Geophysical Research Abstracts,
Vol. 11, EGU2009-9072, 2009
EGU General Assembly 2009

A novel technique for high-precision analysis of triple oxygen isotope ratios in carbon dioxide

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Precise measurement of triple oxygen isotope ratios in carbon dioxide is a promising tool in tracing interactions between the troposphere and the biosphere. Thus, exact triple oxygen isotope determination of tropospheric CO_2 might play a major role in improving geochemical modelling of terrestrial gross carbon fluxes [1]. Even though major progress in analysing triple oxygen isotope ratios in carbon dioxide has been made [2-4], the uncertainties in δ^{17}O analysis remain too large to reveal the predicted slight variations of tropospheric CO_2 from the terrestrial fractionation line [1]. Assonov and Brenninkmeijer [2] showed that the triple oxygen isotope composition of CO_2 can be inferred from CO_2-CeO_2 exchange experiments due to the very high oxygen diffusion rates of ceria. They showed that the triple oxygen isotope composition can be deduced by comparing the mass ratios 45/44 and 46/44 of the sample CO_2 before and after equilibration with ceria. In order to enhance precision, we analysed the equilibrated ceria instead of CO_2. We also investigated the temperature dependency of the CO_2-CeO_2 equilibrium fractionation factor.

CO_2-CeO_2 isotope exchange experiments were carried out at temperatures between 600˚C and 900˚C for 0.5 h to 3 h. The molar CO_2-CeO_2 ratio in the exchange system is greater than 100. δ^{18}O analyses of CO_2 before and after equilibration show that the influence of CeO_2 oxygen on the isotopic composition of the bulk system is negligible. After isotopic equilibration with CO_2, the triple oxygen isotope composition of ceria is analysed on a Thermo MAT 253 gas mass spectrometer by IR-laser fluorination. After determination of the fractionation factor between CO_2 and ceria, the triple oxygen composition of the sample CO_2 can be inferred from the isotopic composition of the equilibrated ceria. In order to calibrate the procedure, CO_2 with a known δ^{17}O value is prepared via quantitative conversion of O_2 to CO_2 by combustion of carbon. Terrestrial rocks and minerals with varying δ^{18}O values are analysed defining the terrestrial fractionation line (TFL). Thus, oxygen isotope anomaly of CO_2 can be expressed as $\Delta^{17}O_{CO2}$= $(\beta_{TFL} - \beta_{CO2-CeO2}) \times \Delta^{18}O_{CO2-CeO2} + \Delta^{17}O_{CeO2}$.

Analysis of rocks and minerals (N = 126) defines the slope of the TFL (β_{TFL})as 0.5247. $\beta_{CO2-CeO2}$ accounts for the triple oxygen equilibrium fractionation between equilibrated ceria and CO_2. Experimental determination of $\beta_{CO2-CeO2}$ requires equilibration of ceria and CO_2 with known δ^{17}O abundance. This parameter has not been determined yet, but it will be presented at the conference. $\Delta^{18}O_{CO2-CeO2}$ accounts for the equilibrium fractionation between CO_2 and CeO_2. Isotopic exchange between CO_2 and CeO_2 is temperature dependent resulting in an equilibrium fractionation factor $1000 \times \ln \alpha_{CO2-CeO2}$ of $15.04 \pm 0.06\,(1\sigma)$, $12.69 \pm 0.10\,(1\sigma)$ and $11.63 \pm 0.10\,(1\sigma)$ at 600˚C, 700˚C and 900˚C respectively. $\Delta^{17}O_{CeO2}$ describes the deviation of equilibrated CeO_2 from the TFL. Our data show that the reproducibility of a single ceria analysis is ± 0.03 ‰. Untreated ceria shows an oxygen isotope anomaly of Δ^{17}O = -0.20 ‰± 0.03 (1σ). Equilibration of ceria with ordinary technical CO_2 (δ^{18}O = 15.2 ‰) gives $\Delta^{17}O_{CeO2}$values of 0.04 ‰± 0.04 (1σ), 0.07 ‰± 0.06 (1σ) and 0.14 ‰± 0.10 (1σ) at 600˚C, 700˚C and 900˚C respectively. Taking all available data into account, $\Delta^{17}O_{CO2}$ is likely to be determined with a precision of approximately 0.05 ‰ of a single experiment.

Our data confirm that ceria is an excellent oxygen-exchange medium in CO_2 exchange experiments and that full equilibrium is reached after a short period of time of 0.5 h to 3 h at temperatures ranging between 600˚C and 900˚C. Our technique can also be used to determine equilibrium fractionation factors between other oxygen-bearing gaseous components (e.g. CO_2-O_2) via equilibration with CeO_2. Most importantly, our data suggest that direct measurement of equilibrated ceria is a suitable tool to precisely determine Δ^{17}O variations of CO_2. This new analytical technique is accurate and straightforward. It opens up a new field for investigating the triple oxygen composition of various types of atmospheric CO_2. These data will be acquired in the course of the ongoing project.

References:

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