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Kinetics of CO$_2$(g)–H$_2$O(l) isotopic exchange, including mass 47 isotopologues

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Highlights

The kinetics of CO$_2$(g)–H$_2$O(l) isotopic exchange were studied with lab experiments.

- The rate-limiting step is dissolution of CO$_2$ in the water.
- The rates of exchanged were identical for $^{12}$C$^{16}$O$^{18}$O and $^{13}$C$^{16}$O$^{18}$O.

Abstract

The analysis of mass 47 isotopologues of CO$_2$ (mainly $^{13}$C$^{18}$O$^{16}$O) is established as a constraint on sources and sinks of environmental CO$_2$, complementary to $\delta^{13}$C and $\delta^{18}$O constraints, and forms the basis of the carbonate clumped isotope thermometer. This measurement is commonly reported using the $\Delta_{47}$ value — a measure of the enrichment of doubly substituted CO$_2$ relative to a stochastic isotopic distribution. Values of $\Delta_{47}$ for thermodynamically equilibrated CO$_2$ approach 0 (a random distribution) at high temperatures (≥ several hundred degrees C), and increase with decreasing temperature, to ≈ 0.9% at 25 °C. While the thermodynamic properties of doubly substituted isotopologues of CO$_2$ (and, similarly, carbonate species) are relatively well understood, there are few published constraints on their kinetics of isotopic exchange. This issue is relevant to understanding both natural processes (e.g., photosynthesis, respiration, air–sea or air–groundwater exchange, CO$_2$ degassing from aqueous solutions, and possibly gas–sorbate exchange on cold planetary surfaces like Mars), and laboratory handling of CO$_2$ samples for $\Delta_{47}$ analysis (e.g., re-equilibration in the presence of liquid water, water ice or water adsorbed on glass or metal surfaces). We present the results of an experimental study of the kinetics of isotopic exchange, including changes in $\Delta_{47}$ value, of CO$_2$ exposed to liquid water between 5 and 37 °C. Aliquots of CO$_2$ gas were first heated to reach a nearly random distribution of its isotopologues and then exposed at low pressure for controlled periods of time to large excesses of liquid water in sealed glass containers. Containers were held at 5, 25 and 37 °C and durations of exchange ranging from 5 min to 7 days. To avoid the formation of a boundary layer that might slow exchange, the tubes were vigorously shaken during the period of exchange. At the end of each experiment, reaction vessels were flash frozen in liquid nitrogen. CO$_2$ gas was then recovered from the head space of the reaction vessel, purified and analyzed for its $\Delta_{47}$, $\delta^{13}$C and $\delta^{18}$O by gas source isotope ratio mass spectrometry. Equilibrium was reached for both $\delta^{18}$O and $\Delta_{47}$ after durations of a few hours to tens of hours. $\delta^{18}$O values at equilibrium were consistent with known fractionation factors for the CO$_2$–H$_2$O system. The evolution of $\delta^{18}$O and $\Delta_{47}$ with experiment duration were consistent with first-order reactions, with rate constants equal to each other
(within error), averaging 0.19 h⁻¹ at 5 °C, 0.38 h⁻¹ at 25 °C and 0.65 h⁻¹ at 37 °C. We calculate an activation energy for this isotopic exchange reaction of 26.2 kJ/mol. By comparison, Mills and Urey (1940) measured the rate of ¹⁸O exchange between CO₂(aq) and water to have a rate of 11 h⁻¹ at 25 °C and an activation energy of 71.7 kJ/mol. Our finding of a slower rate and lower activation energy is consistent with the rate limiting step of our experiment being the CO₂(g)–CO₂(aq) exchange, even when samples are shaken during the partial equilibration. Our results broadly resemble those from the study of (Affek, 2013), though this prior study found a lower rate constant for Δ₄⁷. We propose that the difference is due to analytical uncertainties and explore the theoretical consequences of unequal reaction rates between ¹²C¹⁸O¹⁶O and ¹³C¹⁸O¹⁶O with a forward model.

1. Introduction

The carbon dioxide budget in the atmosphere is constrained by carbon and oxygen isotopic compositions of CO₂ (Francey and Tans, 1987, Ciais et al., 1995a, Ciais et al., 1995b, Francey et al., 1995, Ciais et al., 1997, Peylin et al., 1999, Cuntz et al., 2003). Such data can help distinguish between land and ocean fluxes (using δ¹³C, Ciais et al., 1995a, Ciais et al., 1995b, Francey et al., 1995), and terrestrial primary production from soil respiration (using δ¹⁸O, Yakir and Wang, 1996, Peylin et al., 1999, Welp et al., 2011). Additionally the amount of ¹⁴C can be used to constrain the origin of carbon in CO₂ (e.g., Mayorga et al., 2005). However, due to the large number and variability of fluxes that influence the atmospheric budget, it is not possible to fully constrain the CO₂ budget with those measurements alone.

The development of clumped isotope measurement techniques – i.e., methods for analysis of multiply-substituted isotopologues – enables additional constraints on CO₂ budgets (Eiler and Schauble, 2004, Affek and Eiler, 2006, Affek et al., 2007, Yeung et al., 2009). Such methods compare the abundance of molecules containing two or more heavy isotopes to the abundances that would be present if all isotopes in that sample were randomly distributed among all possible isotopologues (the ‘stochastic distribution’). In the case of CO₂, we are interested in the mass anomaly of molecules with m/z = 47, dominated by ¹²C¹⁸O¹⁶O, which is reported using the variable Δ₄⁷, defined as follows:

$$
\Delta_{47} = \left( \frac{R_{17}^{47}}{2R_{13}^{13}R_{18}^{18} + 2R_{17}^{17}R_{18}^{18} + R_{13}^{13}(R_{17}^{17})^2} - 1 \right)
$$

(1)

where \(R^{47}\) refers to the ratio of isotopologues of the corresponding mass to mass 44 measured on a mass spectrometer, \(R_{13}\) and \(R_{18}\) are the bulk isotopic ratios, determined using traditional methods, and \(R^{17}\) is estimated by assuming a specific mass law for mass-dependent O-isotope fractionation (e.g., Eiler and Schauble, 2004, Affek and Eiler, 2006, Huntington et al., 2009, this last constraint can be relaxed if the \(\Delta_{17}O\) value of the sample is known: Guo et al. (2009)).

In a CO₂ sample that has achieved an internal isotopic equilibrium, the enrichment in mass-47 isotopologues (i.e., the \(\Delta_{47}\) value) is a function of temperature only (Eiler and Schauble, 2004, Wang et al., 2004). Gas phase isotopic exchange in pure CO₂ is extremely slow at temperatures below several hundred degrees Celsius, and thus it is difficult for gaseous CO₂ to achieve a temperature-
dependent equilibrium. However, the presence of water catalyzes isotopic exchanges through reactions such as:

\[ ^{12}C^{16}O^{15}O + H_2^{18}O \rightleftharpoons H_2^{12}C^{16}O^{16}O^{18}O \rightleftharpoons ^{12}C^{16}O^{18}O + H_2^{16}O \] (2a)

\[ ^{13}C^{16}O^{15}O + H_2^{18}O \rightleftharpoons H_2^{13}C^{16}O^{16}O^{18}O \rightleftharpoons ^{13}C^{16}O^{18}O + H_2^{16}O \] (2b)

which will take place readily at temperatures reached at Earth surface and atmosphere. For this reason, the interpretation of \( \Delta_{\alpha} \) values of atmospheric CO\(_2\) depends critically on our understanding of the kinetics of these reactions. The reaction rate of the CO\(_2\)–H\(_2\)O oxygen isotope exchange has been studied previously (e.g., Mills and Urey, 1940, although it must be noted that they studied the reaction of dissolved, not gaseous, CO\(_2\) with water) and a recent study presented the first investigation of the rate of equilibration of \( \Delta_{\alpha} \) for gaseous CO\(_2\) in the presence of liquid water (Affek, 2013). Here we build on the results of Affek (2013) by presenting new data that add additional constraints on the temperature dependence of rates of reaction for the equilibration of CO\(_2\) isotopologues in the presence of water. In particular, we extend the range of studied temperatures down to 5 °C, therefore more precisely define the activation energy over the temperature range of interest to studies of the earth’s surface, and we present evidence that evolution in \( \delta^{18}O \) and clumped isotope composition are more tightly coupled than was suggested by this earlier work.

2. Experimental setup

The aim of the experiments we present is to quantify parameters that define the rate of changes in \( \delta^{18}O \) and \( \Delta_{\alpha} \) in CO\(_2\) vapor in the presence of H\(_2\)O, where the CO\(_2\) is initially out of equilibrium with respect to both clumped isotope and oxygen isotope CO\(_2\)–water equilibrium, at controlled, known temperatures relevant for earth-surface processes. Firstly, CO\(_2\) aliquots with a near-stochastic distribution of isotopologues were created by heating aliquots of \( \approx 50 \) μmol of CO\(_2\) contained in sealed silica tubes at 1000 °C for 2 h. The \( \Delta_{\alpha} \) of the gas after this procedure is equal to 0.0266‰ (reported on the absolute reference frame of Dennis et al., 2011). The oxygen isotope composition (i.e., \( \delta^{18}O \) value) of the gas variably decreases over the course of this procedure. This is most likely due to isotopic exchange with oxygen in the silica tube. This effect has been observed previously and results in heated CO\(_2\) aliquots displaying a range of \( \delta^{18}O \) values (e.g., a range of \( \delta^{18}O \) of 1.5 permil observed by Affek, 2013).

The heated gas aliquots were then introduced in \( \approx 200 \) mm-long silica tubes (ID 4 mm) containing 0.1 mL of de-ionized water. This gas handling was performed on a glass vacuum line and the water was frozen by immersing the end of the tube in liquid nitrogen, so the tube was under vacuum when CO\(_2\) was first introduced. 0.1 mL of water corresponds to about 5000 μmol, meaning the abundance ratio of H\(_2\)O to CO\(_2\) is roughly 50:1. This ensures that the isotopic composition of CO\(_2\) will, at equilibrium, be buffered by the \( \delta^{18}O \) of the water, with limited variations in \( \delta^{18}O \) of water over the course of the experiment. After CO\(_2\) was frozen into the tube along with water (i.e., creating a physical mixture of water ice and CO\(_2\) ice), the tubes were flame-sealed and held for variable durations at controlled temperatures (5, 25 and 37 °C). To minimize the effects of exchange at low temperature
while the ice thawed, the tubes were immersed in water held at the right temperature, which melted the very small volume of ice in a few seconds. Samples held at 25 and 37 °C were attached horizontally in temperature-controlled shakers moving at 250 RPM. Samples held at 5 °C were attached to an apparatus flipping the tubes upside-down sharply every 0.5 s. In both setups the water was clearly agitated in the tubes. A previous study of the rates of CO₂–H₂O exchange found that shaking at rates higher than 2 Hz does not affect the reaction rates (Fortier, 1994). The aim of the shaking is to prevent the formation of a diffusive boundary layer above the liquid which would limit the rate of reaction in a different fashion for each tube, depending on its exact length and the exact amount of CO₂ it contains.

Experiments were conducted with two waters with different oxygen isotope compositions (‘water 1’: δ¹⁸O = −11.0 ± 0.2 permil; ‘water 2’: δ¹⁸O = +23.0 ± 0.2 permil, both versus V-SMOW. ‘Water 2’ was enriched by fractional evaporative distillation). When the chosen duration for a given experiment was over (from 5 min to 10 days), both gas and liquid were frozen in the sealed tube by immersing one extremity in liquid nitrogen. The tube was then connected to a vacuum line through a tube cracker. The liquid nitrogen was replaced with a dry ice–ethanol slush to keep water frozen and release the CO₂. The gas was then purified by passing twice through a dry ice–ethanol slush, removing traces of water, before being trapped in a silica tube with a liquid N₂ trap. Some of the CO₂ dissolved in the water may stay trapped in the water ice during this step. During our experiments, assuming chemical equilibrium is reached, up to 10% of the gas is dissolved in the water during the experiment, with HCO₃⁻ being the dominant species in solution (10 > pH > 4). If some CO₂ stayed trapped in water ice, it would be reflected in the δ¹³C of the recovered gas, as at equilibrium HCO₃⁻ is enriched in ¹³C compared to CO₂(g) by 7 to 10 permil in the temperature range of our experiments (Zeebe and Wolf-Gladrow, 2001). We note below that this effect seems to be negligible, suggesting that CO₂ is quantitatively outgassed during freezing and gas separation. For a subset of samples, the purified CO₂ was quantified using a Baratron® vacuum gauge, showing that 99 ± 3% of the initial CO₂ is recovered with our setup (n = 8).

The gas aliquots were then analyzed for the abundance of the isotopologues of CO₂ of atomic masses 44 to 49 using a Thermo-Finnigan MAT-253 gas source mass spectrometer linked to an automated system as described in Passey et al. (2010). The gas was first purified using a gas chromatograph, following Huntington et al. (2009). Masses 48 and 49 were used to check for adequate sample purification. The data was used to calculate δ¹³C, δ¹⁸O and Δ₄₇, following methods described by Huntington et al. (2009) and Dennis et al. (2011). All measurements of experimental products are standardized based on concurrent analyses of CO₂ having a range of bulk isotopic compositions and equilibrated at 1000 or 25 °C, as well as two intralaboratory carbonate standards. Δ₄₇ values are reported using the absolute reference frame of Dennis et al. (2011).

3. Results

The results of our experiments are presented in Table 1 and Fig. 1, Fig. 2. Overall, we find that the δ¹³C_PGE stayed constant during the experiments, and that both δ¹⁸O and Δ₄₇ of the CO₂ evolved from the initial state towards the values consistent with internal isotopic equilibrium in all sets of
experiments. The reaction proceeded faster at higher temperatures and equilibrium was reached after hours to tens of hours. The details for each isotopic system are developed below.

Table 1. Variations of the isotopic composition of CO$_2$ after exchange with water for controlled durations.

<table>
<thead>
<tr>
<th>Duration (h)</th>
<th>Δ$^13$C (‰)</th>
<th>δ$^{18}$O$_{SMOW}$ (‰)</th>
<th>δ$^{13}$C$_{PDB}$ (‰)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>0.011</td>
<td>29.5</td>
<td>−10.7</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>25 °C, shaking on rotating table, 250 RPM, δ$^{18}$O of water + 23‰ (Fig. 1c)</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.228</td>
<td>43.0</td>
<td>−10.4</td>
</tr>
<tr>
<td>1</td>
<td>0.298</td>
<td>42.2</td>
<td>−10.2</td>
</tr>
<tr>
<td>2</td>
<td>0.371</td>
<td>47.9</td>
<td>−10.3</td>
</tr>
<tr>
<td>5</td>
<td>0.774</td>
<td>60.6</td>
<td>−10.6</td>
</tr>
<tr>
<td>37 °C, shaking on rotating table, 250 RPM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.164</td>
<td>36.6</td>
<td>−10.9</td>
</tr>
<tr>
<td>1</td>
<td>0.468</td>
<td>49.9</td>
<td>−10.4</td>
</tr>
<tr>
<td>2</td>
<td>0.569</td>
<td>54.1</td>
<td>−11.3</td>
</tr>
<tr>
<td>5</td>
<td>0.841</td>
<td>60.1</td>
<td>−10.5</td>
</tr>
<tr>
<td>6</td>
<td>0.780</td>
<td>60.3</td>
<td>−10.6</td>
</tr>
<tr>
<td>40</td>
<td>0.859</td>
<td>61.8</td>
<td>−10.5</td>
</tr>
<tr>
<td>37 °C, shaking on rotating table, 250 RPM</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>0.50</td>
<td>0.340</td>
<td>28.6</td>
<td>−10.5</td>
</tr>
<tr>
<td>4</td>
<td>0.774</td>
<td>28.3</td>
<td>−10.4</td>
</tr>
<tr>
<td>6</td>
<td>0.716</td>
<td>27.8</td>
<td>−10.2</td>
</tr>
<tr>
<td>22</td>
<td>0.856</td>
<td>28.0</td>
<td>−9.7</td>
</tr>
<tr>
<td>45</td>
<td>0.865</td>
<td>28.0</td>
<td>−10.8</td>
</tr>
<tr>
<td>5 °C, shaking by flipping the tube every 0.5 s</td>
<td></td>
<td></td>
<td></td>
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<tr>
<td>0.25</td>
<td>0.133</td>
<td>29.6</td>
<td>−10.7</td>
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<tr>
<td>0.50</td>
<td>0.196</td>
<td>30.2</td>
<td>−10.5</td>
</tr>
<tr>
<td>2</td>
<td>0.330</td>
<td>30.3</td>
<td>−10.8</td>
</tr>
<tr>
<td>Duration (h)</td>
<td>$\Delta_f$ (%)</td>
<td>$\delta^{18}O_{SMOW}$ (%)</td>
<td>$\delta^{13}C_{PDB}$ (%)</td>
</tr>
<tr>
<td>-------------</td>
<td>----------------</td>
<td>---------------------------</td>
<td>-------------------------</td>
</tr>
<tr>
<td>3</td>
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<tr>
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<td>0.766</td>
<td>33.0</td>
<td>-9.9</td>
</tr>
<tr>
<td>87</td>
<td>0.993</td>
<td>34.4</td>
<td>-10.7</td>
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<tr>
<td>95</td>
<td>1.044</td>
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<td>-10.8</td>
</tr>
<tr>
<td>289</td>
<td>1.050</td>
<td>34.5</td>
<td>-10.7</td>
</tr>
</tbody>
</table>

25 °C, shaking on rotating table, 250 RPM

$\delta^{18}O$ of water − 11‰ (Fig. 1b)

<table>
<thead>
<tr>
<th></th>
<th>$\Delta_f$ (%)</th>
<th>$\delta^{18}O_{SMOW}$ (%)</th>
<th>$\delta^{13}C_{PDB}$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>0.122</td>
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<tr>
<td>0.25</td>
<td>0.126</td>
<td>31.0</td>
<td>-10.9</td>
</tr>
<tr>
<td>0.25</td>
<td>0.111</td>
<td>30.8</td>
<td>-9.6</td>
</tr>
<tr>
<td>0.45</td>
<td>0.082</td>
<td>30.6</td>
<td>-10.7</td>
</tr>
<tr>
<td>0.50</td>
<td>0.366</td>
<td>31.1</td>
<td>-10.7</td>
</tr>
<tr>
<td>0.50</td>
<td>0.224</td>
<td>30.6</td>
<td>-10.5</td>
</tr>
<tr>
<td>2</td>
<td>0.384</td>
<td>31.6</td>
<td>-10.8</td>
</tr>
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<td>0.507</td>
<td>30.0</td>
<td>-10.1</td>
</tr>
<tr>
<td>3</td>
<td>0.622</td>
<td>30.9</td>
<td>-10.7</td>
</tr>
<tr>
<td>6</td>
<td>0.818</td>
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<td>-9.6</td>
</tr>
<tr>
<td>20</td>
<td>0.896</td>
<td>29.8</td>
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<td>0.933</td>
<td>29.9</td>
<td>-11.1</td>
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<td>0.956</td>
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<td>-10.6</td>
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<td>44</td>
<td>0.924</td>
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<tr>
<td>46</td>
<td>0.904</td>
<td>29.8</td>
<td>-10.6</td>
</tr>
</tbody>
</table>
1. Download full-size image

Fig. 1. δ\(_{18}^O\) versus time for the experiments: a) 5 °C, flipping at 2 Hz; b) 25 °C, water 1, shaking table; c) 25 °C, water 2, shaking table; d) 37 °C, water 1, shaking table; e) 37 °C, water 2, shaking table. The thick lines are fit of the data to first-order rate functions (see text). Resulting rate constants are found in Table 2.
Fig. 2. $\Delta_{47}$ versus time for the experiments: a) 5 °C; b) 25 °C; c) 37 °C. In b) and c), runs done with water 1 are represented by empty symbols, those done with water 2 with solid symbols. They do not define significantly different trends in those diagrams.

$\delta^{13}$C PDB values of CO$_2$ recovered at the end of the water-exchange experiments averaged $-10.6 \pm 0.3$ permil (1σ). These values vary by significantly more than analytical precision (the external error of a single mass spectrometric measurement is typically better than $\pm 0.01\%o$). Some of this variability was likely created during the heating stage that preceded water equilibration; aliquots of CO$_2$ gas heated using our procedures typically vary in $\delta^{13}$C by $\pm 0.11\%o$ — less than our observed range but still significant. We hypothesize that the additional variability seen in our experimental products was created by a trace contaminant associated with the tubes and/or waters used in the water equilibration. We tested this hypothesis by pre-treating the tubes used for the last six experiments (all run at 5 °C) by heating them at 1200 °C for 2 h before being filled with water and CO$_2$. Values of $\delta^{13}$C for CO$_2$ at the end of these experiments was more constant ($-10.76 \pm 0.06\%o$, 1σ), suggesting the pre-treatment removed the contaminant (perhaps an organic compound, trapped air or carbonate that was converted to CO$_2$ over the course of the experiment). Other sources of errors might be the sample cleaning steps, and, for the equilibration experiments, CO$_2$ dissolved in the introduced water. Whatever the origin of this subtle C isotope variability, it seems unrelated to the range in $\delta^{18}$O and $\Delta_{47}$ with experimental time and temperature, and so we ignore it through the rest of our discussion. It should be noted that these results are not consistent with some of the CO$_2$ remaining...
trapped in the water. As explained in the previous section, if some CO$_2$ was left behind in the ice, the average $\delta^{13}$C of our experiments would be consistently lower than the average $\delta^{13}$C of the aliquots of heated CO$_2$ (−10.75‰, see Table 1).

The $\delta^{18}$O values of CO$_2$ experimental products evolve systematically with time from an initial value of 29.5‰ vs SMOW (±0.9‰, the large range being due to variable exchange with glass during heating to 1000 °C before the experiments, as explained above) and towards different values depending on temperature and isotopic composition of the water used, as illustrated in Fig. 1. Time invariant $\delta^{18}$O values are achieved after a few hours to tens of hours. The set of experiments conducted at 25 °C with water 1 are an exception (see panel b of Fig. 1): the $\delta^{18}$O of CO$_2$ evolves little with time for this series of experiments because the initial $\delta^{18}$O is quite close to the final equilibrium $\delta^{18}$O. It should be noted that the large range in $\delta^{18}$O at short times (duration < 5 h) for this time-series reflects the variable starting $\delta^{18}$O of our heated CO$_2$ gases. Values of $\delta^{18}$O reached at the longest times in all time-series are consistent with the isotopic composition of the waters and the equilibrium oxygen isotope fractionation between CO$_2$ and water (45.3, 41.1 and 38.8‰ at respectively 5, 25 and 37 °C, see Brenninkmeijer et al., 1983), demonstrating that heterogeneous isotopic equilibrium between CO$_2$ gas and liquid water was reached for the longest experiments at all temperatures.

Values of $\Delta_{47}$ start, in all experiments, at the value corresponding to 1000 °C equilibrium and increase with time towards the equilibrium value for each experimental temperature (Fig. 2). There is no obvious difference in the trends between experiments done with water 1 or water 2; i.e., the time evolution in $\Delta_{47}$ appears to be independent of the evolution in $\delta^{18}$O, across a large range in $\delta^{18}$O. As with $\delta^{18}$O, equilibrium is reached in a few hours (for 37 °C) to a few tens of hours (5 °C). Because the final (i.e., time-invariant) $\Delta_{47}$ values reflect equilibration of the CO$_2$ with respect to its homogeneous isotope exchange equilibria, these values were used to help construct the absolute reference frame for this data set (Dennis et al., 2011). This has no significant impact on our examination of the kinetics of isotopic exchange reflected in these data, but means they do not provide an independent measure of the temperature dependence of the equilibrium $\Delta_{47}$ value in CO$_2$(i.e., we axiomatically assume the theoretically predicted temperature dependence of Wang et al., 2004, which underlies the Dennis et al., 2011, reference frame, is correct). As with $\delta^{18}$O, equilibrium is reached in a few hours (for 37 °C) to a few tens of hours (5 °C).

4. Reaction rates

Fig. 1, Fig. 2 illustrate that the timescales for equilibration of both $\delta^{18}$O and $\Delta_{47}$ in our experimental CO$_2$-water systems are on the order of hours to tens of hours. This is generally consistent with previous studies of oxygen isotope equilibration between water and carbon dioxide (Mills and Urey, 1940, Usdowski et al., 1991, Usdowski and Hoefs, 1993, Lécuyer et al., 2009, Affek, 2013), and with the one prior experimental study of equilibration in $\Delta_{47}$ values in this system (Affek, 2013). The time-evolution of the isotopic composition of gaseous CO$_2$ observed here reflects the combined effects of dissolution, solvation, hydration of the dissolved CO$_2$ and reactions between the different species of
dissolved carbonate. The experiments we present do not isolate any of the various relevant steps; i.e., we constrain and focus here only on the net rate of all reactions. However, previous studies (Mills and Urey, 1940, Lécuyer et al., 2009, Affek, 2013) suggest the rate-limiting step is the first i.e., dissolution of CO₂ from the gas phase.

An important question addressed by this study (and the similar previous study of Affek, 2013) is whether rate constants for changes in δ¹⁸O and Δ⁴⁷ are identical or different. In principle, these two should differ only if there is a significant carbon isotope effect on the rate of oxygen isotope exchange between water and CO₂. I.e., these two rates should differ only if there is a measurable difference between ¹³CO₂ and ¹²CO₂ in rate of oxygen isotope exchange (see reactions 2a and 2b). Prior experimental evidence suggests this is unlikely: Zeebe and Wolf-Gladrow (2001) previously showed that carbon isotopic equilibrium can be established between gaseous CO₂ and dissolved inorganic carbon species on time scales of seconds to minutes (28s at 25 °C and pH = 8). Given that oxygen isotope equilibration appears to be several orders of magnitude slower (Fig. 1, and similar previous results), we might expect that the abundance of ¹³C¹⁸O¹⁶O will approach its equilibrium value at a rate indistinguishable from that for ¹²C¹⁸O¹⁶O. Thus, it would be reasonable to assume that the rate of change of δ¹⁸O should equal that for Δν in a sample of CO₂ vapor that is approaching equilibrium with co-existing water. This is consistent with the previous study of Affek (2013): although the rates measured were on average higher for for ¹²C¹⁸O¹⁶O than for the clumped species, the authors concluded that the rates were indistiguishable. We examine this question in more detail in the following discussion, using our data to place limits on the possible range of carbon isotope effects on the oxygen isotope exchange rate.

4.1. Evolution of δ¹⁸O

The evolution in δ¹⁸O of CO₂ having natural isotopic abundances should closely track the evolution in the concentration of ¹²C¹⁴O¹⁶O (i.e., because the concentrations of other relevant species – ¹²C¹⁶O₂, H₂¹⁶O and H₂¹⁸O – are approximately constant over time). And, we examine our data with the initial assumption that this concentration will evolve from the initial value towards the equilibrium following a first-order rate law:

\[
\frac{d[¹²C¹⁸O¹⁶O]}{dt} = -k_1[¹²C¹⁸O¹⁶O]
\]  (3)

Moreover, if the concentration of ¹²C¹⁴O₂ is treated as a constant, the δ¹⁸O of the gas will change with time according to the following equation:

\[
δ¹⁸O_{CO₂}(t) = δ¹⁸O_{CO₂, eq} + (δ¹⁸O_{CO₂, ini} - δ¹⁸O_{CO₂, eq}) × exp(-k_1 × t)
\]  (4)

where t is time and k₁ is the rate constant of the reaction. Classically one would examine the early stage of reaction to calculate the rate constant, as the largest changes in concentration and isotopic composition with time occur at the beginning of the reaction. However, it would be inadequate to do so when interpreting the results of our experiments due to the range of initial δ¹⁸O in our CO₂ gas (i.e., because of the exchange with silica glass during
the preparatory heating to 1000 °C). Moreover, the experiments run at 25 and 37 °C with the water 1 do not exhibit a large contrast in δ²⁰O between the initial and the equilibrium isotopic values. We therefore focus our attention on the data for experiments at 25 and 37 °C with water 2 and at 5 °C with water 1. In all cases, we used the Matlab non-linear least-squares Gauss–Newton fitting algorithm to calculate the rate constants. Data from each series were fitted to a first-order rate law where the only parameter was the rate constant, as both initial and final δ²⁰O were known (though with a significant associated error in the case of the initial δ²⁰O). Errors were calculated by the fitting software and reflect the steepness of the sum of the residuals around the value giving the best fit (here given at the 1σ level).

The best-fit curves are displayed in Fig. 2 and the calculated rate constants are given in Table 2. It is worth noting that, even if a precise calculation were not possible for the series at 37 °C with water 1, the predicted curve using the rate constant calculated at the same temperature but with water 2 is consistent with the data generated by exchange with water 1 at the same temperature (Fig. 2).

Table 2. Rate constants determined for the equilibration of carbon dioxide with water.

<table>
<thead>
<tr>
<th>T (°C)</th>
<th>kδ¹⁸O (h⁻¹)</th>
<th>kΔ⁴⁷ (h⁻¹)</th>
<th>Shaking</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>5</td>
<td>0.17</td>
<td>0.22</td>
<td>Yes</td>
<td>This study</td>
</tr>
<tr>
<td>25</td>
<td>0.41</td>
<td>0.35</td>
<td>Yes</td>
<td>This study</td>
</tr>
<tr>
<td>37</td>
<td>0.64</td>
<td>0.66</td>
<td>Yes</td>
<td>This study</td>
</tr>
<tr>
<td>25</td>
<td>0.38</td>
<td>0.34</td>
<td>Yes</td>
<td>Affek (2013)</td>
</tr>
<tr>
<td>42</td>
<td>0.62</td>
<td>0.51</td>
<td>Yes</td>
<td>Affek (2013)</td>
</tr>
<tr>
<td>22</td>
<td>0.15</td>
<td>0.12</td>
<td>No</td>
<td>Affek (2013)</td>
</tr>
</tbody>
</table>

The rate constants are equal to 0.17 ± 0.03, 0.41 ± 0.11 and 0.64 ± 0.05 h⁻¹ at 5, 25 and 37 °C respectively. This indicates higher reaction rates for warmer temperatures, as we might expect.

4.2. Evolution of Δ₄⁷

The evolution of Δ₄⁷ with time is illustrated in Fig. 2, Fig. 3, and the shape of its evolution appears, at first glance, to also reflect first-order kinetics. Nevertheless, Δ₄⁷ has a complex definition (Eq. (1)) that makes it even less suitable than δ²⁰O as a proxy for concentration. Therefore, the form of the empirical relationships in Fig. 2, Fig. 3 could be misleading. Instead, it is preferable to track the evolution in abundance of individual isotopologues undergoing exchange reactions such as Eq. (3) (i.e., the actual abundances of the specific reactants and products whose chemical kinetics control the evolution of Δ₄⁷). In particular, the evolution of ¹³C¹⁸O¹⁶O is responsible for 97% of mass 47 signal, and thus its variations are most important to controlling the Δ₄⁷ value. Its concentration is controlled by the following equation:

\[ ¹³C¹⁸O¹⁶O(t) = ¹³C¹⁸O¹⁶O(t)_{equ} + \left( ¹³C¹⁸O¹⁶O(t)_{ini} - ¹³C¹⁸O¹⁶O(t)_{equ} \right) \times exp(-k_2 \cdot t) \]  

(5)
where \( k_2 \) is the rate constant for the equilibration of this isotopologue.

For bulk isotopic compositions close to natural isotopic abundances, Eq. (1) can be approximated as:

\[
(6) \Delta_{47} \approx 103.13C_{18O16O2.13R.18R-1}
\]

where \(^{13}R\) and \(^{18}R\) refers to the isotopic ratios of carbon and oxygen in carbon dioxide. In our experiments, \(^{13}R\) stays constant and \(^{18}R\) varies by at most 35‰. Eq. (6) can be rewritten to a reasonable approximation as:

\[
(7) \Delta_{47} \approx 10313C_{18O16O_{\text{equ}}} + [(13C_{18O16O})_{\text{ini}} - 13C_{18O16O_{\text{equ}}}] \times \exp(-k_2 \cdot t) \cdot 18R_{\text{equ}} + 18R_{\text{ini}} - 18R_{\text{equ}} \cdot \exp(-k_1 \cdot t) - 1
\]

where \( k_i \) is the rate constant for the evolution of the clumped isotopologue, and \( k_i \) the rate constant for the evolution of bulk \( \delta^{18}O \).

Thus the time evolution of \( \Delta_{47} \) depends on both the rate constant for the bulk oxygen isotope ratio \( (^{18}R) \) and on the rate constant for the clumped species. Importantly, for limited variations of \(^{18}R\) (and thus of \( \delta^{18}O \)), only \( k_2 \) will be of importance. For the case of our experiments (where isotope abundances are in the natural range and variations are modest), it is therefore acceptable to treat the evolution of \( \Delta_{47} \), as we treated that of \( \delta^{18}O \), i.e., to use the following expression:

\[
\Delta_{47}(t) = \Delta_{47_{\text{equ}}} + (\Delta_{47_{\text{ini}}} - \Delta_{47_{\text{equ}}}) \times \exp(-k_2 \cdot t).
\]

This expression is more straightforward to fit to the experimental results than it was for the analogous expression describing the evolution of \( \delta^{18}O \). This is because all experiments began with closely similar initial \( \Delta_{47} \) values, and all evolved strongly to their final \( \Delta_{47} \) values (i.e., by a large multiple of analytical precision). Therefore, it is possible to use the early stages of reaction to obtain the rate constants, as illustrated on Fig. 3. The rate constants are equal to 0.20 ± 0.04, 0.35 ± 0.02 and 0.66 ± 0.04 h\(^{-1}\) (1 σ) at 5, 25 and 37 °C, respectively. Those values are, within errors, equal to the ones calculated above for the kinetics of the oxygen isotope exchange.
The rate constants obtained at 25 °C (0.41 and 0.35 h\(^{-1}\) for \(\delta^{18}O\) and \(\Delta_{47}\)) are very similar to those obtained by Affek (2013) (respectively 0.38 and 0.34 h\(^{-1}\)), despite differing reaction vessels (the ones used in Affek (2013) are 25 times bigger) and differing ratio of carbon dioxide to water (the study of Affek (2013) used 10 times more water for a comparable amount of carbon dioxide). However, the rates obtained by their study at 42 °C (0.62 and 0.51 h\(^{-1}\)) are lower than or equal to those obtained here at 37 °C (0.64 and 0.66 h\(^{-1}\)). Additionally, Affek (2013) had also made measurements at 22 °C with no shaking. They found rates of reaction (0.15 and 0.12 h\(^{-1}\)) even lower than the ones measured here at 5 °C (0.17 and 0.22 h\(^{-1}\)), highlighting the importance of the boundary layer in controlling the rate of isotopic exchange.

Significantly, we find at all temperatures that the rates of evolution of \(\delta^{18}O\) and \(\Delta_{47}\) are indistinguishable within uncertainties, as did Affek (2013).

During our derivation, we assumed that the differences between the starting and the initial \(\delta^{18}O\) of the gas were small enough that we could neglect them (Eqs. 7, 8). However it is worth verifying to what extent this approximation is correct. We therefore performed a sensitivity test for this approximation: we calculated how \(\Delta_{47}\) evolved with time, from a stochastic distribution towards a value of + 1‰, using both Eqs. 7, 8 and equal rate constants (\(k1 = k2\) in Eq. 7). The contrasts in \(\delta^{18}O\) ranged from 0 to + 10000‰. When the final \(\delta^{18}O\) is enriched compared to the starting values, a transient positive anomaly in \(\Delta_{47}\) is observed, i.e, the clumped species is approaching its equilibrium value faster than the bulk isotopic composition at the beginning of the reaction (see Fig. 4). This anomaly reaches a maximum value of 0.01‰ (similar to the error on our measurement) for a \(\delta^{18}O\) contrast of 41‰. It should be noted that the anomalies are only transient and disappear when equilibrium is reached. It is not likely that this effect will be important in nature, as it is only relevant for systems far from equilibrium in which the contrasts in bulk oxygen isotopic compositions will be of 50‰ or more.
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Fig. 4. Comparison of $\Delta_{47}$ calculated from Eq. (7) at different contrasts between initial and final bulk $\delta^{18}\text{O}$, indicated by the numbers on the figure. Dashed lines: $\Delta_{47}$ calculated from Eq. (7), continuous lines: differences between calculations from Eqs. (7), (8). Although we show only curves for large contrasts in $\delta^{18}\text{O}$, there is a potentially measurable difference for contrasts higher than 41‰ (see text for details).

4.3. Potential consequences of unequal rates of reaction

As discussed above, the evolution of $\Delta_{47}$ must depend on the rate of exchange of $^{18}\text{O}$ and the effect of $^{13}\text{C}$ substitution on the $^{18}\text{O}$ exchange rate. Our data suggest that the rate constants for $^{12}\text{C}^{18}\text{O}^{16}\text{O}$ and $^{13}\text{C}^{18}\text{O}^{16}\text{O}$ are indistinguishable, but with large error bars associated to the calculated values.

Here we investigate this issue further by constructing a model in which there is a significant effect of carbon isotope substitution on the rate of $^{18}\text{O}$ exchange, and then compare the predictions of that model to our data to place limits on the possible size of any such effect. Specifically, we built a forward model of the change in both $\delta^{18}\text{O}$ and $\Delta_{47}$ in carbon dioxide, from an initial state that is far from oxygen isotope equilibrium with water and having a random internal isotopic distribution, towards a final composition that is in both oxygen isotope equilibrium with water and internal equilibrium at an arbitrary temperature (chosen so that the final $\Delta_{47}$ is equal to + 1 permil). We assumed, for simplicity, that $\delta^{13}\text{C}$ was constant, that the water isotopic composition stayed constant with a $\Delta^{17}\text{O}$ equal to 0 and that very low abundance isotopologues (e.g., $^{12}\text{C}^{17}\text{O}^{18}\text{O}$) were distributed stochastically and that the oxygen isotope fractionation follows a strict canonical mass dependent law (with a mass exponent equal to 0.528) before, during and at the end of the exchange process. The results are presented in **Fig. 5**.
1. **Download full-size image**

Fig. 5. Modeled results of $\Delta_{47}$ evolution with time when the rates for of reactions 3a and 3b are not equal. a) Model with arbitrary time and reaction rates and a 10‰ bulk $\delta^{18}O$ contrast. Continuous line: equal rates, dashed lines: one of the rates is 10% higher than the other, dotted line: one is 20% higher than the other. See explanations in text. b) and c) Illustration with the dataset obtained in this study: the dashed line is the predicted line using the rates calculated for the 25 °C series (b)) and the 37 °C series (c)) when the water 2 is used ($\approx$ 30‰ bulk $\delta^{18}O$ contrast), see Table 2, the continuous line is the curve obtained for equal rate constants. In b), equilibration of the clumped species proceeds more slowly than equilibration of the non-clumped species. The reverse is true in c). See text for details.

Panel 4a) provides an example scenario when the rate constants of oxygen isotope exchange differ by some specified amount between $^{12}$CO$_2$ and $^{13}$CO$_2$. We find that if $^{13}$CO$_2$ species equilibrate 10% (or more) more slowly than the $^{12}$CO$_2$ species, $\Delta_{47}$ initially decreases sharply to negative values early in the exchange process before reversing and approaching the final equilibrated state. If, instead, $^{13}$CO$_2$ species exchange faster than $^{12}$CO$_2$ species, $\Delta_{47}$ values rise too sharply early in the exchange process, and in the illustrated case even exceed the final equilibrium value before eventually drifting back down to that equilibrated state. These effects may seem counter intuitive but arise naturally from the definition of $\Delta_{47}$: the $\Delta_{47}$ value measures (mostly) the difference between the actual $^{13}$C$^{\delta^{18}O}$ abundance and the abundance of $^{13}$C$^{\delta^{18}O}$ expected for a sample where $^{18}O$ atoms are randomly distributed between $^{12}$C and $^{13}$C bearing molecules. Thus, if $^{13}$C$^{\delta^{18}O}$ increases when $^{13}$C$^{\delta^{18}O}$ remains fixed, $\Delta_{47}$ must decrease. And, conversely, if $^{13}$C$^{\delta^{18}O}$ increases when $^{13}$C$^{\delta^{18}O}$
remains fixed, $\Delta_{47}$ must rise. It is worth noting that in the case of our model the amplitude of the peculiar deviations from a first-order rate law in the $\Delta_{47}$ evolution depend both on the strength of the carbon isotope effect we assume and the amplitude of change in $\delta^{18}$O of CO$_2$ between its initial and final equilibrium states. When the $\delta^{18}$O contrast is smaller than 1 permil, the 'hump' due to a 10% relative difference in the reaction rates would no longer be analytically resolvable.

Panels b) and c) of Fig. 5 compare models of this type to our data. This allows us to place constraints on the amplitude of possible effect of carbon isotope substitution on the rate of $\delta^{18}$O exchange. Experimental data for the 25 °C (panel b)) and 37 °C (panel c)) series are plotted, along with the curves corresponding to equal rate constants (continuous lines). The dotted lines illustrate the expected evolution with water 2 (which has a strong contrast between starting and ending $\delta^{18}$O) using the exact rate constants fitted to our data (see Table 2). Importantly, our data do not show the dips and 'humps' displayed by the forward model with the experimental rates differing by 10% or more. Moreover, there is no apparent difference between the experiments performed with water 1 or with water 2. We can therefore constrain the isotopic effect of carbon on CO$_2$–water exchange. The series most sensitive to a difference in the reaction rates are those at 25 and 37 °C with water 2, as they are the ones with the highest $\delta^{18}$O contrast. Based on this model, we find that the relative difference in the reaction rates cannot be greater than 0.5%, with no constraint on the sign of this difference. In the study of Affek (2013), taken at face value, the calculated rates differed by 16% on average, while the $\delta^{18}$O contrast between initial and final composition varied from 8 to 13‰. As their evolution of $\Delta_{47}$ with time has a shape compatible with a first-order rate law, we conclude that the apparent differences in rate constants are due to analytical uncertainties.

4.4. Thermodynamic parameters of the exchange reactions

One of the purposes of our study is to allow for the calculation of the rate of CO$_2$ exchange for a given temperature. Fig. 6 is an Arrhenius plot where the rate constants obtained in this study are displayed, along with those measured by Affek (2013). The rate constants measured at the different temperatures in our study form a line ($R^2 = 0.96$) that can be used to calculate the Arrhenius parameters, $A_0$ (pre-exponential factor) and $E_a$ (activation energy), consistent with the relationship:

$$k = A_0 \cdot exp\left(\frac{-E_a}{RT}\right)$$ (9)

where $R$ is the ideal gas constant and $T$ is the temperature in Kelvin. If we assume that there is strictly no carbon isotope effect on the rate of oxygen isotope exchange, and give equal weight to measured rate constants from $\delta^{18}$O and $\Delta_{47}$ data, we calculate that $E_a$ is equal to 26.2 ± 4.1 kJ/mol and $\ln(A_0)$ is equal to 9.77 ± 1.5 (both 1σ), with $A_0$ in h$^{-1}$. The same calculation can be done with the data of Affek (2013); in this case there are only two different temperatures, so errors are calculated using the uncertainties on the calculated rate constants. These data suggest an $E_a$ of 26.3 ± 7.6 kJ/mol and a $\ln(A_0)$ of 8.8 ± 2.7, using the $\delta^{18}$O data, and an $E_a$ of 21.8 ± 2.6 kJ/mol and a $\ln(A_0)$ of 7.0 ± 1.0, using the $\Delta_{47}$ data, which are within 2σ of our results. The similarity of our results with those of Affek.
show that the differences in vessel geometry and water/CO$_2$ ratios between these two sets of experiments have little or statistically no influence on the rate of CO$_2$-water exchange.

1. **Download full-size image**

Fig. 6. Arrhenius plot, showing the rate constants calculated from the experiments from this study (squares, values derived from oxygen isotopes data, diamonds from $\Delta_{47}$ measurements), and least-squares fit line through the 6 rate constants calculated. See text for details. Also plotted are rate constants from [2] (small crosses from $\delta^{18}O$ data, stars from $\Delta_{47}$ for shaken series, circles from an unshaken experiment).

By comparison, **Mills and Urey (1940)** studied the kinetics of oxygen isotope equilibration between dissolved CO$_2$ and water. Their experiments started with vigorous shaking to dissolve the CO$_2$ in the solution, and they analyzed the evolution of the isotopic composition of this dissolved CO$_2$ with time. They found an activation energy of 71.7 kJ/mol and a rate constant of 11 $h^{-1}$ at 25 °C (compared to 0.38 in this study). The lower rate constant we observe is consistent with the interpretation that the rate limiting step in the system we have studied is the exchange of CO$_2$ between the gas and the liquid phase. Other previous studies of oxygen isotope exchange between CO$_2$ and water show that, with shaking, $\approx 10$ h are needed to reach equilibrium between water and carbon dioxide (**Fortier, 1994, Zeebe and Wolf-Gladrow, 2001, Lécuyer et al., 2009**) at room temperature. This result is semi-quantitative, but generally consistent with our findings and those of **Affek (2013)**.

5. **Perspectives**

Knowledge of the chemical kinetics of isotopic exchange, including $\Delta_{47}$ changes, between carbon dioxide vapor and co-existing liquid water can potentially provide insight into a variety of chemical, biochemical and geochemical processes. The data presented here may be useful where one has poor knowledge of the $\delta^{18}O$ of water in the environment of interest (and thus cannot easily evaluate whether or not a CO$_2$ sample is in oxygen isotope exchange equilibrium with that water), but the temperature is known (i.e., so the $\Delta_{47}$ value CO$_2$ should have at equilibrium is known). A key result of our study is that the measured rates are similar to those obtained with other geometries (**Fortier, 2013**).
This implies that in a variety of interface conditions, we can use those rate constants quantitatively.

One area of application of this data is the atmospheric CO\textsubscript{2} budget. Clumped isotope signatures (i.e., $\Delta_{47}$ values) of atmospheric CO\textsubscript{2} have been used previously to help to constrain the sources and fluxes in urban environments (Affek and Eiler, 2006, Affek et al., 2007) and stratospheric air (Yeung et al., 2009). The experiments presented here constrain the rates at which exchange with liquid water (sea surface, leaf water, aerosols, etc.) may drive the $\Delta_{47}$ value of atmospheric CO\textsubscript{2} towards equilibrium at the local ambient temperature. These experiments, combined with appropriate models for other limiting factors (e.g., surface area and film thickness of water; diffusion of CO\textsubscript{2} through air) can be used to define the residence time of CO\textsubscript{2} with respect to exchange processes of interest. For example, in models of air–sea exchange, atmospheric CO\textsubscript{2} is assumed to equilibrate with CO\textsubscript{2} dissolved in ocean surface water (e.g., Cuntz et al., 2003). These models assume a rate of reaction derived from the Mills and Urey (1940) experiments, which imply e-folding times of a few minutes for the equilibration of CO\textsubscript{2}. However, these experiments constrain the exchange between dissolved CO\textsubscript{2} and water, which, according to our data, does not appear to be the rate limiting step in exchange between gaseous CO\textsubscript{2} and water. Exchange between the sea and the atmosphere is further complicated by the changing nature of the ocean surface and its impact on the speed of atmosphere–ocean CO\textsubscript{2} exchanges (e.g., Takahashi et al., 2002, Wanninkhof et al., 2002). Nevertheless, taken at face value, our results would imply an e-folding time of a few hours to tens of hours depending on the temperature. However, compared to the residence time that characterize exchange of oxygen atoms between the ocean and the atmosphere (≈ 8 years Farquhar et al., 1993) and the scale of those global models, the experiments we present do not imply a significant revision to models of the stable isotope geochemistry of air–sea exchange of CO\textsubscript{2}.

The oxygen isotope composition of CO\textsubscript{2} in the atmosphere is also strongly influenced by the exchange with leaf water (exchange time of O atoms between leaf water and atmospheric CO\textsubscript{2} being ≈ 2 years, Farquhar et al., 1993). This time scale is however not relevant, as although the average residence time of CO\textsubscript{2} in a leaf stomata is 0.02 s (Ciais et al., 1997), the presence of the enzyme carbonic anhydrase ensures that O isotopic equilibrium is reached between the CO\textsubscript{2} and leaf water (Keeling, 1995, Cuntz et al., 2003).

One could also imagine using the data presented here to interpret values of $\Delta_{47}$ and $\delta^{18}$O for CO\textsubscript{2} in environments other than the atmosphere. For example, Affek and Eiler (2006) showed that the $\Delta_{47}$ of CO\textsubscript{2} in car exhaust was equal to 0.45‰. This is much higher than the value expected for the combustion temperature, and was suggested to reflect re-equilibration at 170 °C, mediated by the water also produced during combustion.

One could imagine using the known kinetics of CO\textsubscript{2}(v)–H\textsubscript{2}O(l) exchange to place limits on the physical conditions of this re-equilibration (surface area of water aerosol, etc.). There are other 'micro-
environments' of this type where similar observations and interpretations could be made, including CO₂ emitted from gas- and coal-fired power plants. It may be particularly interesting to compare car exhaust to natural gas combustion to coal burning; these fuels differ markedly in their C/H ratios and conditions of burning and so their exhaust streams may differ markedly in the effectively blocking temperature for CO₂(v)–H₂O(l) exchange. The geometry of the combustion gas exhaust may also play a role, as it will partially control the cooling rate of the gases.

Another observation that may benefit from kinetic data of the type we present is the recent finding that CO₂ in the polar stratosphere can have Δ₄⁷ value up to 1.5‰ (the highest known for a natural material, Yeung et al., 2009). The two leading hypothesis to explain the high Δ₄⁷ values are either a not yet identified photochemical fractionation of CO₂ in the stratosphere, or temperature-dependent isotopic exchange on polar stratospheric clouds. The measured Δ₄⁷ are consistent with CO₂ at equilibrium at polar stratospheric temperatures, which could be reached through exchange mediated by aqueous aerosols or by liquid water layers on particle surfaces (Yeung et al., 2009). It may be possible to use measurements of fundamental rates of isotopic exchange, such as those presented here, to place limits on this hypothesis. Our results imply that if the second hypothesis is correct, the δ¹⁸O of stratospheric CO₂ should be in equilibrium with the δ¹⁸O of the water present as aerosols or on aqueous surfaces. Careful collection of aerosols and particles to measure the oxygen isotopic composition of the water that can exchange with stratospheric CO₂ would be necessary. One of the complications that arise in this case is that aqueous stratospheric aerosol commonly has high concentrations of dissolved salts, which are known to influence rates of exchange between CO₂ and water (Fortier, 1994, Lécuyer et al., 2009).

Finally, the clumped isotope geochemistry of respired sources of CO₂ (e.g., from soil; in human breath) are little understood but the few observations that are available suggest their Δ₄⁷ values are not in equilibrium at their formation temperatures (Affek and Eiler, 2006). This implies that respiration involves one or more kinetic isotope effects (chemical and/or transport), and that escape to a non-exchangeable form (i.e., in air) must occur faster than isotopic equilibration mediated by soil or body water. Again, knowledge of the fundamental rates of CO₂(v)–H₂O(l) exchange may allow one to use clumped isotope observations to place constraints on the mechanisms of respiration. As is the case with stratospheric CO₂, it would be key for soil respiration to recover the water that exchange with the CO₂ and measure its δ¹⁸O, as a disequilibrium in Δ₄⁷ should be reflected by a disequilibrium in oxygen isotope ratios. It is worth noting that in previous data on human breath (Affek and Eiler, 2006), Δ₄⁷ value did not reflect the body temperature while the difference in δ¹⁸O between body water and exhaled CO₂ did. This seems contradictory with the results of our experiments, and more work on the isotopic composition of CO₂ in exhaled air is necessary, especially regarding Δ₄⁷.

6. Summary and conclusions

We investigated the kinetics of isotopic exchange between liquid water and gaseous carbon dioxide, including δ¹⁸O and mass 47 isotopologues, at 5, 25 and 37 °C. We found that equilibrium between
gaseous CO₂ and liquid water was reached after durations of a few hours (for 37 °C series) to tens of hours (for the 5 °C series). δ¹⁸O values at equilibrium were consistent with known fractionation factors for the CO₂-H₂O system. Rate constants were calculated and are equal for the evolution of δ¹⁸O and Δ₄⁷ at each temperature (within error). They average 0.19⁻¹ at 5 °C, 0.38 h⁻¹ at 25 °C and 0.65 h⁻¹ at 37 °C. Those results are broadly consistent with the previous study of (Affek, 2013), which suggests that the geometry of the reaction vessels only plays a small role and that the measured rate constants can be applied to natural world questions. We calculate an activation energy for this isotopic exchange reaction of 26.2 kJ/mol. By comparison, Mills and Urey (1940) measured the rate of ¹⁸O exchange between CO₂(aq) and water to have a rate of 11 h⁻¹ at 25 °C and an activation energy of 71.7 kJ/mol. Combination of the data presented here with that in Mills and Urey suggest that in systems containing CO₂ vapor and liquid water, dissolution of carbon dioxide is the rate-limiting step. Theoretical modeling of the reaction, when compared with our experimental data, show that the rate constants for oxygen isotope exchange are essentially identical for ¹³CO₂ and ¹²CO₂, otherwise the evolution of Δ₄⁷ during exchange would exhibit peculiar rises or dips that violate first-order kinetics and differ from the evolution in δ¹⁸O.

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