Systematics of O and H isotopes in Animals

Presentation modified by Nadine Quintana Krupinski
Background

- $\delta^{18}O$ and $\delta D$ values correlate strongly with local precipitation isotopic value.
- Precip isotopic value varies with latitude and elevation.
- Local water isotopic value also affected by aridity (evaporation effect).
Oxygen in animals

- $\delta^{18}$O measured in tissues (body water, hair) and tooth enamel (bone not generally used)
- Hair is isotopically offset from body water $\delta^{18}$O (hair is more positive)
- Food effect
- Enamel and bone have a constant offset from body water $\delta^{18}$O
Major O Fluxes

IN
- Drinking and food water (not fractionated during uptake)
- Atmosphere O$_2$
- Food solids

OUT
- Respired CO$_2$ (fractionated)
- Water in urine and feces
- Water lost in exhalation, sweat, evaporation (fractionated)
δ¹⁸O in bioapatite

- Measured from PO₄ and CO₃ in bioapatite and CO₃ in carbonate (bone)
- Apatite: Ca₅(PO₄)₃(OH, F, Cl)
- CO₃ can substitute for PO₄ or for OH (also in other places)
- O in PO₄ and CO₃ rapidly equilibrates with body water O
- Either PO₄ or CO₃ is selected for analysis, depending on the diagenetic history of the bioapatite
Apatite $\delta^{18}O$ “vital” effects

- $\delta^{18}O_{\text{Apatite}}$ depends on the *temperature* and *fluid composition* (in $\delta^{18}O$) at which the biomineral precipitates.
- For homeotherms (mammals, birds), assume constant body temp. and derive info about the animal’s environment.
- For heterotherms, as temp. $\downarrow$, bioapatite $\delta^{18}O \uparrow$ and carbonate $\delta^{18}O$ values $\uparrow$.
- In mammal apatite, constant offset btw. $\delta^{18}O$ of body water and $\text{PO}_4$ ($\sim 18\%$), btw. $\text{PO}_4$ and $\text{CO}_3$ ($\sim 8\%$).
Box model for animals

Fig. 1. Mass balance model of oxygen fluxes and isotopic composition of body water in mammals, modified after Luz et al. (1984). Oxygen uptake occurs as ingested water ($F_w$), metabolic oxygen derived from food ($F_F$) and atmospheric O$_2$ ($F_A$). Principal internal reactions are carbohydrate, fat, and protein metabolism, exemplified by oxidation reactions for glucose, palmitic acid, and alanine, respectively. Water outfluxes are as water vapor ($F_{VW}$), liquid water ($F_{LW}$), and CO$_2$ ($F_{CO2}$).
Mass balance model

output

\[ 0.25 \times [\delta^{18}O_{BW} + 38.65] + 0.4 \times [\delta^{18}O_{BW} + 0] + 0.25 \times [\delta^{18}O_{BW} - 8.5] + 0.1 \times [\delta^{18}O_{BW} - 18] \]

\[ = \]

input

\[ 0.25 \times 15 + 0.45 \times [\delta^{18}O_{LW} + 26.2 \times (1 - h)] + 0.3 \times \delta^{18}O_{LW} \]

\[ \text{BW} = \text{body water} \]

\[ \text{LW} = \text{local water} \]
Models for O in body water

- Portion of O from food, air (Ehleringer):
  \[ p_{fd} = 0.33 * p_{mw} \quad p_{O_2} = 0.67 * p_{mw} \]

- Isotopic ratio of body water (same eqn. for O&H, Podlesak):
  \[ R_{bw} = \frac{\sum_{i=1}^{n} r_{in,i} \cdot R_{in,i}}{\sum_{j=1}^{n} r_{out,j} \cdot \alpha_{out,j}} \]
  
  \( r = \) molar quantity of the input or output,
  \( R = \) ratio of the heavy isotope to the light isotope
  \( A = \) fractionation between body water and the output

Alternatively, in \( \delta \) notation (Ehleringer):

\[ \delta^{18}O_{wb} = (a \cdot \delta^{18}O_{we} + b \cdot \delta^{18}O_d + c \cdot [\alpha_{O_2}(1,000 + \delta^{18}O_{O_2}) - 1,000]) / (h \cdot \alpha_{fwlo} + j \cdot \alpha_{co2} + k), \]
**δ^{18}O in hair**

- Hair (keratin) $\delta^{18}O$ is related to gut water $\delta^{18}O$ (Ehleringer):

  $$\delta^{18}O_h = \alpha_{ow} \cdot (1,000 + \delta^{18}O_{wg}) - 1,000$$

**OR, in R notation** (same eqn. for O&H; Podlesak):

  $$R_{fw} = \frac{(R_{bw} \times 0.81 + R_{fd} \times 0.19)}{(0.76 + 0.24 \times 1)}$$

- $R_{fw}$ = isotopic ratio of follicle water
- $R_{bw}$ = isotopic ratio of body water
- $R_{fd}$ = isotopic ratio of food
δ$^{18}$O in tooth enamel

- Tooth isotopic composition is derived from body water composition
- Equilibrium fractionation yields a constant, temperature-dependent offset from body water
- Podlesak use a model for continually growing teeth (e.g. rats) - large time-averaging of tooth isotopic signal
- General tooth model using known input and output δ$^{18}$O values (Kohn & Cerling):

$$\delta^{18}O(BW) = 9.85 \pm 4.6 - 11.8 \pm 3.9 \times h + 0.75 \pm 0.3 \times \delta^{18}O(LW)$$
Rats with a change in drinking water $\delta^{18}$O

Body water

Enamel

Hair

- Food
- Enriched water
- Depleted water

$\delta^{18}$O (per mil)

Time (days)

C) #23 Upper incisor

la = 1.8 mm
lm = 5.9 mm
Growth rate = 0.7 mm day$^{-1}$

Time (hrs)

$\delta^{18}$O (per mil)

Time (days)
Geographic patterns in human hair $\delta^{18}\text{O}$

- Tap water $\delta^{18}\text{O}$ varies
- Diet constant: “continental supermarket” diet w/ $\delta^{18}\text{O} 26\%$

Above: Geographic Information System-generated maps of the predicted average $\delta^{18}\text{O}$ of human scalp hair across the continental United States.

Ehleringer et al. 2008
Hydrogen in animals

- δD measured in tissues (hair, feathers, chitin), body water, breath, tooth enamel or bone collagen
- Hair is isotopically offset from body water δD
- Food effect “removed” in these studies
H sources and sinks

• IN
  – Drinking water
  – Food water
  – Food (important! But may be controlled)
  – Small portion (10-15%) of H in synthesized hair exchanges w/ water

• OUT
  – Urine and feces
  – Water lost in exhalation, sweat, evaporation (fractionated)
δD in tissues and body water

- Hair follicle δD is a mix of blood water and food water δD:
  \[ \delta^2 H_{wf} = e \cdot \delta^2 H_{wb} + (1 - e) \cdot \delta^2 H_d \]

- Fraction of H atoms from food:
  \[ f_d = (1 - f_e) \cdot (1 - f_s) \]

- Body water δD:
  \[ \delta^2 H_{wb} = (d \cdot \delta^2 H_{we} + (1 - d) \cdot \delta^2 H_d)/(m \cdot \alpha_{fwlh} + n) \]

Equations from Ehleringer et al. 2008
Rats with a change in drinking water δD

Body water

Hair
Geographic patterns in human hair $\delta D$

- Tap water $\delta D$ varies
- Diet constant: “continental supermarket” diet w/ $\delta Dd 115\%$

Above: Geographic Information System-generated maps of the predicted average $\delta D$ of human scalp hair across the continental United States.

Ehleringer et al. 2008
Extra slides
Changes in hair $\delta^{18}\text{O}$, $\delta\text{D}$ with "migration"

Fig. 4. Time sequence plots of the H ($\delta^2\text{H}$) and O ($\delta^{18}\text{O}$) isotope ratios of human scalp hair along a basal-to-tip transect for an individual that moved from Beijing, China, to Salt Lake City, Utah.

Ehleringer et al. 2008