

# Leaf-scale quantification of the effect of photosynthetic gas exchange on $\Delta^{17}\text{O}$ of atmospheric $\text{CO}_2$

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## 1. Discrimination against $^{13}\text{C}$ of $\text{CO}_2$

The isotope discrimination against  $^{13}\text{C}$  ( $\Delta_A^{13}\text{C}$ ) associated with photosynthesis for the three-plant species is shown in Figure S8 a) and b) as a function of  $c_c/c_a$  and  $c_i/c_a$  for  $\text{C}_3$  and  $\text{C}_4$  plants, respectively. For the  
15  $\text{C}_3$  plants,  $c_c$  is calculated following (Farquhar and Cernusak, 2012) as:

$$c_c = c_i - \left( \frac{1 - t^{13}}{1 + t^{13}} \right) \left( \frac{(\Delta_A^{13}\text{C}_i - \Delta_A^{13}\text{C}_{\text{obs}})Pc_a}{\left( b - a_m - \frac{\alpha_b}{\alpha_e} e \frac{R_d}{R_d + A} \right)} \right) \quad (\text{S1})$$

where  $\Delta_A^{13}\text{C}_{\text{obs}}$  is the observed discrimination against  $^{13}\text{C}$  and  $\Delta_A^{13}\text{C}_i$  is the discrimination that can be  
20 calculated for infinite mesophyll conductance (no mesophyll resistance).  $t^{13}$  is a ternary correction factor (considers the collisions between air and  $\text{CO}_2$ , air and  $\text{H}_2\text{O}$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ ),  $b$  the fractionation due to uptake by Rubisco, and  $a_m$  the sum of the fractionations associated with  $^{13}\text{CO}_2$  dissolution in and diffusion through water, respectively.  $e$ ,  $R_d$ ,  $\alpha_e$ ,  $\alpha_b$  and  $P$  are the fractionations during day respiration (decarboxylation), the day respiration rate, the fractionation factor for day respiration with respect to net  
25 assimilation, the fractionation factor for  $\text{C}_3$  carboxylation, and the pressure of the air surrounding the leaf, respectively. A detailed description of the equations, best fit parameters and definitions of discrimination factors are given in Table S3.

Experiments at different light intensities are shown in different colors, blue for LL and yellow for HL.  
30 For ivy and sunflower,  $\Delta_A^{13}\text{C}$  and  $c_c/c_a$  are linearly correlated. As irradiance increases,  $c_c/c_a$  and  $\Delta_A^{13}\text{C}$  decrease.  $\Delta_A^{13}\text{C}$  for ivy increases from 13‰ to 16‰ when  $c_c/c_a$  increases from 0.34 to 0.55 while for sunflower  $\Delta_A^{13}\text{C}$  ranges from 13‰ to 25 ‰ for  $c_c/c_a$  ratios of 0.37 to 0.8. This is due to the lower assimilation rate and generally higher back-diffusion flux at a higher  $c_c/c_a$  ratio. When irradiance increases, the assimilation rate increases,  $c_c/c_a$  decreases, and less of the  $\text{CO}_2$  that has entered the stomata  
35 diffuses back to the atmosphere. As a result,  $\Delta_A^{13}\text{C}$  decreases with an increase in light intensity. For maize,

$\Delta_A^{13}\text{C}$  is much smaller than for the  $\text{C}_3$  plants, ranging from 2.4‰ to 3.5‰ for  $c_i/c_a$  ratios of 0.42 to 0.55, and we did not observe a strong correlation between  $\Delta_A^{13}\text{C}$  and  $c_i/c_a$ .  $\Delta_A^{13}\text{C}$  vs  $c_i/c_a$  is shown in Figure S9 of the for both  $\text{C}_3$  plants (sunflower and ivy) and a  $\text{C}_4$  plant (maize).

## 40 2. Leaf cuvette model

In the simple leaf cuvette model, we partitioned the leaf into three different compartments: the intercellular air space, the mesophyll cell, and the chloroplast, as shown in Figure S6. For this model, we assumed an infinite boundary conductance. The conductance from the intercellular air space to the chloroplast, where assimilation takes place (mainly for the  $\text{C}_3$  plants), is represented by  $g_{m13}$ . The  
 45 conductance from the intercellular air space to the mesophyll, where the  $\text{CO}_2\text{-H}_2\text{O}$  exchange occurs is expressed as  $g_{m18}$ .

### **CO<sub>2</sub> balance**

50 First, we solve for the  $\text{CO}_2$  mole fractions in the atmosphere ( $c_a$ ), the intercellular air space ( $c_i$ ), the mesophyll cell ( $c_m$ ) and the chloroplast ( $c_c$ ). The main assumptions in the leaf cuvette model are: -

- The system is in steady state ( $\frac{dc_i}{dt} = 0 = g_s c_a + g_{m18} c_m - g_i c_i - g_{m13} c_i$ )
- The mixing in the cuvette is perfect (i.e.  $c_a = c_o$ )
- Boundary layer resistance can be neglected
- 55 - The conductance between intercellular space and mesophyll is assumed to be 3 times higher than the conductance between intercellular space and chloroplast (i.e.  $g_{m18} = 3 \times g_{m13}$ ).

Furthermore, we used a 100 ppm drawdown of  $\text{CO}_2$  for each photosynthesis experiment. The mixing ratio of  $\text{CO}_2$  entering the cuvette and leaving the cuvette is 500 ppm and 400 ppm, respectively. The leaf area,  
 60 flowrate and assimilation rate used for the model are  $30 \text{ cm}^2$ ,  $0.7 \text{ L min}^{-1}$  and  $20.0 \text{ mol m}^{-2}\text{s}^{-1}$ , respectively. The  $\text{CO}_2$  mole fractions in all leaf reservoirs are calculated for each given  $c_m/c_a$  ratio, by assuming  $g_{m18} = 0.3 \text{ mol m}^{-2}\text{s}^{-1}$ ).

Next, we assume a value for the  $\text{C}^{18}\text{OO}$  mole fraction inside the cuvette ( $c_{a,\text{C}^{18}\text{OO}}$ ). From the mole fractions  
 65  $c_{a,\text{C}^{18}\text{OO}}$  and  $c_{m,\text{C}^{18}\text{OO}}$  and the conductance  $g_{s,\text{C}^{18}\text{OO}}$  and  $g_{m18,\text{C}^{18}\text{OO}}$  we can calculate the inflow of  $\text{C}^{18}\text{OO}$  into the intercellular air space. Since the system is in steady state, the inflow and outflow of  $\text{C}^{18}\text{OO}$  for the intercellular air space are equal and hence we can determine the mole fraction  $c_{i,\text{C}^{18}\text{OO}}$ . The ingoing  $\text{C}^{18}\text{OO}$  is known from the airflow rate and  $c_{e,\text{C}^{18}\text{OO}}$ , the outgoing  $\text{C}^{18}\text{OO}$  depends on the airflow rate and  $c_{a,\text{C}^{18}\text{OO}}$  and the plant uptake of  $\text{C}^{18}\text{OO}$  is  $A_{n,\text{C}^{18}\text{OO}} = g_{s,\text{C}^{18}\text{OO}} \times (c_{a,\text{C}^{18}\text{OO}} - c_{i,\text{C}^{18}\text{OO}})$ . By using an iterative  
 70 procedure we can improve our estimate for  $c_{a,\text{C}^{18}\text{OO}}$ . Note that for each update in  $c_{a,\text{C}^{18}\text{OO}}$ , we also update the corresponding  $c_{i,\text{C}^{18}\text{OO}}$

### **<sup>13</sup>CO<sub>2</sub> balance**

75 Next, we calculate the steady state  $^{13}\text{CO}_2$  mole fractions in the different model reservoirs and subsequently, we determine the discrimination  $\Delta^{13}\text{C}$ . The additional assumptions used are:

- For the fractionation factors we use  $a_{13s} = 4.4$ ,  $a_m = 1.8$  ‰ and  $b = 29$ ‰
- The uptake of  $^{13}\text{CO}_2$  scales linearly with the  $^{13}\text{CO}_2$  mole fraction in the chloroplast ( $A_n = k \times c_c$ ) and similarly for  $^{13}\text{CO}_2$  we have:  $A_{n,13\text{CO}_2} = k \times (1 - b) \times C_{c,13\text{CO}_2}$

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We solve the steady state  $^{13}\text{CO}_2$  balance by performing 2 nested iterations. First, we do an initial guess for the atmospheric  $^{13}\text{CO}_2$  mole fraction ( $C_{a,13\text{CO}_2}$ ). Next, we do an initial guess for the photosynthetic uptake of  $^{13}\text{CO}_2$  ( $A_{n,13\text{CO}_2}$ ). In the ‘inner’ iteration loop we use  $c_{a,13\text{CO}_2}$  and  $A_{n,13\text{CO}_2}$  to calculate the  $^{13}\text{CO}_2$  mole fractions in all leaf reservoirs. From the  $^{13}\text{CO}_2$  mole fraction in the chloroplast ( $c_{c,13\text{CO}_2}$ ) and the linear assimilation factor ( $k \times (1 - b)$ ) we can calculate the corresponding  $A_{n,13\text{CO}_2}$  and compare this to our initial guess. Using an iterative procedure, we can find the  $A_{n,13\text{CO}_2}$  that corresponds to the assumed  $c_{a,13\text{CO}_2}$ .

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The ‘outer’ iteration loop is aimed at finding the steady state atmospheric  $^{13}\text{CO}_2$  mole fraction ( $c_{a,13\text{CO}_2}$ ) using a mass balance for  $^{13}\text{CO}_2$ . We know the  $^{13}\text{CO}_2$  mole fraction of the ingoing air ( $c_{in,13\text{CO}_2}$ ), we have assumed value for outgoing air ( $c_{a,13\text{CO}_2}$ ) and have calculated the corresponding photosynthetic uptake ( $A_{n,13\text{CO}_2}$ ). From the resulting imbalance, we can come up with a new guess for  $c_{a,13\text{CO}_2}$ . After each update of our estimate for  $c_{a,13\text{CO}_2}$ , we repeat the ‘inner’ iteration loop to update  $A_{n,13\text{CO}_2}$ .

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## 95 $\text{C}^{18}\text{OO}$ balance

To solve the  $\text{C}^{18}\text{OO}$  balance, we assume on top of the earlier mentioned assumptions:

- For the fractionation of  $\text{C}^{18}\text{OO}$  for diffusion through stomata and diffusion into the mesophyll cell, we used  $a_{18s} = 8.8$  ‰ and  $a_{18w} = 0.8$ ‰, respectively
- The isotopic exchange between  $\text{CO}_2$  and water in the mesophyll is fast enough to reach complete equilibration, which is a function of temperature
- Isotopic equilibration between  $\text{CO}_2$  and water does not occur in the intercellular air space

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We assume for the leaf water signature  $\delta^{18}\text{O}_{\text{leaf}} = 10.467$ ‰ VSMOW and for the leaf water temperature  $T_{\text{leaf}} = 22^\circ\text{C}$ , from which we can calculate the  $\delta^{18}\text{O}$  signature and therefore (using  $c_m$  from above) the  $\text{C}^{18}\text{OO}$  mole fraction in the mesophyll ( $c_{m,C18OO}$ ). Next, we assume a starting value for the  $\text{C}^{18}\text{OO}$  mole fraction inside the cuvette ( $c_{a,C18OO}$ ). From the steady state mass balance, we can then determine the mole fraction  $c_{i,C18OO}$  ( $c_i = \frac{g_s c_a + g_m 18 c_m}{g_s + g_m}$ ). The ingoing  $\text{C}^{18}\text{OO}$  is known from the airflow rate and  $c_{e,C18OO}$ , the outgoing  $\text{C}^{18}\text{OO}$  depends on the airflow rate and  $c_{a,C18OO}$  and the plant uptake of  $\text{C}^{18}\text{OO}$  is  $A_{n,C18OO} = g_{s,C18OO} \times (c_{a,C18OO} - c_{i,C18OO})$ .

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A similar mass balance is implemented for  $\text{C}^{17}\text{OO}$ , the fractionation of  $\text{C}^{17}\text{OO}$  for diffusion through stomata and diffusion into the mesophyll cell we used  $a_{17s} = 4.4$  ‰ and  $a_{17w} = 0.382$ ‰, respectively. We assume for the leaf water signature  $\delta^{18}\text{O}_{\text{leaf}} = 5.39$ ‰ VSMOW.

115

```

def
clumpy_e170(key1, var1, Cin, d17Oin, d18Oin, An, Aleaf, key2, var2, gm13C, d17O_leaf, d18O_lea
120  f, print_table=False):
    """
    -----
    ---

    Description:

125  CLUMPy (Clumped isotopes Leaf Uptake Model in Python) calculates the outgoing
D17O signature for a leaf in the cuvette experiment as described by Adnew et al.

130  List of input variables:

    - Experimental conditions

        *airflow      rate of air entering cuvette [L/min]
135  *drawdown      CO2 drawdown [ppm]

    - Ingoing air characteristics

140  Ce            ingoing CO2 mixing ratio [ppm]
    d17Oe         ingoing d17O signature [permil VSMOW]
    d18Oe         ingoing d18O signature [permil VSMOW]

    - Leaf properties

145  An            net assimilation rate [umol/(m2s)]
    Aleaf         leaf area [cm2]
    **gs          stomatal conductance [mol/(m2s)]
    **Ci_Ca       CO2-in-intercellular-space to CO2-in-atmosphere ratio [-]
    **Cm_Ca       CO2-in-mesophyll to CO2-in-amountosphere ratio [-]
150  gm13C        conductance between intercellular space and chloroplast
[mol/(m2s)]

    - Leaf water characteristics

155  d17O_leaf     leaf water d17O signature [permil VSMOW]
    d18O_leaf     leaf water d18O signature [permil VSMOW]

    Notes:

160  *   The user can call the function with the value of airflow or drawdown for
var1. The user is
        required to specify which input parameter is given by using the key1
variable.

165  **  The user can call the function with the value of gs, Ci_Ca or Cm_Ca for
var2. The user is required

```

to specify which input parameter is given by using the key2 variable.

```
-----  
170 ---  
    ""  
  
175 #####  
    # #  
    # INITIALIZATION #  
    # #  
    #####  
  
180 # -- Import statement  
import numpy as np  
  
# -- Output settings  
185 print_diag_d170a = False  
print_diag_d180a = False  
  
#####  
190 # #  
# MODEL SETTINGS #  
# #  
#####  
  
# -- Test key1  
195 if (key1=='airflow'):  
    airflow = var1 # L/min  
elif (key1=='drawdown'):  
    drawdown = var1 # ppm  
else:  
200     print ('Error: key1 not recognized')  
    return  
  
# -- Test key2  
if (key2=='gs'):  
205     gs = var2 # mol/(m2s)  
if (key2=='Ci_Ca'):  
    Ci_Ca = var2 # -  
elif (key2=='Cm_Ca'):  
    Cm_Ca = var2 # -  
210 else:  
    print ('Error: key2 not recognized')  
    return  
  
#####  
215 # #  
# MODEL PARAMETERS #  
# #  
#####
```

```

220 # -- Isotope reference
R17_VSMOW = 0.0003799 # -
R18_VSMOW = 0.0020052 # -

# -- Reference line
225 RL = 0.528 #

# -- Physical constants
Vm = 24.5 # L/mol

# -- 17O fractionations
230 lambda_kinetic = 0.509 # (Young et al., 2002)
lambda_equilibration = 0.5229 # (Barkan and Luz, 2012)

# -- 18O fractionations
235 a180_diff = 8.8 # permil (Farquhar et al., 1993)
a180_liq = 0.8 # permil (Farquhar et al., 1993)
a180_eq = 42.2 # permil (Brenninkmeijer et al., 1983)

#####
#
240 # CALCULATION #
# #
#####

# ==== CO2 MIXING RATIOS

245 # -- CO2 assimilation
CO2_assimilation = An*1.0e-6*Aleaf*1.0e-4 # molCO2/s

# -- Test key1
250 if (key1=='airflow'):

# -- CO2 fluxes
CO2_inflow = airflow/60.0/Vm*Ce*1.0e-6 # molCO2/s
CO2_outflow = CO2_inflow-CO2_assimilation # molCO2/s
255 # -- Cuvette condition
Ca = CO2_outflow/(airflow/60.0)*Vm*1.0e6 # ppm

# -- Test key1
260 if (key1=='drawdown'):

# -- Airflow
airflow = CO2_assimilation*60.0*Vm/(drawdown*1.0e-6) # L/min

265 # -- Cuvette condition
Ca = Ce-drawdown # ppm

# -- Mesophyll conductance

```

```

270 gm180 = 3.0*gm13C # mol/(m2s)
# -- Test key2
if (key2=='gs'):
275     # -- Intercellular CO2 mixing ratio
    Ci = Ca-An/gs # ppm
    # -- Mesophyll CO2 mixing ratio
    Cm = Ci-An/gm180 # ppm
280 # -- Test key2
if (key2=='Ci_Ca'):
    # -- Intercellular CO2 mixing ratio
285     Ci = Ci_Ca*Ca # ppm
    # -- Mesophyll CO2 mixing ratio
    Cm = Ci-An/gm180 # ppm
    # -- Stomatal conductance
290     gs = An/(Ca-Ci) # mol/(m2s)
# -- Test key2
if (key2=='Cm_Ca'):
295     # -- Mesophyll CO2 mixing ratio
    Cm = Cm_Ca*Ca # ppm
    # -- Combined stomatal-mesophyll conductance
300     gtot = An/(Ca-Cm) # mol/(m2s)
    # -- Stomatal conductance
    gs = 1.0/(1.0/gtot-1.0/gm180) # mol/(m2s)
    # -- Intercellular CO2 mixing ratio
305     Ci = Ca-An/gs # ppm
# ==== C1700 MIXING RATIOS
# -- Mesophyll C1700 mixing ratio
310 d170m =
1000.0*((d170_leaf/1000.0+1)*((a180_eq/1000.0+1.0)**lambda_equilibration)-1.0) #
permil VSMOW
R17m = (d170m/1000.0+1.0)*R17_VSMOW # -
Cm_170 = 2*R17m*Cm # ppm
315 # -- C1700 conductances
gs_170 = gs*((1.0-a180_diff/1000.0)**lambda_kinetic) # mol/(m2s)
gm180_170 = gm180*((1.0-a180_liq/1000.0)**lambda_kinetic) # mol/(m2s)

```

```

320 # -- Ingoing C1700 mixing ratio
R17e = (d17Oin/1000.0+1.0)*R17_VSMOW # -
Ce_170 = 2*R17in*Ce # ppm

# -- C1700 signature
325 d170a = d17Oin # permil VSMOW
max_qq = 100 # -
relax_qq = 0.5 # -
for qq in np.arange(max_qq):

330 # -- Atmospheric C1700 mixing ratio
R17a = (d170a/1000.0+1.0)*R17_VSMOW # -
Ca_170 = 2*R17a*Ca # ppm

# -- Intercellular d170 signature
335 Ce_170 = (Ca_170*gs_170+Cm_170*gm180_170)/(gs_170+gm180_170) # ppm
R17i = 0.5*Ci_170/Ci # -
d170i = 1000.0*(R17i/R17_VSMOW-1.0) # permil VSMOW

# -- Calculate C1700 fluxes
340 inflow_C1700 = airflow/60.0/Vm*Ce_170*1.0e-6 # molC1700/s
leafuptake_C1700 = (Ca_170-Ci_170)*gs_170*1.0e-6*Aleaf*1.0e-4 # molC1700/s
outflow_C1700 = inflow_C1700-leafuptake_C1700 # molC1700/s

# -- Copy previous d170a signature
345 d170a_prev = d170a # permil VSMOW

# -- Calculate new d170a signature
Ca_170 = outflow_C1700/(airflow/60.0)*Vm*1.0e6 # ppm
R17a = 0.5*Ca_170/Ca # -
350 d170a_diff = 1000.0*(R17a/R17_VSMOW-1.0)-d170a # permil VSMOW
d170a = d170a+relax_qq*d170a_diff # permil VSMOW

# -- Print diagnostics
if (print_diag_d170a):
355 print ('-----')
print ('d170a iteration ', qq+1)
print ('-----')
print ('Ca_170          ', Ca_170)
print ('Ci_170          ', Ci_170)
360 print ('Cm_170          ', Cm_170)
print ('R17a            ', R17a)
print ('R17i            ', R17i)
print ('R17m            ', R17m)
print ('d170in          ', d170e)
365 print ('d170a            ', d170a)
print ('d170i            ', d170i)
print ('d170m            ', d170m)
print ('-----')
print()
370

```



```

# -- Clear loop index
del qq

# -- Determine convergence
375 conv_d170a = np.abs((d170a-d170a_prev)/d170a_prev) # -

# -- Test convergence
if (conv_d170a > 1.0e-6):
380     print ('WARNING: Convergence in outgoing d170 signature less than 1.0e-6')
     print ('conv ', conv_d170a)
     print()

# ==== C1800 MIXING RATIOS

385 # -- Mesophyll C1800 mixing ratio
d180m = 1000.0*((d180_leaf/1000.0+1)*(a180_eq/1000.0+1.0)-1.0) # permil VSMOW
R18m = (d180m/1000.0+1.0)*R18_VSMOW # -
Cm_180 = 2*R18m*Cm # ppm

390 # -- C1800 conductances
gs_180 = gs*(1.0-a180_diff/1000.0) # mol/(m2s)
gm180_180 = gm180*(1.0-a180_liq/1000.0) # mol/(m2s)

# -- Ingoing C1800 mixing ratio
395 R18e = (d180e/1000.0+1.0)*R18_VSMOW # -
Ce_180 = 2*R18in*Ce # ppm

# -- C1800 signature
400 d180a = d180e # permil VSMOW
max_pp = 100 # -
relax_pp = 0.5 # -
for pp in np.arange(max_pp):

    # -- Atmospheric C1800 mixing ratio
405 R18a = (d180a/1000.0+1.0)*R18_VSMOW # -
    Ca_180 = 2*R18a*Ca # ppm

    # -- Intercellular d180 signature
410 Ci_180 = (Ca_180*gs_180+Cm_180*gm180_180)/(gs_180+gm180_180) # ppm
    R18i = 0.5*Ci_180/Ci # -
    d180i = 1000.0*(R18i/R18_VSMOW-1.0) # permil VSMOW

    # -- Calculate C1800 fluxes
415 inflow_C1800 = airflow/60.0/Vm*Cin_180*1.0e-6 # molC1800/s
    leafuptake_C1800 = (Ca_180-Ci_180)*gs_180*1.0e-6*Aleaf*1.0e-4 # molC1800/s
    outflow_C1800 = inflow_C1800-leafuptake_C1800 # molC1800/s

    # -- Copy previous d180a signature
420 d180a_prev = d180a # permil VSMOW

    # -- Calculate new d180a signature

```

```

Ca_180 = outflow_C1800/(airflow/60.0)*Vm*1.0e6 # ppm
R18a = 0.5*Ca_180/Ca # -
d180a_diff = 1000.0*(R18a/R18_VSMOW-1.0)-d180a # permil VSMOW
425 d180a = d180a+relax_pp*d180a_diff # permil VSMOW

# -- Print diagnostics
if (print_diag_d180a):
430     print ('-----')
         print ('d180a iteration ', pp+1)
         print ('-----')
         print ('Ca_180          ', Ca_180)
         print ('Ci_180          ', Ci_180)
         print ('Cm_180          ', Cm_180)
435     print ('R18a           ', R18a)
         print ('R18i           ', R18i)
         print ('R18m           ', R18m)
         print ('d180in         ', d180e)
         print ('d180a          ', d180a)
440     print ('d180i          ', d180i)
         print ('d180m          ', d180m)
         print ('-----')
         print()

445 # -- Clear loop index
del pp

# -- Determine convergence
conv_d180a = np.abs((d180a-d180a_prev)/d180a_prev) # -
450

# -- Test convergence
if (conv_d180a > 1.0e-6):
         print ('WARNING: Convergence in outgoing d180 signature less than 1.0e-6')
455     print ('conv ', conv_d180a)
         print()

# ==== EXCESS-170

# -- Calculate e170 in regions
460 e170e = 1.0e6*(np.log(d170e/1000.0+1.0)-RL*np.log(d180e/1000.0+1.0)) # per meg
e170a = 1.0e6*(np.log(d170a/1000.0+1.0)-RL*np.log(d180a/1000.0+1.0)) # per meg
e170i = 1.0e6*(np.log(d170i/1000.0+1.0)-RL*np.log(d180i/1000.0+1.0)) # per meg
e170m = 1.0e6*(np.log(d170m/1000.0+1.0)-RL*np.log(d180m/1000.0+1.0)) # per meg

465 #####
#
# RESULTS
#
#####

470 # -- Test print settings
if print_table:

```

```

# -- Print parameters
475 print ('=====')
print ('CO2 mixing ratios')
print ('  ingoing      Ce      %8.1f   ppm' %(Ce))
print (' atmosphere   Ca      %8.1f   ppm' %(Ca))
480 print (' intercellular Ci      %8.1f   ppm' %(Ci))
print (' mesophyll     Cm      %8.1f   ppm' %(Cm))
print
print ('d17O signatures')
print ('  ingoing      d17Oe %8.1f   permil VSMOW' %(d17Oe))
485 print (' atmosphere   d17Oa %8.1f   permil VSMOW' %(d17Oa))
print (' intercellular d17Oi %8.1f   permil VSMOW' %(d17Oi))
print (' mesophyll     d17Om %8.1f   permil VSMOW' %(d17Om))
print
print ('d18O signatures')
490 print ('  ingoing      d18Oe %8.1f   permil VSMOW' %(d18Oe))
print (' atmosphere   d18Oa %8.1f   permil VSMOW' %(d18Oa))
print (' intercellular d18Oi %8.1f   permil VSMOW' %(d18Oi))
print (' mesophyll     d18Om %8.1f   permil VSMOW' %(d18Om))
print
print ('e17O signature')
495 print ('  ingoing      e17Oe %8.2f   per meg' %(e17Oe))
print (' atmosphere   e17Oa %8.2f   per meg' %(e17Oa))
print (' intercellular e17Oi %8.2f   per meg' %(e17Oi))
print (' mesophyll     e17Om %8.2f   per meg' %(e17Om))
print ('=====')
500 print()

```

```

return d17Oa, d18Oa, e17Oa

```

505

### 3. Derivation of the <sup>18</sup>O-photosynthetic discrimination

Following (Farquhar and Lloyd, 1993), the assimilation rate for C<sup>16</sup>O<sup>16</sup>O is calculated as:

510

$$A = \frac{c_a - c_m}{r_m} \quad (\text{S2})$$

where  $A$ ,  $r_m$ ,  $c_a$ ,  $c_m$  are the assimilation rate, resistance as CO<sub>2</sub> diffuses from the leaf surrounding to the CO<sub>2</sub>-H<sub>2</sub>O exchange site, the mole fraction of CO<sub>2</sub> in the air surrounding the leaf and at the CO<sub>2</sub>-H<sub>2</sub>O exchange site, respectively. The assimilation rate for C<sup>18</sup>O<sup>16</sup>O is calculated as:

515

$${}^{18}\text{R}_A \times A = \frac{{}^{18}\text{R}_a \times c_a - {}^{18}\text{R}_m \times c_m}{\alpha^{18}_m \times r_m} \quad (\text{S3})$$

where  $\alpha^{18}_m$  is the fractionation factor as  $\text{C}^{18}\text{O}^{16}\text{O}$  diffuses from the leaf surrounding to the  $\text{CO}_2\text{-H}_2\text{O}$  exchange site. Dividing equation 2 by equation 1 leads to:

520

$${}^{18}\text{R}_A = \frac{{}^{18}\text{R}_a \times c_a - {}^{18}\text{R}_m \times c_m}{\alpha^{18}_m \times (c_a - c_m)} \quad (\text{S4})$$

$$\frac{{}^{18}\text{R}_A}{{}^{18}\text{R}_a} = \frac{c_a - \frac{{}^{18}\text{R}_m}{{}^{18}\text{R}_a} \times c_m}{\alpha^{18}_m \times (c_a - c_m)} \quad (\text{S5})$$

$$\frac{{}^{18}\text{R}_a}{{}^{18}\text{R}_A} = \frac{\alpha^{18}_m \times (c_a - c_m)}{c_a - \frac{{}^{18}\text{R}_m}{{}^{18}\text{R}_a} \times c_m} \quad (\text{S6})$$

$$\frac{{}^{18}\text{R}_a}{{}^{18}\text{R}_A} - 1 = \frac{\alpha^{18}_m \times (c_a - c_m)}{c_a - \frac{{}^{18}\text{R}_m}{{}^{18}\text{R}_a} \times c_m} - 1 \quad (\text{S7})$$

Using the definitions

525

$$\Delta_A {}^{18}\text{O}_{\text{FM}} = \frac{{}^{18}\text{R}_a}{{}^{18}\text{R}_A} - 1 \quad (\text{S8})$$

And

$$\delta^{18}\text{O}_{\text{ma}} = \frac{{}^{18}\text{R}_m}{{}^{18}\text{R}_a} - 1 \quad (\text{S9})$$

This can be rewritten as

$$\Delta_A {}^{18}\text{O}_{\text{FM}} = \frac{\alpha^{18}_m \times (c_a - c_m)}{c_a - c_m \times (\delta^{18}\text{O}_{\text{ma}} + 1)} - 1 \quad (\text{S10})$$

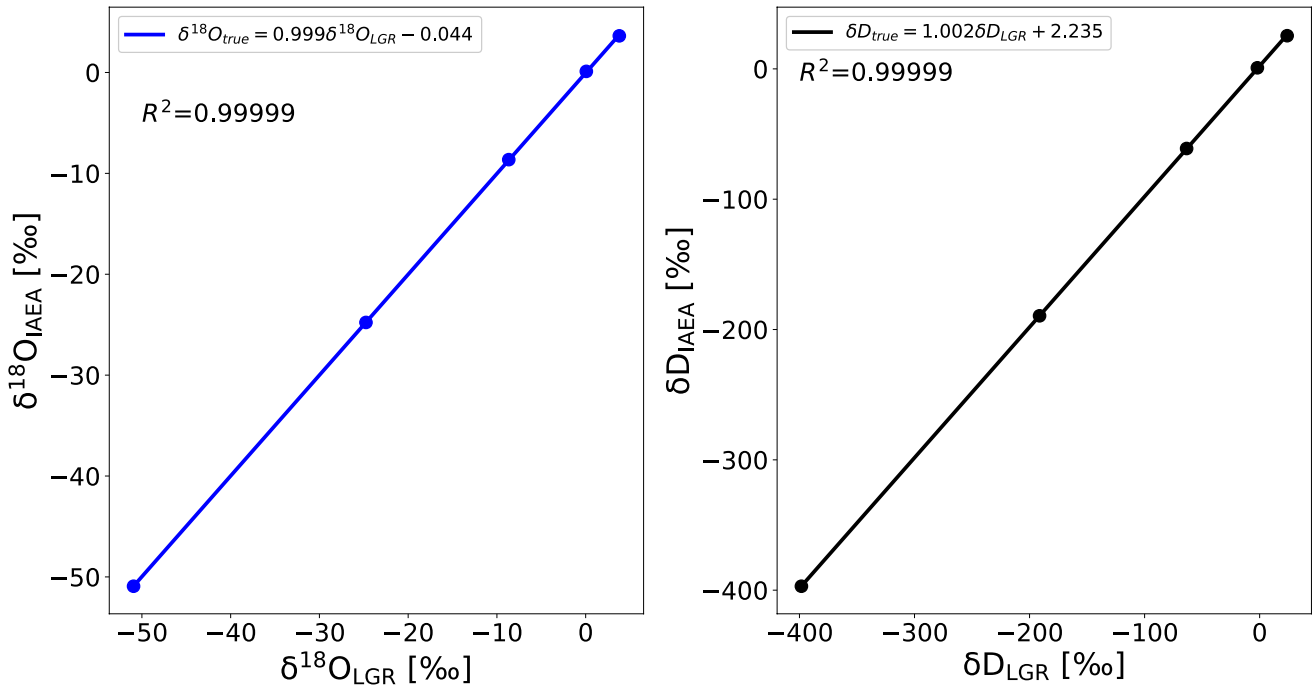
530

$$\Delta_A^{18}\text{O}_{\text{FM}} = \frac{\bar{a}_{18} + \frac{c_m}{c_a - c_m} \times \delta^{18}\text{O}_{\text{ma}}}{1 - \frac{c_m}{c_a - c_m} \times \delta^{18}\text{O}_{\text{ma}}} \quad (\text{S11})$$

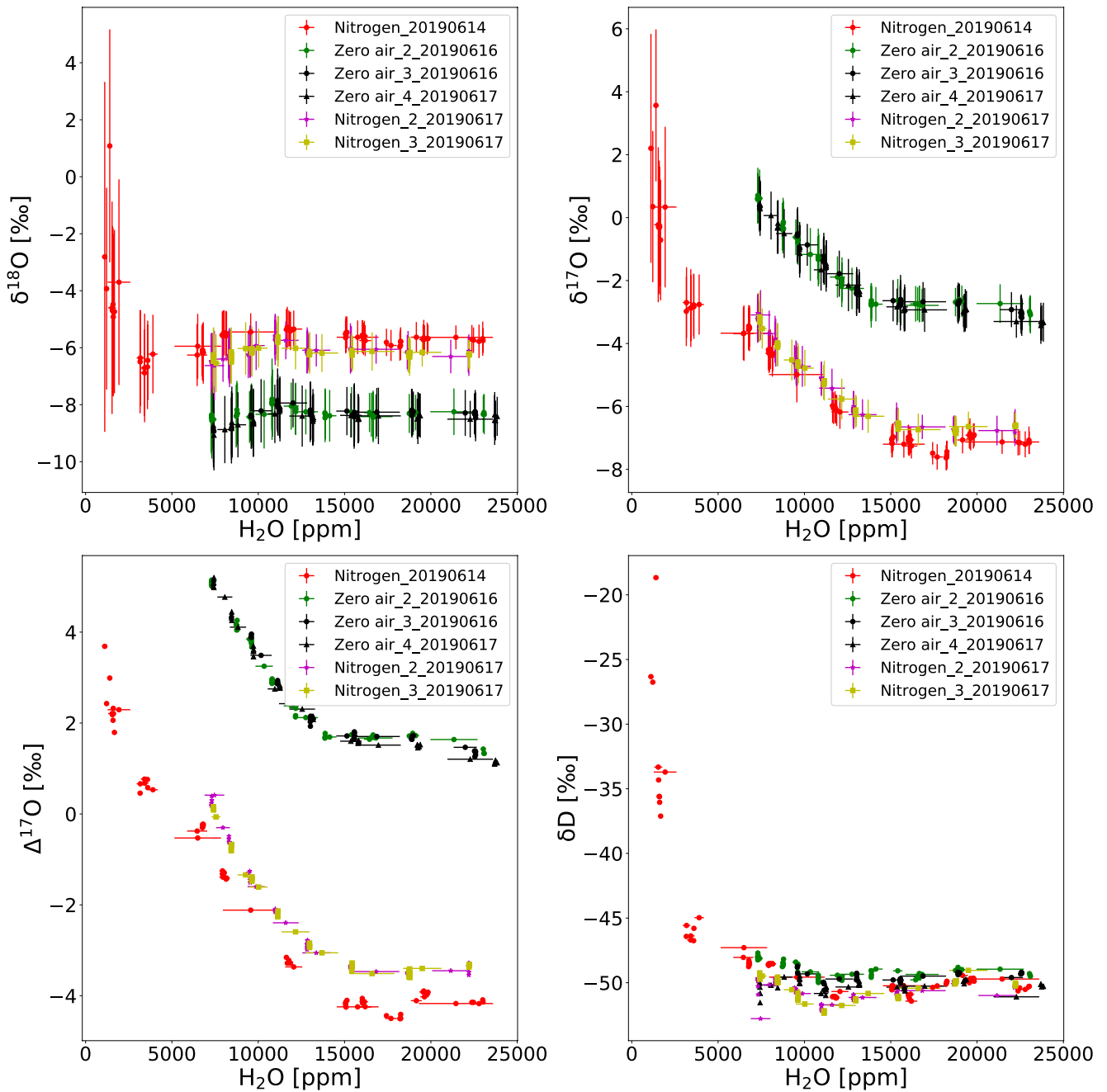
$\Delta_A^{17}\text{O}_{\text{FM}}$  can be calculated analogous to  $\Delta_A^{18}\text{O}_{\text{FM}}$ .

535

$$\Delta_A^{17}\text{O}_{\text{FM}} = \frac{\bar{a}_{17} + \frac{c_m}{c_a - c_m} \times \delta^{17}\text{O}_{\text{ma}}}{1 - \frac{c_m}{c_a - c_m} \times \delta^{17}\text{O}_{\text{ma}}} \quad (\text{S12})$$

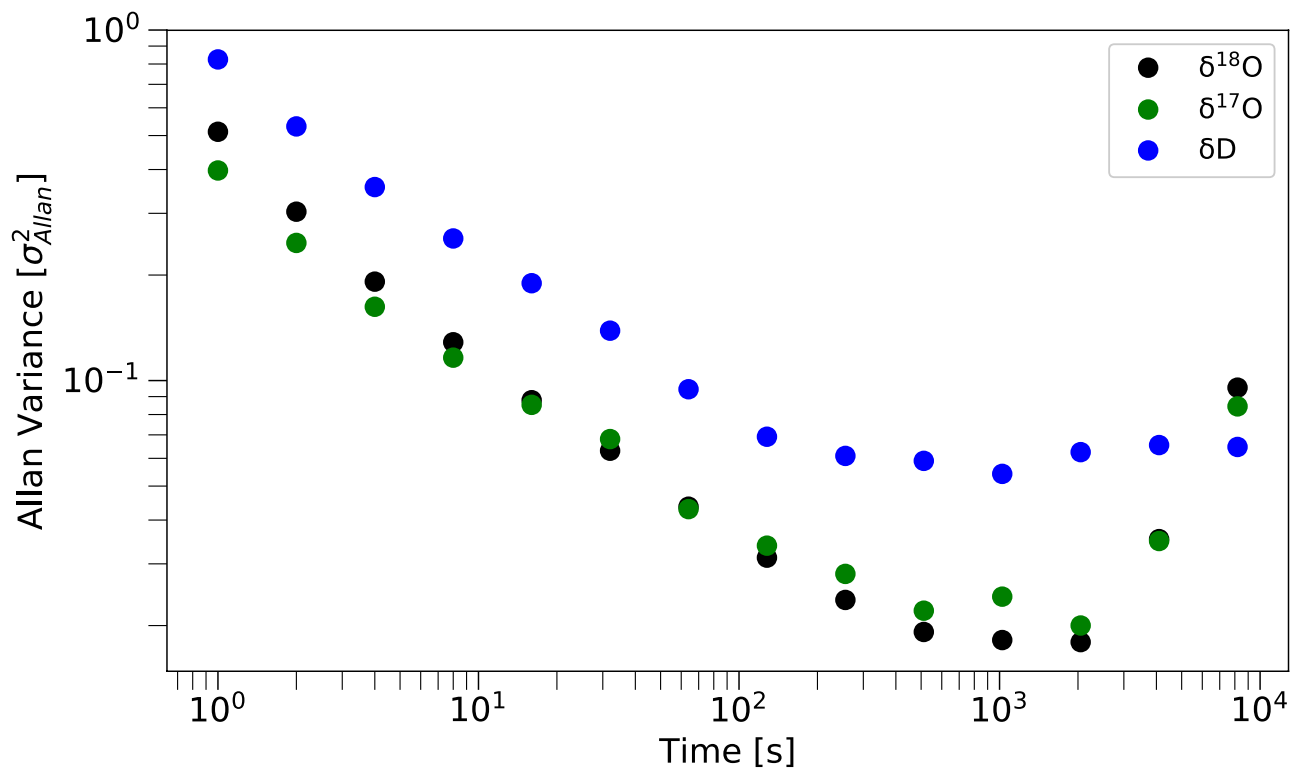


540 Figure S1. Calibration of the LGR water isotope analyser for the measurement of  $\delta^{18}\text{O}$  and  $\delta\text{D}$  of water vapor. a)  $\delta^{18}\text{O}_{\text{IAEA}}$  is the value assigned by IAEA while  $\delta^{18}\text{O}_{\text{LGR}}$  is the value reported by the LGR instrument. b)  $\delta\text{D}_{\text{IAEA}}$ , is the value assigned by IAEA while  $\delta\text{D}_{\text{LGR}}$  is the value reported by the LGR instrument.

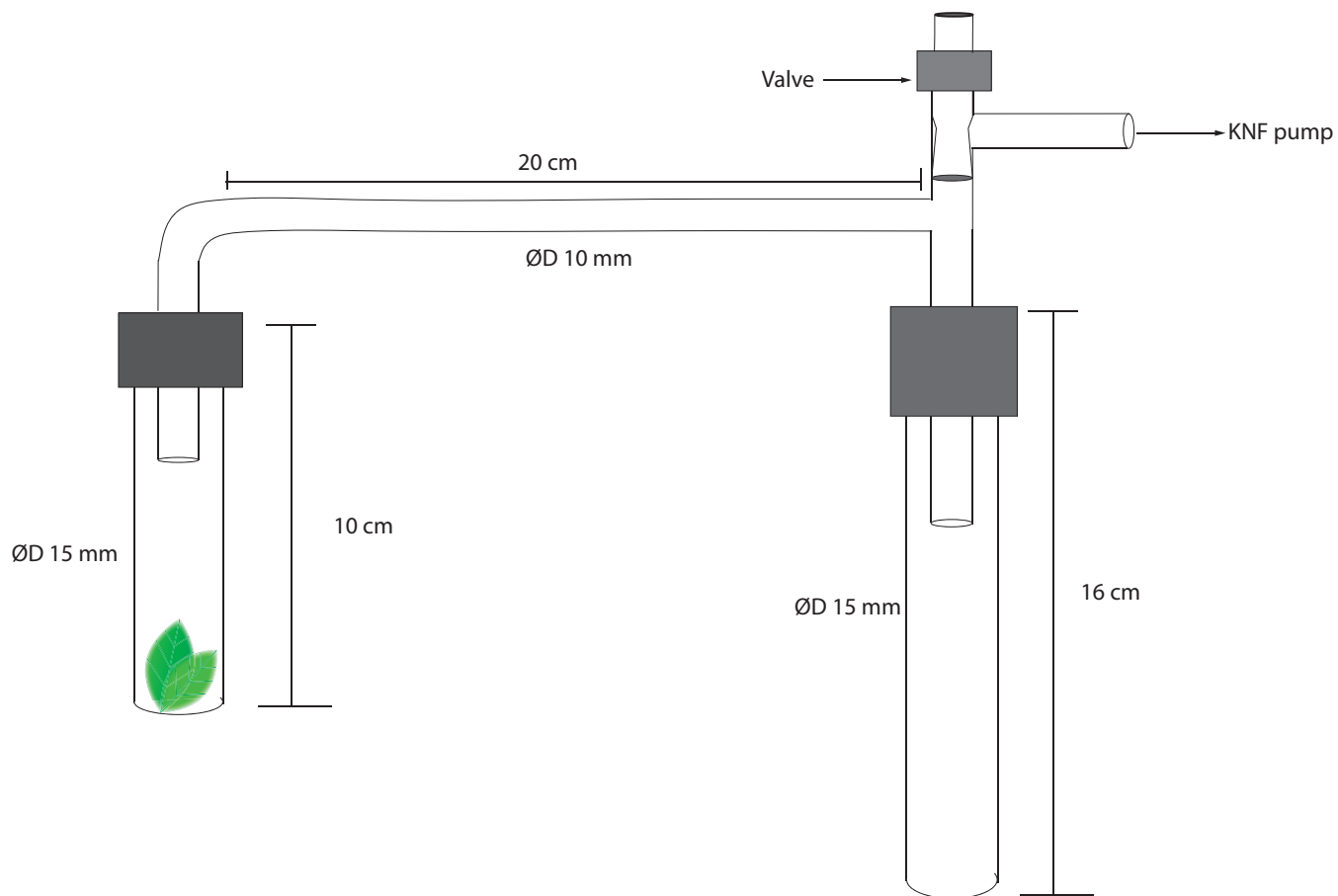


545

Figure S2 Dependency of isotope composition of water vapour on the water vapor concentration and the carrier gas used for the water vapor standard source for  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ ,  $\Delta^{17}\text{O}$  and  $\delta\text{D}$ .



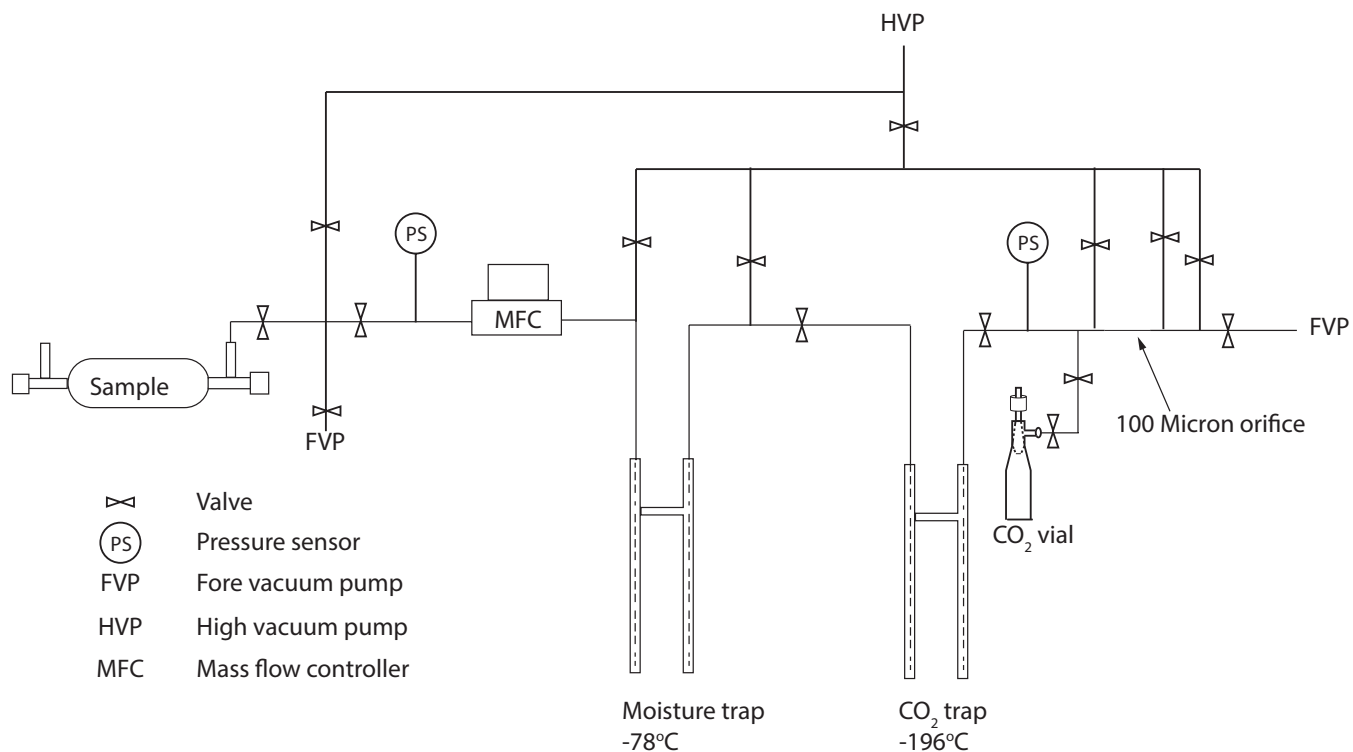
550 Figure S3 Allan variance curves of  $\delta\text{D}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for measurement at 20000 ppm water vapor concentration.



555

**Figure S4** Schematic drawing of the setup used for the extraction of leaf water. The vial containing the leaf is heated to 60°C while the other vial is immersed in the liquid nitrogen to collect the water vapor.





560

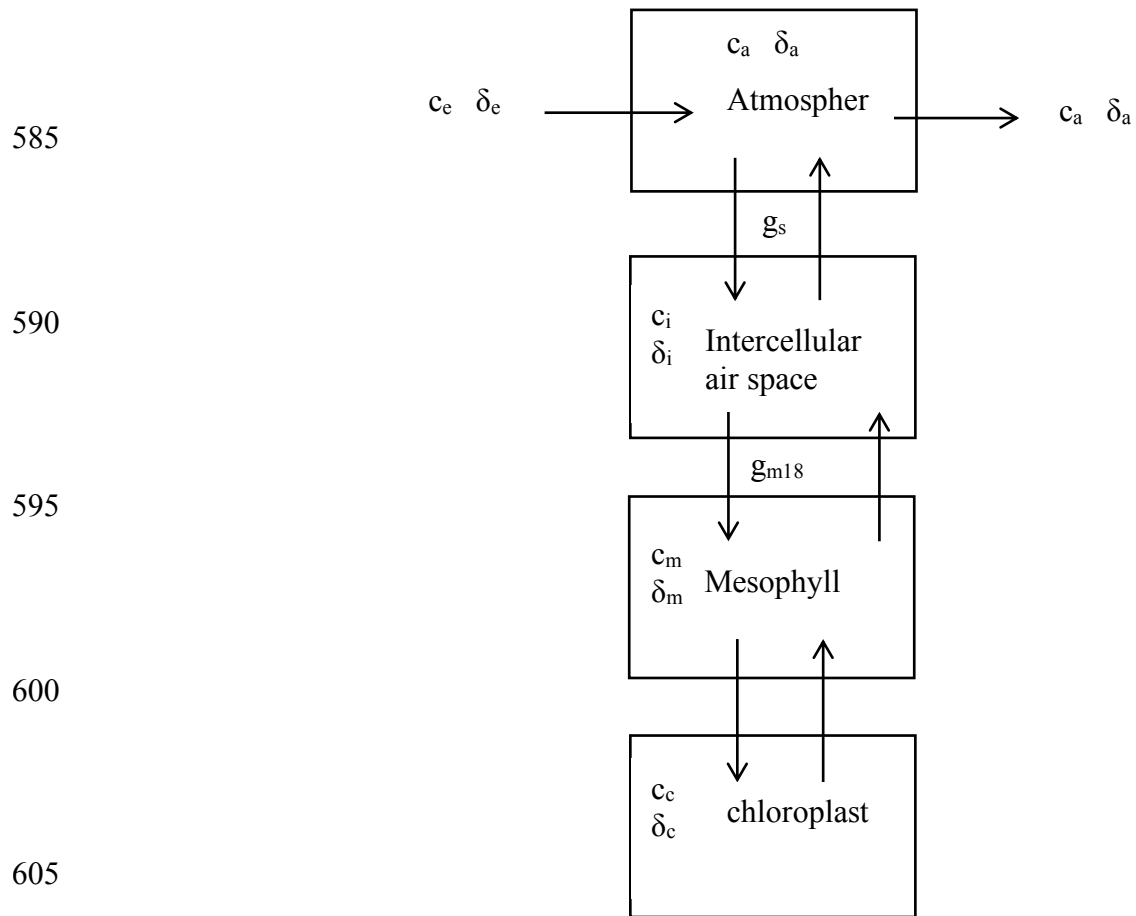
**Figure S5** Schematic diagram of the system used for the extraction of carbon dioxide from air samples. The moisture trap is cooled by a dry ice-ethanol mixture while the CO<sub>2</sub> trap is cooled by liquid nitrogen.

565

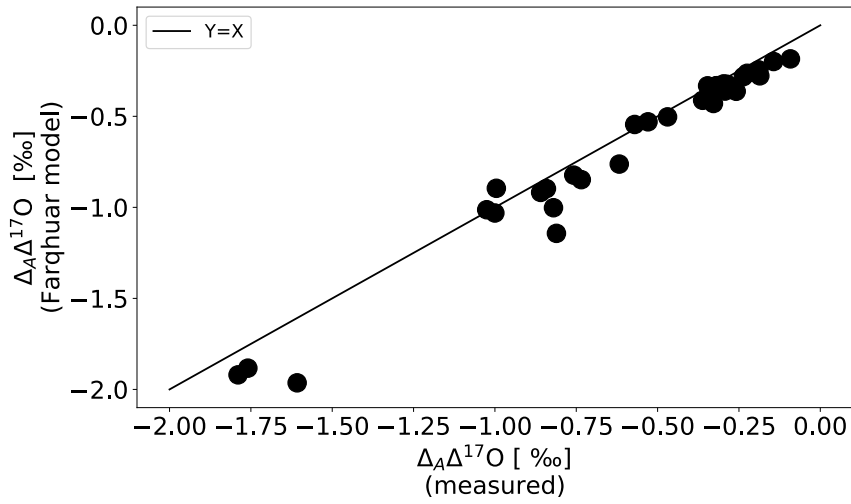
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610 Figure S6 Schematic diagram of the conceptual leaf-cuvette model.  $\delta$  and  $c$  are the oxygen isotope composition and mixing ratio of  $\text{CO}_2$ . The subscript  $e, a, i, m, c$  represents  $\text{CO}_2$  entering the cuvette, leaving the cuvette, the intercellular air space, the mesophyll and the chloroplast, respectively.



615

Figure S7 The correlation between the observed  $\Delta_A \Delta^{17}\text{O}$  (calculated using equation 12) and  $\Delta_A \Delta^{17}\text{O}$  estimated from the Farquhar model ( $\Delta_A \Delta^{17}\text{O}_{\text{FM}} = \ln(\Delta_A^{17}\text{O}_{\text{FM}} + 1) - 0.528 \times \ln(\Delta_A^{18}\text{O}_{\text{FM}} + 1)$ ).

620

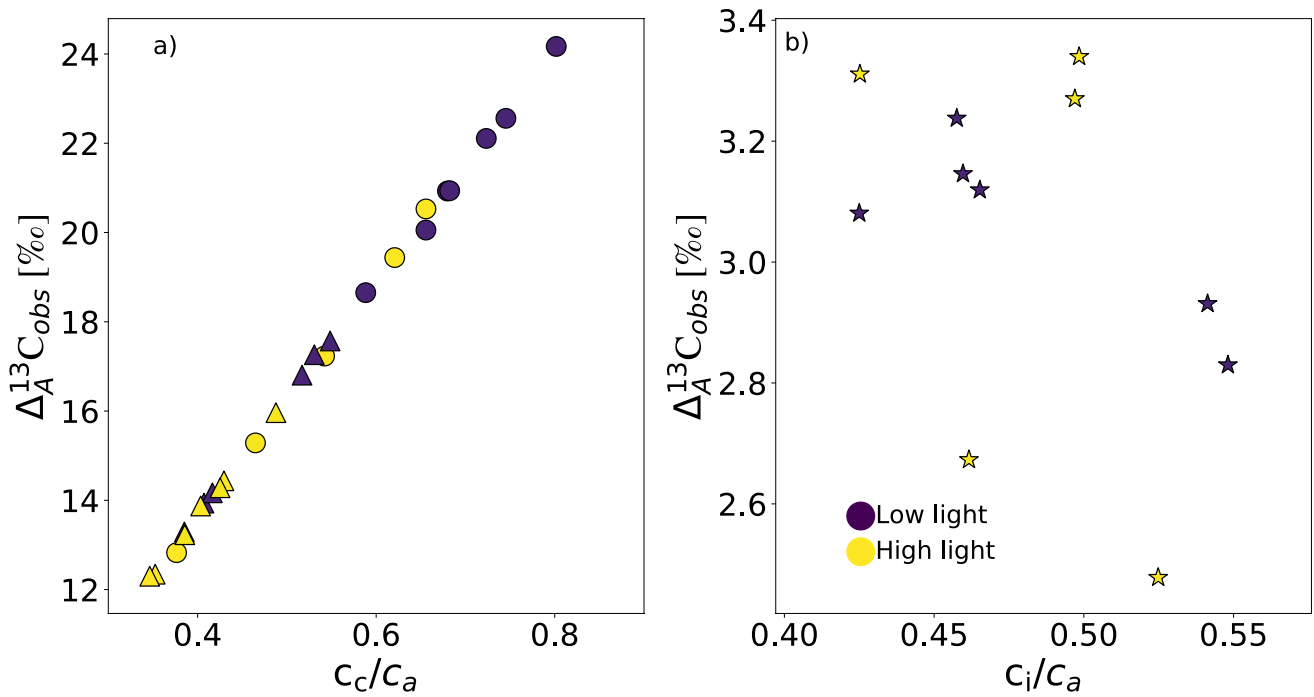


Figure 8.  $\Delta_A^{13}\text{C}$  of carbon dioxide during photosynthesis. a) The  $\Delta_A^{13}\text{C}$  of the two  $\text{C}_3$  plants sunflower (circles) and ivy (triangles) at two different irradiances. b) The  $\Delta_A^{13}\text{C}$  of maize at two different irradiances. 625 The measurement error in  $\Delta_A^{13}\text{C}_{\text{obs}}$  is 0.15‰ (SD), calculated using error propagation.

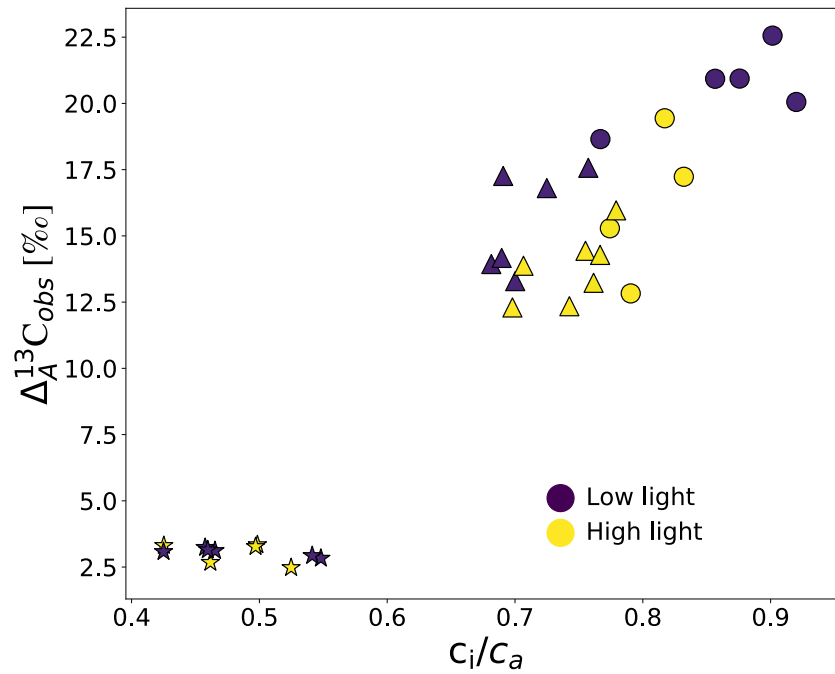
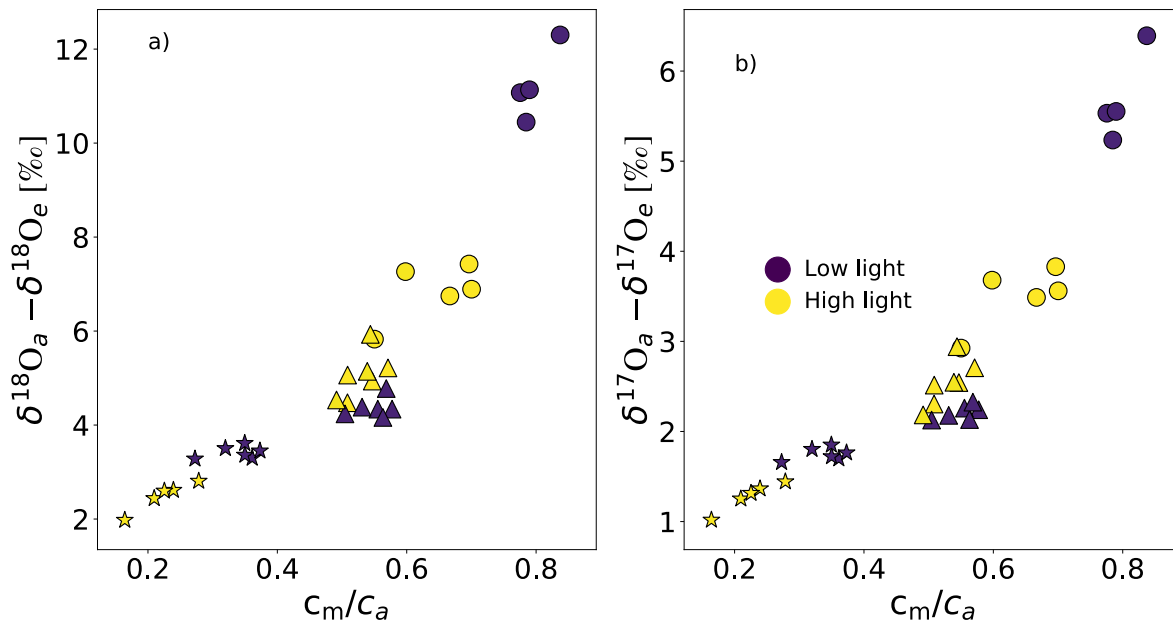


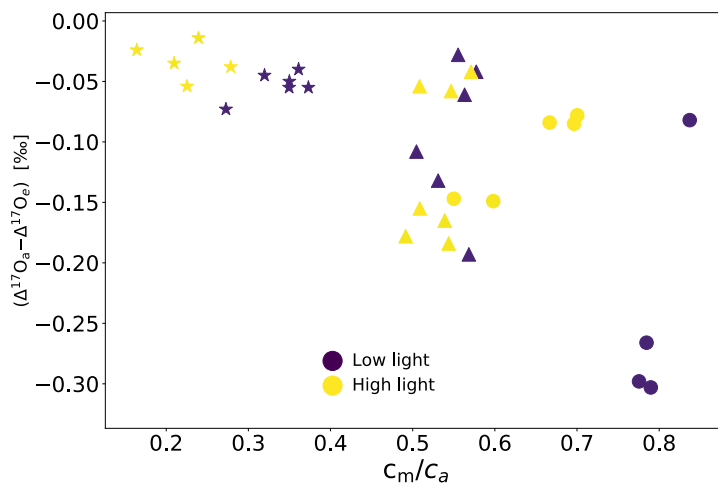
Figure S9.  $\Delta_A^{13}\text{C}$  of carbon dioxide during photosynthesis. The  $\Delta_A^{13}\text{C}$  of the two  $\text{C}_3$  plants sunflower (circle) and ivy (triangles) and a  $\text{C}_4$  plant maize (stars). 630



635

Figure S10. The relative difference in  $\delta^{17}\text{O}$  (a) and  $\delta^{18}\text{O}$  (b) of  $\text{CO}_2$  leaving (index a) and entering (index e) the leaf cuvette during experiments with two  $\text{C}_3$  plants, sunflower (circles) and ivy (triangles) and a  $\text{C}_4$  plant maize (stars) as a function of the  $c_m/c_a$  ratio. The experiments were performed at low light ( $300 \mu\text{mol m}^{-2}\text{s}^{-1}$ , purple) and high light ( $1200 \mu\text{mol m}^{-2}\text{s}^{-1}$ , yellow) conditions.

640



645

Figure S11 The difference in  $\Delta^{17}\text{O}$  of the  $\text{CO}_2$  leaving (index a) and entering (index e) the cuvette as a function of  $c_m/c_a$  for sunflower (circles), ivy (triangles) and maize (stars).

650

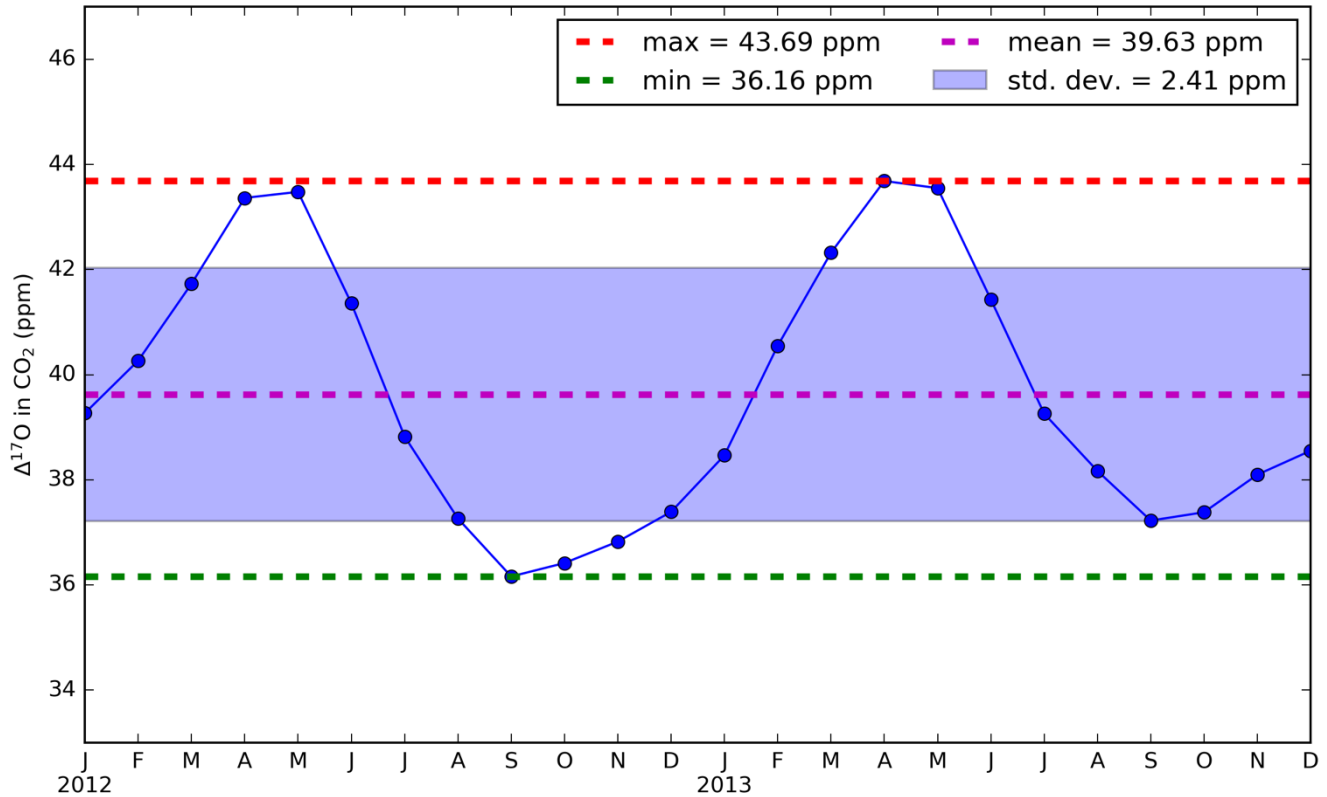


Figure S12. 3D model result for the global average seasonal cycle of  $\Delta^{17}\text{O}$  of atmospheric  $\text{CO}_2$  for the years 2012 and 2013 (Koren et al., 2019). Note that  $\Delta^{17}\text{O}$  value is reported here with  $\lambda$  value of 0.5229.

655 To convert to the  $\lambda$  value of 0.528,  $\Delta^{17}\text{O}(\text{CO}_2)_{\lambda=0.528} = \Delta^{17}\text{O}(\text{CO}_2)_{\lambda=0.5229} + (0.5229 - 0.528) \times \ln(\delta^{18}\text{O}(\text{CO}_2) + 1)$ . In the 3D global model,  $\delta^{18}\text{O}(\text{CO}_2)$  is 41.5‰.

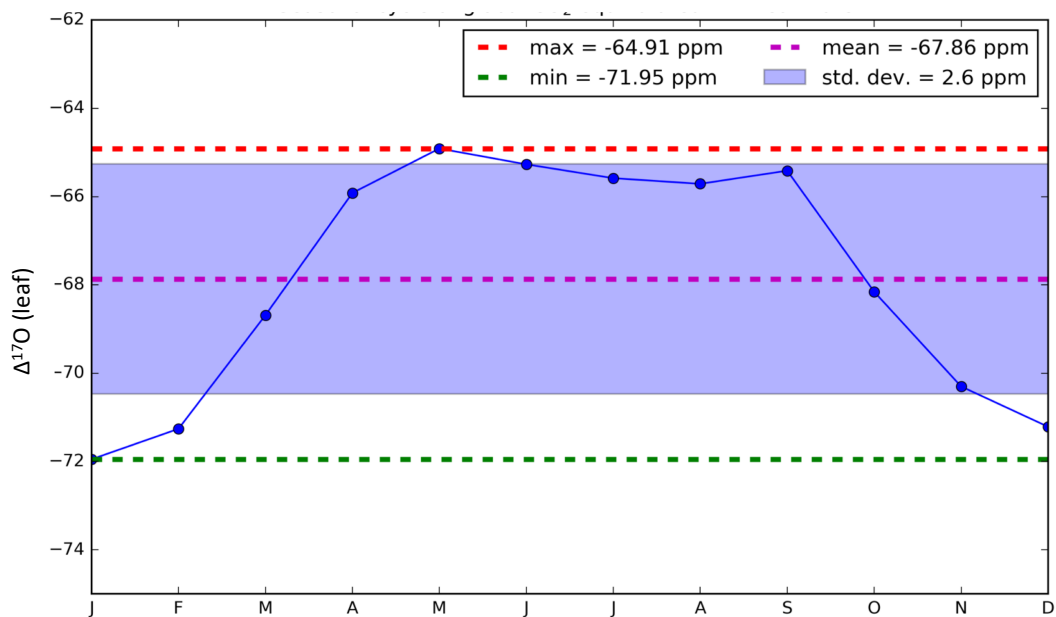
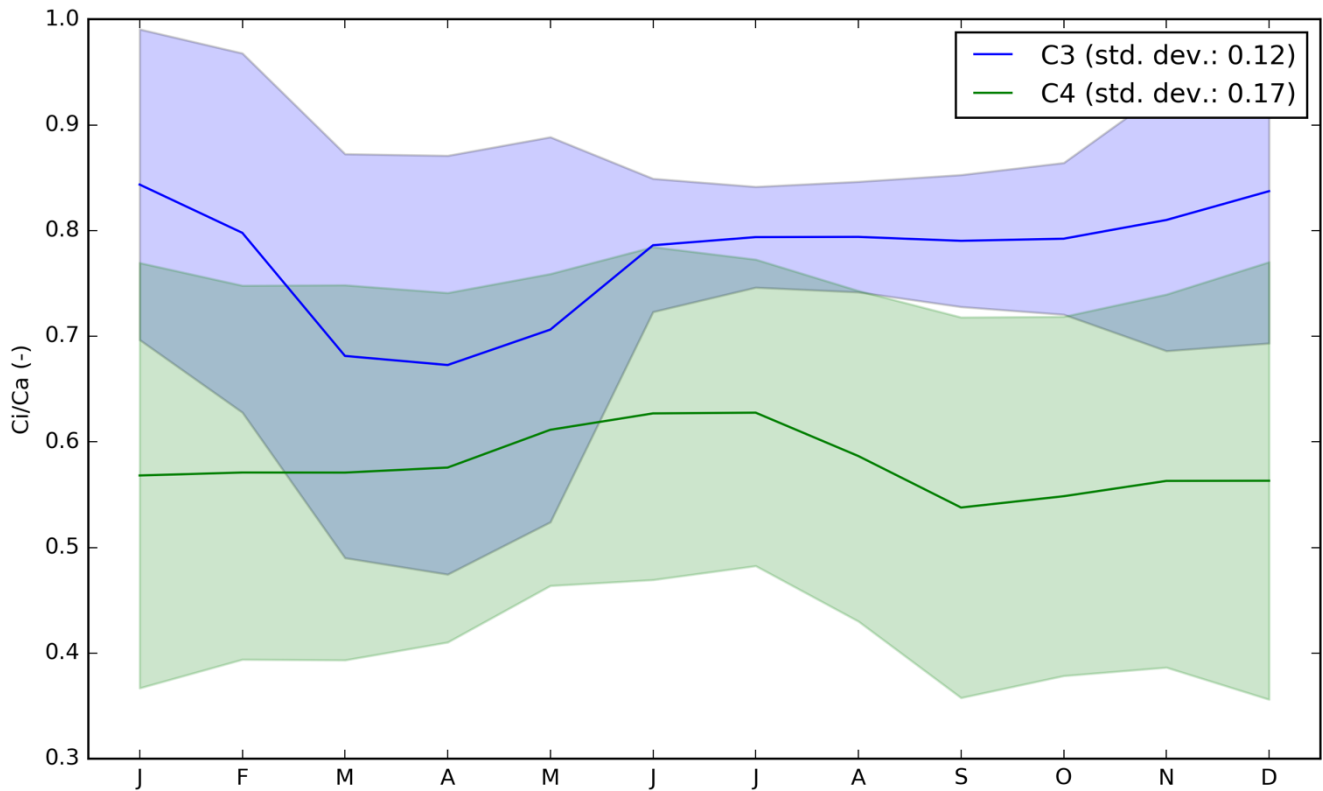


Figure S13. A 3D model result for the seasonal cycle of the global  $\Delta^{17}\text{O}$  value of leaf water for the year 2012 (Koren et al., 2019). Note that  $\Delta^{17}\text{O}$  value is reported here with  $\lambda$  value of 0.5229. To convert to the  $\lambda$  value of 0.528,  $\Delta^{17}\text{O}(\text{leaf})_{\lambda=0.528} = \Delta^{17}\text{O}(\text{leaf})_{\lambda=0.5229} + (0.5229 - 0.528) \times \ln \alpha_{\text{trans}}$ .  $\alpha_{\text{trans}} = 1/0.9917$  (Koren et al., 2019; Hofmann et al., 2017).



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Figure S14 Annual variability of  $c_i/c_a$  ratio for C<sub>4</sub> and C<sub>3</sub> plants from SiBCASA model (Schaefer et al., 2008;Koren et al., 2019).

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Table S1 Reproducibility of the extraction system and the CO<sub>2</sub>-O<sub>2</sub> exchange system. Extraction reproducibility experiments were performed using compressed air. To establish the reproducibility of the CO<sub>2</sub>-O<sub>2</sub> isotope exchange system we used pure CO<sub>2</sub> (SCOTT, Air Products, Germany). *SE and SD* is a standard error and standard deviation. All the isotope values given in the table are in per mill [‰].

675

Extraction system reproducibility				
Extraction	$\delta^{18}\text{O}$	SE	$\delta^{13}\text{C}$	SE
03/03/2019	41.411	0.005	-8.636	0.004
03/03/2019	41.352	0.006	-8.642	0.003
03/03/2019	41.355	0.020	-8.636	0.005
04/03/2019	41.314	0.008	-8.647	0.007
04/03/2019	41.359	0.007	-8.651	0.004
05/03/2019	41.297	0.006	-8.648	0.004
05/03/2019	41.330	0.008	-8.652	0.004



05/03/2019	41.387	0.005	-8.648	0.004			
06/03/2019	41.368	0.010	-8.660	0.004			
06/03/2019	41.369	0.007	-8.653	0.004			
06/03/2019	41.329	0.008	-8.652	0.003			
07/03/2019	41.373	0.007	-8.646	0.004			
07/03/2019	41.324	0.007	-8.646	0.004			
07/03/2019	41.352	0.007	-8.643	0.002			
Mean $\pm$ SD	41.351 $\pm$ 0.030		-8.647 $\pm$ 0.007				
CO <sub>2</sub> -O <sub>2</sub> exchange system reproducibility							
EXP	Pre-exchange O <sub>2</sub>		Post-exchange O <sub>2</sub>		Pre-exchange CO <sub>2</sub>		
	$\delta^{17}\text{O}_i$	$\delta^{18}\text{O}_i$	$\delta^{17}\text{O}_f$	$\delta^{18}\text{O}_f$	$\delta^{18}\text{O}_i$	$\delta^{17}\text{O}_i$	$\Delta^{17}\text{O}_i$
1	9.254	18.542	10.949	21.591	25.803	13.3967	-0.143
2	9.254	18.542	10.986	21.649	25.803	13.4066	-0.134
3	9.254	18.542	10.972	21.638	25.803	13.3907	-0.149
4	9.254	18.542	10.967	21.637	25.803	13.3823	-0.158
5	9.254	18.542	10.934	21.571	25.803	13.3894	-0.151
6	9.254	18.542	10.942	21.575	25.803	13.4006	-0.140
7	9.254	18.542	11.080	21.818	25.803	13.4061	-0.134
8	9.254	18.542	11.038	21.760	25.803	13.3868	-0.153
9	-20.85	-38.2	-4.373	-7.288	25.803	13.401	-0.139
10	-20.85	-38.2	-4.210	-6.9804	25.803	13.3978	-0.142
11	-20.85	-38.2	-4.497	-7.520	25.803	13.4003	-0.140
12	-20.85	-38.2	-3.987	-6.573	25.803	13.4103	-0.130
Mean $\pm$ SD						13.398 $\pm$ 0.009	-0.142 $\pm$ 0.008

Table S2: The ratio of stomatal conductance to mesophyll conductance and weighted mean fractionation of  $^{12}\text{C}^{18}\text{O}^{16}\text{O}$  as it diffuses from the  $\text{CO}_2\text{-H}_2\text{O}$  exchange site ( $\bar{a}_{18}$ ) for numerous species determined in previous investigations.

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$g_s/g_m$	$\bar{a}_{18}$	Plant type	Reference
1.56	3.93	<i>S. viridis</i> (C <sub>4</sub> )	(Osborn et al., 2017)
1.26	4.33	<i>S. viridis</i> (C <sub>4</sub> )	(Osborn et al., 2017)
0.22	7.37	Tobacco (C <sub>3</sub> )	(Gillon and Yakir, 2000)
0.16	7.71	Soya (C <sub>3</sub> )	(Gillon and Yakir, 2000)
0.47	6.23	Oak (C <sub>3</sub> )	(Gillon and Yakir, 2000)
0.17	7.76	Tobacco (C <sub>3</sub> )	(Barbour et al., 2016)
0.06	8.32	Cotton (C <sub>3</sub> )	(Barbour et al., 2016)
0.32	7.04	Wheat (C <sub>3</sub> )	(Barbour et al., 2016)
0.06	8.27	Maize (C <sub>4</sub> )	(Barbour et al., 2016)
0.24	7.29	<i>S. Viridis</i> (C <sub>4</sub> )	(Barbour et al., 2016)
0.29	7.21	<i>F. bidentis</i> (C <sub>4</sub> )	(Barbour et al., 2016)
0.88	5.05	Sunflower (C <sub>3</sub> )	This study
0.55	5.96	Ivy (C <sub>3</sub> )	This study
0.27	7.12	Maize (C <sub>4</sub> )	This study
1.2	4.18	<i>A. edulis</i> (C <sub>4</sub> )	(Cousins et al., 2006)
2.1	3.74	<i>A. edulis</i> (C <sub>4</sub> )	(Cousins et al., 2006)
0.13	7.90	<i>A. edulis</i> (C <sub>4</sub> )	(Cousins et al., 2007)

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ble S3 List of symbols and equations used for  $^{13}\text{C}$  discrimination calculation

Symbol	description	Unit/calculation/value	Ref
Gas exchange			
$t^{13}$	Ternary correction for	$\frac{(1+a_{13bs})E}{2g_{CO_2}^t}$	(Farquhar and Cernusak, 2013)
$eRd$	Dark respiration rate	$0.8 \mu\text{mol m}^{-2}\text{s}^{-1}$ [measured]	
$Rd$	Day respiration rate	$1.5 \mu\text{mol m}^{-2}\text{s}^{-1}$	(Cernusak et al., 2004)
Carbon isotope effects			
$a_{13b}$	Fractionation in $^{13}\text{CO}_2$ as $\text{CO}_2$ diffuses through the boundary layer	2.9‰	(Farquhar and Lloyd, 1993)
$a_{13s}$	Fractionation in $^{13}\text{CO}_2$ as $\text{CO}_2$ diffuses through the stomata	4.4‰	(Vogel.J.C., 1980;Farquhar et al., 1982;Farquhar and Lloyd, 1993)
$a_m$	fractionation factor for dissolution and diffusion through water	1.8‰	(Farquhar et al., 1982;Wingate et al., 2007)
$f$	a fractionation factor for photorespiration (decarboxylation of glycine)	16‰	(Evans and von Caemmerer, 2007)
$e$	The fractionation factor for day respiration	$eRd + e^*$ , ‰	(Wingate et al., 2007;Bickford et al., 2009)
$e^*$	The apparent fractionation for day respiration	$\delta^{13}\text{C}_a - \Delta_A^{13}\text{C} - \delta^{13}\text{C}_{\text{substrate}}$ , ‰	(Wingate et al., 2007;Cernusak et al., 2013)
$b$	Fractionation factor for uptake by RubisCO	29‰	(Farquhar et al., 1982;Farquhar and Lloyd, 1993)
$\alpha_f$	a fractionation due to photorespiration (decarboxylation of glycine)	$1+f$	
$\alpha_e$	fractionation due to day respiration	$1+e$	
$\alpha_b$	Fractionation due to uptake by RubisCO	$1+b$	
Isotopic composition			
$\delta^{13}\text{C}_{\text{subst rate}}$		$\frac{\delta^{13}\text{C}_a - \Delta_A^{13}\text{C}}{\Delta_A^{13}\text{C} + 1}$ , ‰	(Farquhar et al., 1989)
$\Delta_A^{13}\text{C}$	$^{13}\text{C}$ -photosynthetic discrimination	$\frac{\zeta(\delta^{13}\text{C}_a - \delta^{13}\text{C}_e)}{1 + \delta^{13}\text{C}_a - \zeta(\delta^{13}\text{C}_a - \delta^{13}\text{C}_e)}$ , ‰	(Evans et al., 1986)

$\Delta A^{13}C_{obs}$	$^{13}\text{C}$ -photosynthetic discrimination (Farquhar model)	$\left(\frac{1}{1-t}\right) \left[ a_{13bs} \frac{c_a - c_i}{c_a} \right]$ $+ \left(\frac{1+t}{1-t}\right) \left[ a_m \frac{c_i - c_c}{c_a} + b \frac{c_c}{c_a} \right]$ $- \frac{\alpha_b}{\alpha_e} e \frac{R_d}{R_d + A} \frac{c_c - \Gamma^*}{c_a} - \frac{\alpha_b}{\alpha_f} f \frac{\Gamma^*}{c_a}$	(Farquhar and Cernusak, 2010)
$\Delta A^{13}C_i$	$^{13}\text{C}$ -photosynthetic discrimination (assuming the no mesophyll conductance, i.e $c_i=c_c$ )	$\left(\frac{1}{1-t}\right) \left[ \bar{a} \frac{c_a - c_i}{c_a} \right]$ $+ \left(\frac{1+t}{1-t}\right) \left[ b \frac{c_i}{c_a} - \frac{\alpha_b}{\alpha_e} e \frac{R_d}{R_d + A} \frac{c_i - \Gamma^*}{c_a} \right]$ $- \frac{\alpha_b}{\alpha_f} f \frac{\Gamma^*}{c_a}$	(Farquhar and Cernusak, 2010)

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