Development of a high-precision measurement system for the triple oxygen isotopic compositions of atmospheric carbon dioxide

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The triple oxygen isotopic compositions ($\Delta^{17}O$) of tropospheric carbon dioxide (CO_2) can be a useful tracer to quantify carbon cycle in terrestrial environments. Traditionally, CO_2 must be converted to O_2 to determine $\Delta^{17}O$ precisely. However, toxic and dangerous reagents such as fluoride must be needed for the reactions to convert CO_2 to O_2. Alternative safer, more simple, and more easy techniques should be needed for the routine measurements on the $\Delta^{17}O$ of tropospheric CO_2. In this study, I developed an alternative new method for the high precision measurements on the $\Delta^{17}O$ of CO_2 using Cavity Ring-Down Spectroscopy (CRDS) for H_2O. First of all, atmospheric sample with CO_2 was introduced into pre-evacuated line and separated from atmospheric nitrogen (N_2), oxygen (O_2) and water (H_2O) using the differences in the boiling points. Then, N_2O having the similar molecular weight and the similar boiling point with CO_2 was separated from CO_2 using a PorapakPS column (3m long, 0.31cm i.d.) under -70 ˚C. By reacting the purified CO_2 with H_2 at 600 ˚C under the existence of the nickel catalysts, CO_2 was converted to methane (CH_4) and water (H_2O). Subsequent to purify H_2O from CH_4, $\Delta^{17}O$ of H_2O was measured in CRDS. In this study, I developed this new vacuum line to purify atmospheric CO_2 and to convert CO_2 into H_2O. Then, I determined the optimum conditions for the purification of CO_2, the reduction of CO_2, and the analysis of H_2O.The new system developed in this study has several advantages over the conventional methods, such as (1) safe and easy operations, (2) less than 50 min for the analysis, and (3) comparable precisions with previous methods. By using the new system developed in this study, we can determine $\Delta^{17}O$ of tropospheric CO_2 with precision better than 0.015 ‰(1σ). By using the new system developed in this study, I determined the difference in the $\Delta^{17}O$ values between tropospheric CO_2 in Nagoya and that in car exhaust, and found that tropospheric CO_2 in Nagoya was 0.22‰ higher in $\Delta^{17}O$ than that in car exhaust.

Keywords: carbon dioxide, high precision, triple oxygen isotope