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Oxygen Isotope Exchange between O₂ and CO₂ over Hot Platinum: An Innovative Technique for Measuring $\Delta^{17}\text{O}$ in CO₂

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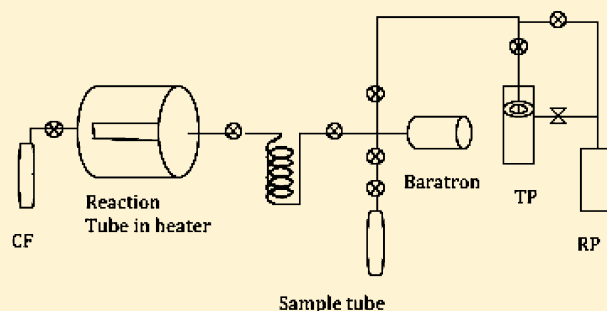
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ABSTRACT: The isotopic composition of carbon dioxide provides a powerful tool and has been widely used for constraining the sources and sinks of atmospheric CO₂. In this work, we demonstrate a simple, rapid, and clean way for measuring the triple oxygen isotope ratio of carbon dioxide with high precision. The method depends on isotope exchange between O₂ and CO₂ in the presence of platinum at high temperature and allows rapid measurement of $\Delta^{17}\text{O}$ of CO₂. The method has been established and confirmed through several tests by using artificially made CO₂ with known $\Delta^{17}\text{O}$ values. The analytical precision obtained for determining $\Delta^{17}\text{O}$ in CO₂ is 0.045‰ (1 – σ standard deviation).



Molecules of O₂ and CO₂ in gas phase do not react or exchange their isotopes in normal laboratory conditions.¹ The free energy change associated with exchange is small and cannot drive the reaction at a significant rate.² However, in the atomic phase, hyperthermal O-atom exchange with CO₂ is known to occur through CO₄ intermediate complex.³ These two gases can react on a gold surface at low temperature via CO₃ formation (by reaction of CO₂ with atomic oxygen), which dissociates at relatively higher temperature.⁴ Long ago, Morita and Titani⁵ reported that the heavy isotope of oxygen is transferred from O₂ to CO₂ on a heated platinum sponge. They placed the two gases in a chamber containing platinum at various temperatures and collected the O₂ afterward. The O₂ was converted to water in a hydrogen reactor. By comparing the density of water formed before and after the transfer, they estimated the transfer coefficient of heavy oxygen isotopes as a function of temperature. This early experiment brought to light the possibility that heated platinum can be used as a catalyst to initiate isotope exchange between CO₂ and O₂. If the exchange can be made efficiently and quantitatively, the process can be used to determine the ¹⁷O/¹⁶O and ¹⁸O/¹⁶O ratios of CO₂ via those of O₂. This would open up new areas of research because the $\Delta^{17}\text{O}$ of CO₂ provides an important parameter for studying biogeochemical cycles of CO₂ in the atmosphere, biosphere, and hydrosphere.

Various methods were developed in the past to determine the $\Delta^{17}\text{O}$ of CO₂. Two decades ago, Bhattacharya and Thieme⁶ obtained O₂ from CO₂ by reacting it with BrF₃ at ~800 °C for 48 h and measured the oxygen isotope ratios of the liberated O₂. The reported uncertainty in this method is about 0.1‰. In a more complex method, CO₂ was first

converted to methane and water, and then the latter was reacted with fluorine to obtain H₂ and O₂. The oxygen isotope ratios of O₂ would represent those in CO₂ if the conversion is complete in both cases. The precision in this method is stated to be about 0.2‰.⁷ Although these two methods are apparently precise enough, they are time-consuming and labor intensive. Additionally, for small CO₂ samples the possibility of unknown fractionation in the attendant chemical conversions cannot be ruled out.

The method of equilibration of CO₂ with hot metal oxide was introduced by Assonov and Brenninkmeijer⁸ to determine the $\Delta^{17}\text{O}$ of CO₂. CeO₂ is an ideal exchange medium as it is water free, exchanges oxygen with CO₂ in a reasonably short time, and produces minimal contamination. Despite its potential the quoted error is large ($\pm 0.33\%$), and the method needed further improvement for application to atmospheric CO₂. The online analytical system developed by Kawagucci et al.⁹ relies on the same principle of transition metal oxide and CO₂ exchange but uses CuO instead of CeO₂. The standard deviation of this method turns out to be larger ($\sim 0.35\%$). Recently, Mahata et al.¹⁰ improved the Assonov and Brenninkmeijer method to a precision better than 0.1‰. However this improved method remains labor intensive and time-consuming. Moreover, for application in atmospheric CO₂, the analyzed gas needs to be purified to ensure the conservation of carbon isotope during the exchange with hot CeO₂.

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In a variant of the CeO_2 method, Hofmann and Pack¹¹ developed a method based on CeO_2 exchange with a large amount of CO_2 and analyzed the equilibrated CeO_2 instead of equilibrated CO_2 . An online laser fluorination system was used to obtain O_2 from CeO_2 . They analyzed the O_2 gas using continuous flow isotope ratio mass spectrometry. In this method, two important parameters are involved to determine the $\Delta^{17}\text{O}$ of CO_2 , namely, the slope of terrestrial fractionation line (β_{TFL}) and the slope of CO_2 – CeO_2 fractionation line ($\beta_{\text{CO}_2\text{--CeO}_2}$). Hofmann and Pack determined β_{TFL} using a large number of analyses of rocks and minerals, varying in $\delta^{18}\text{O}$ over a range of about 20‰. They also determined the $\beta_{\text{CO}_2\text{--CeO}_2}$ using a set of CO_2 gases with known $\Delta^{17}\text{O}$. The method is highly precise, but the major drawback is the requirement of a large amount of CO_2 gas (about 3.5 mmol). For atmospheric analysis, it would imply collection of a large volume air sample and extraction and purification of CO_2 from a large amount of moisture.

Very recently, Barkan and Luz¹² have developed a method for high-precision measurements of $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios in about a 70 μmol CO_2 sample. This method is based on oxygen isotope exchange between CO_2 and H_2O followed by water fluorination to produce O_2 . The oxygen is collected at liquid helium temperature and analyzed in a mass spectrometer. This method involves several parameters like amount of water ($\sim 2.5 \mu\text{L}$), absolute humidity, and fractionation factors, which are necessary for final calculation of δ -values. Moreover, dealing with CoF_3 and water needs special attention. Despite these issues, they obtained an impressive precision of 5 per meg.

Here we present a new and by far the simplest method for high-precision measurements of $^{17}\text{O}/^{16}\text{O}$ ratio in CO_2 . The method is based on equilibrium isotopic exchange between CO_2 and O_2 gas in a quartz tube containing platinum at elevated temperature. We give below the considerations that prompted us to try out this novel procedure and some details of the experimental method.

Isotope Exchange between CO_2 and O_2 . The isotopic exchange between gaseous molecules takes place via simple molecular collision followed by formation of intermediates, which decays back to the starting molecules. In low-density gas-phase reactions, the probability of each of these steps is not high and therefore such exchanges have rarely been studied. The standard theoretical methods of isotope exchange reactions² treat each molecule as an independent entity, but the experiments on isotope exchange usually involve solid or liquid phases. For example, the exchange of CO_2 and H_2O has been studied using gaseous CO_2 and liquid water or CO_2 and moisture in presence of a glass surface.¹³ On a theoretical level, the presence of solid or liquid phases adds another level of complexity for analysis of the chemical reaction.

The adsorption of gaseous O_2 molecules on platinum at low temperature is well-known,¹⁴ and catalytic converters are used to convert CO to CO_2 . This process is known to occur by formation of atomic oxygen from adsorbed O_2 molecules, which react quickly with CO in presence of platinum. Similarly, trace amounts of CO_3 have been detected by reaction of CO_2 and O_2 on a silver surface at low temperature.⁴ Based on the earliest isotope transfer study of Morita and Titani,⁵ we thought that isotope exchange between CO_2 and O_2 can also occur if aided by a catalytic platinum surface. This may take place if O-atoms formed by dissociation of adsorbed O_2 molecules can react with CO_2 to form transient species of CO_3 , which would

decay back to give rise to O_2 and CO_2 . The newly formed CO_2 would have 1/3 probability of hosting the O-atom that came from O_2 , and thus isotope mixing between O_2 and CO_2 would take place if the process is fast. Exchange of energetic atomic oxygen with CO_2 is known to occur by collision from an atomic beam study of Perri et al.¹⁵ A host of transitional metals could probably enhance isotope exchange for gaseous molecules, but platinum has several advantages over others. It is relatively cheap and available in various forms and can be cleaned easily if contaminated.¹⁶

The Reaction System and Gas Handling Method. The CO_2 and O_2 exchange was carried out in a reaction tube made of quartz (60 cm in length and 6.5 mm in diameter (OD) and positioned horizontally inside a cylindrical heater having a total length of ~ 25 cm). The length of the quartz tube is kept much longer than the heating zone since two ultratorr connectors (with Viton O-rings) are used to attach two Pyrex stopcocks at two ends of the tube. In this way, the O-rings do not get heated. One of the stopcocks connects with the vacuum line and the other separates a coldfinger used to take the CO_2 sample (Figure 1). Strips of thin platinum sheet (length ~ 2 cm and

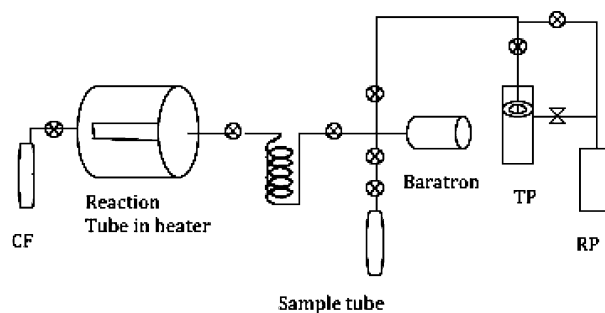


Figure 1. Schematic diagram of the vacuum line used for isotopic exchange of CO_2 and O_2 to determine the $\delta^{17}\text{O}$ of CO_2 samples (TP = turbo-pump, RP = rotary pump, CF = coldfinger). The reaction tube contains small platinum strips that catalyze the exchange at 670 °C. The CO_2 and O_2 are sequentially introduced from the same port as sample tube. First, the CO_2 sample is taken completely at the coldfinger and isolated. The O_2 fraction is taken next and introduced in the reaction tube by expansion. The volumes of the relevant parts are such that about 80% of the O_2 gas goes in. The reaction tube is then isolated from the line, and the CO_2 from coldfinger is released for exchange reaction.

width ~ 2 mm) are kept in the reaction tube whose central zone (~ 10 cm) is maintained at a temperature of 670 °C by a temperature controller. The temperature at the end of the heater drops to about 600 °C. In principle, the reaction system can be miniaturized because the exchange takes place only on the surface of the small platinum pieces.

The gas intake procedure is as follows. A given amount of CO_2 sample is first measured in the mass spectrometer and then taken back in a sample tube from the mass spectrometer using LN_2 . The amount of this retrieved CO_2 is measured accurately using a Baratron manometer placed in the calibrated volume of a section of the vacuum line. This CO_2 is then frozen completely in the coldfinger (Figure 1) and kept isolated. The method was tested by using about 30 μmol of CO_2 , close to the amount of CO_2 that we normally obtain from a 2-L air sample collected in our atmospheric CO_2 program. In this method, the sample CO_2 is exchanged with a given amount of O_2 having a given isotopic composition, and therefore the choice of O_2

amount and composition is important, because they would play a crucial role in the accuracy of the method. It is expected that the higher the difference of $\delta^{18}\text{O}$ between CO_2 and O_2 is better would be the $\Delta^{17}\text{O}$ precision. This is because (as will be seen later) the $\delta^{17}\text{O}$ of the initial CO_2 is calculated from an expression (see eq 4) that depends on the ratio of the $\delta^{18}\text{O}$ differences of CO_2 and O_2 multiplied by the $\delta^{17}\text{O}$ difference of the O_2 . Hence, the accuracy of the $\delta^{17}\text{O}$ of CO_2 determination would be higher when the initial compositional differences are larger and better determined. The $\delta^{18}\text{O}$ value of the CO_2 sample being known (from its measured δ^{46} value), it is possible to choose a suitable O_2 sample. We took an aliquot of O_2 from the tanks available in our laboratory with known isotopic composition such that the difference in $\delta^{18}\text{O}$ is as high as possible. In our present strategy, the O_2 amount is targeted to be equal to that of the CO_2 amount. However, taking (isotopically unaltered) aliquots of exactly equal amounts of these two gases is not straightforward because some gas handling steps can potentially introduce unknown fractionation. With these constraints, we could take aliquots of O_2 and CO_2 equal to within $9.7\% \pm 7.1\%$ (see Table 2); in four instances, the O_2 amount was lower and in 12 instances the CO_2 amount was lower. For typical amounts of 30–40 μmol the difference between the two aliquots was less than 7 μmol . Based on the data shown in Table 2, it is noted that such small deviations (less than 10%) from equality do not affect the final result.

The aliquot of O_2 is first taken in the calibrated manometer section of the vacuum line, and its amount is measured. It is then expanded in the reaction tube for a few minutes so that the gases in the line and reaction zone are isotopically the same. The initial amount of the aliquot is adjusted such that the reacting amount of O_2 approximately equals (within 10%) the CO_2 amount. After isolating the reaction zone (containing O_2) from the vacuum line and allowing the CO_2 kept in the side coldfinger to enter, we allowed the reaction between O_2 and CO_2 to proceed for a period of 2 h. This period was considered sufficient for exchange equilibrium based on a set of control experiments (Table 1 and Figure 2). After the reaction, the gas

Table 1. Test To Determine the Required Time To Reach Steady State in Exchange of O_2 and CO_2 by Platinum Catalyst Method^a

expt no.	reaction time, min	initial CO_2 $\delta^{18}\text{O}$	initial O_2 $\delta^{18}\text{O}$	exchanged CO_2 $\delta^{18}\text{O}$	exchanged O_2 $\delta^{18}\text{O}$	difference in $\delta^{18}\text{O}$
1	10	32.26	13.06	24.84	22.06	−2.78
2	40	26.61	12.92	20.24	21.75	1.51
3	60	15.12	13.57	13.30	14.67	1.37
4	120	16.36	32.38	25.44	23.52	1.92
5	120	32.99	15.49	23.83	22.71	1.12

^aNote that after about 40 min, the difference between the $\delta^{18}\text{O}$ values of the two gases reach nearly constant value indicating attainment of a steady state. The δ -values are relative to VSMOW in ‰.

mixture was passed through a spiral trap containing LN_2 to retain the CO_2 and let the O_2 fraction to be collected in a bottle containing molecular sieves (using LN_2) kept downstream. The bottle with molecular sieves at -196°C acted essentially as a pump to collect O_2 , and the procedure was carried out slowly to avoid possible escape of CO_2 from the spiral trap. The CO_2 was then collected back in the calibrated volume to check the amount and ensure $\sim 100\%$ yield. This CO_2 is then reanalyzed in the mass spectrometer. The O_2 fraction is heated to 60°C

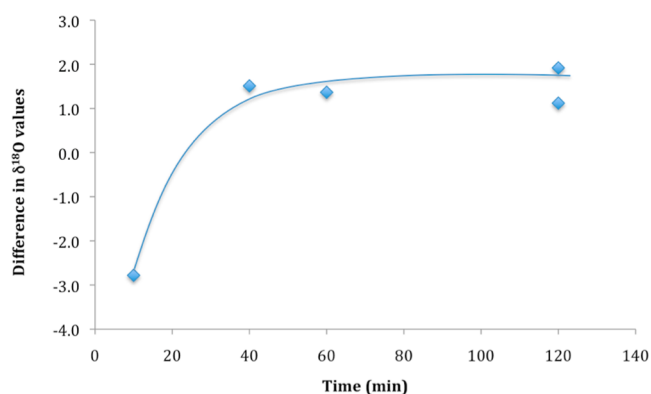


Figure 2. Chart showing the time required to attain a steady state in the isotopic exchange of O_2 and CO_2 . It is seen that after about 40 min, the difference in $\delta^{18}\text{O}$ of O_2 and CO_2 remains nearly constant indicating that a steady state has been reached. In our experiment, we take 120 min as the reaction time to ensure attainment of steady state.

for 10 min to avoid fractionation prior to analysis in the mass spectrometer.¹⁷ After each use, the molecular sieves in the bottle was cleaned in vacuum at about 250°C . We used only two to three pellets of 5 Å molecular sieves to minimize fractionation associated with O_2 absorption.

Mass Spectrometry. The isotopic analyses were done using a FINIGAN MAT 253 mass spectrometer in the dual inlet mode. The O_2 fraction is measured for $\delta^{17}\text{O}$ and $\delta^{18}\text{O}$ before and after the reaction. Similarly, the CO_2 is measured for δ^{45} and δ^{46} before and after the reaction. Strictly speaking, the δ -values of the final CO_2 are not needed in the approach that we follow. However, the data provides a check on the isotopic integrity of the sample to show that no unwanted isotopic contamination or loss has taken place. The measurement protocol for each sample in the mass spectrometer is as follows. First, the sample CO_2 is analyzed in the mass spectrometer relative to an aliquot of working reference (WR) gas. Then the gas is frozen back in a sample tube and taken to the vacuum line for exchange reaction. The modified CO_2 is measured again with respect to the same WR gas kept in the variable reservoir of the mass spectrometer. We use an aliquot of fresh WR gas for each sample. The precision of the mass spectrometric analysis for δ^{45} is better than 0.005‰ and is close to 0.03‰ for δ^{46} . Similarly, an aliquot of O_2 is taken from a large reservoir (either tank or O_2 gas specially prepared and kept in a flask) and measured in the mass spectrometer using a WR of O_2 . This O_2 is then expanded in the reaction chamber and used for exchange as explained before. After the reaction, the O_2 fraction is taken back and remeasured relative to the same WR gas. The measurement precision for a single analysis (using 12 cycles and 8 s integration time) is better than 0.01‰. Over the course of this work, we used several CO_2 and O_2 gases both as working reference and as samples in order to obtain a set of gases with variable isotopic composition for checking the procedure (see Mahata et al.¹⁰). Both the WR gases were calibrated using commercially available OZTECH gases (OZTECH Trading Corporation, Safford, Arizona 85546, USA) as primary standards. OZTECH CO_2 has $\delta^{13}\text{C} = -3.59\text{‰}$ (VPDB) and $\delta^{18}\text{O} = 24.97\text{‰}$ (VSMOW). OZTECH O_2 has $\delta^{18}\text{O} = 27.54\text{‰}$ (VSMOW) and $\delta^{17}\text{O} = 14.02\text{‰}$ (VSMOW).

Control Tests. Several control tests have been performed to ensure the data quality. Before the system was used for experiments, the reaction tube containing platinum strips was

Table 2. Analytical Data Showing the Results of Determination of $\Delta^{17}\text{O}$ of CO_2 Test Samples (19 in total) by Platinum Catalyst Method^a

sample no.	CO_2 amount, μmol	δ -values of initial CO_2 , true value			O_2 amount, μmol	δ -values of initial O_2			δ -values of exchanged O_2			exchanged CO_2 , δ^{46}	initial CO_2 , estimated		estimated difference from true $\Delta^{17}\text{O}$ value	
		$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$		$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	$\delta^{18}\text{O}$	$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$		$\delta^{17}\text{O}$	$\Delta^{17}\text{O}$	first order	second order
1		15.12	8.89	1.11		27.56	14.08	-0.05	21.55	11.44	0.37		8.62	0.83	-0.28	-0.01
2	24.5	15.12	8.89	1.11	23.8	30.92	15.94	0.10	23.36	12.45	0.46	22.81	8.64	0.86	-0.25	0.02
3		16.36	10.05	1.64		30.85	15.91	0.11	24.36	13.14	0.63	23.52	9.72	1.30	-0.33	-0.07
4	40.0	16.36	10.05	1.64	46.9	32.38	16.71	0.13	25.44	13.72	0.67	23.52	9.82	1.40	-0.24	0.03
5	35.1	16.36	10.05	1.64	36.3	26.17	14.18	0.75	21.68	12.19	1.05	21.10	9.82	1.40	-0.23	0.04
6	40.4	16.36	10.05	1.64	40.8	32.64	16.87	0.16	25.09	13.59	0.71	24.07	9.80	1.38	-0.26	0.01
7	24.5	15.75	8.42	0.33	29.3	32.36	16.72	0.15	25.33	13.12	0.12		8.19	0.10	-0.23	0.04
8	38.1	15.75	8.42	0.33	40.3	32.45	16.75	0.14	24.78	12.85	0.13	23.96	8.25	0.15	-0.18	0.09
9	38.6	31.54	16.36	0.21	46.2	15.47	7.81	-0.14	23.25	11.79	-0.14	22.59	16.03	-0.12	-0.33	-0.06
10	27.4	32.99	17.06	0.17	32.5	15.49	7.81	-0.15	23.83	12.08	-0.15	22.71	16.76	-0.12	-0.29	-0.02
11	31.9	15.59	8.14	0.12	31.9	32.33	16.70	0.14	24.39	12.53	0.02	23.57	7.91	-0.10	-0.22	0.04
12	34.0	6.58	3.51	0.12	39.4	33.16	17.12	0.14	21.79	11.19	0.01	20.75	3.26	-0.12	-0.24	0.02
13	38.6	15.33	7.71	-0.17	41.2	26.12	14.16	0.75	21.35	11.17	0.21	20.66	7.40	-0.48	-0.31	-0.04
14		15.33	7.71	-0.17		32.68	16.87	0.14	24.91	12.63	-0.15	24.21	7.39	-0.48	-0.32	-0.05
15	37.4	15.42	7.76	-0.17	40.5	32.70	16.91	0.17	24.90	12.65	-0.12	23.75	7.48	-0.45	-0.28	-0.01
16	46.7	15.42	7.76	-0.17	43.2	33.24	17.10	0.08	25.30	12.78	-0.19	24.07	7.40	-0.52	-0.35	-0.08
17	37.6	15.50	7.83	-0.14	43.6	32.87	17.01	0.18	25.24	12.85	-0.09	24.38	7.55	-0.42	-0.28	-0.01
18	37.7	15.35	7.75	-0.14	38.4	32.79	16.95	0.15	24.89	12.66	-0.11	23.62	7.48	-0.41	-0.27	0.00
19	39.0	15.45	7.77	-0.17	34.6	32.57	16.83	0.16	24.26	12.33	-0.12	23.49	7.55	-0.39	-0.22	0.05
mean difference																
stdev (1 - σ)																
0.045																
0.000																
0.045																

^aThe interpolation method underestimates the true value of $\Delta^{17}\text{O}$ by $-0.268\text{‰} \pm 0.045\text{‰}$ on the first order. The reason for this is explained in the text. The correct value of $\Delta^{17}\text{O}$ on 2nd order is obtained by adding 0.268‰ to the first order value. The uncertainty (standard deviation) of $\Delta^{17}\text{O}$ determination is estimated to be 0.045‰ . The δ -values are relative to VSMOW in ‰ .

kept under vacuum at high temperature for several hours. In a blank experiment, O_2 gas alone was kept in the reaction zone and analyzed before and after. No noticeable change was seen either in the isotope ratios or in the amount. A similar check was done for CO_2 . We also kept the $O_2 + CO_2$ gas mixture without heating the reaction tube, and no observable change was found. The possibility of quartz and oxygen isotope exchange was tested by putting the mixture in the hot quartz tube without the platinum strips. No appreciable changes in δ -values were observed, confirming the earlier work by Schauer et al.¹⁸ and Barkan and Luz.¹⁹

Several experiments were done to select the time and the temperature of the reaction. The data show that some exchange can take place even at a lower temperature of 370 °C and a shorter time of 10 min (Table 1 and Figure 2). However, the exchange is rapid at higher temperature, and we chose 670 °C based on the paper by Morita and Titani.⁵ A period of 2 h was chosen because it was not only sufficient for equilibration but also suitable for experimental convenience.

Preparation of CO_2 Gases with Known Oxygen Isotopic Composition. To check the efficacy of the method, several CO_2 gases were made with enriched and normal $\delta^{17}O$ (as described in Mahata et al.¹⁰). The enriched CO_2 was made from enriched O_2 and the latter was made from ozone (made by Tesla discharge of tank oxygen) to act as a source of anomalously enriched oxygen. The $\Delta^{17}O$ of ozone (as converted oxygen) was first determined and then diluted to the desired extent by mixing oxygen from the same tank. We made several such oxygen samples with different $\Delta^{17}O$ values, which is defined as: $\Delta^{17}O = 1000 \times \ln(1 + \delta^{17}O/1000) - 1000 \times 0.516 \times \ln(1 + \delta^{18}O/1000)$. These anomalous oxygen gases were analyzed for isotope ratios and their δ -values were determined precisely. The $\Delta^{17}O$ values of O_2 gas samples thus prepared are 1.630‰, 1.108‰, 0.326‰, 0.208‰, 0.124‰, and -0.169‰. Next, these oxygen gases were converted to CO_2 by reacting with hot graphite in the presence of platinum catalyst at 700 °C.¹⁹ The yield was always more than 98%. Following earlier studies,¹⁰ we assume that this conversion step preserves the $\Delta^{17}O$ value in the product CO_2 . Aliquots of these CO_2 gases were used as unknown samples to test whether we are able to obtain their $\Delta^{17}O$ values sufficiently accurately. In practice, it is easier to determine $\Delta^{17}O$ values rather than $\delta^{17}O$ though mathematically one can be used to obtain the other as long as the slope coefficient is known.

DISCUSSION OF THE EXPERIMENTAL DATA

Our data (Table 2) show dramatic changes in the isotopic composition of both O_2 and CO_2 when they are placed together as a mixture in the reaction tube containing hot platinum. In the present set of experiments, we consider only the case when the amounts of these two gases are equal and their $\delta^{18}O$ values differ by more than 10‰. In a set of 19 experiments, the O_2 fraction was initially heavier in 16 cases and the CO_2 fraction heavier in 3 cases (Table 2). But whatever the relative isotope ratios of the two gases, the compositions of the two gases approach each other with time and remain nearly constant (indicating a steady state) after about 40 min (Table 1 and Figure 2). In steady state, there remains a small difference between the two compositions. The final CO_2 $\delta^{18}O$ values are slightly less than that of the final O_2 , the magnitude varying from 0.55‰ to 1.27‰ (Table 2). We note that in a normal gas phase exchange of O_2 and CO_2 the modified Urey theory predicts that at 700 °C the CO_2 would be enriched in ^{18}O by

about 6.5‰.² Clearly, the catalytic exchange on the platinum surface involves a more complex exchange mechanism, which results in a reverse effect where the O_2 fraction is more enriched. Notwithstanding this complexity, our data demonstrates that the two gases exchange oxygen isotopes almost to the point of reaching isotopic homogeneity and this can happen despite having a large initial δ -difference, which can be as high as 27‰ in $\delta^{18}O$ (sample 12 in Table 2). The $\delta^{18}O$ values of exchanged CO_2 samples plotted against the $\delta^{18}O$ values of corresponding exchanged O_2 samples shows excellent correlation, and the best fit line deviates from the 1:1 line only by about 0.622‰ (Figure 3). The fact that isotopic equilibrium is attained can be used to derive the $\delta^{17}O$ of initial CO_2 from that of the O_2 fraction, as described below.

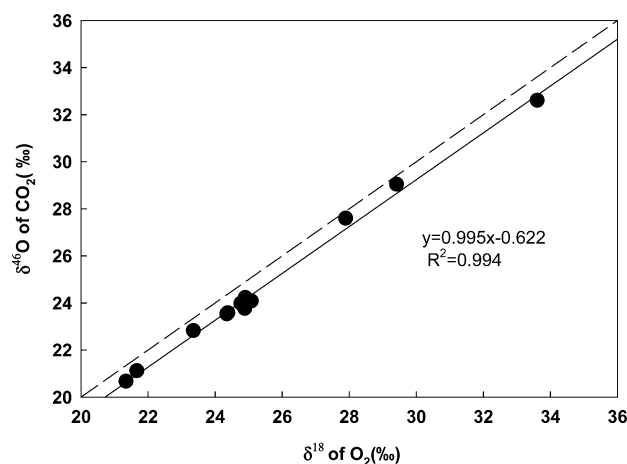


Figure 3. $\delta^{18}O$ (δ^{46}) of CO_2 plotted against $\delta^{18}O$ values of O_2 after exchange in the presence of hot platinum. After exchange, the two gases acquire nearly the same isotope ratios except for a small kinetic fractionation that lowers the $\delta^{18}O$ of CO_2 by about 0.6‰.

Origin of the Depletion in CO_2 Fraction: A Speculation. One can speculate about the origin of the small negative fractionation associated with the exchange process, which depletes the $^{18}O/^{16}O$ ratio of the CO_2 fraction relative to the O_2 fraction by about 1‰. If the exchange takes place via the formation of CO_3^* in the adsorbed state, the following processes may take place (in parentheses we mention whether the net effect of the particular process on the final CO_2 is depletion or enrichment): (1) migration of CO_2 molecules to the platinum surface from the gas phase via diffusion and their collision with platinum surface (depletion); (2) sticking of the impinging CO_2 molecules (enrichment); (3) migration and collision of O_2 molecules with the platinum surface (depletion); (4) sticking of the O_2 molecules on the platinum surface (enrichment); (5) dissociation of the O_2 to $O + O$ on the platinum surface (depletion); (6) collision of the adsorbed CO_2 with adsorbed O -atom forming CO_3^* (depletion); (7) dissociation of the newly formed CO_3^* to CO_2 and O -atom after a certain period (life time) and emission of CO_2 back to the gas phase (enrichment).

Since all CO_3^* molecules finally dissociate and all oxygen atoms are simply redistributed among the O_2 and CO_2 phase, there is no overall fractionation as far as the total oxygen reservoir is concerned in steps 1–7.

The data show that the net result is the formation of a slightly lighter CO_2 . The magnitude of the net CO_2 fractionation is expected to be small due to the cancellation

of one step of enrichment with depletion in another step. For example, step 6 involves differential mobility of O-atom dictated by breaking and forming of Pt–O bonds preferring lighter O-atom movement and interaction, while the step 7 involves break down of CO_3^* (i.e., $\text{CO}_2 + \text{O}$) bonds preferring enrichment of CO_2 . The magnitudes of these two are also not expected to be very different at high temperature of the platinum. For example, one can compare the β -values of CO_2 and CO in Table 12 of Richet et al.,² which are 16.3‰ and 17.4‰, respectively, at 700 °C. As yet we do not have a physical model of the chemical processes involved in the above steps. Therefore, it is difficult to infer the magnitude or even the direction of the net fractionation between the two gas phases using a model of fractionation and overall exchange.

Mathematical Formalism Based on Isotope Mass Balance. The exchange of the oxygen isotopes between the two gases O_2 and CO_2 must obey the mass conservation rule for both $^{17}\text{O}/^{16}\text{O}$ and $^{18}\text{O}/^{16}\text{O}$ ratios. For simplicity, we consider below only $^{18}\text{O}/^{16}\text{O}$. If the oxygen isotope ratios are expressed by $\delta^{18}\text{O}_i$ before exchange and $\delta^{18}\text{O}_f$ after exchange and the amounts are given by m (in μmol), we have

$$\begin{aligned} m(\text{O}_2)\delta^{18}\text{O}_i(\text{O}_2) + m(\text{CO}_2)\delta^{18}\text{O}_i(\text{CO}_2) \\ = m(\text{O}_2)\delta^{18}\text{O}_f(\text{O}_2) + m(\text{CO}_2)\delta^{18}\text{O}_f(\text{CO}_2) \end{aligned} \quad (1)$$

Using $\Delta\delta^{18}\text{O}$ to indicate the shift in $\delta^{18}\text{O}$ value, we can write,

$$\Delta\delta^{18}\text{O}(\text{CO}_2) = -[m(\text{O}_2)/m(\text{CO}_2)]\Delta\delta^{18}\text{O}(\text{O}_2) \quad (2)$$

So the magnitude of the positive change in $\delta^{18}\text{O}$ of CO_2 is proportional to the magnitude of change (negative) in $\delta^{18}\text{O}$ of O_2 , the mass ratio being the proportionately constant. In particular, if the masses are equal (in μmol units), the two changes will be equal (Figure 4a), and the same would be true for $\delta^{17}\text{O}$.

The above information, however, is not enough to determine the initial and final $\delta^{17}\text{O}$ values of CO_2 since only the shift can be determined but not the individual values. For this, we need additional information like fractionation between the two gases at the end.

Fortunately, we note from our experimental data that after the exchange the $\delta^{18}\text{O}$ values of the final O_2 and CO_2 are nearly equal when the temperature is kept constant and the two masses are equal. This means the final δ -values are close to the simple average of the starting δ -values of the two. In other words, the net fractionation is quite small (close to 1‰ in $\delta^{18}\text{O}$) when the masses are equal despite the complexity of the processes leading to the exchange. This is an intriguing observation and needs to be further investigated especially for cases when the masses differ by a significant amount. Expressed mathematically this means that

$$\delta^{17}\text{O}_f(\text{O}_2) = \delta^{17}\text{O}_f(\text{CO}_2) + \epsilon^{17} \quad (3)$$

where ϵ^{17} indicates a net positive fractionation in $^{17}\text{O}/^{16}\text{O}$ ratio whose order is about 0.5‰. Since the fractionation is small, we can use a simple calibration method (based on CO_2 samples with known composition) to determine the $^{17}\text{O}/^{16}\text{O}$ ratio of unknown CO_2 samples. We describe below the applicability of the method by checking the consistency in the case of CO_2 samples with known δ -values.

Calculation of $\delta^{17}\text{O}$ Value of Initial CO_2 . As mentioned before, in the present work, we always strived to have equal amounts of CO_2 and O_2 . For convenience, we apply a graphical extrapolation method to determine the composition of the

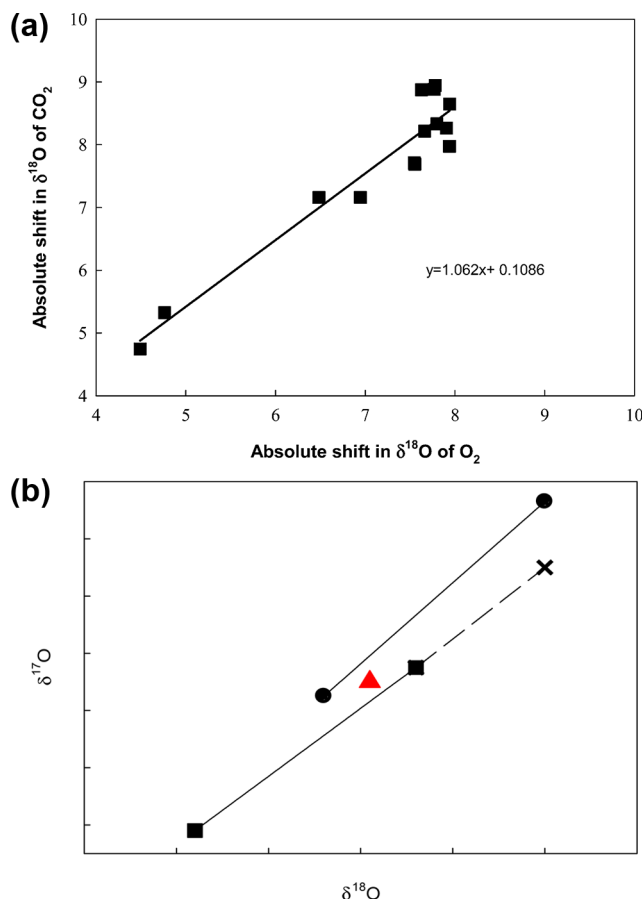


Figure 4. (a) When CO_2 and O_2 are allowed to exchange over hot platinum, the $\delta^{18}\text{O}$ of the two gases shift and in equilibrium attain a value close to the average δ -value as if the oxygen isotopes have been almost homogenized. At the final stage a small difference (actually depletion) is noted in the CO_2 δ -value relative to the O_2 δ -value as seen in the diagram and the equation of the best fit line. (b) Schematic diagram showing changes in isotopic composition (in the $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$ space) of O_2 and CO_2 caused by isotopic exchange of the two gases over hot platinum. The squares show the initial and final δ -values of O_2 , the circles show the same for CO_2 . The triangle corresponds to the mass balance point of the two reservoirs, and the cross shows the intersection point obtained by extending the line joining the two O_2 points and the vertical line at $\delta^{18}\text{O}$ of initial CO_2 . The cross gives the first order estimate of $\delta^{17}\text{O}$ value of the initial CO_2 . The true $\delta^{17}\text{O}$ value of CO_2 is obtained by a small correction as described in the text.

initial CO_2 . For calculation of the $\delta^{17}\text{O}$ value of CO_2 , a two stage approach is taken. We first assume that the gases O_2 and CO_2 completely homogenize after exchange (disregarding the fact this is not strictly true) and their composition is dictated by the isotopic mass balance. Therefore, on first order, the composition of the O_2 fraction after exchange equals the mass balance composition. In the $\delta^{17}\text{O}$ – $\delta^{18}\text{O}$ space, three points representing the initial O_2 , final O_2 , and initial CO_2 should lie on a common line (see schematic given in Figure 4b). This line can be drawn by connecting the initial and final compositions of the O_2 fraction. Since we know the initial $\delta^{18}\text{O}$ of CO_2 , it is easy to obtain the $\delta^{17}\text{O}$ from the point of intersection of this line and a vertical line at $\delta^{18}\text{O}$ of the initial CO_2 shown graphically in Figure 4b. Mathematically, the $\delta^{17}\text{O}$ value of initial CO_2 can be obtained by a simple extrapolation equation:

$$\delta^{17}\text{O}_i(\text{CO}_2) = \frac{(\delta^{17}\text{O}_f(\text{O}_2) - \delta^{17}\text{O}_i(\text{O}_2))}{[\delta^{18}\text{O}_f(\text{O}_2) - \delta^{18}\text{O}_i(\text{O}_2)] + \delta^{17}\text{O}_f(\text{O}_2)} \quad (4)$$

where the subscripts i and f denote initial (before exchange) and final (after exchange) states. Table 2 shows the mass spectrometric data obtained for the set of 19 samples and the derived $\delta^{17}\text{O}$ and $\Delta^{17}\text{O}$ values along with the true values of the samples. The precision for the method is then affected by two factors: (1) degree of isotope exchange (e.g., see Figure 2) and (2) precision for measuring the δ -values of CO_2 and O_2 in eq 4.

Correction for Deviation from Simple Mixing Line. As mentioned before, the two gases do not attain a common isotopic composition and in particular the $\delta^{18}\text{O}$ difference can be easily obtained from the $\delta^{18}\text{O}$ of final O_2 and the δ^{46} (which equals $\delta^{18}\text{O}$ to a high precision) of the final CO_2 . It is to be noted that CO_2 extracted by trapping after exchange and taken in a sample bottle for analysis is potentially liable to be fractionated and their δ^{46} values have larger dispersion for this reason. As mentioned earlier, the value of $[\delta^{18}\text{O}_f(\text{O}_2) - \delta^{46}_f(\text{CO}_2)]$ varies from 0.55‰ to 1.27‰ (neglecting one high value, 1.92‰), and the mean is $0.88\text{‰} \pm 0.23\text{‰}$. This means that the line connecting two O_2 points lies to the right of the simple mixing line, and the $\delta^{17}\text{O}$ estimate obtained from eq 1 would be lower than the true value (Figure 4b). The deviation in $\delta^{17}\text{O}$ or $\Delta^{17}\text{O}$ from the true value ranges from 0.18‰ to 0.35‰ (Table 2). Collecting all 19 values together reveals that the mean and standard deviation in $\Delta^{17}\text{O}$ deviation is $0.268\text{‰} \pm 0.045\text{‰}$ (Table 2 and Figure 5a). This mean value can be used as a correction, which needs to be added to the $\Delta^{17}\text{O}$ value obtained in the first order estimate given above. Alternatively, one can use the best fit equation relating the true value and the calculated first order value obtained from Figure 5a, that is,

$$\Delta^{17}\text{O}(\text{first order value}) = 1.017\Delta^{17}\text{O}(\text{true value}) - 0.290 \quad (5)$$

to derive the true $\Delta^{17}\text{O}$ value. After this correction, the difference in $\Delta^{17}\text{O}$ values (on second order) from the true values ranges from -0.08‰ to $+0.09\text{‰}$ with a mean value of 0.00‰ (Table 2 and Figure 5b) and the uncertainty (based on the current data set) to determine the $\Delta^{17}\text{O}$ of an unknown sample of CO_2 turns out to be 0.045‰ at the $1 - \sigma$ standard deviation level.

Advantage over the CeO_2 Method. In the CeO_2 – CO_2 exchange method,^{8,10} the analyzed gas is CO_2 . CO_2 is measured before and after exchange with cerium oxide. Clearly, there being no carbon source in the system, the $\delta^{13}\text{C}$ of CO_2 ought to remain the same even after exchange, and this is the premise used to determine the $\Delta^{17}\text{O}$ of CO_2 . Therefore, precision in the CeO_2 method depends solely on the validity of the above assumption in the adopted experimental set up. It is quite possible for small fractionation to occur in the $^{13}\text{C}/^{12}\text{C}$ ratio due to absorption by powder of CeO_2 used to effect the equilibration. Unfortunately, even a small change in the $\delta^{13}\text{C}$ value is magnified in the uncertainty of $\Delta^{17}\text{O}$ determination by about a factor of 15. Despite this, Mahata et al.¹⁰ showed that it is possible to achieve a precision better than 0.1‰. Experimentally, this method is quite complex because it requires complete conditioning of CeO_2 prior to each exchange experiment. Complete oxygen replacement is an important

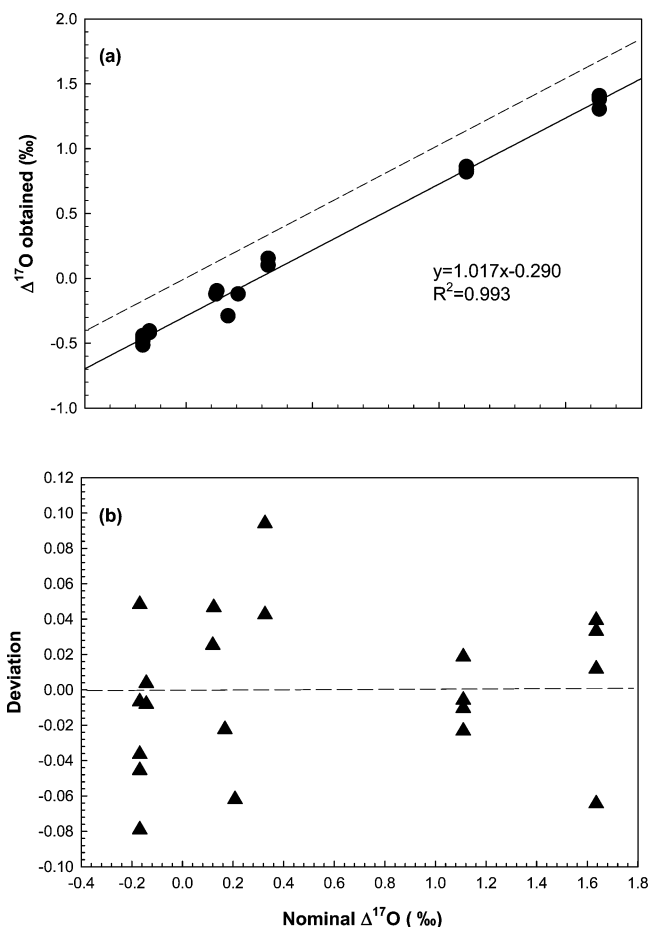


Figure 5. (a) First order estimate of $\Delta^{17}\text{O}$ versus expected $\Delta^{17}\text{O}$ for all the artificially made CO_2 mixtures. Note that the estimate is lower than the true value on an average by 0.268‰ (see Table 2). (b) Deviation from the expected value plotted against the expected value after adding a correction of 0.268‰ . The dotted line is the fit to the points and shows that the mean deviation is 0.00‰ and the uncertainty is 0.045‰ (Table 2).

requirement of the procedure, which involves passing of large amount of tank oxygen over hot CeO_2 . In practice, only the top surface of the grains undergoes easy equilibration, leaving bulk of the CeO_2 compound in uncertain state.

In comparison, the present method is simple, easy, and fast. Here two analyses of the O_2 fraction and one analysis of the CO_2 fraction are needed. The procedure requires handling of easily separable gases carried out in a simple vacuum system. These gases do not interact with each other and are fairly inert in a vacuum system. It is possible to use repeatedly the same platinum strips for catalytic exchange without contamination in the high temperature zone where it is placed. Some samples were analyzed using both CeO_2 method and the platinum method, and good agreement was obtained between the results.

CONCLUSIONS

A novel method has been developed to determine the $^{17}\text{O}/^{16}\text{O}$ isotopic ratio in a CO_2 gas sample, which can be as small as $20\text{--}30\text{ }\mu\text{mol}$. The method is based on isotopic exchange between the CO_2 sample and an aliquot of tank O_2 in the presence of hot platinum and mass spectrometric analysis of the exchanged O_2 gas sample to obtain the isotope ratio of the CO_2 sample. It is shown that the reproducibility of $\Delta^{17}\text{O}$

determination at $1 - \sigma$ standard deviation level is 0.045‰. This promises to be a rapid, simple, and efficient way to determine the $^{17}\text{O}/^{16}\text{O}$ ratio of atmospheric CO_2 samples with sufficient precision for application in isotope mass balance model.

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Notes

The authors declare no competing financial interest.

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