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Temperature dependence of the triple oxygen isotope equilibrium fractionation between carbon dioxide and water and its implication on the triple oxygen isotope signature of tropospheric carbon dioxide

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Stratospheric CO_2 possesses a large oxygen isotope anomaly [1], whereas the oxygen isotope composition of tropospheric CO_2 is to a great extent controlled by mass-dependent oxygen isotope exchange between CO_2 and water in plants [2]. Thus, investigations of the CO_2-water equilibrium are essential to understand the triple oxygen isotope signature of tropospheric CO_2. High precision analysis of the $\Delta^{17}O$ signature of tropospheric CO_2 is a valuable tool to investigate the terrestrial gross carbon fluxes [3] and to test predictions on the stratosphere-troposphere exchange flux. Here, we present data on the exponent β for equilibrium fractionation between $CO_{2(g)}$ and water at 2, 23 and 37°C and data on $\Delta^{17}O$ of tropospheric CO_2. The analytical data on ambient air CO_2 sampled in Göttingen (Germany) are compared to an oxygen isotope mass-balance model for tropospheric CO_2.

For each CO_2-water equilibration experiment, about 14 mmol of CO_2 were equilibrated with 3.3 mol of local distilled tap water (molar $H_2O_{(l)}/CO_{2(g)}$ ratio > 200). We conducted 1 experiment at 2°C, 5 experiments at 23°C and 4 experiments at 37°C. The triple oxygen isotope composition of CO_2 was analyzed based on CO_2-CeO_2 equilibration and subsequent mass spectrometric analysis of CeO_2 by infrared laser fluorination [4]. Each CO_2 analysis is based on 3-5 CeO_2 analyses. We assume that our tap water ($\delta^{18}O$ = –8.1‰) falls on the meteoric water line with a slope of β = 0.528 and an intercept of γ = +0.033‰ [5]. β (CO_2-water) was determined as 0.5196±0.0008 (1σ), 0.5220±0.0008 (1σ) and 0.5214±0.0008 (1σ) at 2, 23 and 37°C, respectively. Thus, the data do not show a temperature dependence in the investigated temperature range. The experimentally determined exponent β (for 2°C $\leq$ t $\leq$ 37°C) is significantly lower than the high temperature limit of 0.529 [6].

Taking into account that β ($CO_{2(g)}$-$H_2O_{(g)}$) = 0.5235 [7], β ($H_2O_{(l)}$-$H_2O_{(g)}$)=0.529 [8], $\alpha_{CO2(g)-H2O(l)}$=1.041 [9] and $\alpha_{H2O(l)-H2O(g)}$=1.009 [10] at 25°C, one can estimate the exponent β ($CO_{2(g)}$-water) as 0.522±0.001. This demonstrates that our experimental results are consistent with theoretical and experimental data on β ($CO_{2(g)}$-$H_2O_{(g)}$) and β ($H_2O_{(l)}$-$H_2O_{(g)}$) [7, 8].

CO_2 from ambient air was sampled in 2-week intervals starting in August 2010 in Göttingen. The CO_2 was extracted from about 450 L air using a Russian doll type cryogenic trap [11]. The CO_2 was dried using P_2O_5 and $Mg(ClO_4)_2$. Subsequently, the CO_2 was analyzed for its triple oxygen isotope composition using the CO_2-CeO_2 exchange method [4]. All data on $\Delta^{17}O$ are given relative to the rocks- and minerals defined terrestrial fractionation line with a slope of 0.5251±0.0007 and an intercept of –0.014±0.008‰ . Each CO_2 sample was analyzed with a precision < ±0.04‰ . The $\Delta^{17}O$ of ambient air CO_2 is on average –0.09±0.04‰ (N=11). Our results are 0.11‰ higher than the prediction from Hoag et al. [3] who give $\Delta^{17}O$ of global tropospheric CO_2 of –0.20 ‰ (relative to our TFL). We reevaluated the model from Hoag et al. [3] assuming that CO_2 from the hydro- and biosphere fractionates mass-dependently according to our experimentally determined exponent β ($CO_{2(g)}$-$H_2O_{(l)}$). The model allows us to estimate the effect of CO_2 influx from the stratosphere, biosphere and hydrosphere on the global triple oxygen isotope composition of tropospheric CO_2.

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