

Global long-term mean triple oxygen isotope composition of tropospheric CO₂

M. Hofmann, B. Horváth, and A. Pack

Georg-August-Universität, Göttingen, Germany (magdalena.hofmann@geo.uni-goettingen.de)

Introduction: The oxygen and carbon isotope composition (¹⁸O/¹⁶O and ¹³C/¹²C) of tropospheric CO₂ is an excellent tool to investigate the atmospheric CO₂ cycle. Hoag et al. [1] suggested that the triple oxygen isotope composition (¹⁷O/¹⁶O and ¹⁸O/¹⁶O) of tropospheric CO₂ is a potential new tracer for terrestrial gross primary production (GPP). Here, we investigate in detail the global long-term mean triple oxygen isotope composition of tropospheric CO₂ and discuss its sensitivity to the major CO₂ fluxes, in particular GPP and stratospheric CO₂ influx.

Method: We conduct mass balance calculations for both $\delta^{18}\text{O}$ and $\Delta^{17}\text{O}_{TFL}$ of tropospheric CO₂ in order to reconcile the assumptions for ¹⁸O/¹⁶O and ¹⁷O/¹⁶O fractionation of atmospheric CO₂. In doing so, we carefully assign triple oxygen isotope signatures to the main CO₂ sources and sinks. For CO₂-water exchange, we implement the triple oxygen isotope exponent $\theta_{CO_2/water} = 0.522 \pm 0.002$ [2] and we take into account that the main water reservoirs that exchange with atmospheric CO₂ (ocean, soil and leaf water) have a distinct $\Delta^{17}\text{O}_{TFL}$ signature [3, 4]. For kinetically fractionated CO₂ sources and sinks we assume that the exponent $\lambda_{kinetic} = 0.509$ [5]. We test the sensitivity to the main carbon fluxes and fractionation processes by carrying out a Monte Carlo simulation. We also compare the mass balance calculations to the long-term mean triple oxygen isotope composition of ambient air sampled in Göttingen (NW Germany) and with samples from remote locations. The triple oxygen isotope composition of these CO₂ samples was analyzed using a CO₂-CeO₂ equilibration technique published previously [2, 6]. All triple oxygen isotope data are reported relative to the terrestrial fractionation line (TFL) with a slope $\lambda_{TFL} = 0.5251$ and zero intercept.

Results: For our base scenario, we calculate a global triple oxygen isotope composition of tropospheric CO₂ with $\delta^{18}\text{O}_{VSMOW} = 41.3\text{‰}$ and $\Delta^{17}\text{O}_{TFL} = -0.12\text{‰}$. Ambient air CO₂ from Göttingen has a long-term mean triple oxygen isotope composition with $\delta^{18}\text{O}_{VSMOW} = 41.5 \pm 0.9\text{‰}$ (SD) and $\Delta^{17}\text{O}_{TFL} = -0.12 \pm 0.06\text{‰}$ (SD).

Discussion: Several studies on $\delta^{18}\text{O}$ of atmospheric CO₂ demonstrated that assimilation and respiration are the two opponents controlling the global mean $\delta^{18}\text{O}$ of tropospheric CO₂ [7-10]. Here, we show that assimilation is the main driver that tends to decrease the $\Delta^{17}\text{O}_{TFL}$ of tropospheric CO₂ whereas both soil respiration and stratospheric influx are the main drivers that tend to increase the $\Delta^{17}\text{O}_{TFL}$ value. The model output for our base scenario is in excellent agreement with the long-term mean triple oxygen isotope composition of ambient air from Göttingen. The sensitivity tests show that $\Delta^{17}\text{O}_{TFL}$ of tropospheric CO₂ is slightly sensitive to changes in GPP and stratospheric CO₂ influx, and thus, has the potential to complement $\delta^{18}\text{O}$ modeling of atmospheric CO₂.

References:

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