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

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The abundance of the isotopologue $^{18}$O$^{13}$C$^{16}$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 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 $^{18}$O$^{13}$C$^{16}$O in atmospheric air. The main assumption is that the exchange between CO$_2$ and water within the mesophyll cells will imprint a $\Delta_{47}$ value on the back-diffusing CO$_2$ that reflects the leaf temperature. Additionally, kinetic effects due to CO$_2$ diffusion into and out of the stomata are thought to play a role. We investigated the effect of photosynthesis on the residual 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 CO$_2$ using two C3 and one C4 plant species: (i) sunflower (Helianthus annuus), a C3 species with a high leaf conductance for CO$_2$ diffusion, (ii) ivy (Hedera hibernica), a C3 species with a low conductance, and (iii) maize (Zea mays), a species with the C$_4$ photosynthetic pathway. We also investigated the effect of different light intensities (photosynthetic photon flux density of 200, 700 and 1800 µmol m$^{-2}$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 CO$_2$ with a $\Delta_{47}$ value of 0 to 0.1‰, with CO$_2$ free air to set the 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 CO$_2$ concentration at the outlet was 400 ppm and varied between 0.6 and 1.5 L min$^{-1}$. CO$_2$ and H$_2$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 CO$_2$ for the C3 species sunflower and ivy was proportional to the effect on $\delta^{18}$O of the residual CO$_2$. The difference in $\Delta_{47}$ between the in- and outgoing CO$_2$ was between 0.13 and 0.47‰, varying with the CO$_2$ concentration in the chloroplasts relative to the bulk air ($C_a/C_i$). The $C_a/C_i$ depends on conductance and photosynthetic activity, and was different for the two species and was manipulated with the light intensity. No effect on $\Delta_{47}$ was observed for the C$_4$ species maize. This may be related to its lower $C_a/C_i$ 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 CO$_2$.