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Fractionation of clumped isotopes of CO_2 during photosynthesis

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Stable isotope ($\delta^{13}C$ and $\delta^{18}O$) and mole fraction measurements of CO_2 are used to constrain the carbon cycle. However, the gross fluxes of the carbon cycle, especially photosynthesis and respiration, remain uncertain due to the challenging task of distinguishing individual flux terms from each other. The clumped isotope composition (Δ_{47}) of CO_2 has been suggested as an additional tracer for gross CO_2 fluxes since it depends mainly on temperature but not on the bulk isotopic composition of leaf, soil and surface water, unlike $\delta^{18}O$ of CO_2.

In this study, we quantify the effect of photosynthetic gas exchange on Δ_{47} of CO_2 using leaf cuvette experiments with two C_3 and one C_4 plants and discuss challenges and possible applications of clumped isotope measurements. The experimental results are supported by calculations with a leaf cuvette model. Our results demonstrate how the effect of gas exchange on Δ_{47} is controlled by CO_2-H_2O isotope exchange (using plants with different carbonic anhydrase activity), and kinetic fractionation as CO_2 diffuses into and out of the leaf (using plants with different stomatal and mesophyll conductance). We experimentally confirm the previously suggested dependence of Δ_{47} on the stomatal conductance and back-diffusion flux.