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# The impact of soil microorganisms on the global budget of $\delta^{18}\text{O}$ in atmospheric $\text{CO}_2$

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**Improved global estimates of terrestrial photosynthesis and respiration are critical for predicting the rate of change in atmospheric  $\text{CO}_2$ . The oxygen isotopic composition of atmospheric  $\text{CO}_2$  can be used to estimate these fluxes because oxygen isotopic exchange between  $\text{CO}_2$  and water creates distinct isotopic flux signatures. The enzyme carbonic anhydrase (CA) is known to accelerate this exchange in leaves, but the possibility of CA activity in soils is commonly neglected. Here, we report widespread accelerated soil  $\text{CO}_2$  hydration. Exchange was 10–300 times faster than the uncatalyzed rate, consistent with typical population sizes for CA-containing soil microorganisms. Including accelerated soil hydration in global model simulations modifies contributions from soil and foliage to the global  $\text{CO}^{18}\text{O}$  budget and eliminates persistent discrepancies existing between model and atmospheric observations. This enhanced soil hydration also increases the differences between the isotopic signatures of photosynthesis and respiration, particularly in the tropics, increasing the precision of  $\text{CO}_2$  gross fluxes obtained by using the  $\delta^{18}\text{O}$  of atmospheric  $\text{CO}_2$  by 50%.**

carbon cycle | water cycle | carbonic anhydrase | oxygen isotopes | terrestrial biosphere

The Earth's climate system is intimately connected to the movement of water and carbon across the planetary surface. As global warming proceeds, it is expected that photosynthetic  $\text{CO}_2$  uptake will increase in colder regions of the world and diminish in those regions that are already warm and dry (1). At the same time, warming is expected to increase microbial activity, at least where water is not limiting, and therefore lead to an enhanced breakdown of organic matter in the soil, producing a large respiratory flux of  $\text{CO}_2$  back to the atmosphere (2). Because terrestrial ecosystems presently sequester about a quarter of the  $\text{CO}_2$  emissions associated with fossil fuel burning (7.1 GtC $\text{y}^{-1}$ ) (1), it is critical that we understand how large-scale, climate-driven changes will affect the carbon sequestration of the terrestrial biosphere. Currently, the precise response of terrestrial  $\text{CO}_2$  sources and sinks to changes in climate remains uncertain (3) and its understanding requires the ability to quantify the amount of  $\text{CO}_2$  taken up during photosynthesis separately from the amount released by respiration.

The oxygen isotope composition of atmospheric  $\text{CO}_2$  ( $\delta_a$ ) was shown to be a powerful tracer of photosynthetic and respiratory  $\text{CO}_2$  fluxes while at the same time providing information on the intensity of water cycling within terrestrial ecosystems (4–6). This tracing property occurs because the oxygen isotope composition ( $\delta^{18}\text{O}$ ) of leaf and soil water pools is transferred to

atmospheric  $\text{CO}_2$  during photosynthetic and respiratory  $\text{CO}_2$  exchange, via an isotopic exchange during  $\text{CO}_2$  hydration (7):  $\text{CO}_{2\text{aq}} + \text{H}_2^{18}\text{O} \rightleftharpoons \text{CO}^{18}\text{O}_{\text{aq}} + \text{H}_2\text{O}$ . Despite the short residence time of  $\text{CO}_2$  in leaves,  $\text{CO}_2$  involved in photosynthesis is nearly completely relabeled by  $^{18}\text{O}$ -enriched leaf water because of the enzyme carbonic anhydrase (CA; EC 4.2.1.1), a very efficient catalyst of  $\text{CO}_2$  hydration and isotopic exchange (4, 5, 8, 9). Typically the  $\delta^{18}\text{O}$  of leaf and soil water pools are very different. There is a tendency for the heavier molecules of water to accumulate more readily in leaves than in soils during evapotranspiration because of the difference in water pool size (10, 11). Because the  $\text{CO}_2$ - $\text{H}_2\text{O}$  exchange in leaves (associated with photosynthesis) or soils (associated with soil respiration) produces such contrasting  $^{18}\text{O}$  signals, estimates of the amount of  $\text{CO}_2$  exchanged during photosynthesis and respiration can in principle be constrained by using the  $\delta^{18}\text{O}$  signal of atmospheric  $\text{CO}_2$  (6, 12).

However, our ability to partition gross fluxes of  $\text{CO}_2$  may be complicated because the  $\delta^{18}\text{O}$  of soil water ( $\delta_{\text{sw}}$ ) can often display a strong vertical gradient at the soil surface because soil evaporation also leads to an enrichment of heavy water molecules in the uppermost layers (13–15). Thus, to determine the  $\delta^{18}\text{O}$  of  $\text{CO}_2$  exchanged between soils and the atmosphere accurately it becomes necessary to know the shallowest depth ( $z_{\text{eq}}$ ) where diffusing  $\text{CO}_2$  molecules (from the atmosphere or produced by soil respiration; Fig. 1A) have enough time to fully equilibrate isotopically with soil water. With increasing temperature and moisture,  $\text{CO}_2$  hydration increases relative to the diffusion rate so that  $z_{\text{eq}}$  moves closer to the surface, and toward more enriched  $\delta^{18}\text{O}$  values (see *Methods*, Eq. 4). Although we know that CA accelerates the rate of hydration in leaves, the possibility of CA activity in soils is commonly neglected (4, 15),

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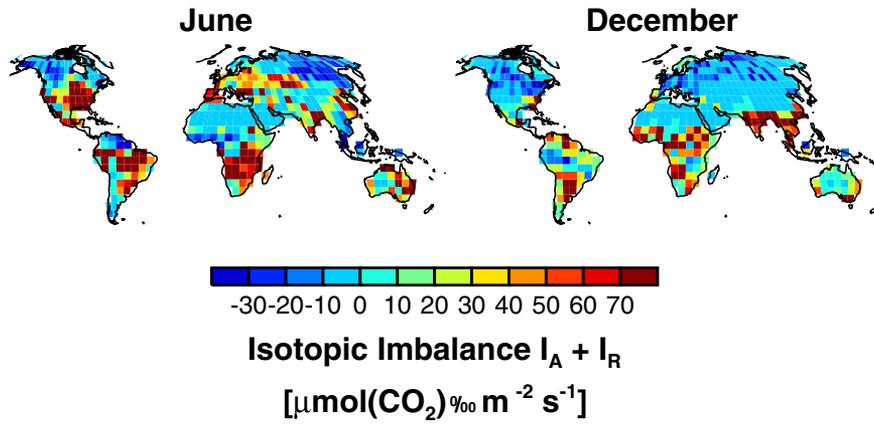
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**Fig. 4.** Global distribution in the extent of isotopic imbalance ( $I_A + I_R$ ) across continental surfaces for June and December simulated by the global model Mecbeth for the most enhanced soil  $\text{CO}_2$  hydration scenario ( $f_{CA} = 300$ ). Regions where  $I_A + I_R$  is the most different from zero correspond to regions of strong isotopic imbalance where biospheric gross  $\text{CO}_2$  fluxes are expected to be the most constrained by  $\delta^{18}\text{O}$  data.

**Future Directions for Global Isotope-Enabled Models.** This study demonstrates that enhanced rates of  $\text{CO}_2$  hydration occur at the soil surface and appreciably impact the oxygen isotope composition of atmospheric  $\text{CO}_2$ . This enhanced exchange in the soil brings into focus our limited ability to predict the isotopic enrichment of soil water near the surface (18, 29), highlighting a need for future improvements in this research area. Also, although we provided the basic observations and parameterization, more work is now needed to further assess the variability in  $f_{CA}$  in different ecosystems, plant functional types, or regions within the global model, including attempts to establish the mechanistic basis to underpin the observed differences in CA activity between ecosystems. Developments on these fronts will greatly enhance our capabilities to use the  $\delta^{18}\text{O}$  of atmospheric  $\text{CO}_2$  to quantitatively inform us of large-scale changes in the intensity of carbon and water cycling in terrestrial ecosystems.

## Methods

**Soil  $\text{CO}^{18}\text{O}$  Budget Equation.** In a given soil layer, the number of moles of  $\text{CO}^{18}\text{O}$  changes as a result of (i)  $\text{CO}^{18}\text{O}$  production during heterotrophic and autotrophic respiration, (ii) diffusion of these molecules through the soil layer, and (iii) oxygen isotopic exchange with the surrounding soil water (30–32):

$$\theta_t \frac{\partial C\mathcal{R}}{\partial t} = \mathcal{R}_c S_c + \frac{\partial}{\partial z} \left[ D_{c,\text{iso}} \frac{\partial C\mathcal{R}}{\partial z} \right] + k_{h,\text{iso}} B \theta_w C (\mathcal{R}_{\text{eq}} - \mathcal{R}), \quad [1]$$

where  $C$  [ $\text{mol}\cdot\text{mol}^{-1}$ ] is the  $\text{CO}_2$  mole fraction in soil air,  $\mathcal{R}$ ,  $\mathcal{R}_c$ , and  $\mathcal{R}_{\text{eq}}$  are the  $^{18}\text{O}/^{16}\text{O}$  ratios of the  $\text{CO}_2$  in soil air, respired  $\text{CO}_2$ , and  $\text{CO}_2$  in isotopic equilibrium with the surrounding soil water, respectively,  $S_c$  ( $\text{mol}\cdot\text{m}^{-3}\cdot\text{s}^{-1}$ ) is the respiration rate density,  $D_{c,\text{iso}}$  ( $\text{m}^2\cdot\text{s}^{-1}$ ) is the effective diffusivity of  $\text{CO}^{18}\text{O}$  in soil air,  $\theta_w$  ( $\text{m}^3\cdot\text{m}^{-3}$ ) is the volumetric soil water content,  $B$  is the  $\text{CO}_2$  solubility coefficient, and  $\theta_t$  ( $\text{m}^3\cdot\text{m}^{-3}$ ) is the total  $\text{CO}_2$  porosity. Denoting by  $\theta_a$  the soil air porosity we have (31):  $\theta_t = \theta_a + B\theta_w$ . The solubility coefficient  $B$  depends on soil temperature  $T_s$  (K) according to ref. 33:  $B = 1.739\exp(-0.039(T_s - 273.15) + 0.000236(T_s - 273.15)^2)$ .  $\mathcal{R}_{\text{eq}}$  is related to the  $^{18}\text{O}/^{16}\text{O}$  ratio in soil water  $\mathcal{R}_{\text{sw}}$  through  $\mathcal{R}_{\text{eq}} = (1 + \varepsilon_{\text{eq}})\mathcal{R}_{\text{sw}}$ , where  $\varepsilon_{\text{eq}} = 17.604/T_s - 0.01793$  is the  $\text{CO}_2$ - $\text{H}_2\text{O}$  equilibrium fractionation (22). Because there are three oxygen atoms present in the bicarbonate intermediate, the isotopic exchange rate during  $\text{CO}_2$  hydration equals one-third the hydration rate (7):  $k_{h,\text{iso}} = f_{CA}k_{h,\text{uncat}}/3$ , where (34)  $k_{h,\text{uncat}} = 0.037 \times \exp(0.118(T_s - 298.15))$ . In this framework, CA activity is expressed as an enhancement factor ( $f_{CA}$ ) of the uncatalyzed  $\text{CO}_2$  hydration rate ( $k_{h,\text{uncat}}$ ). The effective  $\text{CO}^{18}\text{O}$  diffusivity in soil air is calculated as  $D_{c,\text{iso}} = D_{c,\text{eff}} \alpha_d$ , where  $\alpha_d = 0.9913$  is the isotopic discrimination during molecular diffusion of  $\text{CO}_2$  in air and  $D_{c,\text{eff}}$  ( $\text{m}^2\cdot\text{s}^{-1}$ ) is the effective  $\text{CO}_2$  diffusivity in soil air. Several parameterizations of this effective diffusivity exist in the literature that differ mostly for wet soils (35). Results presented in this study use ref. 31:  $D_{c,\text{eff}} = 0.66 \times \theta_a \times 1.4 \cdot 10^{-5} (T_s/298.15)^{1.75}$ .

**Full Equilibration Depth.** The budget equation above contains two time scales. One time scale indicates the half-life of  $\text{CO}_2$  molecules before being isotopically equilibrated with the surrounding water:

$$\tau_k = \ln 2 \cdot \left( \frac{\theta_t}{k_{h,\text{iso}} B \theta_w} \right) \quad [2]$$

and another time scale indicates the time required for a plume of  $\text{C}^{18}\text{O}$  molecules to diffuse through the soil over a given distance  $z$ :

$$\tau_d(z) = \frac{\theta_t z^2}{2D_{c,\text{iso}}} \quad [3]$$

Full equilibration within a soil layer of thickness  $z$  is satisfied when the time scale for isotopic equilibration is smaller than the time scale for diffusion through this layer, i.e.,  $\tau_k \ll \tau_d(z)$ . When  $\tau_k = \tau_d(z)$ , full equilibration can occur if the soil layer has uniform soil temperature, moisture content, and isotopic composition. However, in the top centimeters of the soil, strong gradients of  $T_s$ ,  $\theta_w$ , and  $\mathcal{R}_w$  are more likely. The shallowest depth of full equilibration,  $z_{\text{eq}}$ , must therefore satisfy the inequality:  $\tau_k < \tau_d(z_{\text{eq}})$ . In the following we will define  $z_{\text{eq}}$  as:  $\tau_k = \tau_d(z_{\text{eq}})/4$ , or similarly:

$$z_{\text{eq}} = 2 \sqrt{\frac{2 \ln 2 D_{c,\text{iso}}}{k_{h,\text{iso}} B \theta_w}} \quad [4]$$

The factor 4 was determined by matching the value of  $f_{CA}$  deduced in Fig. 2 with that obtained from simulations using the full numerical model (Eq. 1), i.e.,  $f_{CA} \approx 300$  for the Mediterranean evergreen site (14) and  $f_{CA} \approx 20$  for the montane evergreen site (15). Eq. 4 with  $f_{CA} = 20$  also provides seasonal variations of  $z_{\text{eq}}$  at the temperate evergreen site that correspond to the depth where  $\delta^{18}\text{O}$  in soil air  $\text{CO}_2$  ( $\delta_{\text{sa}}$ ) and  $\delta_{\text{sw}} - \varepsilon_{\text{eq}}$  (estimated using the full numerical model, Eq. 1) start to diverge by  $>0.3$  ‰ (a threshold chosen for practical purposes to represent the overall precision of soil water isotope measurements).

Other studies (14, 35) use a different formulation for  $D_{c,\text{iso}}$ , leading to values of this diffusivity 5-fold smaller in saturated soils. Using this other formulation does not fundamentally change the results presented in Fig. 2.

**Soil  $\text{CO}_2$  Isoflux.** In the steady state, and assuming isothermal and uniform soil water conditions, Eq. 1 can also be solved analytically (30–32). In this framework, the isotopic composition of the soil  $\text{CO}_2$  flux  $\delta_{\text{flux}}$  is:

$$\delta_{\text{flux}} = \delta_{\text{eq}} + \varepsilon_{d,\text{eff}} + (\delta_{\text{eq}} - \delta_a) v_{\text{inv}} \frac{C_a}{F_R}, \quad [5]$$

where  $\varepsilon_{d,\text{eff}}$  is the effective isotopic fractionation during diffusion,  $F_R$  is the soil  $\text{CO}_2$  efflux, and  $v_{\text{inv}} = \sqrt{B\theta_w k_{h,\text{iso}} D_{c,\text{iso}}}$  has the dimensions of a velocity ( $\text{m}\cdot\text{s}^{-1}$ ) that when multiplied by  $C_a$  gives the soil invasion flux  $F_{\text{inv}}$ . The product  $(\delta_{\text{flux}} - \delta_a)F_R$  is called the soil  $\text{CO}_2$  isoflux. It can be seen as the sum of two isotope fluxes: a respiration isoflux,  $I_R = (\delta_{\text{eq}} + \varepsilon_{d,\text{eff}} - \delta_a)F_R$ , and an invasion isoflux,  $I_{\text{inv}} = (\delta_{\text{eq}} - \delta_a)F_{\text{inv}}$ , sometimes defined as abiotic because it is independent of

$F_R$ . Assuming a uniform soil  $\text{CO}_2$  production  $S_c$  over a soil column of depth  $z_0$ ,  $\varepsilon_{d,\text{eff}}$  can be estimated as (31):  $\varepsilon_{d,\text{eff}} = \varepsilon_d(1 - z_1/z_0(1 - \exp(-z_0/z_1)))$ , where  $z_1 = (2\sqrt{2\ln 2})^{-1} z_{\text{eq}}$ . Eq. 5 can then be inverted to estimate  $\delta_{\text{eq}}$  as a function of  $\delta_{\text{flux}}$ ,  $C_a$ ,  $\delta_a$ , and  $F_R$  measurements:

$$\delta_{\text{eq}} = \frac{\delta_{\text{flux}} - \varepsilon_{d,\text{eff}} + v_{\text{inv}}C_a/F_R\delta_a}{1 + v_{\text{inv}}C_a/F_R} \quad [6]$$

**Oxygen Isotope Composition of the Net  $\text{CO}_2$  Flux from Soil Chambers.** The steady-state oxygen isotope signal of the net soil  $\text{CO}_2$  flux during chamber closure ( $\delta_{\text{ch}}$ ) was calculated by using a simple isotopic mass balance:

$$\delta_{\text{ch}} = \frac{\delta_{\text{out}}C_{\text{out}} - \delta_{\text{in}}C_{\text{in}}}{C_{\text{out}} - C_{\text{in}}}, \quad [7]$$

where  $C_{\text{out}}$ ,  $C_{\text{in}}$  and  $\delta_{\text{out}}$ ,  $\delta_{\text{in}}$  are the mole fractions and isotopic compositions of  $\text{CO}_2$  in the air leaving and entering the chamber, respectively. In the case of the two sites that used closed chambers (subtropical evergreen and semiarid grassland),  $C_{\text{out}}$ ,  $C_{\text{in}}$  and  $\delta_{\text{out}}$ ,  $\delta_{\text{in}}$  are the mole fractions and isotopic compositions of  $\text{CO}_2$  at the start and end of a defined chamber closure period, respectively.

To derive  $\delta_{\text{eq}}$  values from soil chamber data, we use Eq. 6, neglect chamber effects, and make the common assumption that the atmosphere inside the chamber is well mixed ( $C_a = C_{\text{out}}$  and  $\delta_a = \delta_{\text{out}}$ ).

**Oxygen Isotope Composition of Soil Water.** Depth-resolved soil samples were collected at each experimental site within proximity of the soil chamber and at approximately the same time as gas exchange measurements. In the case of the Mediterranean evergreen, subtropical evergreen, and both temperate ever-

green sites, soil water was extracted cryogenically from bulk soil samples and  $\delta^{18}\text{O}$  analysis of  $\text{CO}_2$  equilibrated with the extracted water was completed (14). For the montane evergreen, subtropical deciduous, and semiarid grassland sites  $\text{CO}_2$  with a known isotopic composition was equilibrated directly with fresh soil samples and stored in gas-tight containers for 12 h. Equilibrated  $\text{CO}_2$  was then sampled from the container and analyzed for its  $\delta^{18}\text{O}$  composition (15).

**Global Model Simulations.** The global model Mecbeth calculates the sources and sinks of  $\text{CO}_2$ , water, and their respective isotopes and transports them in the atmosphere (18, 19). It merges a description of the biospheric energy, water, and carbon fluxes with a global climate and water isotope model. The atmosphere and biosphere are dynamically coupled to account for feedbacks of the accelerated equilibration of  $\text{CO}_2$  with soil water on  $\delta_a$  and the isotopic signatures of leaf and other fluxes. The model parameterization of soil water isotopes was improved in this study to provide depth-resolved descriptions of soil water and soil water isotopes (35), a necessary step if CA activity occurs in soils containing strong vertical gradients in  $\delta_{\text{sw}}$  (14). Several soil layers of varying thickness were included in the model. The most important upper layers relevant to this study consisted of a top layer at 0–6 cm and another layer at 6–20 cm.

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