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*Supplement of*

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

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## Gas exchange parameters

15 Leaf exchange parameters are calculated following von Caemmerer and Farquhar (1981). The transpiration rate ( $E$ ) is calculated from the air flowrate, leaf area and concentration of water vapor entering and leaving the cuvette as:

$$E = \frac{u_e}{s} \times \left( \frac{w_a - w_e}{1 - w_a} \right) \quad (\text{S1})$$

where  $w_e$ ,  $w_a$  are the mole fractions of water entering ( $e$ ) and leaving ( $a$ ) the cuvette,  $u_e$  is the flowrate of air entering the cuvette and  $s$  is the leaf surface area. The assimilation rate ( $A_N$ ) is calculated as:

$$A_n = \frac{u_e}{s} \times \left( c_e - c_a \times \left( \frac{1 - w_e}{1 - w_a} \right) \right) \quad (\text{S2})$$

20 where  $c_e$  and  $c_a$  are the mole fractions of  $\text{CO}_2$  leaving and entering the cuvette. The total conductance for water vapor ( $g_{wa}^t$ ) is calculated as:

$$g_{wa}^t = E \times \left( \frac{1 - \left( \frac{w_i + w_a}{2} \right)}{w_i - w_a} \right) \quad (\text{S3})$$

where  $w_i$  is the water vapor mole fraction in the intercellular air space (calculated assuming saturation at ambient temperature) and  $w_a$  is the mole fraction of water vapor leaving the cuvette. The mole fraction of  $\text{CO}_2$  in the intercellular air space is calculated as:

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$$c_i = \frac{\left( g_{ac}^t - \frac{E}{2} \right) \times c_a - A_n}{\left( g_{ac}^t + \frac{E}{2} \right)} \quad (\text{S4})$$

where  $g_{ca}^t$  is the total conductance for  $\text{CO}_2$ . For a detailed derivation of the leaf exchange parameters, the reader is referred to von Caemmerer and Farquhar (1981).

## Isotopic composition of water at the evaporation site

- 30 Using mass balance for the air entering and leaving the cuvette, the  $\delta^{18}\text{O}$  of the transpired ( $\delta^{18}\text{O}_{\text{trans}}$ ) water is calculated according to (Harwood et al., 1998):

$$\delta^{18}\text{O}_{\text{trans}} = \left( \frac{w_a}{w_a - w_e} \right) \times (\delta^{18}\text{O}_{w_a} - \delta^{18}\text{O}_{w_e}) + \delta^{18}\text{O}_{w_e} \quad (\text{S5})$$

- 35 where  $\delta^{18}\text{O}_{w_e}$  and  $\delta^{18}\text{O}_{w_a}$  are  $\delta^{18}\text{O}$  values of water vapor entering and leaving the cuvette and  $w_a$  and  $w_e$  are the mole fractions of water vapor entering and leaving the cuvette.  $\delta^{17}\text{O}$  is calculated based on the triple isotope relationship for transpiration,  $\alpha^{17} = (\alpha^{18})^{\lambda_{\text{trans}}}$  where  $\lambda_{\text{trans}} = 0.522 - 0.008 \times h$  (Landais et al., 2006).  $h$  is the relative humidity,  $0.3 \leq h \leq 1$ , which is calculated as  $h = \frac{w_a}{w_i}$ ;  $w_i$  is the saturation mole fraction of water vapor in the intercellular air space.

- 40 Leaf water at the site of evaporation becomes enriched during evaporation and/or transpiration since the heavier isotopologues diffuse slower than the lighter ones (Flanagan et al., 1991; Flanagan, 1993; Yakir and Sternberg, 2000). The degree isotopic enrichment due to the phase change from water to vapor (evaporation) and diffusion is described by the modified Craig and Gordon model (Craig and Gordon, 1965), including resistance to boundary layer and stomata diffusion as described by (Farquhar et al., 1989; Flanagan et al., 1991; Flanagan, 1993). Measurement of the isotopic composition of air entering and leaving the cuvette allows determining the isotopic composition of water at the evaporation site even if it is not in steady state as described in (Farquhar et al., 1989; Flanagan et al., 1991; Harwood et al., 1998). The  $\delta^{18}\text{O}$  of leaf water at the site of evaporation ( $\delta^{18}\text{O}_{\text{wes}}$ ) is:

$$\delta^{18}\text{O}_{\text{wes}} = \delta^{18}\text{O}_{\text{trans}} + \varepsilon^{18}_k + \varepsilon^{18}_{\text{equ}} + \frac{w_a}{w_i} \times (\delta^{18}\text{O}_{w_a} - \varepsilon^{18}_k + \delta^{18}\text{O}_{\text{trans}}) \quad (\text{S6})$$

- 50 where  $\varepsilon^{18}_k$  and  $\varepsilon^{18}_{\text{equ}}$  are the kinetic fractionation of water vapor in air and the equilibrium fractionation between liquid and gas phase water, respectively. The equilibrium fractionation is temperature dependent (Bottinga and Craig, 1968) and calculated as:

$$\varepsilon^{18}_{\text{equ}} = 2.644 - 3.206 \times \left( \frac{10^3}{T} \right) + 1.534 \times \left( \frac{10^6}{T} \right) \quad (\text{S7})$$

- 55 where  $T$  is the temperature in Kelvin.  $\text{H}_2^{18}\text{O}$  has a lower vapor pressure and diffuses slower than  $\text{H}_2^{16}\text{O}$  (Farquhar and Lloyd, 1993). The kinetic isotope effect due to diffusion  $\varepsilon_k$ , is the weighted sum of the fractionations of water isotopologues during diffusion through the stomata in the air ( $\varepsilon_{ks}$ ) and through the boundary layer ( $\varepsilon_{kb}$ ) (Farquhar and Lloyd, 1993). According to Merlivat (1978) and (Barkan and Luz, 2007) the fractionation factor for  $\text{H}_2^{18}\text{O}$  as it diffuses through stomata is 28 ‰ ( $\varepsilon^{18}_{ks}$ ). According to (Farquhar and Lloyd, 1993)  $\varepsilon_{kb} = (\varepsilon_{ks})^{\frac{2}{3}}$ , i.e., the fractionation factor as  $\text{H}_2^{18}\text{O}$  diffuses through the boundary layer is 19 ‰ ( $\varepsilon^{18}_{kb}$ ). The kinetic fractionation of  $\text{H}_2^{18}\text{O}$  as it diffuses through stomata and boundary layer is given by equation S8 (Farquhar and Lloyd, 1993).

$$\varepsilon^{18}_k = \frac{28 \times g_b + 19 \times g_s}{g_b + g_s} \quad (\text{S8})$$

65 where  $g_b$  and  $g_s$  are boundary layer conductance and stomatal conductance respectively. The fractionation factors for  $\text{H}_2^{17}\text{O}$  for diffusion through stomata and boundary layer are 14.6 ‰ and 9.7 ‰, respectively (Barkan and Luz, 2007).  $\delta^{17}\text{O}_{\text{wes}}$  can be calculated using a similar equation as  $\delta^{18}\text{O}_{\text{wes}}$  if  $\delta^{17}\text{O}_{\text{wa}}$  and  $\delta^{17}\text{O}_{\text{we}}$  are known, for this study we calculated  $\delta^{17}\text{O}_{\text{wes}}$  assuming that the irrigation water (IRW) is the same as soil water.

$$\delta^{17}\text{O}_{\text{wes}} = \left( \frac{\delta^{18}\text{O}_{\text{wes}} + 1}{\delta^{18}\text{O}_{\text{IRW}} + 1} \right)^{\lambda_{\text{trans}}} \times (\delta^{17}\text{O}_{\text{IRW}} + 1) - 1 \quad (\text{S9})$$

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### Mole fraction of $\text{CO}_2$ at the site of $\text{CO}_2\text{-H}_2\text{O}$ exchange

75 The  $\text{CO}_2$  mole fraction at the site of  $\text{CO}_2\text{-H}_2\text{O}$  exchange is calculated as shown in equation S10 following (Farquhar and Cernusak, 2012; Osborn et al., 2017; Barbour et al., 2016).

$$c_m = c_i \left( \frac{\delta^{18}\text{O}_i - a_{18w} - \delta^{18}\text{O}_A \times (1 + a_{18w})}{\delta^{18}\text{O}_m - a_{18w} - \delta^{18}\text{O}_A \times (1 + a_{18w})} \right) \quad (\text{S10})$$

where  $\delta^{18}\text{O}_i$  is  $\delta^{18}\text{O}$  of  $\text{CO}_2$  in the intercellular airspace (Farquhar and Cernusak, 2012),

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$$\delta^{18}\text{O}_i = \frac{\delta^{18}\text{O}_{\text{io}} + t^{18} \times \left( \delta^{18}\text{O}_A \times \left( \frac{c_a}{c_i} + 1 \right) - \delta^{18}\text{O}_a \times \frac{c_a}{c_i} \right)}{1 + t^{18}} \quad (\text{S11})$$

The ternary correction factor  $t^{18}$  is calculated as:

$$t^{18} = \frac{(1 + a_{18bs}) \times E}{2g_{ac}} \quad (\text{S12})$$

85  $g_{ac}$  is the conductance as  $\text{CO}_2$  diffuses through the boundary layer and stomata,  $a_{18bs}$  is the weighted  $^{18}\text{O}$  fractionation for  $\text{CO}_2$  diffusion across the boundary layer and stomata in series.

$$a_{18bs} = \frac{(c_a - c_s) \times a_{18b} + (c_s - c_i) \times a_{18s}}{c_a - c_i} \quad (\text{S13})$$

$\delta^{18}\text{O}_{\text{io}}$  is the  $\delta^{18}\text{O}$  of  $\text{CO}_2$  in the intercellular air spaces ignoring the ternary correction and it is given by (Farquhar and Cernusak, 2012).

$$\delta^{18}\text{O}_{\text{io}} = \delta^{18}\text{O}_A \times \left(1 - \frac{c_a}{c_i}\right) \times (1 + a_{18\text{bs}}) + \frac{c_a}{c_i} \times (\delta^{18}\text{O}_a - a_{18\text{bs}}) + a_{18\text{bs}} \quad (\text{S14})$$

90

where  $a_{18w}$  is the  $^{18}\text{O}$  fractionation of  $\text{CO}_2$  for dissolution and diffusion in water (0.8 ‰) and  $a_{18s}$  and  $a_{18b}$  are the  $^{18}\text{O}$  fractionation of  $\text{CO}_2$  as it diffuses through stomata (8.8 ‰) and the boundary layer (5.8 ‰), respectively (Farquhar et al., 1982; Farquhar and Lloyd, 1993). The oxygen isotope composition of the assimilated  $\text{CO}_2$  is calculated from a mass balance using the mole fraction and isotope composition of  $\text{CO}_2$  entering and leaving the cuvette:

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$$\delta^{18}\text{O}_A = \frac{\delta^{18}\text{O}_a - \Delta_A^{18}\text{O}}{\Delta_A^{18}\text{O} + 1} \quad (\text{S15})$$

$a_{18w}$  is the fractionation of  $\delta^{18}\text{O}$  of  $\text{CO}_2$  during diffusion and dissolution in water (0.8 ‰) (Farquhar and Lloyd, 1993),  $\delta^{18}\text{O}_A$  is the  $\delta^{18}\text{O}$  of the assimilated  $\text{CO}_2$  and  $\delta^{18}\text{O}_m$  is the  $\delta^{18}\text{O}$  of  $\text{CO}_2$  in equilibrium with leaf water at the  $\text{CO}_2$ - $\text{H}_2\text{O}$  exchange site. Assuming that the isotopic composition of leaf water at the  $\text{CO}_2$ - $\text{H}_2\text{O}$  exchange site is the same as the  $\delta^{18}\text{O}$  of leaf water at the evaporation site,  $\delta^{18}\text{O}_m$  can be calculated as:

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$$\delta^{18}\text{O}_m = (\delta^{18}\text{O}_{\text{wes}} + 1) \times (1 + \varepsilon_w^{18}) - 1 \quad (\text{S16})$$

The equilibrium fractionation between  $\text{CO}_2$  and water ( $\varepsilon_w^{18}$ ) is temperature dependent and is calculated after Brenninkmeijer et al. (1983) as:

105

$$\varepsilon_w^{18} = \frac{17604}{T} - 17.93 \quad (\text{S17})$$

where  $T$  is leaf temperature. Analogous to  $\delta^{18}\text{O}$ , the mole fraction of  $\text{CO}_2$  in the mesophyll cell can be calculated using  $\delta^{17}\text{O}$  values. The  $^{18}\text{O}$  fractionation ( $\alpha^{18}-1$ ) for dissolution is -0.8 ‰ (Vogel.J.C. et al., 1970). The corresponding  $^{17}\text{O}$  fractionation is -0.418 ‰, calculated from the  $^{18}\text{O}$  fractionation due to equilibrium dissolution using  $\lambda_{\text{CO}_2\text{-H}_2\text{O}} = 0.5229$  (Barkan and Luz, 2012). We assume that the  $^{17}\text{O}$  fractionation during diffusion in water is the same as the fractionation against  $^{13}\text{CO}_2$  (Farquhar and Lloyd, 1993) and use the average fractionation determined for  $^{13}\text{CO}_2$  of 0.8 ‰ (average of 0.7 ‰ (O'Leary, 1984) and 0.9 ‰ (Jähne et al., 1987)). The  $^{17}\text{O}$  fractionation due to the sum of the equilibrium dissolution and diffusion in water is then  $a_{17w} = 0.382$  ‰. Similar to (Farquhar and Lloyd, 1993), using the principle of binary diffusivities (Mason and Marrero, 1970),  $a_{17s}$  and  $a_{17b}$  are 4.4 ‰ and 2.9 ‰ using the power of 2/3 relationship between the boundary layer and stomatal conductance fractionation ( $\alpha_b = \alpha_s^{2/3}$ ) obtained by Farquhar and Lloyd (1993).

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120 For calculating the isotopic composition at the site of oxygen isotope exchange, we assume that the isotopic composition of CO<sub>2</sub> is fully equilibrated with water at the evaporation site. This includes the implicit assumption that the isotopic composition of the leaf water at the CO<sub>2</sub>-H<sub>2</sub>O exchange site is the same as at the site of evaporation. The δ<sup>17</sup>O of CO<sub>2</sub> at the CO<sub>2</sub>-H<sub>2</sub>O exchange site (δ<sup>17</sup>O<sub>m</sub>) is then calculated using the triple oxygen isotope ratio relationship,  $\alpha^{17} = (\alpha^{18})^{\lambda_{\text{CO}_2\text{-H}_2\text{O}}}$ .

$$\delta^{17}\text{O}_m = \left( \frac{\delta^{18}\text{O}_m + 1}{\delta^{18}\text{O}_{\text{wes}} + 1} \right)^{\lambda_{\text{CO}_2\text{-H}_2\text{O}}} \times (\delta^{17}\text{O}_{\text{wes}} + 1) - 1 \quad (\text{S18})$$

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where  $\lambda_{\text{CO}_2\text{-H}_2\text{O}}$  is 0.5229 (Barkan and Luz, 2012).

### Mole fraction of CO<sub>2</sub> at the site of assimilation

130 For the C<sub>3</sub> plants,  $c_c$  is calculated following (Farquhar and Cernusak, 2012) as:

$$c_c = c_i - \left( \frac{1 - t^{13}}{1 + t^{13}} \right) \left( \frac{(\Delta_A^{13}\text{C}_i - \Delta_A^{13}\text{C}_{\text{obs}})Pc_a}{\left( b - a_m - \frac{\alpha_b}{\alpha_e} e \frac{R_d}{R_d + A} \right)} \right) \quad (\text{S19})$$

135 where  $\Delta_A^{13}\text{C}_{\text{obs}}$  is the observed discrimination against <sup>13</sup>C and  $\Delta_A^{13}\text{C}_i$  is the discrimination that can be calculated for infinite mesophyll conductance (no mesophyll resistance).  $t^{13}$  is a ternary correction factor (considers the collisions between air and CO<sub>2</sub>, air and H<sub>2</sub>O, CO<sub>2</sub> and H<sub>2</sub>O),  $b$  is the fractionation due to uptake by Rubisco, and  $a_m$  is the sum of the fractionations associated with <sup>13</sup>CO<sub>2</sub> 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 assimilation, the fractionation factor for C<sub>3</sub> 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 3.

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### Derivation of the <sup>18</sup>O- and <sup>17</sup>O-photosynthetic discrimination

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The assimilation rate for C<sup>16</sup>O<sup>16</sup>O is calculated as:

$$A_n = \frac{c_a - c_m}{r_m} \quad (\text{S20})$$

150 where  $A_n$ ,  $r_m$ ,  $c_a$ ,  $c_m$  are the assimilation rate, the resistance as CO<sub>2</sub> diffuses from the air surrounding the leaf 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 (Farquhar and Lloyd; 1993). The assimilation rate for C<sup>18</sup>O<sup>16</sup>O is calculated as:

$${}^nR_A \times A_n = \frac{{}^nR_a \times c_a - {}^nR_m \times c_m}{\alpha^n_m \times r_m} \text{ where } n \text{ is } 17 \text{ or } 18 \quad (\text{S21})$$

155  $\alpha^n_m$  is the fractionation factor as  $C^{18}O^{16}O$  or  $C^{17}O^{16}O$  diffuse from the air surrounding the leaf to the  $CO_2$ - $H_2O$  exchange site. Dividing equation S22 by equation S29 leads to:

$${}^nR_A = \frac{{}^nR_a \times c_a - {}^nR_m \times c_m}{\alpha^n_m \times (c_a - c_m)} \quad (\text{S22})$$

$$\frac{{}^nR_A}{{}^nR_a} = \frac{c_a - \frac{{}^nR_m}{{}^nR_a} \times c_m}{\alpha^n_m \times (c_a - c_m)} \quad (\text{S23})$$

$$\frac{{}^nR_a}{{}^nR_A} = \frac{\alpha^n_m \times (c_a - c_m)}{c_a - \frac{{}^nR_m}{{}^nR_a} \times c_m} \quad (\text{S24})$$

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$$\frac{{}^nR_a}{{}^nR_A} - 1 = \frac{\alpha^n_m \times (c_a - c_m)}{c_a - \frac{{}^nR_m}{{}^nR_a} \times c_m} - 1 \quad (\text{S25})$$

Using the definitions

$$\Delta_A {}^nO_{FM} = \frac{{}^nR_a}{{}^nR_A} - 1 \quad (\text{S26})$$

165 and

$$\delta^n O_{ma} = \frac{{}^nR_m}{{}^nR_a} - 1 \quad (\text{S27})$$

this can be rewritten as

$$\Delta_A {}^nO_{FM} = \frac{\alpha^n_m \times (c_a - c_m)}{c_a - c_m \times (\delta^n O_{ma} + 1)} - 1 \quad (\text{S28})$$

$$\Delta_A^{nO_{FM}} = \frac{\bar{a}_n + \frac{c_m}{c_a - c_m} \times \delta^n O_{ma}}{1 - \frac{c_m}{c_a - c_m} \times \delta^n O_{ma}} \quad (S29)$$

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### Comparison of equations used in global models and in this study to calculate $\Delta^{17}O$ -photosynthetic discrimination

175 The discrimination against  $\Delta^{17}O$  associated with assimilation in global models, assuming complete equilibration between  $CO_2$  and  $H_2O$ , is calculated from equation S30 (Hofmann et al., 2017; Liang et al., 2017; Koren et al., 2019).

$$\Delta_A \Delta^{17}O = (\lambda_{diffusion} - \lambda_{RL}) \times \ln(\bar{a}_{18} + 1) + (\Delta^{17}O_m - \Delta^{17}O_a) \frac{c_m}{c_a - c_m} \quad (S30)$$

180  $\bar{a}_{18}$ , is the weighted mean discrimination occurring during the diffusion of  $^{12}C^{18}O^{16}O$  from the ambient air to the  $CO_2$ - $H_2O$  exchange site and it is estimated to be 7.4 ‰ (Farquhar et al., 1993). This value has been adopted in several global studies of  $\delta^{18}O(CO_2)$  (Ciais et al., 1997a; 1997b; Cuntz et al., 2003a; 2003b) and the global  $\Delta^{17}O$  studies (Hofmann et al., 2017; Liang et al., 2017; Koren et al., 2019).  $\lambda_{diffusion}=0.509$  is the three-isotope coefficient associated with fractionation of  $C^{17}OO$  as it diffuses through air relative to  $C^{18}OO$  (Young et al., 2002) and  $\lambda_{RL}=0.528$  (the reference slope used in this study).  $\Delta^{17}O_m$  and  $c_m$  are the oxygen isotope anomaly and mole fraction of  $CO_2$  at the  $CO_2$ - $H_2O$  exchange site, respectively.

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A good approximation for the observed  $^{18}O$ -discrimination can be derived from the leaf exchange parameters (Farquhar and Lloyd, 1993):

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$$\Delta_A^{18O_{FM}} = \frac{\bar{a}_{18} + \frac{c_m}{c_a - c_m} \times \delta^{18}O_{ma}}{1 - \frac{c_m}{c_a - c_m} \times \delta^{18}O_{ma}} \approx \bar{a}_{18} + \frac{c_m}{c_a - c_m} \times (\delta^{18}O_m - \delta^{18}O_a) \quad (S31)$$

The subscript *FM* stands for Farquhar model.  $\delta^{18}O_{ma}$  is the enrichment in  $\delta^{18}O$  of  $CO_2$  in full isotopic equilibrium with water at the exchange site relative to the  $CO_2$  in the surrounding air, calculated as:

$$\delta^{18}O_{ma} = \frac{\delta^{18}O_m - \delta^{18}O_a}{1 + \delta^{18}O_a} \quad (S32)$$

$\delta^{18}O_m$  is the isotope composition of  $CO_2$  in equilibrium with leaf water at the  $CO_2$ - $H_2O$  exchange site (equation S16). In the global models (Hofmann et al., 2017; Liang et al., 2017; Koren et al., 2019),  $\Delta^{17}O$ -

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photosynthetic discrimination shown in equation S30 is derived from  $\Delta_A^{17}\text{O}_{\text{FM}}$  and  $\Delta_A^{18}\text{O}_{\text{FM}}$  as shown from equation S33.

$$\begin{aligned} \Delta_A \Delta^{17}\text{O} &= \left( \bar{a}_{17} + \frac{c_m}{c_a - c_m} (\delta^{17}\text{O}_m - \delta^{17}\text{O}_a) \right) - \lambda_{\text{RL}} \times \left( \bar{a}_{18} + \frac{c_m}{c_a - c_m} (\delta^{18}\text{O}_m - \delta^{18}\text{O}_a) \right) \quad (\text{S33}) \\ &= (\bar{a}_{17} - \lambda_{\text{RL}} \times \bar{a}_{18}) + [(\delta^{17}\text{O}_m - \lambda_{\text{RL}} \delta^{18}\text{O}_m) - (\delta^{17}\text{O}_a - \lambda_{\text{RL}} \delta^{18}\text{O}_a)] \frac{c_m}{c_a - c_m} \\ &= (\bar{a}_{17} - \lambda_{\text{RL}} \times \bar{a}_{18}) + [\Delta^{17}\text{O}_m - \Delta^{17}\text{O}_a] \frac{c_m}{c_a - c_m} \end{aligned}$$

200 Note that,  $\ln(\bar{a}_{18} + 1) \approx \bar{a}_{18}$  and  $(\bar{a}_{17} - \lambda_{\text{RL}} \times \bar{a}_{18}) = (\lambda_{\text{diffusion}} - \lambda_{\text{RL}}) \times \ln(\bar{a}_{18} + 1)$ .

### Calibration and characterization of the water vapor isotope analyzer (WVIA)

Based on the calibration using five water standards, a working standard was prepared to correct for short-term variability and to determine the non-linearity (dependency of  $\delta\text{D}$  and  $\delta^{18}\text{O}$  on the water vapor mole fraction). Each day the WVIA was calibrated with 3 standards that cover the isotopic composition of the samples measured ( $\delta^{18}\text{O}$  value of -24.777 ‰, -8.640 ‰ and 0.11 ‰, provided by IAEA (Wassenaar et al., 2018)), see Figure S2. Figure S3, shows the results of the non-linearity tests. All three isotope signatures of water vapor showed a different dependence on the mole fraction of water vapor measured. The  $\delta^{18}\text{O}$  is independent of the mole fraction above 11000 ppm but decreases at lower mole fraction until 4000 ppm, and then increases again.  $\delta^{17}\text{O}$  is relatively stable for mole fractions higher than 17000 ppm, but increases strongly and in a non-linear manner below. Similarly,  $\delta\text{D}$  is independent of the mole fraction of water vapor above 10000 ppm but increases non-linearly below.  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$  and  $\delta\text{D}$  values measured with the WVIA are dependent on the type of carrier gas used when measuring liquid samples as shown for pure  $\text{N}_2$  and zero air used as a carrier gas, Figure S3 (Johnson and Rella, 2017). To investigate how the precision of the isotope values depends on the averaging time, Allan deviation (square root of Allan variance) curves are shown in Figure S4. All three isotope signatures of water vapor show a similar pattern. The optimum precision is reached at averaging times of 16.7 minutes for  $\delta^{18}\text{O}$  and  $\delta\text{D}$  and 15 minutes for  $\delta^{17}\text{O}$  (Figure S4). Note that the  $\delta^{17}\text{O}$  measurements of water vapor are not calibrated to an international isotope scale for our experiments.

### 220 Water extraction and analysis

The vial containing the leaf was frozen using a liquid nitrogen bath and connected to another empty vial by glass tubing. The system was then evacuated using a membrane pump (KNF Neuberger, Germany), (Figure S5). The pressure was monitored with a Dual pressure sensor (DualTrans transducer, MKS, USA). After the target vacuum was reached (1mbar or below) the extraction system was isolated from the pump. The vial containing the leaf was placed into a heater block (ORI BLOCK DB-1, Techne, England) while

the empty vial was kept at liquid nitrogen temperature for 4 hr (Figure S5). The extracted leaf water, ~ 0.7 ml (determined based on weight by measuring the leaf weight before and after extraction), was collected in a 2 ml vial (Autosampler vials, National Scientific, the Netherlands) using a pipette and kept in the freezer at -20°C before isotopic analysis.

$\Delta^{17}\text{O}$  of leaf water is measured using a fluorination method. The water was converted to  $\text{O}_2$  using  $\text{CoF}_3$  as fluorinating reagent and the  $\text{O}_2$  was collected in a sample tube immersed in liquid Helium (-270°C). Finally,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  of  $\text{O}_2$  were measured with an isotope ratio mass spectrometer (ThermoQuest MAT 253 Finnigan, Germany) in dual inlet mode. The measurement reproducibility for two replicates is 0.015 ‰, 0.010 ‰ and 0.005 ‰ for  $\delta^{17}\text{O}$ ,  $\delta^{18}\text{O}$  and  $\Delta^{17}\text{O}$ , respectively.

### 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 S7. 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 conductance from the intercellular air space to the mesophyll, where the  $\text{CO}_2$ - $\text{H}_2\text{O}$  exchange occurs is expressed as  $g_{m18}$ .

### $\text{CO}_2$ balance

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
- The conductance between intercellular space and mesophyll is assumed to be 3 times higher than the conductance between intercellular space and chloroplast (i.e.  $g_{m18} = 3 \times g_{m13}$ ).

We modeled a 100 ppm drawdown of  $\text{CO}_2$  for each photosynthesis experiment. The mole fractions of  $\text{CO}_2$  entering and leaving the cuvette are 500 ppm and 400 ppm, respectively. The leaf area, flowrate and assimilation rate used in 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 an initial value for the  $\text{C}^{18}\text{OO}$  mole fraction inside the cuvette ( $c_{a,\text{C}^{18}\text{OO}}$ ). From the mole fractions  $c_{a,\text{C}^{18}\text{OO}}$  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

270  $c_{a,C18OO}$  and the plant uptake of  $C^{18}OO$  is  $A_{n,C18OO} = g_{s,C18OO} \times (c_{a,C18OO} - c_{i,C18OO})$ . By using an iterative procedure we can improve our estimate for  $c_{a,C18OO}$ . Note that for each update in  $c_{a,C18OO}$ , we also update the corresponding  $c_{i,C18OO}$

### $^{13}CO_2$ balance

275 Next, we calculate the steady state  $^{13}CO_2$  mole fractions in the different model reservoirs and subsequently, we determine the discrimination  $\Delta^{13}C$ . 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  $CO_2$  scales linearly with the  $CO_2$  mole fraction in the chloroplast ( $A_n = k \times c_c$ ). Similarly for  $^{13}CO_2$  we have:  $A_{n,^{13}CO_2} = k \times (1 - b) \times C_{c,^{13}CO_2}$

280 We solve the steady state  $^{13}CO_2$  balance by performing 2 nested iterations. We start with an initial guess for the atmospheric  $^{13}CO_2$  mole fraction ( $C_{a,^{13}CO_2}$ ) and for the photosynthetic uptake of  $^{13}CO_2$  ( $A_{n,^{13}CO_2}$ ). In the ‘inner’ iteration loop we use  $c_{a,^{13}CO_2}$  and  $A_{n,^{13}CO_2}$  to calculate the  $^{13}CO_2$  mole fractions in all leaf reservoirs. From the  $^{13}CO_2$  mole fraction in the chloroplast ( $c_{c,^{13}CO_2}$ ) and the linear assimilation factor ( $k \times (1 - b)$ ) we can calculate the corresponding  $A_{n,^{13}CO_2}$  and compare this to our initial guess. Using an  
285 iterative procedure, we can find the  $A_{n,^{13}CO_2}$  that corresponds to the assumed  $c_{a,^{13}CO_2}$ .

The ‘outer’ iteration loop is aimed at finding the steady state atmospheric  $^{13}CO_2$  mole fraction ( $c_{a,^{13}CO_2}$ ) using a mass balance for  $^{13}CO_2$ . We know the  $^{13}CO_2$  mole fraction of the ingoing air ( $c_{in,^{13}CO_2}$ ), we have assumed value for outgoing air ( $c_{a,^{13}CO_2}$ ) and have calculated the corresponding photosynthetic uptake ( $A_{n,^{13}CO_2}$ ). From the resulting imbalance, we can come up with a new guess for  $c_{a,^{13}CO_2}$ . After each update  
290 of our estimate for  $c_{a,^{13}CO_2}$ , we repeat the ‘inner’ iteration loop to update  $A_{n,^{13}CO_2}$ .

### $C^{18}OO$ balance

The additional assumptions for solving the  $C^{18}OO$  balance are:

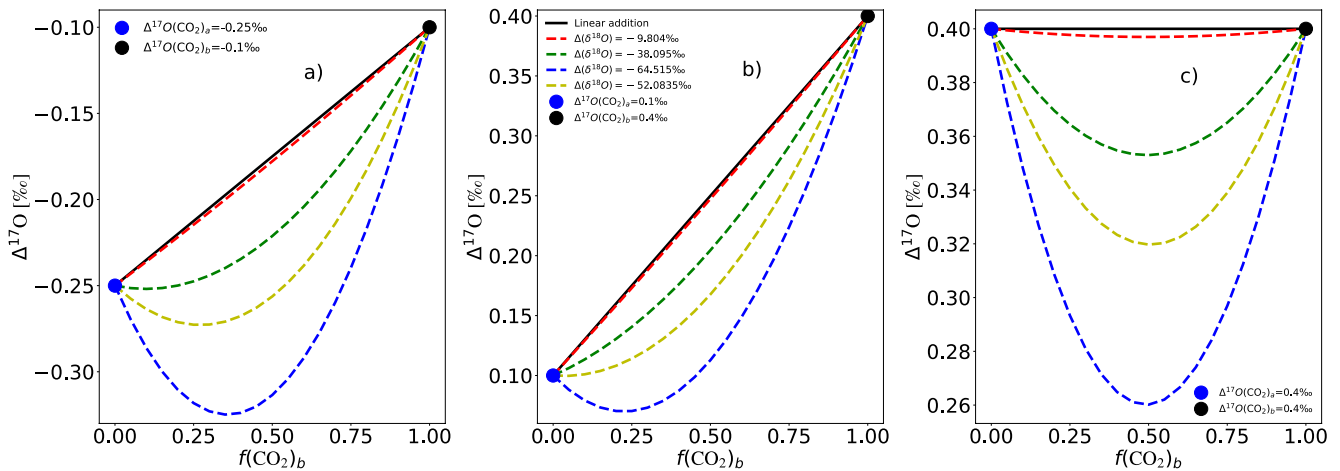
- 295
- For the fractionation of  $C^{18}OO$  for diffusion through stomata and diffusion into the mesophyll cell, we used  $a_{18s} = 8.8$  ‰ and  $a_{18w} = 0.8$  ‰, respectively
  - The isotopic exchange between  $CO_2$  and water in the mesophyll is fast enough to reach complete equilibration, which is a function of temperature
  - Isotopic equilibration between  $CO_2$  and water does not occur in the intercellular air space

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

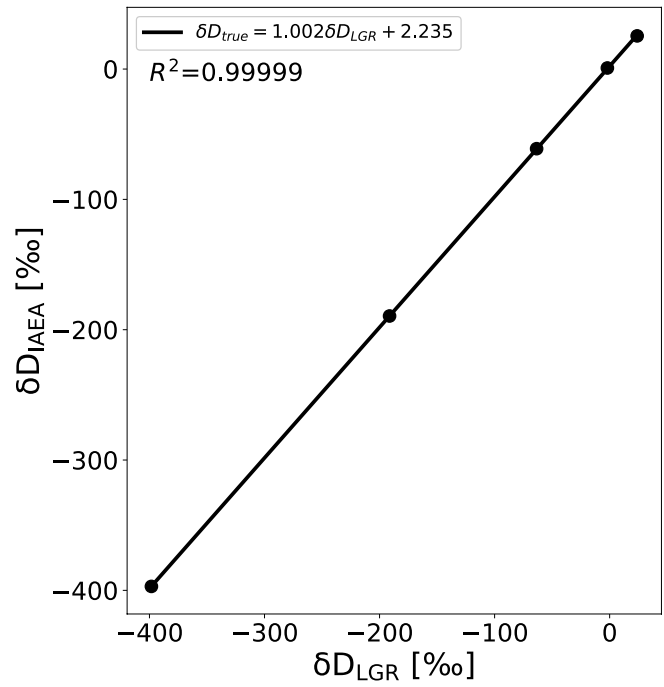
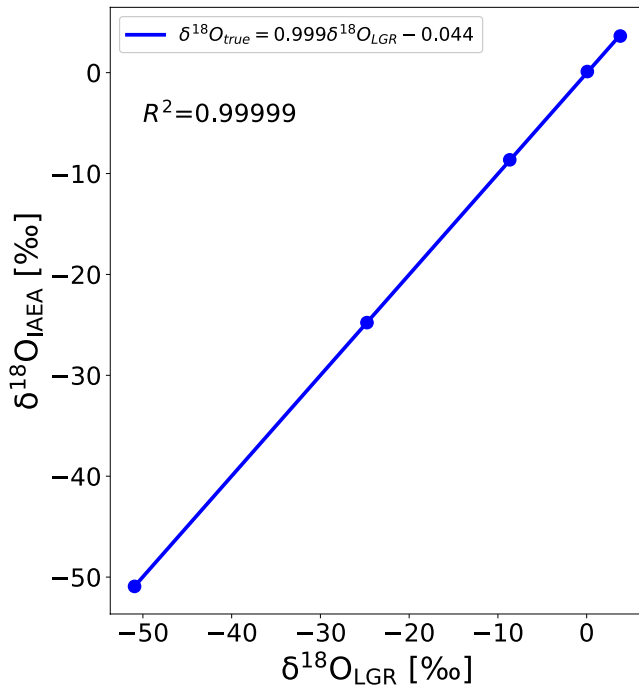
A similar mass balance is implemented for  $C^{17}OO$ , the fractionation of  $C^{17}OO$  for diffusion through stomata is  $a_{17s} = 4.4 \text{ ‰}$  and for diffusion into the mesophyll cell we used and  $a_{18w} = 0.382 \text{ ‰}$ , respectively.  
 310 We set the leaf water signature to  $\delta^{18}O_{\text{leaf}}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

### $^{13}C$ -photosynthetic discrimination

The isotope discrimination against  $^{13}C$  ( $\Delta_A^{13}C$ ) associated with photosynthesis for the three-plant species  
 315 is shown in Figure S8 a) and b) as a function of  $c_c/c_a$  and  $c_i/c_a$  for  $C_3$  and  $C_4$  plants, respectively. Experiments at different light intensities are shown in different colors, blue for LL and yellow for HL. For ivy and sunflower,  $\Delta_A^{13}C$  and  $c_c/c_a$  are linearly correlated. As irradiance increases,  $c_c/c_a$  and  $\Delta_A^{13}C$  decrease.  $\Delta_A^{13}C$  for ivy increases from 13 ‰ to 16 ‰ when  $c_c/c_a$  increases from 0.34 to 0.55 while for sunflower  $\Delta_A^{13}C$  ranges from 13 ‰ to 25 ‰ for  $c_c/c_a$  ratios of 0.37 to 0.8. This is due to the lower  
 320 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  $CO_2$  that has entered the stomata diffuses back to the atmosphere. As a result,  $\Delta_A^{13}C$  decreases with an increase in light intensity. For maize,  $\Delta_A^{13}C$  is much smaller than for the  $C_3$  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  $\Delta_A^{13}C$  and  $c_i/c_a$ .  $\Delta_A^{13}C$  vs  $c_i/c_a$  is shown in Figure S9  
 325 of the for both  $C_3$  plants (sunflower and ivy) and a  $C_4$  plant (maize).



330 Figure S1 Illustration of the changes in  $\Delta^{17}O$  for mixing of two different gases when the  $\Delta^{17}O$  values are calculated in logarithmic form, as a function of the fraction of  $CO_2$  gas b. The blue and black circles show the  $\Delta^{17}O$  values of the mixing end members and the different colors show mixing lines for differences in  $\delta^{18}O$ .



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Figure S2 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.

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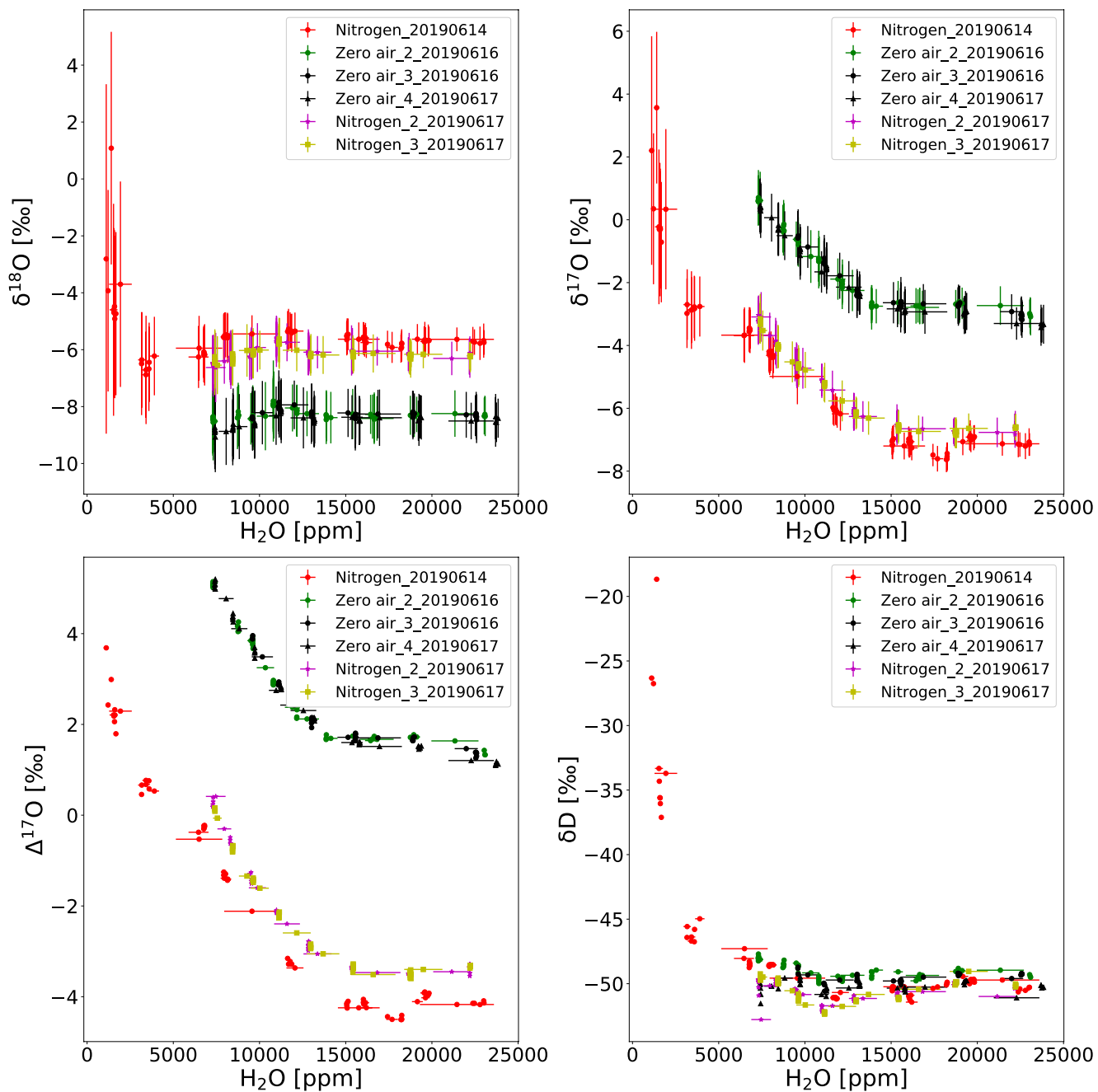
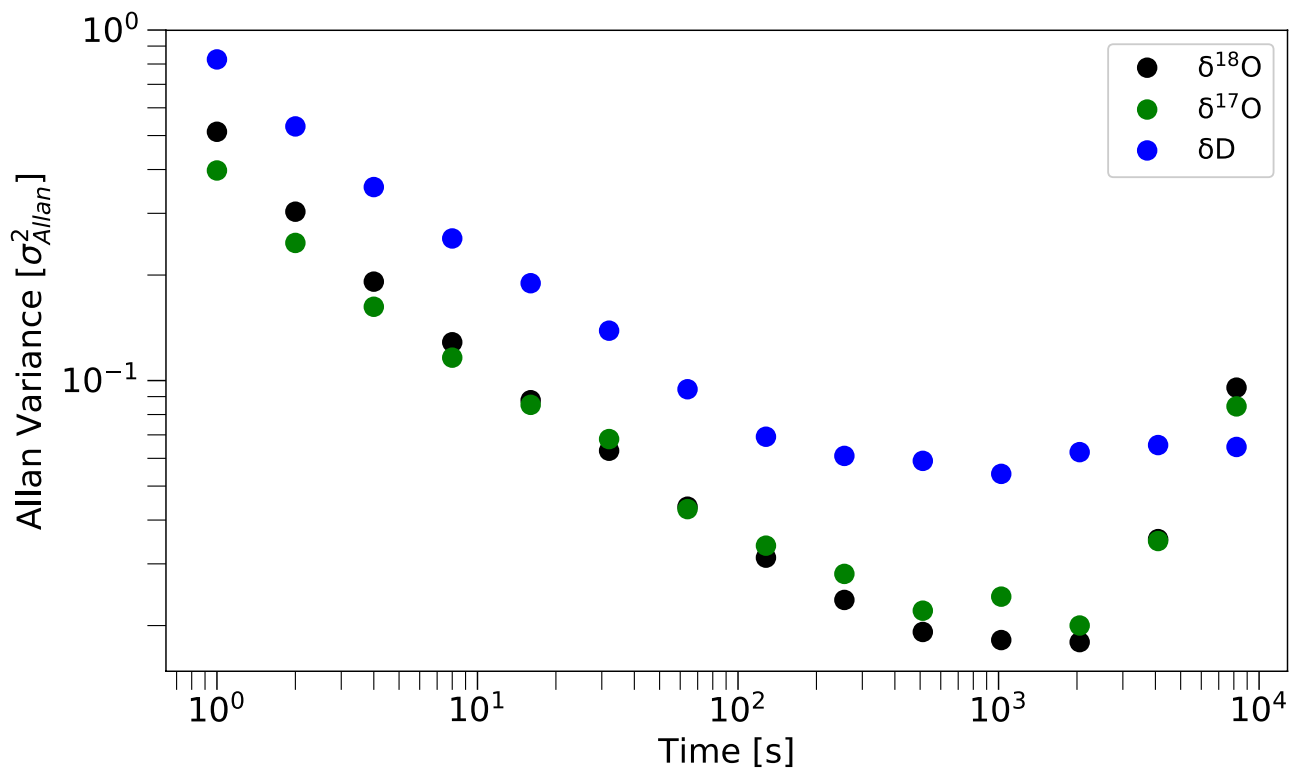
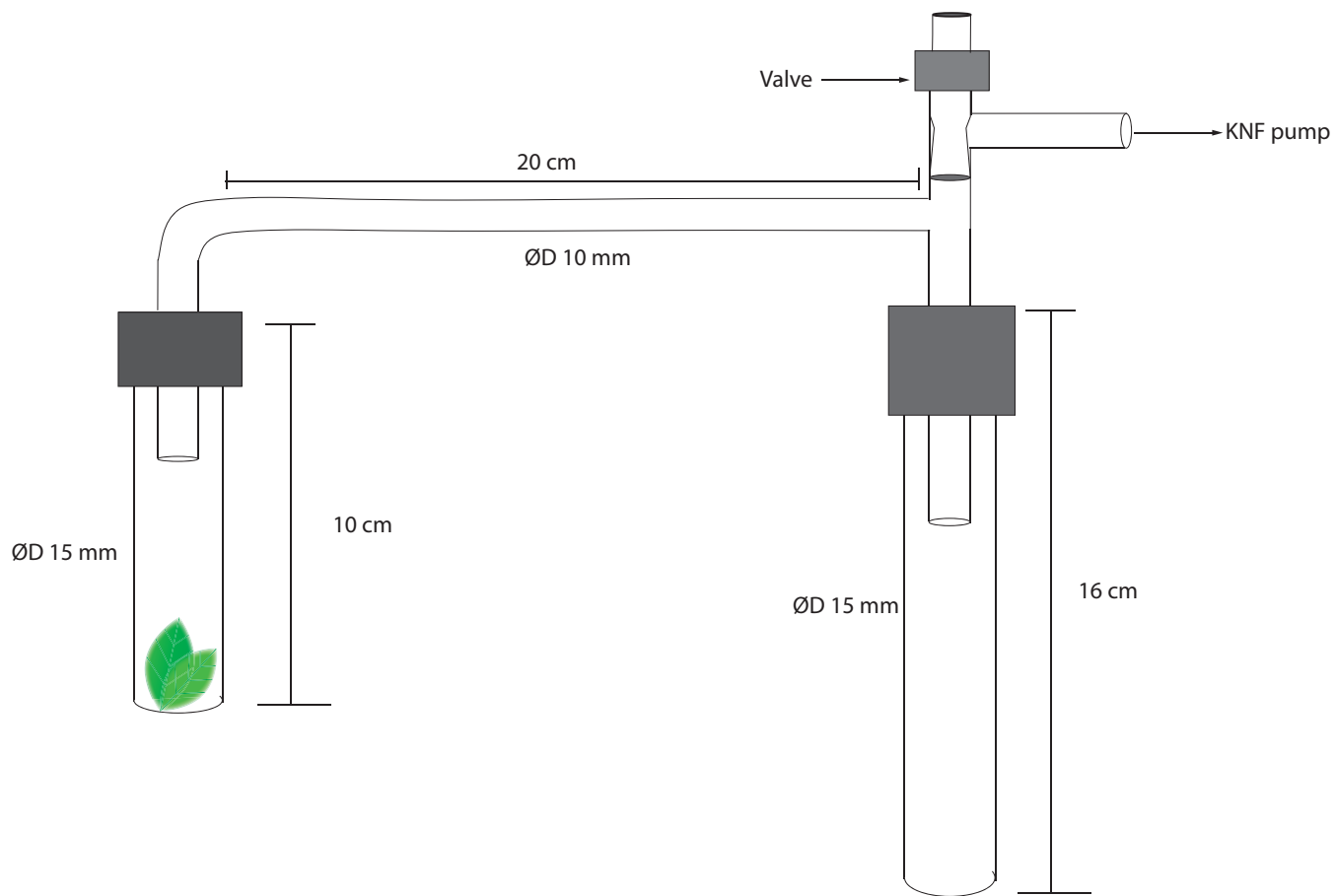


Figure S3 Dependency of isotope composition of water vapour on the water vapor concentration and the carrier gas used for the water vapor standard source for  $\delta^{18}\text{O}$ ,  $\delta^{17}\text{O}$ ,  $\Delta^{17}\text{O}$  and  $\delta\text{D}$ .



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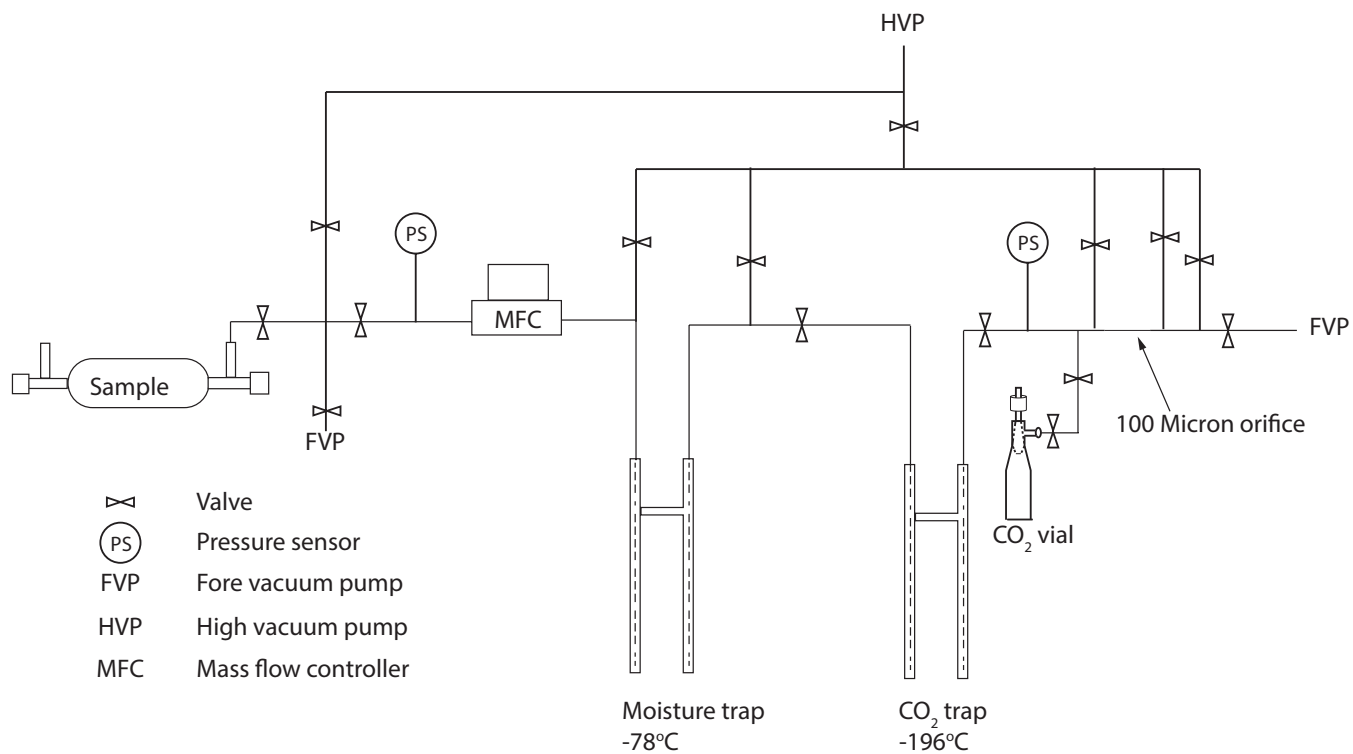
Figure S4 Allan variance curves of  $\delta\text{D}$ ,  $\delta^{17}\text{O}$  and  $\delta^{18}\text{O}$  for measurement at 20000 ppm water vapor concentration.



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**Figure S5** 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.





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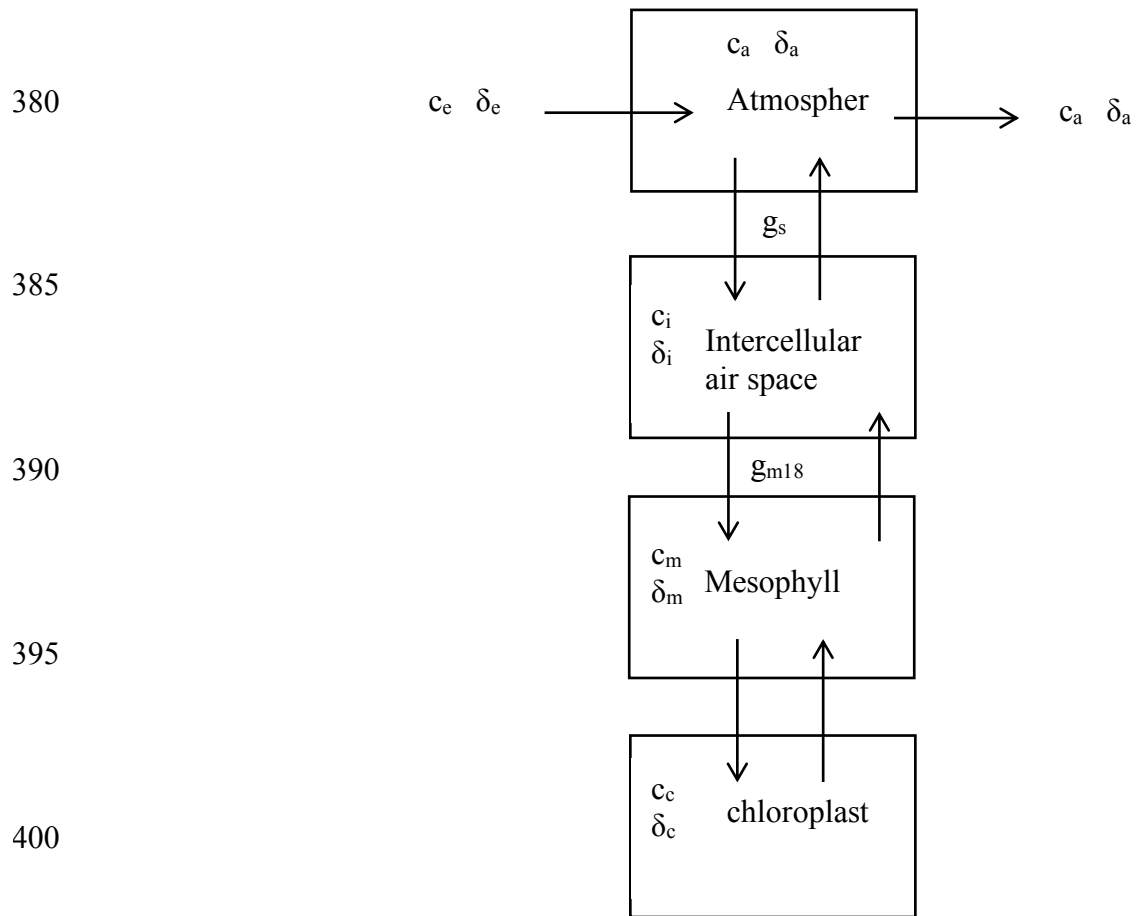
**Figure S6** Schematic diagram of the system used for the extraction of carbon dioxide from air samples. The moisture trap is cooled by a dry ice-ethanol mixture while the CO<sub>2</sub> trap is cooled by liquid nitrogen.

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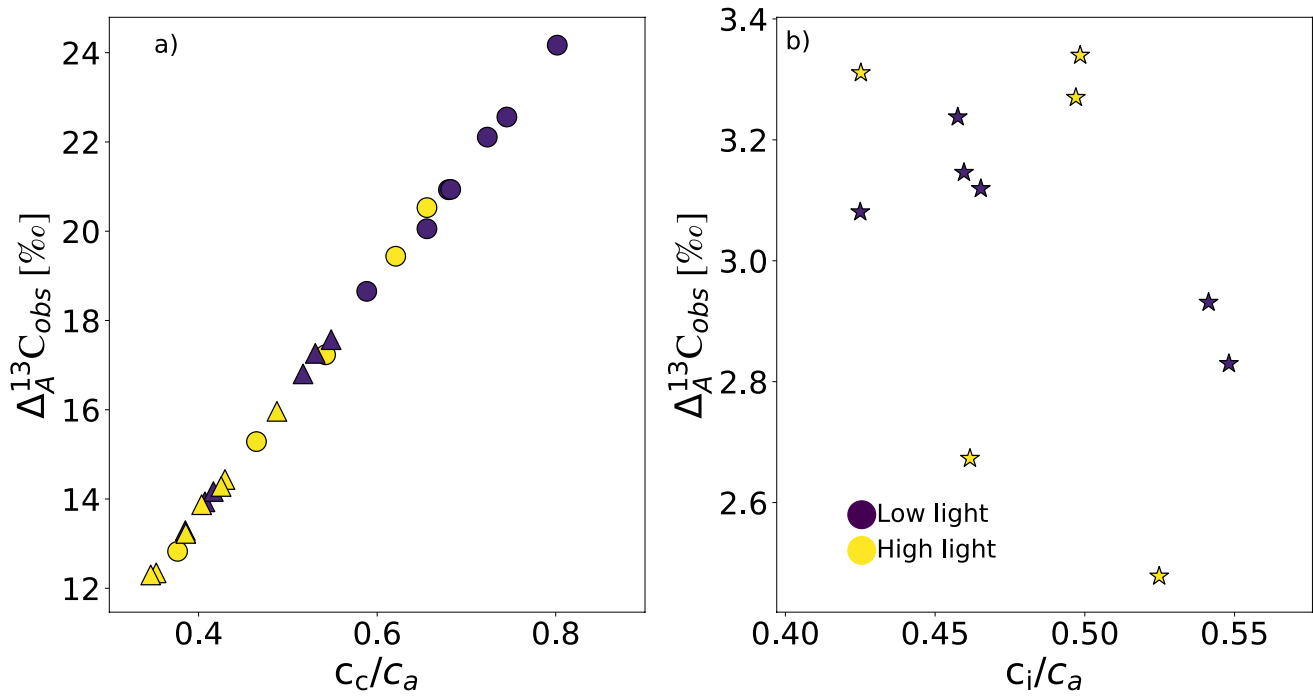
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405 Figure S7 Schematic diagram of the conceptual leaf-cuvette model.  $\delta$  and  $c$  are the oxygen isotope composition and mixing ratio of  $\text{CO}_2$ . The subscripts  $e, a, i, m, c$  represents  $\text{CO}_2$  entering the cuvette, leaving the cuvette, in the intercellular air space, the mesophyll and the chloroplast, respectively.



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Figure S8.  $\Delta_A^{13}C$  of carbon dioxide during photosynthesis. a) The  $\Delta_A^{13}C$  of the two  $C_3$  plants sunflower (circles) and ivy (triangles) at two different irradiances. b) The  $\Delta_A^{13}C$  of maize at two different irradiances. The measurement error in  $\Delta_A^{13}C_{obs}$  is 0.15 ‰ (SD), calculated using error propagation.

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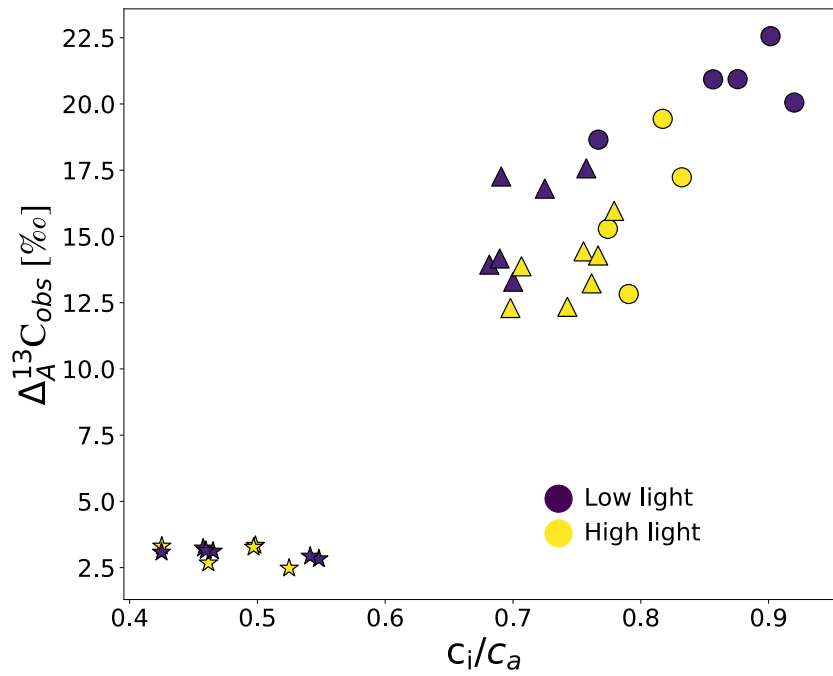
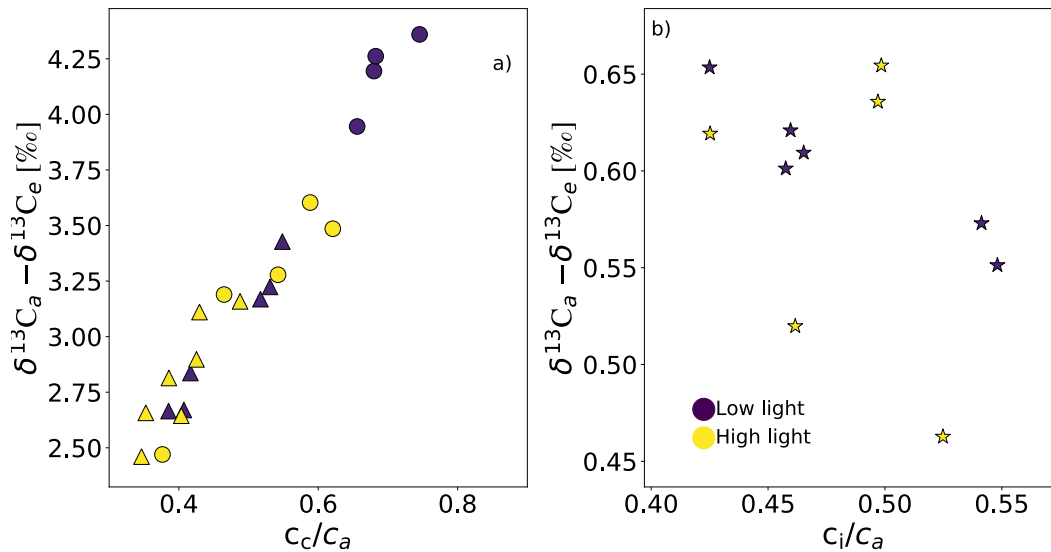
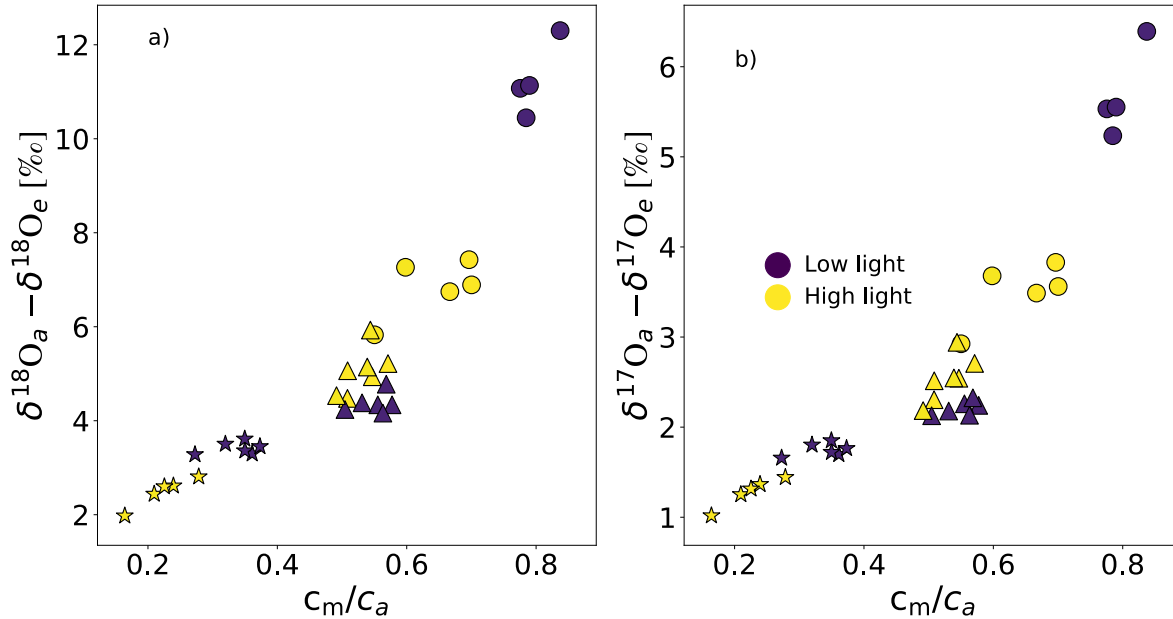


Figure S9.  $\Delta_A^{13}C$  of carbon dioxide during photosynthesis for the two  $C_3$  plants sunflower (circles) and  
 420 ivy (triangles) and a  $C_4$  plant maize (stars).

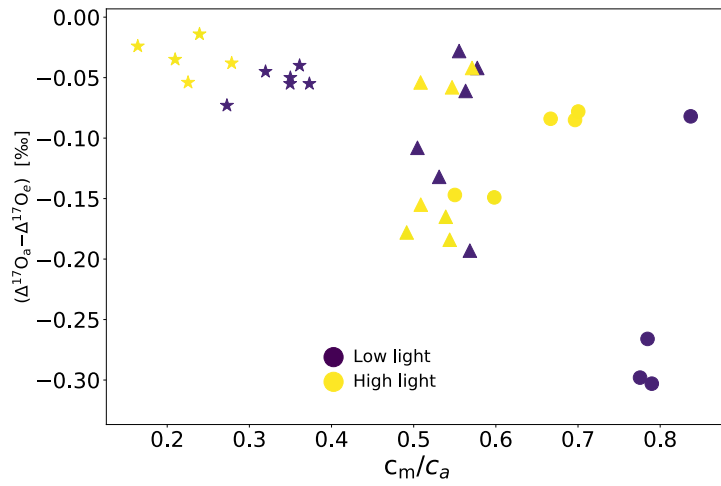


425 Figure S10. Relative difference in  $\delta^{13}\text{C}$  of  $\text{CO}_2$  leaving (index a) and entering (index e) the leaf cuvette during experiments with two  $\text{C}_3$  plants, sunflower (circles) and ivy (triangles) (panel a) as a function of the  $c_e/c_a$  ratio and a  $\text{C}_4$  plant maize (stars) (panel b) as a function of the  $c_i/c_a$  ratio. The experiments were performed under 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.

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435 Figure S11 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 under 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.

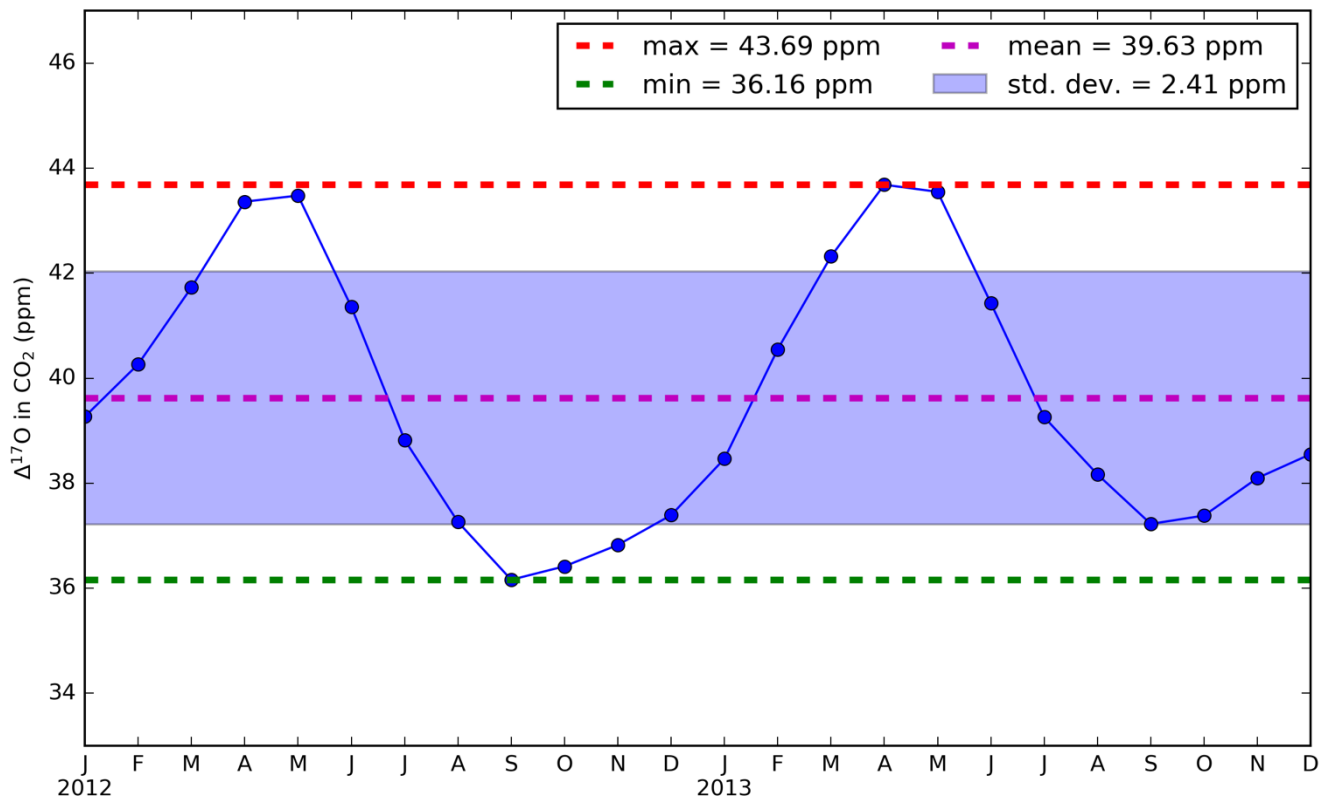


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Figure S12 Difference in  $\Delta^{17}\text{O}$  of the  $\text{CO}_2$  leaving (index a) and entering (index e) the cuvette as a function of  $c_m/c_a$  for sunflower (circles), ivy (triangles) and maize (stars).

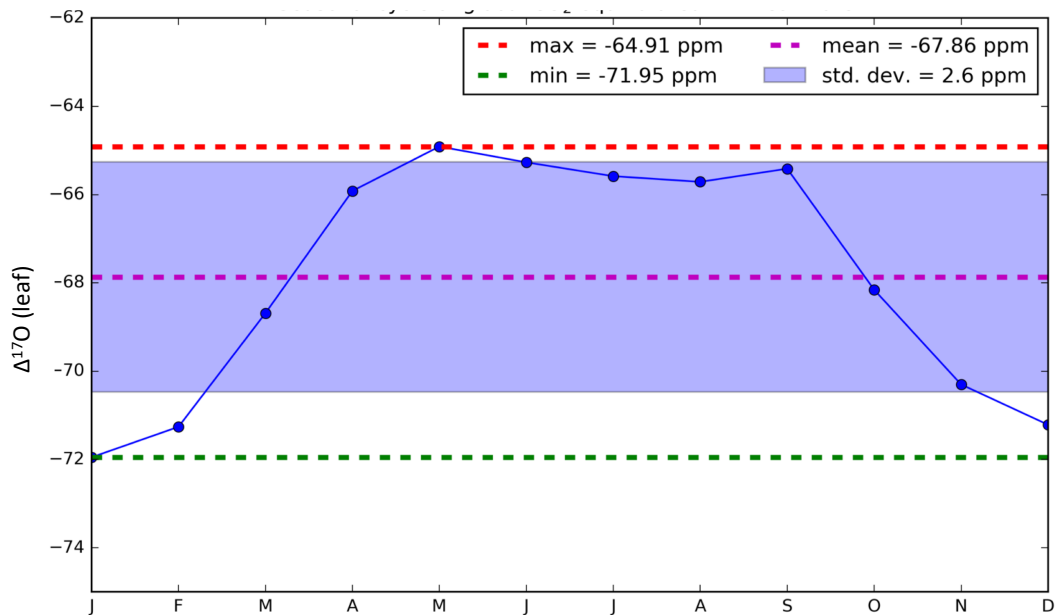
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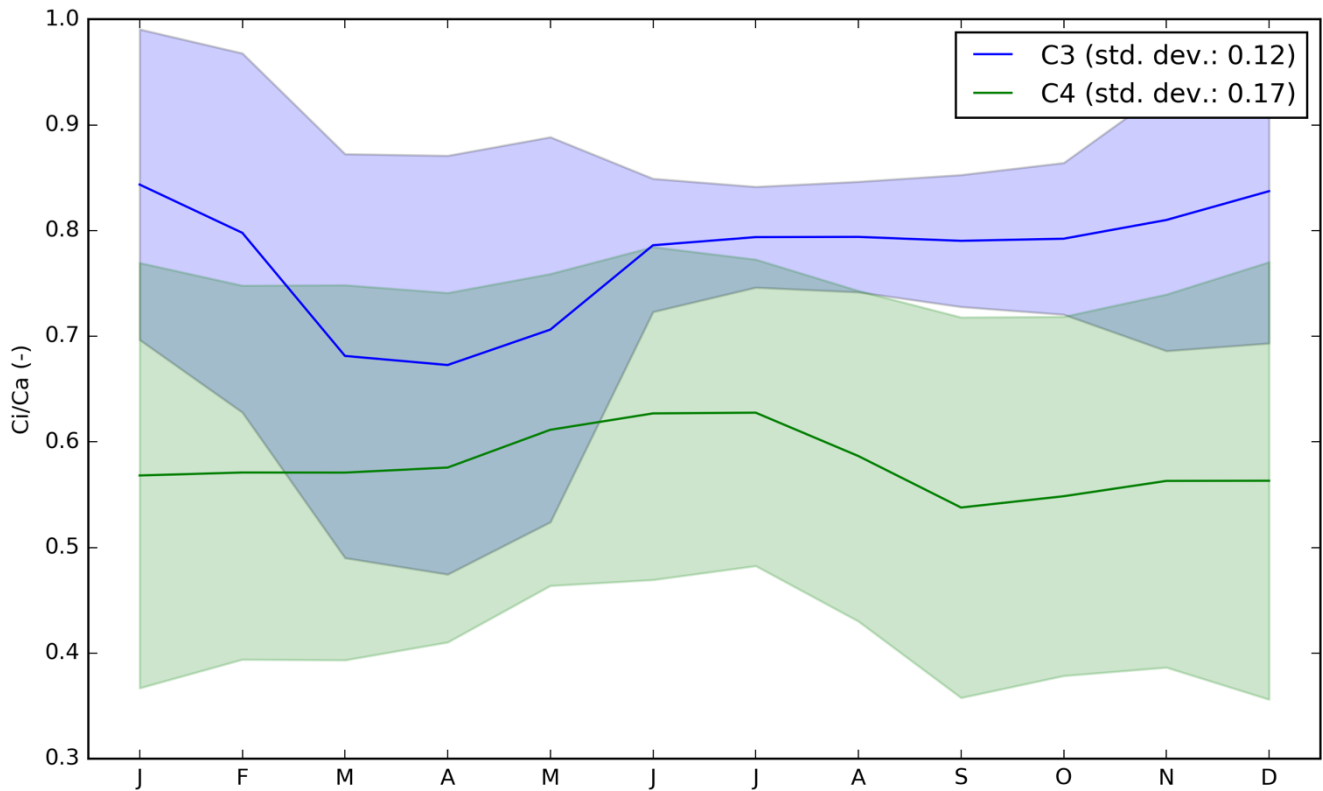
Figure S13. 3D model result for the global average seasonal cycle of  $\Delta^{17}\text{O}$  of atmospheric  $\text{CO}_2$  for the years 2012 and 2013 (Koren et al., 2019). Note that the  $\Delta^{17}\text{O}$  value was calculated in Koren et al. (2019) with  $\lambda = 0.5229$ . To convert to the  $\lambda = 0.528$ , we use  $\Delta^{17}\text{O}(\text{CO}_2)_{\lambda=0.528} = \Delta^{17}\text{O}(\text{CO}_2)_{\lambda=0.5229} + (0.5229 - 0.528) \times \ln(\delta^{18}\text{O}(\text{CO}_2) + 1)$ . In the 3D global model,  $\delta^{18}\text{O}(\text{CO}_2)$  is 41.5‰.



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Figure S14. 3D model result for the seasonal cycle of the global average  $\Delta^{17}\text{O}$  value of leaf water for the year 2012 (Koren et al., 2019). Note that  $\Delta^{17}\text{O}$  value is reported here with  $\lambda = 0.5229$ . To convert to  $\lambda = 0.528$ , we use  $\Delta^{17}\text{O}(\text{leaf})_{\lambda=0.528} = \Delta^{17}\text{O}(\text{leaf})_{\lambda=0.5229} + (0.5229 - 0.528) \times \ln \alpha_{\text{trans}}$ .  $\alpha_{\text{trans}} = 1/0.9917$  (Koren et al., 2019; Hofmann et al., 2017).





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Figure S15 Annual variability of the  $c_i/c_a$  ratio for C<sub>4</sub> and C<sub>3</sub> plants from the SiBCASA model (Schaefer et al., 2008;Koren et al., 2019).

470 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* stand for standard error and standard deviation. All the isotope values given in the table are in per mill [‰].

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

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Table S2: The ratio of stomatal conductance to mesophyll conductance and weighted mean fractionation of <sup>12</sup>C<sup>18</sup>O<sup>16</sup>O as it diffuses from the CO<sub>2</sub>-H<sub>2</sub>O exchange site ( $\bar{a}_{18}$ ) for numerous species determined in previous investigations.

$g_s/g_m$	$\bar{a}_{18}$	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)

480

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