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A comprehensive study of the CO_2-O_2 isotope exchange technique to standardize triple oxygen measurements in CO_2

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Abstract

Triple oxygen isotope ($\Delta'^{17}O$) measurements in CO_2 using the platinum catalysed CO_2-O_2 exchange method require precise determination of oxygen isotope exchange fractionation factors ($^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$). These catalysed exchange fractionation factors are typically determined at elevated temperature (~750 ºC). However, large inter-laboratory inconsistencies have been reported in these factors, primarily attributed to thermal-gradient-induced fractionation arising from portions of the exchange reactor extending beyond the heated zone (hereafter referred to as the cold zone). This study experimentally determines $^{18}\alpha^{Pt}_{CO_2/O_2}$, $^{17}\alpha^{Pt}_{CO_2/O_2}$ and triple oxygen isotope exponent ($\theta^{Pt}_{CO_2/O_2}$) by systematically reducing cold zone over a temperature range of 600 to 1000 °C using novel setup alongside conventional exchange reactor configurations. The novel setup enabled uniform heating of CO_2-O_2 mixture, effectively eliminating thermal gradient and yielded exchange fractionation factors and exponent in near-perfect agreement with the revised theoretical equilibrium values. In the conventional reactors, reduction of the cold zone improved agreement with equilibrium values; nevertheless, notable discrepancies from theoretical predictions remained even at cold zone proportion of 25%. A crossover between $^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$ ($^{17}\alpha^{Pt}_{CO_2/O_2} > {}^{18}\alpha^{Pt}_{CO_2/O_2}$) was observed beyond certain temperature depending on the cold zone, reflecting kinetic effects induced by thermal gradient. These results establish that the theory-experimental discrepancies in exchange fractionation factors are driven by thermal gradient and reveal a robust exponential correlation between these factors and hot zone volumes. Here, we propose a new framework to standardize fractionation factors accounting for the hot and cold zones of the exchange reactor, which is crucial for inter-laboratory consistent $\Delta'^{17}O$ measurements in CO_2.

Keywords: Triple oxygen isotope, fractionation factor, thermal diffusion, cold zone

1. Introduction

The deviations from the expected proportionality between $\delta^{18}O$ and $\delta^{17}O$, though small, have the potential to provide deeper insights into the reaction pathways involved in both mass-dependent and mass-independent realms (Thiemens and Heidenreich, 1983; Thiemens et al., 2012; Bao et al., 2016; Miller and Pack, 2021a). Focusing on the ^{17}O anomaly in CO_2, the signature is increasingly being utilised to estimate stratosphere-troposphere exchange fluxes, atmospheric CO_2 budget, terrestrial and marine gross primary productivity (Thiemens et al., 2014; Laskar et al., 2016, 2019, 2020; Liang et al., 2017a, 2017b, 2023; Koren et al., 2019) and palaeo-hydroclimatic variability (Passey et al., 2014; Passey and Ji, 2019; Bergel et al., 2020; Huth et al., 2022; Sha et al., 2020, 2023, 2024a). However, the isobaric interference of $^{13}C^{16}O^{16}O$ with $^{12}C^{17}O^{16}O$ necessitates an exceptionally high mass resolving power (>56,000). Even at such resolution, achieving high-precision measurements of ^{17}O in CO_2 is challenging due to its low natural abundance and signal suppression by the intense tail of the $^{13}C^{16}O^{16}O$ peak. This technical challenge has spurred the development of several alternative techniques that either produce O_2 from CO_2 or transfer the oxygen isotopic signature of CO_2 to O_2. These include fluorination by BrF_5, methanation-fluorination, CO_2-H_2O exchange-fluorination, CO_2-CeO_2 exchange-laser fluorination and Pt catalysed CO_2-O_2 exchange (Bhattacharya and Thiemens, 1989; Hofmann and Pack, 2010; Barkan and Luz, 2012; Mahata et al., 2013; Passey et al., 2014). The CO_2-O_2 exchange method, which has been first introduced by Mahata et al., 2013 with subsequent modifications by Barkan et al., 2015, remains the most adopted technique due to its clean and simple approach with the best available measurement precision. Mahata et al., 2013 determined the $\delta^{17}O$ of CO_2 by measuring the $\delta^{18}O$ of CO_2 before exchange and $\delta^{18}O$ and $\delta^{17}O$ of O_2 before and after exchange. For that, they used the slope of the line connecting the initial and final isotope ratios and applied a minor correction based on the deviation of the final ratios from this line. Presently, $\delta^{17}O$ of CO_2 is mostly measured using the calibrated isotope exchange fractionation factors ($^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$). The ratio of natural logarithms of the two oxygen isotope fractionation factors is termed as the triple oxygen isotope exponent (θ_{CO_2/O_2}). The deviation of $\delta'^{17}O$ from that expected for a given $\delta'^{18}O$, based on a reference slope, is referred to as the triple oxygen isotope anomaly ($\Delta'^{17}O$). The reference slope is denoted as λ when multiple fractionation processes are involved and as θ when the fractionation process is defined (Passey et al., 2014; Miller and Pack, 2021b; Aron et al., 2021).

$$\theta_{CO_2/O_2} = \frac{\ln {}^{17}\alpha_{CO_2/O_2}}{\ln {}^{18}\alpha_{CO_2/O_2}}$$

$$\Delta'^{17}O = \delta'^{17}O - \lambda_{reference} \times \delta'^{18}O\,;\ \delta' = \ln\left(\frac{R_{sample}}{R_{standard}}\right)$$

The temperature at which the exchange is carried out by most researchers is ~750 °C. The $^{18}\alpha_{CO_2/O_2}$ and $^{17}\alpha_{CO_2/O_2}$, at this temperature, derived from internal partition function ratios using CO_2 datasets from Tashkun and Harvey, 2025 and our oxygen datasets, are 1.004390 and 1.002323, respectively (discussed in section 2.4). Replacing CO_2 datasets with that of Huang et al., 2017, the corresponding values become 1.004490 and 1.002377. The slight differences in the calculated values arise primarily from the uncertainty in the zero-point energy (ZPE) differences between CO_2 isotopologues. But the experimentally determined $^{18}\alpha^{Pt}_{CO_2/O_2}$, $^{17}\alpha^{Pt}_{CO_2/O_2}$ and $\theta^{Pt}_{CO_2/O_2}$, at 750 °C, are far from theory and vary significantly across laboratories, ranging from 1.00051 to 1.00227, 1.00048 to 1.00135 and 0.5 to 0.9, respectively (Barkan et al., 2015; Fosu et al., 2020; Adnew et al., 2022). As the use of the proxy advances with expansion into new fields, establishing high-precision, consistent inter-laboratory values has become increasingly critical. Deviations from the equilibrium conditions were originally thought to derive from heterogeneous processes, but Adnew et al., 2022 ruled out this possibility and suggested that thermal diffusion effects cause these deviations. Following up on this proposition, Wei et al., 2024 conducted thermal-diffusion experiments on pure O_2, pure CO_2 and their mixtures without Pt to isolate thermal gradient effects from exchange reactions. They discussed how $\Delta\delta^{18}O_{hot\text{-}cold}$ and fraction of gas in the hot zone influence the fractionation factors of Pt-catalysed exchange reactions based on their thermal diffusion experiments. However, in their experiments, as only half of the designated hot zone was heated in the furnace, a thermal gradient must have existed within the presumed hot zone itself. The assumption of a simple two-zone (hot and cold) model along the entire extraction line is oversimplified and may have contributed more to the observed discrepancies in $\theta^{TG}_{O_2}$ (fractionation exponent of thermal diffusion for O_2) than a different temperature range in the previous study.

In the present study, we introduce modifications to the existing methods, incorporating key innovations to estimate $\alpha^{Pt}_{CO_2/O_2}$ values across reactors with varying cold zone, ranging from 78.9 to 0%. A key challenge addressed in this study is exchanging CO_2-O_2 in complete absence of thermal gradient effects, which is essential to confirm that any deviation from the theoretical $\alpha^{Pt}_{CO_2/O_2}$ values arise only from such effects. As thermal gradients are unavoidable in reactors used by most laboratories for $\Delta'^{17}O$ measurements in CO_2, it is critical to develop a framework

for standardizing triple oxygen isotope measurements under varying proportions of hot and cold zones to avoid interlaboratory inconsistencies. The specific objectives of this study are to: (i) accurately determine $\alpha^{Pt}_{CO_2/O_2}$ and $\theta^{Pt}_{CO_2/O_2}$ values while progressively minimising the thermal gradient effects to nil, (ii) experimentally verify the underlying reasons for large deviations from theoretical predictions and (iii) recommend appropriate $\alpha^{Pt}_{CO_2/O_2}$ values to establish a standardized method for triple oxygen isotope measurements in CO_2.

2. Materials and methods

2.1 Experimental setup

Figure 1 illustrates the in-house high vacuum setup designed for triple oxygen isotope measurements. High-purity CO_2 and O_2 gases (99.999%), sourced from ATCO Atmospheric and Speciality Gases Private Limited, Ahmedabad, are introduced into the system via stainless steel tubing. The gas pressure during transfer is regulated using Setra™ pressure transducers connected to the vacuum system. The system's main component, the exchange-reactor, consists of two sections separated by a high vacuum valve, necessary for sequential transfer of the two gases before exchange. The CO_2 extracted from various sources such as carbonates, air and water-CO_2 equilibration experiments is cryo-trapped in the lower section of the exchange reactor. An approximately equal amount of O_2 is expanded from an isotopically known tank into the upper section keeping the middle valve closed. The two gases are mixed and heated at the desired temperature keeping only the lower section inside the heater. Heating is performed using Watlow™ ceramic fibre heaters, controlled through an Autonics™ temperature controller and monitored in real time using LabView software.

2.2 CO_2-O_2 exchange experiments under different proportions of hot and cold zones

In order to study the influence of the thermal gradient on the exchange equilibrium, a series of experiments with varying proportions of hot and cold zones have been performed. For all experiments, a 1:1 mixture of CO_2 and O_2 gases with known values of isotopic composition was prepared ($\delta^{18}O_{O_2}$ = 26.399 ‰, $\delta^{17}O_{O_2}$= 13.332 ‰, $\delta^{18}O_{CO_2}$=1.185 ‰ and $\delta^{17}O_{CO_2}$= 0.593 ‰). The isotopic compositions of these CO_2 and O_2 were measured at Academia Sinica, Taiwan. CO_2 was transferred into an evacuated glass flask (to a pressure of ~250 torr), after which O_2 was carefully introduced from the oxygen cylinder through the vacuum line until the total pressure doubled (~500 torr), resulting in equal proportions of CO_2 and O_2 in the flask. The O_2 pressure outside the glass flask was maintained at a significantly higher level to prevent

back-diffusion of CO_2 from the flask. The oxygen isotope fractionation factors of exchange, ${}^{18}\alpha^{Pt}_{CO_2/O_2}$ and ${}^{17}\alpha^{Pt}_{CO_2/O_2}$, and triple oxygen exponent $\theta^{Pt}_{CO_2/O_2}$ were determined at four temperatures across the range of 600 to 1000 °C. Exchange reactors with four different configurations were designed to modify the volume percent remaining outside the heater (referred to as the cold zone hereafter). In the first set of experiments, the mixture was heated in the presence of 150 mg Pt-sponge in the exchange reactor with 78.9% cold zone for 1.5 hours. It has been previously reported through controlled experiments that $\delta^{18}O$ and $\delta^{17}O$ may take longer than an hour to stabilise to the steady-state values within 0.01-0.02% (Mahata et al., 2013; Adnew et al., 2022; Barkan et al., 2015). For the second set, the CO_2-O_2 mixture was exchanged over Pt only in the lower part of the reactor keeping the middle valve closed (see Fig. 1), thereby restricting the cold zone to 62.2%. Further, a special 'reduced cold zone' reactor was devised to constrain the cold zone to 45%. There was no middle valve separating this reactor into two sections, limiting its use to heating a CO_2-O_2 mixture and making it unsuitable for routine sample measurements. We attempted to further reduce the cold zone of this modified reactor to 25% and exchange reactions were conducted at ~700 °C. However, the borosilicate-quartz seal, due to its thermal sensitivity, failed during high-temperature exchange. Also, a few initial high-temperature exchange experiments produced inconsistent results, likely because the Pt at the base was not thermally stable due to the heater-reactor geometry.

During collection after exchange, CO_2 was first trapped in the U-trap (Fig. 1) in liquid nitrogen and O_2 was collected on silica pellets dipped in liquid nitrogen for about 5 minutes. Afterwards, CO_2 was collected from the U-trap. All exchange experiments at each reactor temperature were conducted in at least triplicate. Each sample was measured over five cycles, with signal intensities ranging from 3000 to 4000 mV for O_2 (mass 32) and 6000-8000 mV for CO_2 (mass 44). Measurements were conducted with an integration time of 10 seconds and an idle time of 24 seconds between cycles. The reported errors represent the 1-σ standard deviations from replicate measurements.

To completely eliminate the cold zone, an innovative approach was adopted. The CO_2-O_2 mixture together with conditioned Pt was sealed in quartz tubes which were heated inside a muffle furnace at 650 °C, 700 °C, 750 °C and 800 °C. The furnace ensured homogeneous heating of the tubes forming 'no cold zone' reactors. After heating, the sealed tubes were immediately quenched in water to halt further isotopic exchange, as it is well established that the two gases do not exchange under normal conditions (Katakis and Taube, 1962). The exchanged gases were recollected using a break-seal arrangement in the same vacuum-setup

and analysed, following the procedure described above. To validate the attainment of equilibrium in these experiments, we performed another experiment in which the mixture was heated to 650 °C for two hours and then the temperature was increased to 800 °C for another two hours. After exchange with O_2 at 650 °C, the CO_2 would have attained a higher $\delta^{18}O$ of 17.51 ‰ (Table S2) from its original value of 1.18 ‰ as for the normal heating at 650 ºC. Now when the temperature is increased to 800 °C where the fractionation factors are lower, the $\delta^{18}O$ of CO_2 will have to decrease from its original value to reach the steady-state value rather than increasing from the usual 1.18 ‰. Exchange experiments were limited to temperatures ≤ 800 ºC owing to furnace instability at higher temperatures.

2.3 Determining the oxygen fractionation factors for CO_2-O_2 exchange

The isotopic compositions of the exchanged gases were analysed using a stable isotope ratio mass spectrometer (MAT 253) in dual-inlet mode at Physical Research Laboratory, Ahmedabad. The $\delta^{18}O$ and $\delta^{17}O$ of O_2 were measured directly. The final $\delta^{18}O$ and $\delta^{13}C$ of the CO_2 were measured with an internal precision of 0.05‰. The $\delta^{13}C$ of CO_2 served as a control to identify any fractionation that might have occurred during sample collection, as it is expected to remain constant throughout the exchange. The heaters employed, however, had relatively higher temperature fluctuation of ±5 °C, resulting in added errors across repeated batches. The β values, the CO_2/O_2 molar ratio (Mahata et al., 2013; Barkan et al., 2015), calculated using oxygen mass balance during exchange are close to 1 as expected for a mixture prepared with approximately equal amounts of CO_2 and O_2.

$$\beta = \frac{\delta^{18}O_{\text{Initial}}(O_2) - \delta^{18}O_{\text{Final}}(O_2)}{\delta^{18}O_{\text{Final}}(CO_2) - \delta^{18}O_{\text{Initial}}(CO_2)}$$

The ${}^{18}\alpha^{\text{Pt}}_{CO_2/O_2}$ for exchange could be directly calculated while ${}^{17}\alpha^{\text{Pt}}_{CO_2/O_2}$ was derived from the known initial $\delta^{17}O$ of CO_2 using procedure described in Barkan et al.(Barkan et al., 2015).

$${}^{17}\alpha = \frac{1}{\beta}\left\{\left[\frac{\delta^{17}O_{Initial}\left((CO_2)+1\right)\beta + (\delta^{17}O_{Initial}(O_2)+1)}{[(\delta^{17}O_{Final}(O_2)+1)]}\right] - 1\right\}$$

2.4 Theoretical estimation of ${}^{18}\alpha_{CO_2/O_2}$ and ${}^{17}\alpha_{CO_2/O_2}$

Thermodynamic equilibria for the oxygen isotope exchange between gaseous O_2 and CO_2 is expressed as

220 $$^{i}\mathrm{OO} + \mathrm{CO_2} \rightleftharpoons \mathrm{O_2} + \mathrm{C}^{i}\mathrm{OO}\,,$$

221 where *i* indicates a heavy isotope with mass number 17 or 18, have been calculated according
222 to statistical theory, pioneered by Bigeleisen and Mayer, 1947 and Urey, 1947 (BMU,
223 hereafter). Here, we refine our previous calculations (Adnew et al., 2022; Prokhorov et al.,
224 2019). The fractionation factor for the above isotope exchange equilibrium reaction is given by
225 (Prokhorov et al., 2019; Adnew et al., 2022). The fractionation factor for the above isotope
226 exchange equilibrium reaction is given by

227 $$^{i}\alpha_{\mathrm{CO_2/O_2}} = \frac{Q(\mathrm{O_2})}{Q(^{i}\mathrm{OO})}\frac{Q(\mathrm{C}^{i}\mathrm{OO})}{Q(\mathrm{CO_2})} =$$

228 $$\left(\frac{M(\mathrm{O_2})M(\mathrm{C}^{i}\mathrm{OO})}{M(^{i}\mathrm{OO})M(\mathrm{CO_2})}\right)^{3/2}\frac{Q_{int}(\mathrm{O_2})}{Q_{int}(^{i}\mathrm{OO})}\frac{Q_{int}(\mathrm{C}^{i}\mathrm{OO})}{Q_{int}(\mathrm{CO_2})}\,e^{-\left(\frac{\epsilon_0(\mathrm{O_2})-\epsilon_0(^{i}\mathrm{OO})+\epsilon_0(\mathrm{C}^{i}\mathrm{OO})-\epsilon_0(\mathrm{CO_2})}{kT}\right)} \quad \text{(A)}$$

229 In this equation, M denote molecular masses and ϵ_0 the ZPEs, whereas Q and Q_{int} stand for
230 total and internal partition functions, respectively.

231 $$Q_{int} = \sum_i d_i e^{-\frac{\epsilon_i}{kT}} \quad \text{(B)}$$

232 The internal partition function Q_{int} is the sum over all internal states viz, ro-vibrational and
233 electronic states *i* with state degeneracy d_i and energy ϵ_i above ϵ_0. We note in passing that the
234 relative uncertainty of $^{i}\alpha_{CO2/O2}$ is factually the quadratic sum of four independent contributions:
235 the relative uncertainties of the two internal partition function ratios $Q_{int}(\mathrm{C}^{i}\mathrm{OO})/Q_{int}(\mathrm{CO_2})$
236 and $Q_{int}(^{i}\mathrm{OO})/Q_{int}(\mathrm{O_2})$ and the relative uncertainties of the ZPE difference terms
237 $\exp\left((\epsilon_0(\mathrm{O_2}) - \epsilon_0(^{i}\mathrm{OO})/kT\right)$ and $\exp\left((-\epsilon_0(\mathrm{CO_2}) + \epsilon_0(\mathrm{C}^{i}\mathrm{OO})/kT\right)$. The contributions from
238 atomic and molecular masses in eq. (A) can be safely neglected due to their high accuracy.

239 Electronic excited states will play only a small role in the evaluation of the partition functions
240 and they are just considered in the case of O_2. For di-oxygen, these excited states have adiabatic
241 energies of ~1 eV (7918 cm^{-1}) or more above the ground electronic state and, compared to ro-
242 vibrational states in the ground state, those in the first excited electronic state have therefore
243 an additional relative weight of 1.3×10^{-4} at 1000 °C. The effect on the ratio of partition
244 functions of two isotopologues of the same molecule is smaller, because these have similar
245 state energies on the same potential energy surface and error cancellation occurs when dividing
246 the two similar partition functions. The same arguments apply even more to CO_2 with the
247 lowest excited electronic state energies being ~ 4 to 5 eV (Spielfiedel et al., 1992; Ma et al.,
248 2014). At these energies, the Boltzmann factor in eq. (B) becomes as low as 10^{-16} at 1000 °C,

and these states can thus be completely neglected in the evaluation. If the energies of all states up to a sufficiently high threshold are known to spectroscopic accuracy, one can directly evaluate the above sums (eq. B). We have done so using the CO_2 data provided by Huang et al., 2017, which are based on theoretical molecular calculations, improved by comparison with spectroscopic observations. Note, however, that due to inadvertently using $d_J = J$ instead of $d_J = (2J+1)$ as rotational degeneracy factors in the calculation of partition sums of CO_2 (unpublished work), Adnew et al., 2022 have obtained slightly different results than we do here. Internal partition function ratios, such as $Q_{int}(\mathrm{C}^i\mathrm{OO})/Q_{int}(\mathrm{CO_2})$ from our calculation agree with a former direct sum evaluation (unpublished work) for relevant temperatures above 500 °C to $\lesssim 10^{-4}$ relative, which is close to rounding errors of $\sim 5\times10^{-5}$. Moreover, there is even better agreement with the newly recommended values of $Q_{int}(\mathrm{C}^i\mathrm{OO})/Q_{int}(\mathrm{CO_2})$ from Tashkun and Harvey, 2025, where differences are smaller than 2×10^{-5} over the temperature range between 100 and 1300 K. However, the main uncertainty of α due to CO_2 stems from the ZPE difference terms $\epsilon_0(\mathrm{C}^i\mathrm{OO}) - \epsilon_0(\mathrm{CO_2})$. The two data sets[22,23], yield ZPE differences that differ by 0.06 cm^{-1} and 0.03 cm^{-1} for ^{18}O and ^{17}O containing isotopologues, respectively. This leads to deviations between the two calculations of about 1.1×10^{-4} (for ^{18}O) and 0.6×10^{-4} (for ^{17}O) at low (800 K), and 6.7×10^{-5} and 3.6×10^{-5} at high (1300 K) temperatures. Without any further a-priori knowledge, we use the values at 800 K derived from the two completely independent theoretical approaches to estimate relative uncertainties $u_r(Q_{int}(\mathrm{C}^i\mathrm{OO})/Q_{int}(\mathrm{CO_2}))$ = 0.11 ‰ and 0.06 ‰, for ^{18}O and ^{17}O respectively.

For the partition functions of O_2, we have previously (Huang et al., 2017; Janssen and Tuzson, 2010) used the analytical BMU approach, even though it has not yet been demonstrated whether the approach can actually be applied correctly to O_2. While the BMU method has originally been developed for closed shell molecules, its direct application to molecular oxygen neglects that the molecule has an electronic fine structure due to its non-zero total electron spin, which includes spin-spin and spin-rotation terms (Yu et al., 2012). Even though these fine structure couplings are quite sizable on the order of a few cm^{-1}, they have only a very weak isotope dependence and could possibly cancel in the calculation of partition function ratios. In the case of oxygen, however, quantum mechanical symmetry rules restrict allowed states of the symmetric $^{16}O_2$ isotopologue to odd quantum numbers N for the molecular rotation, while odd and even rotational states of the asymmetric isotopologues ^{17}OO and ^{18}OO are allowed. This implies that the rotational ground state of the homonuclear $^{16}O_2$ molecule has a higher quantum number ($N = 1$) and rotational energy than the heteronuclear molecules in their $N = 0$ states. As

a consequence, one obtains an anomalous ZPE scaling with a difference ratio of $\left(\epsilon_0\left({}^{17}\mathrm{OO}\right) - \epsilon_0(\mathrm{O}_2)\right)/\left(\epsilon_0\left({}^{18}\mathrm{OO}\right) - \epsilon_0(\mathrm{O}_2)\right)$ = (–12.379 cm^{-1}) / (–22.869 cm^{-1}) = 0.541, as compared to (–11.669 cm^{-1}) / (– 22.145 cm^{-1}) = 0.527 when fine structure effects and symmetry restrictions are ignored. Previous calculations that neglected electron spin and symmetry restrictions on the ZPEs therefore must be subject to systematic error, which should become most apparent at low temperatures. In order to avoid such bias, we have included electronic fine-structure effects in our calculation. The details of the calculation will be presented elsewhere (unpublished work). Here, we just summarise the most salient conclusions, and report on the uncertainty estimate in the relevant temperature range between 800 and 1300 K (or about 500 to 1000 °C). The calculations are based on a global evaluation of spectroscopic constants of all O_2 isotopologues made by Yu et al., 2014, 2012, which includes all three lowest electronic states with vibrational states up to $\nu = 35$ for the ground electronic state and $\nu = 17$ for the two lowest excited states. Energy levels for all stable isotopologues are provided in the supplementary material of the study (Yu et al., 2014), but are restricted to rotational quantum numbers N smaller than 66, roughly corresponding to energies below 6080 cm^{-1}. This is too small to accurately calculate partition functions for temperatures up to 1300 K. We have therefore added energies for missing ro-vibrational states in the electronic ground state by extrapolating term energies towards higher rotational excitation using the spectroscopic constants provided by Yu et al., 2014. The validity of this approach has been checked by comparing our calculated internal partition functions for all six isotopologues of O_2 to the results presented in Table 1 of Yu et al., 2012 which cover the temperature range between 9.375 and 300 K, and to the very recent internal partition function of $^{16}O_2$ provided by Furtenbacher et al., 2025. Based on an even larger set of spectroscopic data and more excited electronic states, the latter covers the temperature range between 1 and 5000 K and also specifies uncertainties as a function of temperature. Our calculations agree with the results of Yu et al., 2014 and our agreement with (Furtenbacher et al., 2025) under 1300 K is always better than 5×10^{-7}. The relative standard uncertainty of Q_{int} ($^{16}O_2$) indicated by (Furtenbacher et al., 2025) for this temperature range is 2×10^{-5} or smaller. Even their highest value is smaller than the uncertainties that we have determined in the evaluation of CO_2. The uncertainty of the ZPE differences can be conservatively estimated using the evaluation of ZPEs and their uncertainties from (Irikura, 2007). Based on a smaller set of spectroscopic data and using a less complete and more ancient set of molecular constants than Yu et al., 2014, Irikura, 2007 obtains a standard uncertainty of 4.5×10^{-3} cm^{-1} for the ZPE of $^{16}O_2$ when the Dunham terms up to the

sixth order are available. $\epsilon_0(^i OO) - \epsilon_0(O_2)$ is thus accurate to 0.01 cm^{-1} or better, thus leading to an uncertainty of less than 2×10^{-5} at temperatures as low as 500 °C.

To summarize, in the 500 °C to 1000 °C range, the uncertainties of $^{18}\alpha_{CO_2/O_2}$ and $^{17}\alpha_{CO_2/O_2}$ are dominated by the uncertainty in the ZPE differences between CO_2 isotopologues. They lead to amount to standard uncertainties of 0.11 ‰ and 0.06 ‰ for $^{18}\alpha_{CO_2/O_2}$ and $^{17}\alpha_{CO_2/O_2}$, respectively.

3. Results

3.1 Variations in $^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$ with varying cold zone volumes

Measured $^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$values with varying cold zone volumes are presented in Figure 2 and Supplementary Information Table S2. The values are compared with the theoretically predicted equilibrium values. When no cold zone was present, i.e., the entire CO_2-O_2 mixture was uniformly heated inside the furnace, the measured $^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$ matched the theoretical predictions within experimental uncertainty. Although the experimental values at all temperatures are marginally higher than theoretical estimates, the deviations are insignificant. To confirm that this small offset was not due to incomplete equilibration, an additional experiment was conducted in which the mixture was first equilibrated at 650 °C and subsequently heated to 800 °C. The rationale was that at 650 ºC, $^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$ would attain relatively higher equilibrium values, and subsequent heating at 800 ºC would lower them again. The consistency between this two-step experiment and direct equilibration at 800 ºC confirmed attainment of complete isotopic equilibrium (Fig. 2). The potential causes of the minor systematic deviation have been detailed in the section 4.3. As the hot zone volume decreased, the deviation from the theoretical $^{18}\alpha_{CO_2/O_2}$ and $^{17}\alpha_{CO_2/O_2}$ values became more pronounced. For instance, at a cold zone proportion of approximately 45%, the deviations were ~0.004 for $^{18}\alpha_{CO_2/O_2}$ and ~0.002 for $^{17}\alpha_{CO_2/O_2}$at 750 °C. These discrepancies continued to grow with further increase in cold zone volume, indicating a progressive departure from equilibrium conditions. The $^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$ obtained from the limited exchange done at ~700 °C keeping 25% cold zone still deviated from the corresponding theoretical predictions by 0.002 and 0.001 (Supplementary Information Table S4).

An important observation related to exchanges involving a cold zone is the behaviour of the fractionation factors $^{18}\alpha^{Pt}_{CO_2/O_2}$ and $^{17}\alpha^{Pt}_{CO_2/O_2}$. These values are greater than 1 at lower

temperatures, but drop below 1 once the temperature exceeds a certain threshold (Fig. 2 and 3). Notably, the specific temperature at which this transition occurs depends on the fraction of the cold zone. Similar trends were reported by Adnew et al., 2022 and predicted by the model in Wei et al., 2024 . In setups without a cold zone, the α values consistently remain above 1 and close to the theoretical equilibrium values, gradually approaching 1 as the temperature increases (Fig. 2 and 3). The transition behaviour has been attributed to thermal diffusion effects between the hot and cold regions in setups with a cold zone.

Another intriguing observation is the crossover of α values: at lower exchange temperatures, $^{17}\alpha^{Pt}_{CO_2/O_2}$ is lower than $^{18}\alpha^{Pt}_{CO_2/O_2}$, but at higher temperatures, this trend reverses (Fig. 3). The temperature at which this crossover occurs also depends on the fraction of the hot zone. This crossover is not observed in the absence of a cold zone, consistent with theoretical expectations. Although Adnew et al., 2022 reported that the crossover coincides with the exchange-inflection temperature (temperature at which α transits from >1 to <1), our results show that this is not always the case (Fig. 3). In our experiments, the temperature at which the crossover occurs does not necessarily align with the α = 1 transition point (Fig. 3).

3.2 Comparing $\theta^{Pt}_{CO_2/O_2}$ among reactors with varying cold zones

The average $\theta^{Pt}_{CO_2/O_2}$ value of 0.529 (± 0.015), calculated from the sealed quartz tubes in the temperature range 650 to 800°C, agree well with the theoretical value of 0.529 (Fig. 4, Supplementary Information Table S1 and S2). Conceptually, θ is an intrinsic property of a defined process (Bao et al., 2016). The reaction occurring in conventional exchange reactor is a combination of isotope-exchange and thermal diffusion leading to a large variability in $\theta^{Pt}_{CO_2/O_2}$ values (Fig. 4). These values are much beyond the canonical range in exchange reactions conducted at or above the crossover temperature associated with the respective cold zone. Wei et al., 2024 predicted a relationship between $\theta^{Pt}_{CO_2/O_2}$ and $^{18}\alpha^{Pt}_{CO_2/O_2}$ which is included in Figure 4 using our revised equilibrium $^{18}\alpha_{CO_2/O_2}$ value and $\theta^{TG}_{O_2}$ from their diffusion experiments. Although negative $\theta^{Pt}_{CO_2/O_2}$ have been predicted under conditions of extreme thermal diffusion by their model, increasing cold zones do not produce such behaviour. An exception is the ~880°C experiment with 45% cold zone. The large deviation observed for this data arises from the diverging behaviours of $\theta^{Pt}_{CO_2/O_2}$ (by definition) under these conditions: $\ln^{17}\alpha_{CO_2/O_2}$ approaches zero while $\ln^{18}\alpha_{CO_2/O_2}$ becomes negative (Fig. 4) leading to an amplified and unstable $\theta^{Pt}_{CO_2/O_2}$ value.

4. Discussion

4.1 Experimental versus theoretical $\alpha^{Pt}_{CO_2/O_2}$

Theoretically α_{CO_2/O_2} values for exchange are expected to be larger than 1 and approach unity at very high temperature (Richet et al., 1977; Adnew et al., 2022). Moreover, $^{18}\alpha_{CO_2/O_2}$ should always be greater than $^{17}\alpha_{CO_2/O_2}$. However, in the experimental exchange done in reactors with varying volumes outside the heater, the $\alpha^{Pt}_{CO_2/O_2}$ values are not always greater than 1 due to thermal diffusion between hot and cold zones. The $\alpha^{Pt}_{CO_2/O_2}$ values are higher than 1 at lower temperatures and decrease to less than 1 above a certain temperature in all three reactors with 78.9%, 62.2% and 45% cold zones. The temperature of this exchange-inflection point increased with decreasing cold zones (Fig. 3). Fractionation due to thermal-gradient can explain the selective enrichment of O_2 over CO_2 after the exchange-inflection point. Wei et al., 2024 showed that oxygen isotope fractionation of O_2 is greater than that of CO_2 when subjected to identical thermal gradient conditions and was attributed to isotopic fractionation due to thermal diffusion. The latter topic has been discussed in details by Jones and Furry, 1946. The O_2 in the cold zone of the reactor is more enriched in heavy isotopes compared to CO_2, resulting in values of $^{17}\alpha^{Pt}_{CO_2/O_2}$ and $^{18}\alpha^{Pt}_{CO_2/O_2}$ lower than 1.

A cross over temperature in $\alpha^{Pt}_{CO_2/O_2}$ values was also observed: below this temperature, $^{18}\alpha^{Pt}_{CO_2/O_2}$ is greater than $^{17}\alpha^{Pt}_{CO_2/O_2}$ whereas above it, $^{17}\alpha^{Pt}_{CO_2/O_2}$ exceeds $^{18}\alpha^{Pt}_{CO_2/O_2}$. This inversion, where the abundance of ^{17}O surpasses that of ^{18}O in both CO_2 and O_2, suggests the involvement of a kinetic effect during the exchange process caused by thermal gradient between the cold and hot zones. Such thermal gradient caused a systematic deviation from the isotopic equilibrium, even though thermodynamic equilibrium was attained after 0.5 to 1 hour of heating. All other previous studies (e.g. Mahata et al., 2013; Barkan et al., 2015; Adnew et al., 2022; Wei et al., 2024) that employed setups with distinct hot and cold zones also likely observed thermodynamic equilibirum states that were significantly offset isotopically due to thermal diffusion. The thermal gradient induced kinetic effect was supported by clumped isotope measurements in CO_2 and O_2 following heating of a CO_2 - O_2 mixture in a typical setup with both hot and cold zones (unpublished data; personal communication, Mao-Chang Liang), because $\Delta_{47}(CO_2)$ and $\Delta_{36}(O_2)$ values were far from equilibrium. In our system, the crossover temperature does not coincide with the exchange-inflection temperature. The overlap of these two points observed by Adnew et al., 2022 is likely coincidental and may result from the specific geometry of their experimental setup. Notably, the crossover is not observed in

exchanges conducted within sealed quartz tubes heated uniformly. These experiments attained isotopic equilibrium, showing close agreement with theoretical predictions. The minor discrepancies observed between the theoretical values and those from no-cold zone experiments fall within the expected uncertainty of the experimental values. The experiments in which the gas mixtures were first heated to 650°C for two hours and subsequently at 800 °C for another two hours yielded $\alpha^{Pt}_{CO_2/O_2}$ values indistinguishable from those obtained in experiments heated directly at 800°C, further confirming the attainment of complete equilibrium under uniform heating conditions.

At 750 °C, the offsets in $^{18}\alpha^{Pt}_{CO_2/O_2}$ determined with 0%, 45%, 62.2% and 78.9% cold zones are 0.0003, 0.004, 0.004 and 0.005, respectively, from the theoretical value of 1.00449. This implies that reducing cold zone volumes in the exchange reactor alone may not be sufficient to achieve precise triple oxygen measurements in carbonates. Moreover, the reactor configuration makes it challenging to further minimise the cold zone in routine measurements. Interestingly, the results show a strong dependence of $\alpha^{Pt}_{CO_2/O_2}$ on hot zone volume, offering a potential pathway for standardizing the exchange reactions.

4.2 Relation between $\alpha^{Pt}_{CO_2/O_2}$ and reactor configuration

An exponential relationship between the fractionation factors and the hot zone volumes has been established at 750°C (Fig. 5). Although the exact hot and cold zone volumes are subject to some uncertainty due to the irregular geometry of the reactor tubes, the observed trend remains significant. Further, to test the validity of fractionation factors derived from the exponential relation in figure 5, an isotopically different CO_2 was exchanged with the same O_2. The $\delta^{18}O$ value of this new CO_2 was 37.23 ‰ in contrast to the original CO_2 having $\delta^{18}O$ value of 1.18 ‰. It is to be noted that the $\delta^{18}O$ value of the new CO_2 was higher than that of O_2 (26.40 ‰), unlike the previous case. The exchange was carried out in two different reactors with 41.9% and 62.2% cold zones. The measured $^{18}\alpha^{Pt}_{CO_2/O_2}$ were in good agreement with those expected from the exponential fit (Supplementary Information Table S3). This exponential relationship was also tested at 700°C including fractionation factors from the additional exchange reaction conducted with 25% cold zone proportion (Supplementary Information Figure S1 and Table S4). The observed trend was significant and provided further validation of the proposed framework.

In practical setups, complete elimination of cold zone is not feasible. Therefore, it is essential to calibrate triple oxygen isotope exchange setups based on a fixed configuration of hot and cold zones, and accurately determine the associated fractionation factors. For setups similar to ours, where the hot and cold zone volumes are constrained, the recommended fractionation factors reported here may be applicable. However, before adopting them as standardized factors, this should be verified experimentally by independent groups. We also plotted selected $\alpha^{Pt}_{CO_2/O_2}$ values from previous studies that employed similar experimental setups (Fig. 5). Due to the lack of detailed information regarding the hot and cold zone proportions in those studies, we assumed a 50:50 ratio between the heated and cold sections of the reactors in all the cases. Most of these values showed significant deviations from our fitted curve, with the exception of the data from Adnew et al., 2022 in which the authors explicitly stated that half of the reactor was within the heating zone and results are in good agreement with our fitted line. The discrepancies observed for other studies highlight the importance of accurately characterizing the thermal geometry of the reactor when interpreting fractionation factors.

4.3 Limitations

We observed a small but systematic deviation from the theoretical fractionation values, as discussed earlier. This discrepancy likely stems from a combination of factors, including (i) uncertainties in the theoretical zero-point energy calculations (though these are expected to be small, on the order of ~0.0005), (ii) experimental errors such as potential biases in the $^{18}\alpha_{CO_2/O_2}$ and $^{17}\alpha_{CO_2/O_2}$ values of the CO_2 and O_2 used for exchange, and (iii) slight inaccuracies in assigning the actual experimental temperature. Liang et al., 2023 reported a bias of ~0.001 in θ_{CO_2/O_2} between Academia Sinica and the Hebrew University of Jerusalem, and a difference of ~0.04‰ in $\Delta'^{17}O$. As our CO_2 and O_2 were calibrated in Academia Sinica, small offsets in the $\delta^{17}O$ and $\delta^{18}O$ values of the exchange gases could contribute to the deviations from theoretical expectations. Temperature assignment introduces another potential source of bias. The exchange temperature was taken as that measured when the sealed quartz tube was inside the furnace. However, once the furnace is opened and the tube is rapidly quenched in water, brief partial exchange of the CO_2-O_2 mixture at lower temperatures cannot be completely ruled out. This could introduce a consistent temperature-related offset across all experiments. An exchange occurring at temperatures 30–50 °C lower than assumed would be sufficient to explain the observed discrepancies between theoretical and experimental values. Unfortunately, estimating the actual effective re-equilibration temperature for these setups

remains challenging. Further experiments conducted independently by other laboratories will be essential to refine the exchange fractionation factors and improve the robustness of triple oxygen isotope measurements in CO_2.

4.3 Broader implications for triple oxygen isotopes measurements in CO_2

^{17}O has emerged as a promising proxy that complements ^{18}O in tracing the global hydrological cycle and reconstructing palaeo-environments, particularly in archives where d-excess is not commonly available. Recent studies have used $\Delta'^{17}O$ in carbonates to quantify past relative humidity conditions, for example, parent water derived from speleothems (Sha et al., 2020, 2023) and palaeo-seawater reconstructions from foraminifers (Sha et al., 2024b). These investigations report sensitivities of approximately 1 permeg $\Delta'^{17}O$ per % relative humidity change. Such levels of sensitivity underscore the need for highly precise and inter-laboratory comparable $\Delta'^{17}O$ measurements. However, reported $\Delta'^{17}O$ of international carbonate standards show measurable discrepancies across laboratories (Supplementary Information Table S5 and S6). For instance, $\Delta'^{17}O$ values of CO_2 derived from NBS-18 span a range of ~106 permeg across studies employing Pt-catalysed exchange method (Liang et al., 2017a; Sha et al., 2020; Fosu et al., 2020; Barkan et al., 2019) and are much lower than those obtained using the reduction-fluorination method (Passey et al., 2014; Passey and Ji, 2019; Wostbrock et al., 2020; Huth et al., 2022). Differences in acid digestion temperature between the two methods were initially proposed as a potential source of this discrepancy. However, Wostbrock et al., 2020 performed acid digestion at 25℃ followed by reduction-fluorination and reported values consistent with those obtained at 90℃ by Passey et al., 2014. We suspect that the significantly lower $\Delta'^{17}O$ values measured for NBS-18, NBS-19 and IAEA-603 using Pt-catalysed exchange than reduction-fluorination method may partly reflect kinetic effects induced by thermal gradient. Consequently, consensus $\Delta'^{17}O$ values based on the Pt-catalysed exchange remain ambiguous, as the associated exchange fractionation factors are neither consistent amongst laboratories nor aligned with theoretical predictions. Our novel approach that allows exchange under true equilibrium (0% cold-zone) and has yielded fractionation factors and exponents consistent with theory, can be utilized to verify $\Delta'^{17}O$ values of the standards at true equilibrium. Importantly, the exercise also demonstrates that if setup-specific exchange fractionation factors $\alpha^{Pt}_{CO_2/O_2}$ are used, the final $\Delta'^{17}O$ values should remain consistent across laboratories. We suspect that the exchange fractionation factors used in the above cases were not set-up specific causing the inter-laboratory discrepancies. Further

detailed analysis of the standards using the present approach will help validate and strengthen this methodology.

5. Conclusions

We have experimentally verified that oxygen fractionation factors and exponent during Pt-catalysed CO_2-O_2 exchange in reactors have a combined influence of oxygen isotope-exchange between CO_2 and O_2 and thermal-gradient-induced kinetic fractionation. The fractionation factors and exponent determined from uniformly heated samples show good agreement with the theoretical values based on equilibrium modelling. This gives definitive evidence that isotope exchange reaches to complete isotopic equilibrium during uniform heating whereas the steady state achieved in exchange reactors with cold zones is shifted away from isotopic equilibrium even though thermodynamic equilibrium states were attained. Further θ, supposed to be an intrinsic property of the exchange process, is observed to be varying because of these kinetic effects. These kinetic effects can be further verified by analysing clumped isotopes in exchanged CO_2 and O_2, which can provide a constraint on their effective exchange temperatures. The determined fractionation factors of exchange with varying reactor-configurations showed a defined exponential correlation with the hot zone volumes of the reactor. Thus, we propose a new framework to standardize ${}^{17}\alpha^{Pt}_{CO_2/O_2}$ and ${}^{18}\alpha^{Pt}_{CO_2/O_2}$ accounting for the hot and cold zones of the exchange reactor for accurate triple oxygen measurements in CO_2.

Acknowledgements

We thank Mr. Bankim Pandya for assembling the high-vacuum system used in the exchange experiments. We are also grateful to Dr. Mao-Chang Liang for calibrating our CO_2 and O_2 gas cylinders and for his valuable suggestions during data analysis. Special thanks go to Dr. Getachew A. Adnew and Prof. S. K. Bhattacharya for their insightful guidance during the experimental work and interpretation of the results. We would also like to thank X. Hang and S. Tashkun for valuable discussions on their calculations of partition functions and energy levels of CO_2.

Appendix A. Supplementary material: Table S1-S6 and Figure S1 in this study can be found in Supplementary Information. They contain theoretical predictions of fractionation factors and

results of the Pt-catalysed exchange conducted using isotopically different gas mixtures across a range of temperatures and reactor geometries.

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Figures

Figure 1. Schematic showing the in-house vacuum setup for Pt-catalysed CO_2-O_2 exchange for triple oxygen measurements in CO_2

Figure 2. (a) ${}^{18}\alpha^{Pt}_{CO_2/O_2}$ and (b) ${}^{17}\alpha^{Pt}_{CO_2/O_2}$ values determined with varying cold zone volumes viz. 78.9%, 62.2%, 45% and 0%. The deviation from the theoretical predictions (presented in Supplementary Information Table S1) increases with increasing cold zones. The shaded regions along the theoretical curves represent the uncertainties.

Figure 3. The oxygen isotope fractionation factors, ${}^{17}\alpha^{Pt}_{CO_2/O_2}$ (dashed lines) and ${}^{18}\alpha^{Pt}_{CO_2/O_2}$ (solid lines), determined in four different experimental set-ups with varying cold zone volumes within 600 to 1000 °C temperature range. The crossover temperatures, marked by vertical dotted lines, increase as the cold zone volume decreases from 78.9% to 62.2% to 45%. In the sealed quartz tubes with uniform heating, the $\alpha^{Pt}_{CO_2/O_2}$ values are closely aligned with the theoretical values and do not show any crossing over of ${}^{17}\alpha^{Pt}_{CO_2/O_2}$ and ${}^{18}\alpha^{Pt}_{CO_2/O_2}$.

Figure 4. The $\theta^{Pt}_{CO_2/O_2}$ and ${}^{18}\alpha^{Pt}_{CO_2/O_2}$ determined with varying cold zone volumes viz. 78.9%, 62.2%, 45% and 0% within 600 to 1000°C temperature range. When no cold zone is present, the $\theta^{Pt}_{CO_2/O_2}$ values are closely aligned with the theoretical value of 0.529. The curves show the relationship predicted by Wei et al., 2024 using our revised equilibrium ${}^{18}\alpha_{CO_2/O_2}$ value and $\theta^{TG}_{O_2}$ from their diffusion experiments viz., 0.48 (grey solid line), 0.5 (black solid line) and 0.52 (grey dotted line).

Figure 5. Exponential relations of (a) ${}^{18}\alpha^{Pt}_{CO_2/O_2}$ and (b) ${}^{17}\alpha^{Pt}_{CO_2/O_2}$ with varying hot zone volume fraction at 750 °C. Selected $\alpha^{Pt}_{CO_2/O_2}$ values from previous studies with similar to our experimental setups are also shown, assuming a 50:50 ratio between the heated and cold sections of the reactors. The data from Adnew et al., 2022, in which the authors stated exclusively that approximately half of the reactor was within the heating zone, are in good agreement with our fitted line. For the other studies, hot and cold zone proportions need to be constrained for the reactor geometry. The goodness of fit was evaluated using weighted coefficient of determination (R^2_w).