Articles

Stable Carbon and Oxygen Isotopic Analysis of Atmospheric Carbon Monoxide Using Continuous-Flow Isotope Ratio MS by Isotope Ratio Monitoring of CO

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We have developed a rapid and simple measurement system for both content and stable isotopic compositions (^{13}C and ^{18}O) of atmospheric CO, using continuous-flow isotope ratio mass spectrometry by simultaneously monitoring the CO^+ ion currents at masses 28, 29, and 30. The analytical system consisted sequentially of a sample trapping port (liquid nitrogen temperature silica gel and molecular sieve 5A), a gas dryer, a CO purification column (molecular sieve 5A), a cryofocusing unit, and a final purification column using a GC capillary. Analytical precision of 0.2‰ for ^{13}C and 0.4‰ for ^{18}O can be realized for samples that contain as little as 300 pmol of CO within 40 min for one sample analysis. Analytical blanks associated with the method are less than 1 pmol. The extent of analytical error in $\delta^{13}C$ due to mass-independent fractionation of oxygen in natural CO is estimated to be less than 0.3‰. Based on this system, we report herein a kinetic isotopic effect during CO consumption in soil.

Carbon monoxide is the major substrate of reactions of the hydroxyl radical in the troposphere and hence strongly affects the oxidizing capacity of the atmosphere as well as concentrations of other trace gases. Analyses of the stable isotopic composition of CO have provided important information on the sources and fates of CO in various environments (e.g., refs 1 and 2). Unfortunately, conventional isotopic analysis of CO requires large amounts of material to prepare micromole quantities, and this limitation has prohibited utilization of the isotopic signature of CO in some environments.

Continuous-flow isotope ratio mass spectrometry (CF-IRMS) systems can drastically reduce the sample size and time needed for isotopic analyses.[3,4] They are based on the direct introduction of a sample in a helium stream via a capillary leak to the ion source of a mass spectrometer. Recent reports have also documented the use of CF-IRMS systems to generate accurate and precise isotopic data for CO in natural samples.[5,6]

Both of these previously developed CF-IRMS methods for CO are based on selective and quantitative oxidation of CO to CO_2 using a Schütze reagent (I_2O_5 acidified with sulfuric acid on silica gel[7]). Because the CO_2 is produced by CO reacting with Schütze reagent, the oxygen isotopic composition of the produced CO_2 is different from that of the original CO in the sample.[7] As a result, the original $\delta^{18}O_{CO}$ in the sample is calculated on the basis of the $\delta^{18}O_{CO_2}$ of both the sample and a reference with known $\delta^{18}O_{CO}$.

This method, however, has several problems in determining original isotopic compositions of CO, especially $\delta^{18}O$ of CO: (a) the analytical error of $\delta^{18}O_{CO}$ is doubled with respect to that of the $\delta^{18}O_{CO_2}$ determination through the calculation,[7] (b) blank CO_2 of several tens of picomoles is eluted from the usual Schütze reagent for every analysis,[6] and (c) preparing a low-blank Schütze reagent is very difficult.[6]

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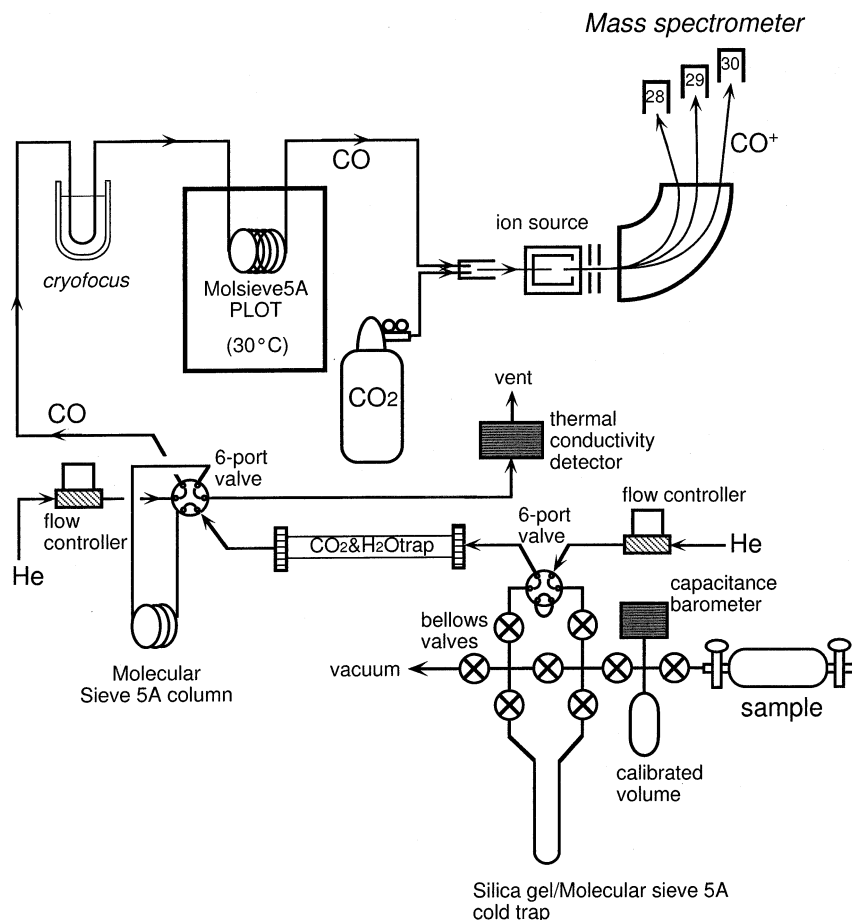
Figure 1. Schematic diagram of the system used for content, $\delta^{13}C$, and $\delta^{18}O$ analysis of atmospheric CO.

Recently, a technique for isotope ratio monitoring of CO has been developed to determine $\delta^{18}O$ of H_2O and organic substances.[8,9] The present study builds upon this research and applies isotope ratio monitoring of CO to the study of trace quantities of CO in natural environments.

In addition, we newly propose the use of CO_2 as a running standard gas for isotope ratio monitoring of CO. For the measurements using CF-IRMS, periodical introduction of a running standard to the mass spectrometer is needed to determine isotopic compositions of samples during each run of sample measurements. All previous techniques for isotope ratio monitoring of CO introduce highly hazardous CO gas as the running standard via a capillary leak to the mass spectrometer (e.g., ref 10). This process is quite hazardous, as only a small portion of the CO gas flowing into the capillary leak is introduced to the mass spectrometer, while most of it escapes into the laboratory atmosphere. We propose herein using CO_2 as an alternative, with CO_2-derived CO fragment ions acting as a running standard in the mass spectrometer.

EXPERIMENTAL SECTION

Instrumentation and Procedure. Mixing ratios and stable isotopic compositions of CO are measured by using a isotope

ratio monitoring gas chromatography/mass spectrometry system (irm-GC/MS; HP6890 equipped with a Molsieve 5A PLOT column and Finnigan MAT 252).[6,11,12] For the measurement of atmospheric samples, the samples are allowed to pass through the original sample purification vacuum line before entry into the irm-GC/MS system (Figure 1) for the purpose of (a) introducing an appropriate amount of air from the sample container into our measurement system, (b) excluding most of the interfering or damaging components, especially N_2 and CH_4, before introduction to the mass spectrometer, and (3) getting a sharp CO peak at the mass spectrometer. To avoid "CO loss"[6] during the CO-transfer procedure, all sample CO pathways are made of passivated Silcosteel treated stainless steel tubes (Restek Corp.) or Pyrex glass tubes with a small number of O-rings made of Viton.

For each measurement, sample air of appropriate volume (100 mL at STP for a 100 ppbv atmosphere, for example) was introduced into the vacuum line and gathered onto a preconcentration column (7-mm i.d.) first packed with silica gel (30−60 mesh, 15 cm long) and then molecular sieve 5A (30−60 mesh, 15 cm long) immersed in liquid nitrogen. The preconcentration column was then gradually heated to room temperature while flushing with ultrapure helium. All ultrapure helium used in our measurements was obtained by passing 99.99995% helium through

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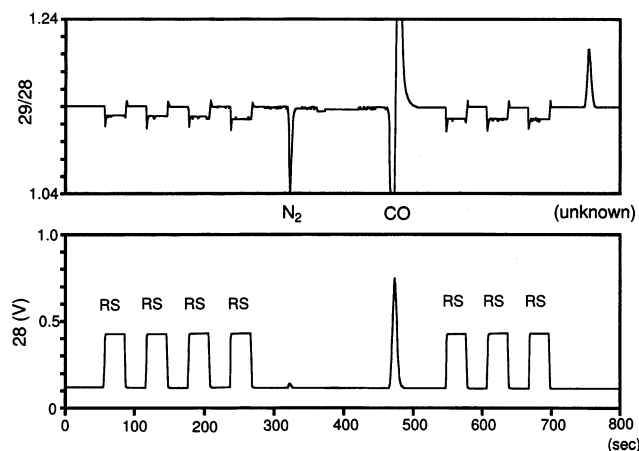
Figure 2. Typical mass traces 28 and the ratio 29/28 of CO. RS, running standard gas.

two stages of active charcoal traps held at liquid nitrogen temperatures just prior to use. After most of the O_2, Ar, N_2, and CH_4 portion is eluted, the finally eluted CO portion is gathered on the second trap, which consists of 15-cm tubing (4-mm i.d.) packed with molecular sieve 5A and cooled with liquid nitrogen, by switching the six-way Valco valve. More than 99% of the moisture and CO_2 are retained in the preconcentration column. In addition, residual H_2O and CO_2 eluted from the preconcentration column is removed from the CO portion by passage through a $Mg(ClO)_4$ (8−24 mesh; Wako Pure Chemical Industries, Ltd., Osaka, Japan) and Ascarite II (20−30 mesh; Thomas Scientific, Swedesboro, NJ) trap during the transfer procedure (Figure 1). Liquid nitrogen is then removed from the second trap, to allow temperature to increase to room temperature to separate CO from residual N_2, CH_4, etc., in the CO portion. Highly purified CO is then injected into the head of the Molsieve 5A PLOT capillary column (0.32 mm i.d. × 1 m; Chrompack Inc.) while the column head is kept at −180 °C. At this temperature, the CO portion becomes enriched at the head of the separation column. The column head is then quickly heated to 80 °C under a continuous helium flow of 0.3 mL/min. The column-separated CO is directly introduced to a mass spectrometer for content and carbon isotope ratio measurements by simultaneous monitoring of the masses ^{28}CO, ^{29}CO, and ^{30}CO (Figure 2).

We also introduce CO_2 into the mass spectrometer just before and after the CO peak while simultaneously monitoring of masses ^{28}CO, ^{29}CO, and ^{30}CO, in order to use the CO_2-derived CO fragment ion in the mass spectrometer as a running standard for $\delta^{13}C$ and $\delta^{18}O$ calculations (Figure 2). Although more than 80% of the ionized species are molecular ions (CO_2^+) when we introduce CO_2 into our mass spectrometer, a significant number of fragment ions (fraction of CO^+ to CO_2^+ is ∼9%, and those of C^+ and O^+, are approximately 8% and 4%) are also formed in the ion source of the mass spectrometer. We use this CO^+ fragment ion for calibrating the isotopic composition of CO.

***δ* Calculation.** The mass spectrometer is computer-controlled, and data acquisition is under software control. In the mass spectrometer, three ion currents are measured simultaneously for CO species at m/z 28, 29, and 30 in each analysis. The baseline and peak boundaries are defined automatically to integrate ion currents for calculating the isotope ratio.[13]

In our mass spectrometry for CO, $^{13}C^{16}O$ and $^{12}C^{17}O$ at m/z 29 are not resolved. The measured ratios of the CO isotopomers (^{28}CO, ^{29}CO, ^{30}CO) can be related to the individual isotopic ratios ^{13}C, ^{17}O, and ^{18}O by the following equations:

$$^{29}R = {}^{13}R + {}^{17}R \tag{1}$$

$$^{30}R = {}^{18}R + {}^{13}R{}^{17}R \approx {}^{18}R \tag{2}$$

where ^iR represents the isotopic or isotopomer ratio for species of mass i to the respective most abundant species; e.g., $^{13}R = {}^{13}C/{}^{12}C$. When neither ^{13}R or ^{17}R values for the sample are known, ^{13}R, ^{17}R, and ^{18}R must be extracted from the determination of only two measured isotopomer ratios, ^{29}R and ^{30}R, and eqs 1 and 2 form an underdetermined system.

Our $\delta^{13}C$ determination therefore relies upon the widely applicable assumption of mass-dependent fractionation in the oxygen isotopes, rendering the measurement of ^{17}O superfluous, by replacing eq 1 with the following equation:

$$^{17}R = ({}^{18}R)^{\alpha}K \tag{3}$$

where α and K are constants characteristic of the relationship between ^{17}R and ^{18}R in the terrestrial oxygen pool. In this study, we adopted 0.516 for α in eq 3. This value had been estimated from the actual $\delta^{17}O$ and $\delta^{18}O$ values of 35 terrestrial samples.[14] Besides, this value almost corresponds with the theoretically estimated α determined by the reduced mass of CO isotopomers.[15] Recently, however, mass-independent oxygen isotope enrichment has been reported in tropospheric CO.[15−17] The influence of this mass-independent fractionation (MIF) on our calculation will be discussed below.

In the usual isotope ratio monitoring runs, running standards with known isotopic ratios are introduced periodically during the sample measurement to allow (a) calibration of isotopic compositions of sample and (b) detection of and correction for drifts in instrumental performance.[13] In our method, however, what we introduce periodically as a running standard differs from what we want to measure, so that it is difficult to calibrate the isotopic composition of sample CO separate from the CO fragment because isotope discrimination that must occur at the ion source alters the $\delta^{13}C$ and $\delta^{18}O$ of the CO fragment ion from those of the initial CO_2.

In our runs, therefore, we measure a working standard gas mixture containing CO of known concentration (245 ppm) and known $\delta^{13}C$ and $\delta^{18}O$ compositions at least once a day in the same manner as the samples themselves. The method for the δ calculations of samples is as follows. By using the peak area ratios of m/z 28 versus 29 and m/z 28 versus 30, we calculate the δ value between the sample and running standard (CO fragment

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ion from CO_2) during sample analysis. For normalization to an international standard, the following relation applies:

$$\delta_{sa-std} = \delta_{sa-rs} + \delta_{rs-std} + (\delta_{sa-rs}\delta_{rs-std})/1000 \quad (4)$$

where δ_{rs-std} is the δ value for the running standard CO fragment against the international standard, which is deduced from the measurement of the working standard gas mixture that contains CO of known δ compositions (δ_{ws-std}) through the following calculation:

$$\delta_{rs-std} = 1000(\delta_{ws-std} - \delta_{ws-rs})/(1000 + \delta_{ws-rs}) \quad (5)$$

CO content in the sample is calculated by comparing each ^{28}CO peak area with that of the working standard gas mixture. The mixing ratio of CO in the working standard was precisely calibrated in the present study by using primary standard gas mixtures that were calibrated by Nihon-Sanso Co. The precision of mixing ratio determinations were estimated to be better than 5%. The isotopic compositions of CO in the working standard were precisely calibrated by using primary 100% CO gas of known $\delta^{13}C$ and $\delta^{18}O$. The $\delta^{13}C$ of the primary 100% CO gas was calibrated by converting CO to CO_2 using CuO within a vacuum line and measured by the usual dual-inlet mass spectrometry. The $\delta^{13}C$ of the produced CO_2 was found to be the same as that of the original CO because the CO_2 derived from CuO combustion is quantitatively produced by the reaction of CO with CuO. The $\delta^{18}O$ of the primary 100% CO gas was calibrated following the method of Brenninkmeijer.[18]

RESULTS AND DISCUSSION

Analytical Blank, Precision, and Accuracy of Concentration and Isotopic Analyses. Compared with our previous method,[6] the new method can reduce drastically the analytical blank associated with the whole analytical procedure. While a usual blank of 21 ± 9 pmol was observed in previously developed methods,[6] it declines to less than 1 pmol in our new method.

To confirm the analytical precision of the determinations of concentration and stable isotopic compositions ($\delta^{13}C$, $\delta^{18}O$), various volumes or pressures of the same atmospheric sample (CO content is 275 ppb) were introduced into the system, as described in Tsunogai et al.[6] The relative error in concentration determinations, using samples ranging from 0.03 to 5.9 nmol, was found to be less than 3%. Variations in peak area from day to day were also within this range.

The results of isotopic analyses of the samples as a function of introduced sample sizes are shown in Figures 3 and 4. The relative variations in $\delta^{13}C$ and $\delta^{18}O$ from the known isotopic compositions are plotted in the figures. As for stable isotopic compositions ($\delta^{13}C$, $\delta^{18}O$), there is no systematic variation in accuracy depending on sample sizes between 150 pmol and 9.6 nmol. The detection limit with $\delta^{13}C$ precision (1σ) of 0.2‰ and $\delta^{18}O$ precision (1σ) of 0.4‰ was 300 pmol. Both the precision and the lowest quantity limit needed to attain the precision were improved compared with the previous method.[6]
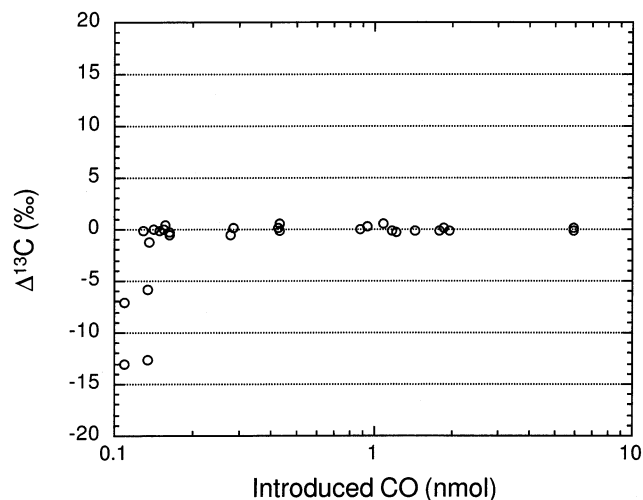
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Figure 3. Relative variability of $\delta^{13}C$ in an atmospheric sample (CO content is 275 ppb) plotted as a function of introduced CO size.
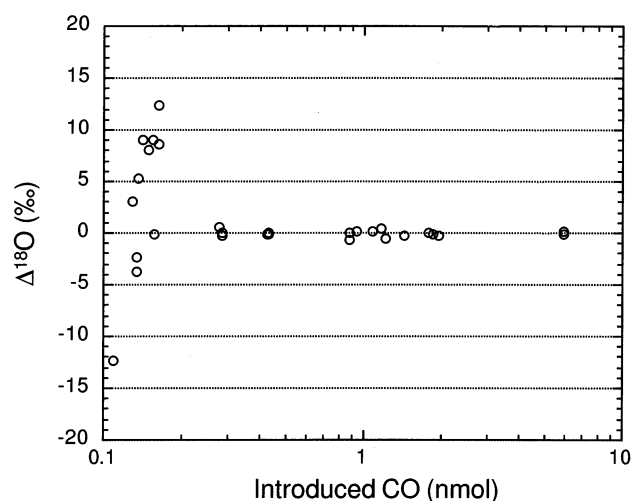

Figure 4. Relative variability of $\delta^{18}O$ in an atmospheric sample (CO content is 275 ppb) plotted as a function of introduced CO size.

To confirm the analytical accuracy of our $\delta^{13}C_{CO}$ measurements, we also analyzed $\delta^{13}C_{CO}$ of duplicate atmospheric samples, based on both our method and the CuO combustion method by using general GC-combustion-isotope ratio mass spectrometry.[6] Because the reacting CO exchanges oxygen atoms with the CuO, it is impossible to deduce the $\delta^{18}O$ of the reacting CO as distinguished from the $\delta^{18}O$ of the produced CO_2. In contrast, the $\delta^{13}C$ of the produced CO_2 is the same as that of the original CO because the CO_2 derived from the CuO combustion is quantitatively produced by the reaction of CO with CuO. Based on the duplicate analyses, we found no systematic difference in $\delta^{13}C$ values obtained using the two different methods.

Error in $\delta^{13}C$ due to the Presence of Mass-Independent Oxygen Isotope Enrichment. In our stable isotope mass spectrometry for CO, $^{13}C^{16}O$ and $^{12}C^{17}O$ at m/z 29 are not resolved. Therefore, as mentioned in the Experimental Section, our $\delta^{13}C$ determination relies upon the widely applicable assumption of mass-dependent fractionation in the oxygen isotopes by using eq 3, to render the complicated ^{17}O measurement superfluous. For atmospheric CO in the troposphere, however, recently published determinations of its oxygen isotopic composition reveal a

significant deviation from mass-dependent fractionation.[15-17] A series of tropospheric CO measurements revealed a pronounced $\Delta^{17}O$ seasonal cycle with maximum $\Delta^{17}O$ values of $+7.5‰$ in summer at a high-latitude region,[17] implying that our determination of $\delta^{13}C$ for atmospheric CO includes some error, as has been the case with past $\delta^{13}C$ data for CO determined by CO_2-based mass spectrometry.[19]

The presence of excess ^{17}O in tropospheric CO implies that the contribution of $^{12}C^{17}O$ to the CO^+ ion beam at m/z 29 in our mass spectrometry is underestimated when eq 3 is employed, so that the inferred $\delta^{13}C_{CO}$ results from eq 1 are correspondingly overestimated. The maximum correction range to the $\delta^{13}C$ values is calculated as follows. We express eq 1 in terms of δ values, yielding

$$^{13}\delta = [1 + (^{17}R_{STD}/^{13}R_{STD})]^{29}\delta - (^{17}R_{STD}/^{13}R_{STD})^{17}\delta \quad (6)$$

where $^{i}R_{STD}$ represents the isotopic ratio of standard material for a species of mass i to the respective most abundant species and $^{i}\delta$ represents $(^{i}R/^{i}R_{STD} - 1) \times 1000$. Thus, for a given $^{29}\delta$ value, a change in $\delta^{17}O$ ($\Delta^{17}O$) causes a corresponding change in $\delta^{13}C$ ($\Delta(^{13}\delta)$) of

$$\Delta(^{13}\delta) = - (^{17}R_{STD}/^{13}R_{STD})\Delta^{17}O \quad (7)$$

The absolute abundances of $^{13}R_{STD}$ and $^{18}R_{STD}$ are estimated to be $^{13}R_{STD} = 0.011\ 237\ 2$ [20] and $^{18}R_{STD} = 0.000\ 402\ 3$,[21] so that we can use $^{17}R_{STD}/^{13}R_{STD} = 0.0358$ to calculate the relation. By substituting the maximum values of $+7.5‰$ for $\Delta^{17}O$ and 0.0358 for $^{17}R_{STD}/^{13}R_{STD}$, the maximum error in $\delta^{13}C$ value is estimated to be $0.27‰$, almost comparable to the 1σ precision of our best $\delta^{13}C$ determination.

In the usual natural system, $\delta^{13}C$ variations of CO are usually much greater than that presented by this range (e.g., refs 1, 2, 5, and 6), so that the effect of mass-independent oxygen isotope enrichment can be ignored in drawing conclusions based on our $\delta^{13}C$ data. We must take care, however, when discussing small-scale variations of less than $0.3‰$.

Field Samples. The method described above has enabled several types of measurements to be made for the first time, primarily by allowing the analysis of much smaller sample volumes than have been possible in the past. An example of such an application is presented below.

Oxidation of atmospheric CO in aerobic soils is an important secondary sink for atmospheric CO. Through isotopic compositions, atmospheric species are traceable to sources and sinks. Use of isotopic information to determine CO sources and sinks requires accurate estimates of the kinetic isotope effect (KIE) during removal of CO in the atmosphere. The KIE is defined as

$$KIE\ (‰) = (k^*_{CO}/k_{CO} - 1) \times 1000 \quad (8)$$

where k^*_{CO} is the rate constant for the reaction of ^{13}CO or $C^{18}O$

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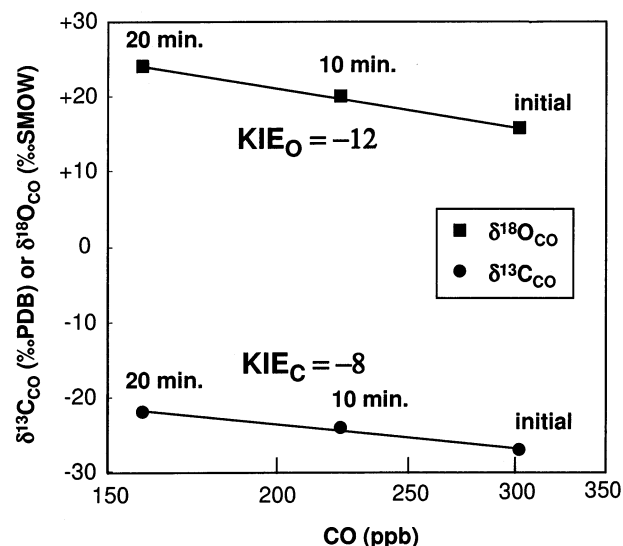**Figure 5.** Temporal variation of concentration and $\delta^{13}C$ or $\delta^{18}O$ in a 30-L hemisphere chamber during the soil oxidation experiment. Kinetic isotope effects (KIEs) calculated from the relation are also presented.

during the removal reaction and k_{CO} is the rate constant for the reaction of ^{12}CO or $C^{16}O$. Isotopic abundance of CO in the atmosphere under steady-state conditions should be equal to the product of the isotopic composition of the source gas times the ratio of the KIE for the sink reactions. The KIEs for carbon and oxygen in the reaction of CO + OH have been determined in many past studies.[17,22,23] As for KIEs during soil uptake, however, an actual data set has not yet been appeared. Nevertheless, only heavy-isotope (^{13}C and ^{18}O) enrichment of residual CO during soil oxidation is expected.[1] In the present study, we preliminarily determined KIEs of carbon and oxygen during uptake into a temperate forested soil of the Tomakomai Experiment Forest, Hokkaido, Japan.

The KIE measurements utilized the static-chamber technique. The KIEs, together with the fluxes of soil, oxidation were measured with a dark glass 30-L hemisphere chamber with an internal diameter of 40 cm. For every 10 and 20 min after deployment, subsamples for content and isotopic analysis were taken in an evacuated 200-mL glass bottle up to 1 atm through a sampling port on the chamber. The chamber also had another port connected to a 1-L aluminum bag in order to compensate for pressure decreases due to the grab sampling in the chamber.

The results of the experiment are plotted in Figure 5. As shown in the figure, large isotopic variations are observed in accordance with soil oxidation of CO. The introduced sizes of CO in the samples are 0.9−1.7 nmol so that it is impossible to account for isotope variation by the analytical error of our analysis. Both of the isotopic compositions show a linear trend with the logarithm of CO concentration, suggesting that the observed temporal variation in concentration and isotopic compositions is due to the KIE. In addition, the linearity of our $\delta^{13}C$ and $\delta^{18}O$ determination can be regarded as highly reliable from the correlation.

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The observed KIEs are estimated to be $-8‰$ for $\delta^{13}C$ and $-12‰$ for $\delta^{18}O$. Two steps must be involved in these KIEs: one is the fractionation during diffusion of CO into the soil pores, while the other is due to actual absorption by the active soil organism. The estimated value resembles the theoretical maximum KIE for the fractionation during diffusion of CO into the soil pores. In addition, the estimated values are completely different from those for the CO + OH reaction, especially for $\delta^{18}O$, suggesting that the KIE is a useful indicator for distinguishing between these two major sink processes of CO. By estimating the average KIE during soil oxidation of CO through similar KIE measurements at different locations or seasons, we can estimate both global and local CO budgets, by balancing CO sources and sinks through the use of $\delta^{13}C$ and $\delta^{18}O$ of CO.

CONCLUSIONS

A new approach for direct introduction of CO to a mass spectrometer has been described that allows precise measurement of $\delta^{13}C$ and $\delta^{18}O$ of atmospheric CO samples by CF-IRMS. Compared with our previously reported method utilizing a combination of CO_2 conversion and CO_2 introduction techniques, this method enhances the precision and reduces the sample amount necessary for analysis. Although we have used this technique for analyses of CO in atmospheric samples, it should be amenable with little modification to isotopic analyses of CO in various environments, including soil pores, natural waters, and ice pores.