CO_2 Reference Gas Prepared in NIES for Intercomparison of Isotope Analysis

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There are several difficulties in determining precise isotopic ratios of CO_2 in the atmosphere. First, there is no gaseous CO_2 standard that has a precise isotope value (e.g., precision <0.01 per mil) relative to VPDB-CO_2. Recently, the U.S. National Institute of Standards and Technology (NIST) supplied three CO_2 reference materials for isotope analysis. These RMs are very useful to check measurement values and the cross contamination effect in mass spectrometers. However, there are uncertainties in the certified values (over 0.03 per mil for $\delta^{13}C$ and 0.1 per mil for $\delta^{18}O$, although these uncertainties may decrease in the future) and, unfortunately, they do not span ambient oxygen isotope ratios for atmospheric CO_2 (about 0 per mil). In such circumstances, NIES decided to make a reference sample for atmospheric CO_2 especially for intercomparison in the CO_2 community. For easy handling, each CO_2 sample was sealed in a 6 mm diameter glass tube. CO_2 was produced from reagent carbonate and the carbon isotope ratio was adjusted to -8.5 per mil. The oxygen isotope ratio of about 0 per mil was obtained by using an equilibrium process with seawater. About 3 L of CO_2 were prepared and about 2 mL of CO_2 were sealed in each glass tube to obtain over 1000 samples. This reference CO_2, called NIES Atmospheric CO_2 Isotope ratio Standard (NACIS), is now being distributed for intercomparison. After the cross contamination effect in isotope analysis by MAT 252 was studied by using NIST RMs, NBS19, and NBS18, an isotope ratio of NACIS was tentatively determined at -8.57 and -0.70 for $\delta^{13}C$ and $\delta^{18}O$ respectively.

Second, the isotopic fractionation of CO_2 in the extraction process from air samples was studied by using NACIS. An air standard was used frequently to ensure traceability of measured values. In this study, the NACIS reference gas was diluted by CO_2 free air to produce an ambient level concentration. This reference air was used to check the extraction process. Several trials showed good agreement in determination of $\delta^{13}C$, but slight deviation (about 0.05 per mil) was sometimes observed in $\delta^{18}O$ analyses. This reference air sample was more useful to assess the extraction process than use of real air.