“Sample 125 poses another problem. This is a sample of grass from southwestern Kansas and the analysis is far heavier than all the others.”
Mean annual plant $\delta^{13}C$
What are plants made of?

- Hydrogen: 6.3%
- Nitrogen: 1.3%
- Carbon: 44%
- Oxygen: 45%
PHOTOSYNTHESIS

$6 \text{ CO}_2 + 6 \text{ H}_2\text{O} \rightarrow \text{C}_6\text{H}_{12}\text{O}_6 + 6 \text{ O}_2$

$\delta^{13}\text{C}$ of atmospheric $\text{CO}_2$?

-8.5%
Photosynthesis takes place in chloroplasts
Light Reactions
convert light energy to chemical energy
produce O₂

Dark Reactions
fix CO₂
produce carbohydrates

Rubisco!

6 CO₂ + 6 H₂O → C₆H₁₂O₆ + 6 O₂
Photosynthesis on land:
Most plant species use C₃ photosynthesis.
The initial product of CO$_2$ fixation is a molecule with **three** carbons.
Carboxylation of RuBP is rate-limiting

Rubisco has a high affinity for $^{12}\text{CO}_2$

$\text{CO}_2$ diffusion in air
$\alpha = 1.0044$
$\varepsilon = 4.4\%$

$\text{CO}_2$ fixation by Rubisco
$\alpha = 1.0270 - 1.0030$
$\varepsilon = 27.0 - 30.0\%$

O’Leary 1988
$\Delta^{13}C = a - (b - a)(c_i / c_a)$

**CO$_2$ diffusion in air**
$\varepsilon = 4.4\%$

**CO$_2$ fixation by Rubisco**
$\varepsilon = 27.0\%$

**Ratio of intracellular to atmospheric partial pressures of CO$_2$**
C₃ Photosynthesis & Fractionation

\[ \delta^{13}\text{C}_{\text{plant}} = \delta^{13}\text{C}_{\text{air}} - a - (b - a)\left(\frac{c_i}{c_a}\right) \]

- CO₂ diffusion in air
  \[ \varepsilon = 4.4\% \]

- CO₂ fixation by Rubisco
  \[ \varepsilon = 27.0\% \]

-8.4‰
\[ \delta^{13}C_{\text{plant}} = \delta^{13}C_{\text{atm.}} - a - (b - a)(c_i / c_a) \]

\[ \delta^{13}C_{\text{atm.}} = -8.4\% \]
\[ a = 4.4\% \]
\[ b = 27.0\% \]
\[ c_i / c_a = 0.7 \]

\[ \delta^{13}C_{\text{atm.}} = -8.4\% \]
\[ a = 4.4\% \]
\[ b = 27.0\% \]
\[ c_i / c_a = 0.9 \]
Impact of $c_i / c_a$ on $\Delta^{13}C$

$$\Delta^{13}C = a - (b - a)(c_i / c_a)$$
Why is there so much variation in the $\delta^{13}C$ values of C$_3$ plants?

Acacia Plants from Australia

Fogel et al. unpublished data
Factors that impact Δ and δ^{13}C in C_3 plants:

- CO₂ Source
- Salinity
- Precipitation
- Degree of Shading
- Level of Aridity

Why is there so much variation in the δ^{13}C values of C_3 plants?
The sources and $\delta^{13}$C values of CO$_2$ impact plant $\delta^{13}$C values

Burning fossil fuels can decrease local atmospheric CO$_2$ $\delta^{13}$C values

Pataki et al. 2007
The sources and $\delta^{13}C$ values of CO$_2$ impact plant $\delta^{13}C$ values

Burning fossil fuels has decreased global CO$_2$ $\delta^{13}C$ values
The sources and $\delta^{13}$C values of CO$_2$ impact plant $\delta^{13}$C values

Use of resired CO$_2$ can decrease $\delta^{13}$C values of understory plants

“The Canopy Effect”

Buchmann et al. 1997
Increasing salinity increases $\delta^{13}\text{C}$ values

If a plant is water-stressed, it will close its stomata to prevent water loss. This decreases $c_i / c_a$ and thus, decreases isotopic discrimination.

Guy et al. 1980
Increasing precipitation decreases $\delta^{13}C$ values

Stewart et al. 1995
Increasing light increases $\delta^{13}\text{C}$ values

Increasing light increases photosynthetic rate.

This decreases isotopic discrimination by reducing $c_i/c_a$
Increasing altitude increases $\delta^{13}$C values

The atmospheric partial pressure of $\text{O}_2$ decreases with increasing altitude.

This leads to increased photosynthetic efficiency, and lower $c_i/c_a$ ratios.

Körner et al. 1988, 1991
How might aridity influence $\delta^{13}$C values?
How might aridity influence $\delta^{13}C$ values?

- For $C_3$ grasses, $\delta^{13}C = -26.7 \pm 2.3 \%$.
- For $C_4$ grasses, $\delta^{13}C = -12.5 \pm 1.1 \%$.
The initial product of CO$_2$ fixation is a molecule with four carbons.

Typically, malate or aspartate is sent to the bundle sheath cell to be decarboxylated.
Kranz Anatomy and $C_4$ Photosynthesis

$C_3$ grass
*Microlaena stipoides*

$C_4$ grass
*Digitaria brownie*

$C_4$ photosynthesis now accounts for almost 25% of terrestrial gross primary productivity despite only occurring in < 5% of plants!
C₄ photosynthesis evolved independently many times

C₄ photosynthesis evolved independently in over 60 plant lineages within both Eudicots and Monocots

The evolution of C₄ photosynthesis depends on the co-occurrence of the necessary external (e.g., climatic conditions) and internal factors (e.g., genetic, structural, and biochemical conditions)

The oldest C₄ lineage (Chloridoideae) is ~30 million years old

Sage et al. 2011
C₄ photosynthesis evolved in a low [CO₂] atmosphere

Rubisco is both a carboxylase (yay!) and an oxygenase (boo!)

Photorespiration occurs when Rubisco fixes O₂ instead of CO₂

Photorespiration is wasteful and energetically expensive

Photorespiration occurs more frequently as [CO₂]/[O₂] decreases
Avoiding photorespiration with C$_4$ photosynthesis

PEP carboxylase evolved in a low CO$_2$/high O$_2$ atmosphere

PEP *carboxylase* fixes CO$_2$ and HCO$_3^-$ (it never interacts with O$_2$)
**C_{4} Photosynthesis**

Diffusion of CO_{2} through the stomata is rate-limiting

PEP carboxylase is not as picky as Rubisco

\[ \alpha = 1.0044 \]
\[ \epsilon = 4.4\% \]

O’Leary 1988, Farquhar et al. 1989
$\Delta^{13}C = a - [b_{\text{PEP}} + b_{\text{RUB}}(\phi) - a](c_i / c_a)$

- $\Delta^{13}C$ = 27.0‰
- Effective discrimination by PEP carboxylase $\varepsilon = -5.7$‰
- Bundle sheath cell "leakiness" $\phi = 0.2$–0.3
- $\text{CO}_2$ diffusion in air $\varepsilon = 4.4$‰
$\delta^{13}C_{\text{plant}} = \delta^{13}C_{\text{atm.}} - a - [b_{\text{PEP}} + b_{\text{RUB}}(\phi) - a](c_i / c_a)$

- CO$_2$ diffusion in air
  \[ \varepsilon = 4.4\% \]

- Effective discrimination by PEP carboxylase
  \[ \varepsilon = -5.7\% \]

- Bundle sheath cell “leakiness”
  \[ \phi = 0.2–0.3 \]

- $\delta^{13}C_{\text{plant}}$

- $\delta^{13}C_{\text{atm.}}$

- $a$

- $b_{\text{PEP}}$

- $b_{\text{RUB}}(\phi)$

- $c_i$

- $c_a$

- $e$ (effective discrimination by Rubisco)
  \[ \varepsilon = 27.0\% \]
\[ \delta^{13}C_{\text{plant}} = \delta^{13}C_{\text{atm.}} - a - [b_{\text{PEP}} + b_{\text{RUB}}(\phi) - a](c_i / c_a) \]

\[ \delta^{13}C_{\text{atm.}} = -8.4\% \]
\[ a = 4.4\% \]
\[ b_{\text{PEP}} = -5.7\% \]
\[ b_{\text{RUB}} = 27.0\% \]
\[ \phi = 0.3 \]
\[ c_i / c_a = 0.4 \]
What leads to variation in $\delta^{13}C$ values in $C_4$ plants?

C$_4$ Grasses from Australia

Count

$\delta^{13}C$

Fogel et al. unpublished data
What leads to variation in $\delta^{13}C$ values in $C_4$ plants?
What leads to variation in δ^{13}C values in C_4 plants?

 getC_4 Grasses from Australia

δ^{13}C

Count

Bundle Sheath Cell “Leakiness”

Metabolic Subtype (e.g., NAD-ME, NADP-ME)