Carbon Isotope Systematics in Soil
Soil Pathway Summary

- Organic matter finds its way into soils and decomposes
- SOM (Soil Organic Matter) is further decomposed by microbes which emit CO$_2$ as a by-product
- Under certain conditions, water and this carbon dioxide can form carbonates
• Each step in this sequence is met with a fractionation of the original carbon.

• Diffusion of CO\textsubscript{2} out of soils and mixing with the atmospheric CO\textsubscript{2} is responsible for the drop in δ\textsuperscript{13}C values of CO\textsubscript{2} (and CaCO\textsubscript{3}) with below the soil surface.

• The cause for the rise in δ\textsuperscript{13}C values of SOM with depth in SOM is debated.
• Since C3 and C4 plants are distributed based on specific environmental parameters…

• And the carbon that is cycled through soils is from these plants…

• $\delta^{13}C$ values in the soil carbon will be representative of these respective photosynthetic pathways. **Caveat:** Do C3 and C4 biomass decompose at the same rate? Potentially big issues for C cycle modeling, paleoecology, etc. if they do not.
What else could possibly contribute a significant amount of carbon to this process?

Parent material
Most carbon in soil carbonates is from soil gas (vegetation, respiration, atmosphere) and not from the parent material that soil is found on.
Phase 1: Enrichment of SOM $\delta^{13}C$ values

- Trees and grass respire
- Roots respire
- Litter in soils gets eaten by bacteria (which respire)

This $CO_2$ is representative of the particular photosynthetic pathway (C3 or C4), and is therefore about -27% or -13% respectively.
Initially, $\delta^{13}C$ values of the SOM look exactly like the plant. But with time and/or depth, SOM $\delta^{13}C$ values rise.
FIG. 4. Carbon isotope ratios of leaves, fresh litter, old litter, and soil organic matter at 5 and 15 cm depths for Pinus contorta, Populus tremuloides, and Acer spp. ecosystems of northern Utah. Vertical lines indicate ±1 se. Lowercase letters indicate statistical differences among components within an ecosystem. The figure is modified from Buchmann et al. (1997b).

FIG. 3. (a) Average profile of soil isotopic enrichment with reference to the first litter layer (L1). (b) Average profile of the logarithm of carbon concentrations by mass. At each depth, mean ± 1 se of the different sites are given. Not all layers were present at all sites.
Why do SOM $\delta^{13}C$ values rise?

1) Suess effect - recent drop in $\delta^{13}C$ values of plants due to fossil fuel burning, etc.
2) Differential loss of components (lipids, lignin, protein, etc.) with different $\delta^{13}C$ values.
3) Progressive $^{13}C$-enrichment of residual SOM due to respiratory loss of $^{12}C$-enriched CO$_2$.
4) Carboxylation in soils in the presence of soil gas that is $^{13}C$-enriched relative to typical plant matter!!
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Fig. 4  Depth profile of %C for archive soils and 1997 soils. The top of the first mineral horizon is the 0 cm depth. Litter is negative depth. Legend: open black squares and dashed lines are archive; solid black circles and lines are modern site 1; solid gray triangles and lines are modern site 2.

Fig. 5  Depth profile of $\delta^{13}C$ for archive soils and 1997 soils for (a) organic carbon only (carbonate removal) and (b) for total carbon (no carbonate removal). The top of the first mineral horizon is the 0 cm depth. Litter is negative depth. Legend as in Fig. 4.

Torn et al. 2002
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4) Carboxylation in soils in the presence of soil gas that is $^{13}C$-enriched relative to typical plant matter!!
• Although there is a rise in the $\delta^{13}C$ values of SOM material at greater depths, most carbon is digested by microbes and released into the soil as CO$_2$, leaving little remaining carbon in deeper SOM.

• This $^{13}C$-enrichment in deeper SOM does not have a great effect on the $\delta^{13}C$ values of soil CO$_2$ because is occurs at such low concentration.
Something else hinky
C3 and C4 don’t respire and rot at the same rate

<table>
<thead>
<tr>
<th></th>
<th>Corn</th>
<th>Alfalfa</th>
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<tbody>
<tr>
<td><strong>Soil moisture</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0–0.05 m</td>
<td>33.2 ± 0.4³</td>
<td>33.2 ± 2.3³</td>
</tr>
<tr>
<td>0.05–0.10 m</td>
<td>48.2 ± 3.5²</td>
<td>25.1 ± 1.5²</td>
</tr>
<tr>
<td>0.10–0.20 m</td>
<td>24.8 ± 2.0³</td>
<td>23.1 ± 0.2³</td>
</tr>
<tr>
<td><strong>Soil temperature</strong></td>
<td></td>
<td></td>
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<tr>
<td>0.10 m</td>
<td>20.4 ± 0.2³</td>
<td>20.4 ± 0.04³</td>
</tr>
<tr>
<td><strong>Soil respiration rate</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.8 ± 0.3³</td>
<td>9.4 ± 1.0²</td>
</tr>
<tr>
<td><strong>δ¹³C</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>canopy air (0.05 m)</td>
<td>-8.6 ± 0.01²</td>
<td>-9.2 ± 0.34³</td>
</tr>
<tr>
<td>leaves</td>
<td>-12.8 ± 0.07²</td>
<td>-28.2 ± 0.20³</td>
</tr>
<tr>
<td>SOC (0–0.05 m)</td>
<td>-15.0 ± 0.73²</td>
<td>-23.6 ± 1.00³</td>
</tr>
<tr>
<td>CO₂ efflux</td>
<td>-22.8 ± 0.47³</td>
<td>-22.3 ± 0.63³</td>
</tr>
<tr>
<td><strong>Carbon-respired</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>% C₄</td>
<td>38</td>
<td>35</td>
</tr>
<tr>
<td>% C₃</td>
<td>62</td>
<td>65</td>
</tr>
</tbody>
</table>

Percentage of C₄ or C₃ carbon respired was estimated using Eq. (5).
Different letters following the means represent significant differences between species (t-test at the 0.05-level).
The year 1995 was the second year of corn cropping, and the fifth year of alfalfa. After five years, crop species are switched at each site.

Buchmann & Ehleringer 1998

Wynn & Bird 2007
Phase 2: Soil CO₂

Via decay of SOM and root respiration, soils are a huge source of CO₂, which diffuses into the atmosphere.

The diffusion of CO₂ has a direct impact on δ¹³C values, and is affected by properties of the soil (porosity, tortuosity, production function with depth, production rate). The pattern produced by diffusion can be modeled to estimate the δ¹³C values of the CO₂ at differing depths.
• There is an initial 4.4‰ enrichment due to diffusion of CO$_2$ out of the soils

• Based on soil properties, atmospheric CO$_2$ plays a role at differing depths in a soil

• $\delta^{13}$C values at depth reflect the respiration, whereas values nearer the surface are more affected by the atmosphere

Cerling & Quade 1993
*Per mil value of CO₂ in the soil as a function of depth

\[
\delta_s(z) = \frac{1}{R_{PDB}} \left( \frac{D^*_s}{D_{13}} \frac{S(z)}{S(z)} \left( 1 - \frac{D_{13}}{D_s} \delta_o \right) + C_a(1 - \delta_d) \right) - 1 \times 1000
\]

Soil Properties:
- Production rate of respired CO₂
- Depth of production
- Soil Tortuosity
- Soil porosity

**Ratio** $^{12}$C to $^{13}$C diffusion in air

**Per mil value for soil-respired CO₂**

**$^{13}$C/$^{12}$C ratio of isotopic standard PDB**

**Per mil value for atmospheric CO₂**

**Concentration of CO₂ in the atmosphere**

**Constructed to put number into delta format**
This equation is set by boundary conditions that limit the function. The uppermost boundary condition is that soil CO$_2$ concentration equals that of the atmosphere (z=0).

CO$_2$ production is modeled with depth and an impermeable lower boundary at some finite $z$. 

\[
\delta_s(z) = \left( \frac{1}{R_{PDB}} \frac{S(z) D_s^{*} \delta_\phi + C_a^{*} \delta_a}{S(z)(1 - \frac{D_s^{*}}{D_{^{13}s}} \delta_\phi) + C_a^{*}(1 - \delta_a)} \right) - 1 \right) \times 1000
\]
In more productive soils (red), the effects of the atmosphere are only seen in the top few cm. Soil gas has a $\delta^{13}$C value = respired CO$_2$ + offset due to diffusion.

In less productive soils, atmospheric affects gas isotope values deep in the soil (blue).
Phase 3: Carbonate Formation

In the presence of water, the soil CO₂ goes through a number of chemical reactions that can result in the formation of soil carbonates.

\[
\begin{align*}
\text{CO}_2 + \text{H}_2\text{O} & \rightleftharpoons \text{H}_2\text{CO}_3 \\
\text{H}_2\text{CO}_3 & \rightleftharpoons \text{H}^+ + \text{HCO}_3^- \\
\text{HCO}_3^- & \rightleftharpoons \text{Ca}^{2+} + 2\text{HCO}_3^- \\
\end{align*}
\]

\[\text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}\]

Acid formed by hydration of soil CO₂ dissolves minerals near the soil surface and is slowly buffered by this process. At deeper levels in the soil, either because of high Ca²⁺ concentration (due to mineral dissolution, seasonal evaporation, or freezing) or simply due to the degassing of CO₂ from soils, the reaction above is driven to the right, leading to soil carbonate precipitation.
The fractionations that occur during carbonate formation are temperature sensitive. Along with the 4.4‰ due to due, the net 13C-enrichment of δ¹³C values relative to SOC is 16.5 and 13.5‰ between 0ºC and 25ºC respectively.

In addition, the δ¹³C is strongly correlated to that of the SOM and overlaying flora.

\[
\text{CO}_2 + \text{H}_2\text{O} \leftrightarrow \text{H}_2\text{CO}_3 \leftrightarrow \text{H}^+ + \text{HCO}_3^- \leftrightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- \leftrightarrow \text{CaCO}_3 + \text{CO}_2 + \text{H}_2\text{O}
\]
How deep a carbonate is when it forms also has an impact on its carbon isotope value. This is directly correlated to the $\delta^{13}C$ value of soil CO$_2$, which differs according to depth.

The model described previously is used in the graph above, and shows a arid C3 environment.
Progression of $\delta^{13}C$ values in soil CO$_2$ to soil carbonate.

~14‰ enrichment in $^{13}C$
Overall Process:

Microbial digestion of SOM and root respiration releases CO$_2$ into soil. Diffusion leads to $^{13}$C enrichment of ~4.4‰ relative to respired CO$_2$. With increasing depth, atmosphere affects $\delta^{13}$C of soil CO$_2$ less and less, and soil CO$_2$ is more representative of vegetation.

As soil CO$_2$ reacts to form soil carbonate, C isotopes are fractionated differently according to temperature. Overall fractionations amount to 13.5 to 16.5 ‰ enrichment relative to plants or soil CO$_2$. 

SOM $^{13}$C-enrichment with depth
Cause unclear, but no large effect overall on $\delta^{13}$C of soil CO$_2$