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Experimental determination of the exponent beta for oxygen triple isotope fractionation between carbon dioxide and water

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Because of the coupling between $\alpha^{18/16}_{CO2-H2O}$ and $\alpha^{17/16}_{CO2-H2O}$ (ln $\alpha^{17/16}_{CO2-H2O} = \beta_{CO2-H2O}$ ln $\alpha^{18/16}_{CO2-H2O}$), not only δ^{18}O, but also δ^{17}O of atmospheric CO_2 is determined by CO_2-water isotope exchange. Thus, fundamental understanding of Δ^{17}O of CO_2 requires precise information on $\beta_{CO2-H2O}$. Here, we present the first experimental data on $\beta_{CO2-H2O}$at 23°C.

We equilibrated bottle CO_2 (δ^{18}O = 27.7‰) with distilled local tap water (Göttingen, December 2009) at 23°C for 68 hours. The molar H_2O/CO_2 ratio was >400. At the end of the experiment, CO_2 was isolated from the water. The resultant δ^{18}O value of the CO_2 was +32.5‰ giving a δ^{18}O value of the tap water of -8.4‰ [1]. This value is typical for local meteoric water and is consistent with preliminary water isotope analyses in the Göttingen laboratory (δ^{18}O = -8‰). The distilled water is assumed to fall on the water fractionation line with β = 0.5279 [2]. The CO_2 gas was analysed for its $\Delta^{17}O_{TFL}$ signature based on CO_2-CeO_2 equilibration at 685°C and subsequent mass spectrometric analysis of CeO_2 by infrared-laser fluorination [3,4]. The $\Delta^{17}O_{TFL}$ values were determined relative to a fractionation line with a slope of 0.5251 ± 0.0085. The exponent β for the triple oxygen isotope fractionation between CO_2 and water can be calculated according to the relation:

$$\beta_{CO2-H2O} = \beta_{TFL} + [(\beta_{CO2-CeO2} - \beta_{TFL})(\delta'^{18}O^{CO2}_{SMOW} - \delta'^{18}O^{CeO2}_{SMOW}) - \Delta^{17}O^{H2O}_{TFL} + \Delta^{17}O^{CeO2}_{TFL}] / (\delta'^{18}O^{CO2}_{SMOW} - \delta'^{18}O^{H2O}_{SMOW})$$

β_{TFL}: slope of the terrestrial fractionation line (TFL) defined by rocks and minerals

$\beta_{CO2-CeO2}$: exponent for the triple oxygen isotope fractionation between CO_2 and CeO_2

$\delta'^{18}O^{x}_{SMOW}$ = 1000 ln ($\delta^{18}O^{x}_{SMOW}$/1000 + 1), where x represents CO_2, CeO_2 or H_2O

$\Delta^{17}O^{y}_{TFL}$: deviations from the TFL, where y represents CeO_2 or H_2O

The CO_2-water equilibration experiment suggests that $\beta_{CO2-H2O}$ = 0.5218 ± 0.0016 at 23°C. Based on theory, Matsuhisa et al. [5] propose $\beta_{CO2-H2O}$ = 0.5235 at 25°C. The data suggest that CO_2 being in equilibrium with seawater (t = 23°C) has a $\Delta^{17}O_{TFL}$ value of -0.14‰

We demonstrate that the equilibrium exponent β can deviate significantly from the high-temperature equilibrium value of 0.529 [6]. Different β values have to be considered when using the Δ^{17}O value of CO_2 for atmospheric modelling [7] or when using Δ^{17}O of skeletal apatite as CO_2-proxy [8,9].

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