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 $^{18}O^{13}C^{16}O$ (Δ_{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 Δ_{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 C_3 and one C_4 plant species: (i) sunflower (*Helianthus annuus*), a C_3 species with a high leaf conductance for CO_2 diffusion, (ii) ivy (*Hedera hibernica*), a C_3 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 Δ_{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_2O concentrations in air were monitored with an IRGA and air was sampled at the outlet with flasks.

We found that the effect on Δ_{47} of the residual CO_2 for the C_3 species sunflower and ivy was proportional to the effect on $\delta^{18}O$ of the residual CO_2. The difference in Δ_{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_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. No effect on Δ_{47} was observed for the C_4 species maize. This 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 Δ_{47} value of atmospheric CO_2.

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