assuming \( GPP_t = GPP_0 \), inferring the paleo-pCO\(_2\).
pCO$_2$ at GPP$_t$ = GPP$_0$
Comparison with other studies

\[ \Delta T(2\times) = 1.5 \text{ °C} \]  
\[ \Delta T(2\times) = 2.8 \text{ °C} \]  
\[ \Delta T(2\times) = 6 \text{ °C} \]

*(Royer et al., 2007)*

![Graph showing CO₂ concentration over time with different markers for different temperature scenarios.](image-url)
### Estimates of $\Delta^{17}O(O_2)$

<table>
<thead>
<tr>
<th>Time</th>
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<th>Min (%)</th>
<th>Max (%)</th>
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\[
\Delta^{17}O(O_2) = -0.2876 - 0.00058 \cdot \left[ \frac{pCO_2}{GPP_t} \right] \]
Inferring $\Delta^{17}O(O_2)$-$pCO_2$-GPP

Modern GPP-$pCO_2$-$\Delta^{17}O(O_2)$ response curve

$\Delta^{17}O(O_2) = -0.405\%$

$\Delta^{17}O(O_2) = -0.450\%$

$GPP_t/GPP_0 = 1$

$pCO_2 = 200-280$ ppm
Inferring $\Delta^{17}\text{O}(\text{O}_2)$-pCO$_2$-GPP

Modern and Later Jurassic GPP-pCO$_2$-$\Delta^{17}\text{O}(\text{O}_2)$ response curve

$\Delta^{17}\text{O}(\text{O}_2) = -1.348\%$

$\Delta^{17}\text{O}(\text{O}_2) = -2.879\%$

Modern

Late Jurassic
Inferring $\Delta^{17}\text{O}(\text{O}_2)$-pCO$_2$-GPP

Modern and Later Jurassic GPP-pCO$_2$-$\Delta^{17}\text{O}(\text{O}_2)$ response curve

Late Jurassic
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 $\Delta^{17}\text{O}$ 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$_2$O.

• We thank Matt Kohn for sharing his body water $^{18}\text{O}/^{16}\text{O}$ model spreadsheet.

• Thank Scott Pitz, Sara Rivero, Naomi Levin, Greg Henkes, and Sophie Lehmann for providing chicken and wild bird eggshells.

• Thank Shuning Li and Haoyuan Ji for helping sample analysis.