

## Effect of photosynthesis on the abundance of $^{18}\text{O}^{13}\text{C}^{16}\text{O}$ in atmospheric $\text{CO}_2$

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The abundance of the isotopologue  $^{18}\text{O}^{13}\text{C}^{16}\text{O}$  ( $\Delta_{47}$ ) in atmospheric air is a promising new tracer for the atmospheric carbon cycle (Eiler and Schauble, 2004; Affek and Eiler, 2006; Affek et al., 2007). The large gross fluxes in  $\text{CO}_2$  between the atmosphere and biosphere are supposed to play a major role in controlling its abundance. Eiler and Schauble (2004) set up a box model describing the effect of air-leaf interaction on the abundance of  $^{18}\text{O}^{13}\text{C}^{16}\text{O}$  in atmospheric air. The main assumption is that the exchange between  $\text{CO}_2$  and water within the mesophyll cells will imprint a  $\Delta_{47}$  value on the back-diffusing  $\text{CO}_2$  that reflects the leaf temperature. Additionally, kinetic effects due to  $\text{CO}_2$  diffusion into and out of the stomata are thought to play a role. We investigated the effect of photosynthesis on the residual  $\text{CO}_2$  under controlled conditions using a leaf chamber set-up to quantitatively test the model assumptions suggested by Eiler and Schauble (2004).

We studied the effect of photosynthesis on the residual  $\text{CO}_2$  using two  $\text{C}_3$  and one  $\text{C}_4$  plant species: (i) sunflower (*Helianthus annuus*), a  $\text{C}_3$  species with a high leaf conductance for  $\text{CO}_2$  diffusion, (ii) ivy (*Hedera hibernica*), a  $\text{C}_3$  species with a low conductance, and (iii), maize (*Zea mays*), a species with the  $\text{C}_4$  photosynthetic pathway. We also investigated the effect of different light intensities (photosynthetic photon flux density of 200, 700 and  $1800 \mu\text{mol m}^{-2}\text{s}^{-1}$ ), and thus, photosynthetic rate in sunflower and maize.

A leaf was mounted in a cuvette with a transparent window and an adjustable light source. The air inside was thoroughly mixed, making the composition of the outgoing air equal to the air inside. A gas-mixing unit was attached at the entrance of the cuvette that mixed air with a high concentration of scrambled  $\text{CO}_2$  with a  $\Delta_{47}$  value of 0 to  $0.1\text{‰}$  with  $\text{CO}_2$  free air to set the  $\text{CO}_2$  concentration of ingoing air at 500 ppm. The flow rate through the cuvette was adjusted to the photosynthetic activity of the leaf so that the  $\text{CO}_2$  concentration at the outlet was 400 ppm and varied between  $0.6$  and  $1.5 \text{ L min}^{-1}$ .  $\text{CO}_2$  and  $\text{H}_2\text{O}$  concentrations in air were monitored with an IRGA and air was sampled at the outlet with flasks.

We found that the effect on  $\Delta_{47}$  of the residual  $\text{CO}_2$  for the  $\text{C}_3$  species sunflower and ivy was proportional to the effect on  $\delta^{18}\text{O}$  of the residual  $\text{CO}_2$ . The difference in  $\Delta_{47}$  between the in- and outgoing  $\text{CO}_2$  was between  $-0.07$  and  $0.49\text{‰}$  varying with the  $\text{CO}_2$  concentration in the chloroplasts relative to the bulk air ( $C_c/C_a$ ). The  $C_c/C_a$  depends on conductance and photosynthetic activity, and was different for the two species and was manipulated with the light intensity. For the  $\text{C}_4$  species maize, a  $\Delta_{47}$  value of  $-0.08 \pm 0.02\text{‰}$  was observed. The slightly negative effect on  $\Delta_{47}$  may be related to its lower  $C_c/C_a$  ratio and possibly a lower carbonic anhydrase activity causing incomplete exchange with leaf water. We will discuss these results in light of the suggested fractionation processes and discuss the implication for the global  $\Delta_{47}$  value of atmospheric  $\text{CO}_2$ .

### References

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