Association between $^{18}\Delta$ and carbonyl sulfide uptake during CO$_2$ exchange between the atmosphere and land plants

Dan Yakir
Earth & Planetary Sciences

A tribute to the memory of Prof Joel Gat
1926-2012
Born 1926, Germany
Young bright, and brash...
The hands-on scientist and the home made lab...

The pre-GNIP collection...
The teacher
(always with jokes)
Going beyond hydrology...
The administrator
(Dept. Chair, Dean)
Meeting with Thatcher, 1986

Meeting with PM Rabin and President Katzir 1970s

The politician...
Joel’s favorite places: Brazil, the Dead Sea, IAEA-Vienna
Joel’s favorite research topics: The Amazon, and...
The Dead Sea: Deepening of the Mixolimnion Signifies the Overture to Overturn of the Water Column

The stable isotope composition of Dead Sea waters

Joel R. Gat
The foundations of isotope hydrology

1929  Discovery of $^{18}$O (Giauque & Johnston)
1932  Discovery of $^2$H (Urey et al.)
1965  Craig-Gordon evaporation model (Craig & Gordon)

\[ \delta = \frac{\alpha \delta_L (1 - E \rho) - h \delta_a - \varepsilon}{(1 - h) + \Delta \varepsilon + \alpha \cdot E \rho} \]
Isotopic variations in meteoric waters

Fig. 9.4 Isotopic data of about 400 samples of rivers, lakes, and precipitation from various parts of the world. The best-fit line was termed the meteoric line. Its equation, as found by Craig (1961a), is $\delta D = 8\delta O^{18} + 10$. The data in the encircled zone of “closed basins” is for East African lakes with intensive evaporation.

Fig. 9.5 Isotopic composition of precipitation in the Pajeu River basin, Brazil: $\circ$, months with rain over 50 mm/month; $\bullet$, months with lower precipitation amounts. A local meteoric line is obtained with the equation $\delta D = 6.4\delta O^{18} + 5.5$ (Salati et al., 1980).
Figure 8  Schematics of the addition of evaporated moisture from surface water into the ambient atmosphere on the δ-diagram. δ_p = δ value of precipitation; δ_w = δ value of the residual water after evaporation; δ_E = the evaporation flux; δ_a and δ_a' are the atmospheric moisture before and after mixing with δ_E.
THE RELATION BETWEEN THE $^{18}$O AND DEUTERIUM CONTENTS OF RAIN WATER IN THE NEGEV DESERT AND AIR-MASS TRAJECTORIES

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Inversion of the Craig-Gordon equation to solve for water bodies in isotopic steady state

\[ \delta_E = (\alpha_{eq} \delta_L - h^* \delta_a + \epsilon_{eq} + \epsilon_k)/(1 - h^* - \epsilon_{eq}) \]

\[ \delta_L = \epsilon_{eq} + \epsilon_k + \delta_i + h^*(\delta_a - \epsilon_{eq} - \delta_i) \]
Latitudinal variation in oxygen-18 of atmospheric CO₂

ROGER J. FRANCEY* & PIETER P. TANS†

Time series showing the relationship between atmospheric carbon dioxide (upper panel), carbon-13 (middle panel) and oxygen-18 (lower panel) isotopic composition in Arctic and Boundary Layer. The measurements were made at NOAA CMDL and the University of British Columbia INSTAAR using samples provided by the NOAA CMDL cooperative air sampling network. Data are shown for Barrow and Samoa, revealing the seasonal variations of the isotopic compositions of carbon-13 and carbon-18 in the carbon dioxide from the VPDB-CO₂ standard, in permil (parts per thousand). Contact: Dr. Jim White, INSTAAR, Boulder, Colorado (303) 492-3695. james.white@colorado.edu.
CO₂ Uptake by Leaf During Photosynthesis

CO₂ is taken up through leaf stomata during photosynthesis.

Carbonic anhydrase

\[ \text{CO}_2 + \text{H}_2\text{O} \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \]

\[ H^{18}_2\text{O} + \text{CO}_2 \overset{\text{CA}}{\rightleftharpoons} \text{H}^+ + [\text{HCO}_3^{18}]^- \overset{\text{CA}}{\rightleftharpoons} \text{H}_2\text{O} + \text{CO}^{18}\text{O} \]
Global distribution of $\theta_{eq}$

Leaf water

ISOSCAPES (West & Bowen)

Gillon & Yakir, 2001

Leaf discrimination

LPJ, J. Kaplan et al.

Leaf water

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Gillon & Yakir, 2001

Global distribution of $\theta_{eq}$

Leaf discrimination

LPJ, J. Kaplan et al.

Leaf water

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Gillon & Yakir, 2001

Global distribution of $\theta_{eq}$

Leaf discrimination

LPJ, J. Kaplan et al.
Leaves ~ +6‰

Ocean ~ 0‰

Soil ~ -5‰

\( \delta^{18}O \) in CO₂

\[ c_a \frac{d \delta_a}{dt} = \langle GPP \Delta_A \rangle + \langle F_R (\delta_s - \delta_a - \epsilon_{eff}) + F_I (\delta_s - \delta_a) \rangle + \langle F_f (\delta_f - \delta_a) \rangle + \langle F_{oa} (\delta_o - \delta_a) + \epsilon_w N_o \rangle \]

\( c_a \)

\( d \delta_a / dt \)

\( \langle GPP \Delta_A \rangle \)

\( \langle F_R (\delta_s - \delta_a - \epsilon_{eff}) + F_I (\delta_s - \delta_a) \rangle \)

\( \langle F_f (\delta_f - \delta_a) \rangle \)

\( \langle F_{oa} (\delta_o - \delta_a) + \epsilon_w N_o \rangle \)

Photosynthesis

Respiration

\( \delta^{18}O \) in \( H_2O \)

\( \delta^{18}O \) in leaves ~ +6‰

\( \delta^{18}O \) in soil ~ -5‰

\( \delta^{18}O \) in ocean ~ 0‰

\( CO_2 + H_2O \rightleftharpoons HCO_3^- + H^+ \)

Francey and Tans 87;
Farquhar et al. 93
Gillon & Yakir, 2001
Global COS Budget

(Gg S a⁻¹; Kettle et al., 2002; Montzka et al., 2007; Berry et al., 2013)

Soil uptake (74-180)

Anthropogenic, direct/indirect (90-266)

Direct COS (110-190)
Indirect CS₂, DMS (149-330)
Unknown (~600)

Leaf uptake (730-1500)

Mean atmospheric concentration ~500 ppt!

Global ocean

BB, wetland (81-119)

Global COS Budget

Stratosphere

COS→SO₂

OH uptake (82-110)

6/24/15

Isotope 2015, Jerusalem
COS Uptake by Leaf During Photosynthesis

**COS** and **CO₂** are taken up through leaf stomata during photosynthesis.

**Diagram:**
- COS and CO₂ enter the leaf through the stomata.
- Inside the leaf, COS is converted to CO₂ and H₂S by Carbonic Anhydrase (CA).
  
  **Chemical Equations:**
  
  **COS + H₂O → CO₂ + H₂S**
  
  **CO₂ + H₂O → HCO₃⁻ + H⁺**
  
  **H¹⁸₂O + CO₂ → H⁺ + [HCO₃¹⁸⁻] → H₂O + CO¹⁸O**
\[ 18\Delta = a + \varepsilon[(\theta(\delta_e - \delta_a) - (1 - \theta)(a/(\varepsilon+1))] \]
PEPc Influence $\theta_{eq}$

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{HCO}_3^- + \text{H}^+ \\
\downarrow\quad\quad\text{PEPc} & \\
\text{CO}_2 & 
\end{align*}
\]

$\rho = \frac{\text{PEPc activity}}{\text{CA activity}}$

\[
\theta_{eq} = 1 - e^{-\left[\frac{\text{CA}_{\text{leaf}}(1-\rho)}{F_{\text{in}}/3}\right]}
\]

$^{18}\Delta = a + \epsilon \left[ (\theta(\delta_e - \delta_a) - (1 - \theta)(a/(\epsilon+1)) \right]$

<table>
<thead>
<tr>
<th>$\rho$</th>
<th>$\text{CA}_{\text{leaf}}$ (µmol m$^{-2}$s$^{-1}$)</th>
<th>$F_{\text{in}}$ (µmol m$^{-2}$s$^{-1}$)</th>
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<tbody>
<tr>
<td>0.18</td>
<td>80-3000</td>
<td>120</td>
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Observed $\theta_{eq} = 0.6$

Predicted (~0.7) mid-range CA activity
Unraveling the contemporary atmospheric CO$_2$ budget
(and the 50% “discount”)

All in billion tons of carbon (Gt C or $10^{15}$ g C)
Final note

• Great scientists like Joel Gat laid the foundations to isotopic hydrology as we know it today

• Isotopic hydrology is the foundation for a powerful tracer
  In environmental sciences,

• This includes key links between the hydrological and the carbon cycles
  Leading to new ‘frontiers’ in Environmental Sciences

Thank you