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Kinetics of $CO_{2(g)}$–$H_2O_{(1)}$ isotopic exchange, including mass 47 isotopologues

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Highlights

- The kinetics of CO_2(g)–H_2O(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 Δ_{47} value — a measure of the enrichment of doubly substituted CO_2 relative to a stochastic isotopic distribution. Values of Δ_{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 Δ_{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 Δ_{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 Δ_{47}, $\delta^{13}C$ and $\delta^{18}O$ by gas source isotope ratio mass spectrometry. Equilibrium was reached for both $\delta^{18}O$ and Δ_{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_2O system. The evolution of $\delta^{18}O$ and Δ_{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 ^{18}O exchange between CO_2(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 CO_2(g)–CO_2(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 Δ_{47}. We propose that the difference is due to analytical uncertainties and explore the theoretical consequences of unequal reaction rates between $^{12}C^{18}O^{16}O$ and $^{13}C^{18}O^{16}O$ with a forward model.

1. Introduction

The carbon dioxide budget in the atmosphere is constrained by carbon and oxygen isotopic compositions of CO_2 (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 $\delta^{13}C$[1], Ciais et al., 1995a, Ciais et al., 1995b, Francey et al., 1995), and terrestrial primary production from soil respiration (using $\delta^{18}O$, Yakir and Wang, 1996, Peylin et al., 1999, Welp et al., 2011). Additionally the amount of ^{14}C can be used to constrain the origin of carbon in CO_2 (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 CO_2 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 CO_2 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 CO_2, we are interested in the mass anomaly of molecules with m/z = 47, dominated by $^{13}C^{18}O^{16}O$, which is reported using the variable Δ_{47}, defined as follows:

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

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 CO_2 sample that has achieved an internal isotopic equilibrium, the enrichment in mass-47 isotopologues (i.e., the Δ_{47} value) is a function of temperature only (Eiler and Schauble, 2004, Wang et al., 2004). Gas phase isotopic exchange in pure CO_2 is extremely slow at temperatures below several hundred degrees Celsius, and thus it is difficult for gaseous CO_2 to achieve a temperature-dependent equilibrium. However, the presence of water catalyzes isotopic exchanges through reactions such as:

$$^{12}C^{16}O^{16}O + H_2^{18}O \rightleftharpoons H_2^{12}C^{16}O^{16}O^{18}O \rightleftharpoons {}^{12}C^{16}O^{18}O + H_2^{16}O \qquad (2a)$$

$$^{13}C^{16}O^{16}O + H_2^{18}O \rightleftharpoons H_2^{13}C^{16}O^{16}O^{18}O \rightleftharpoons {}^{13}C^{16}O^{18}O + H_2^{16}O \qquad (2b)$$

which will take place readily at temperatures reached at Earth surface and atmosphere.
For this reason, the interpretation of Δ_{47} values of atmospheric CO_2 depends critically on our understanding of the kinetics of these reactions. The reaction rate of the CO_2–H_2O 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 Δ_{47} 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 Δ_{47} in CO_2 vapor in the presence of H_2O, 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 ≈ 50 μmol of CO_2 contained in sealed silica tubes at 1000 °C for 2 h. The Δ_{47} 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 ≈ 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_2O 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 CO_2–H_2O 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 CO_2 it contains.

Experiments were conducted with two waters with different oxygen isotope compositions (‘water 1’: $\delta^{18}O = -11.0 \pm 0.2$ permil; ‘water 2’: $\delta^{18}O = +23.0 \pm 0.2$ 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 CO_2. 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 N_2 trap. Some of the CO_2 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 HCO_3^-being the dominant species in solution ($10 > pH > 4$). If some CO_2 stayed trapped in water ice, it would be reflected in the $\delta^{13}C$ of the recovered gas, as at equilibrium HCO_3^- is enriched in ^{13}C compared to CO_2(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 CO_2 is quantitatively outgassed during freezing and gas separation. For a subset of samples, the purified CO_2 was quantified using a Baratron® vacuum gauge, showing that 99 ± 3% of the initial CO_2 is recovered with our setup (n = 8).

The gas aliquots were then analyzed for the abundance of the isotopologues of CO_2 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 $\delta^{13}C$, $\delta^{18}O$ and Δ_{47}, 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 CO_2 having a range of bulk isotopic compositions and equilibrated at 1000 or 25 °C, as well as two intralaboratory carbonate standards. Δ_{47} 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 $\delta^{13}C_{PDB}$ stayed constant during the experiments, and that both $\delta^{18}O$ and Δ_{47} of the CO_2 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.

Duration (h)	**Δ_{47} (‰)**	**$\delta^{18}O_{SMOW}$ (‰)**	**$\delta^{13}C_{PDB}$ (‰)**
Initial value, average of 10 heated gases			
0	0.011	29.5	− 10.7
Standard deviation			
	0.015	0.3	0.04
25 °C, shaking on rotating table, 250 RPM,			
$\delta^{18}O$ of water + 23‰ (Fig. 1c)			
0.50	0.228	43.0	− 10.4
1	0.298	42.2	− 10.2
2	0.371	47.9	− 10.3
5	0.774	60.6	− 10.6
37 °C, shaking on rotating table, 250 RPM			
$\delta^{18}O$ of water + 23‰ (Fig. 1d)			
0.50	0.164	36.6	− 10.9
1	0.468	49.9	− 10.4
2	0.569	54.1	− 11.3
5	0.841	60.1	− 10.5
6	0.780	60.3	− 10.6
40	0.859	61.8	− 10.5
37 °C, shaking on rotating table, 250 RPM			
$\delta^{18}O$ of water − 11‰ (Fig. 1e)			
0.50	0.340	28.6	− 10.5
4	0.774	28.3	− 10.4
6	0.716	27.8	− 10.2
22	0.856	28.0	− 9.7
45	0.865	28.0	− 10.8
Duration (h)	Δ_{47} (‰)	$\delta^{18}O$ (‰)	$\delta^{13}C$ (‰)
5 °C, shaking by flipping the tube every 0.5 s			
$\delta^{18}O$ of water − 11‰ (Fig. 1a)			
0.25	0.133	29.6	− 10.7
0.50	0.196	30.2	− 10.5
2	0.330	30.3	− 10.8

Duration (h)	**Δ_{47} (‰)**	**$\delta^{18}O_{SMOW}$ (‰)**	**$\delta^{13}C_{PDB}$ (‰)**
3	0.399	32.6	− 10.5
4	0.637	31.1	− 10.7
6	0.766	33.0	− 9.9
87	0.993	34.4	− 10.7
95	1.044	34.6	− 10.7
112	1.051	34.7	− 10.9
114	1.064	34.6	− 10.7
215	1.025	34.5	− 10.8
289	1.050	34.5	− 10.7
25 °C, shaking on rotating table, 250 RPM			
$\delta^{18}O$ of water − 11‰ (Fig. 1b)			
0.25	0.122	30.5	− 10.8
0.25	0.126	31.0	− 10.9
0.25	0.111	30.8	− 9.6
0.45	0.082	30.6	− 10.7
0.50	0.366	31.1	− 10.7
0.50	0.224	30.6	− 10.5
2	0.384	31.6	− 10.8
3	0.507	30.0	− 10.1
3	0.622	30.9	− 10.7
6	0.818	31.7	− 9.6
20	0.896	29.8	− 10.7
22	0.933	29.9	− 11.1
34	0.956	29.8	− 10.6
44	0.924	30.0	− 10.4
45	0.931	29.8	− 10.4
46	0.904	29.8	− 10.6

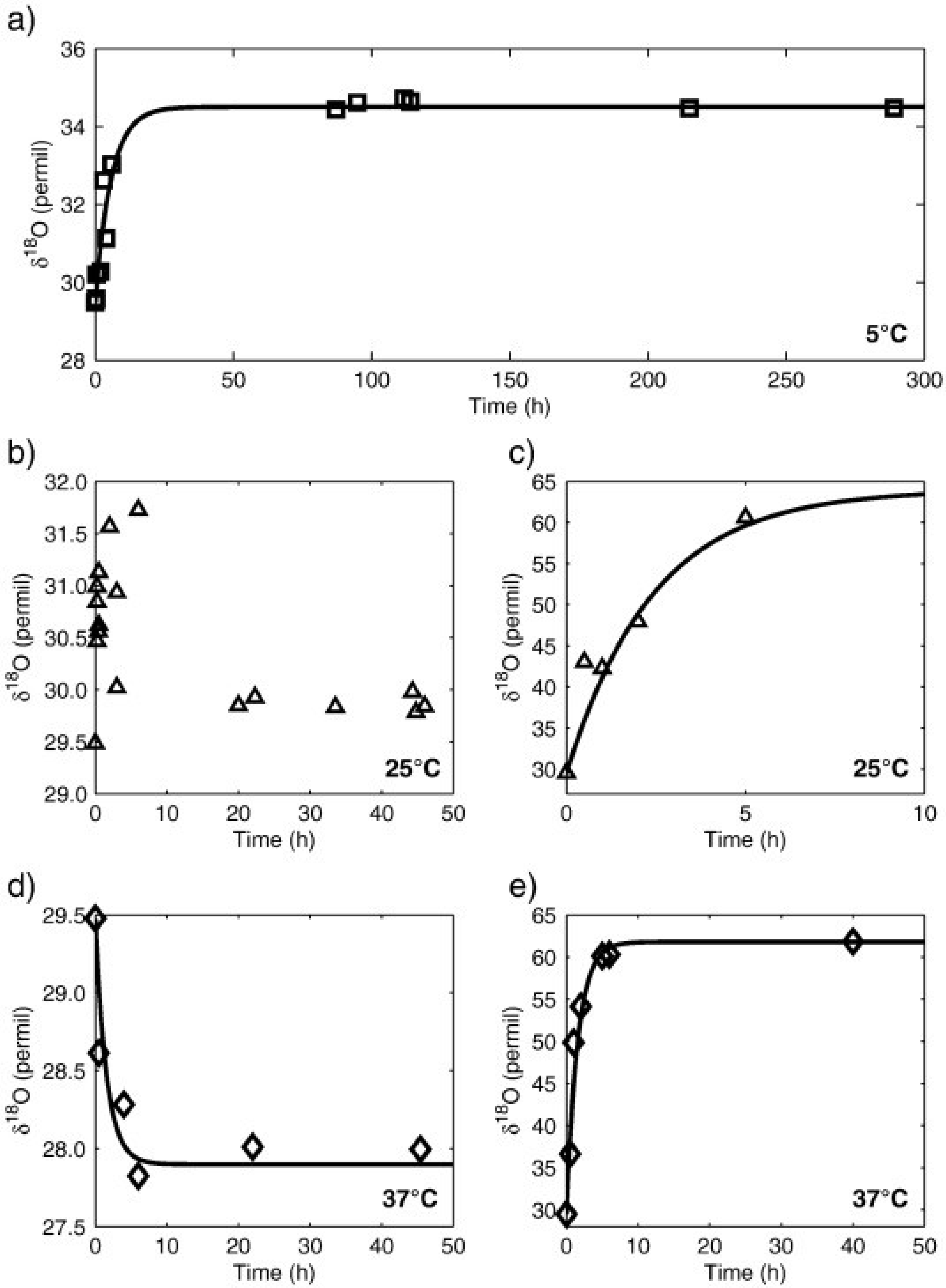

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Fig. 1. $\delta^{18}O$ versus time for the experiments: a) 5 °C, flipping at 2 Hz; b) 25 °C, water 1, shaking table; c) 25 °C, water 2, shaking table; d) 37 °C, water 1, shaking table; e) 37 °C, water 2, shaking table. The thick lines are fit of the data to first-order rate functions (see text). Resulting rate constants are found in Table 2.

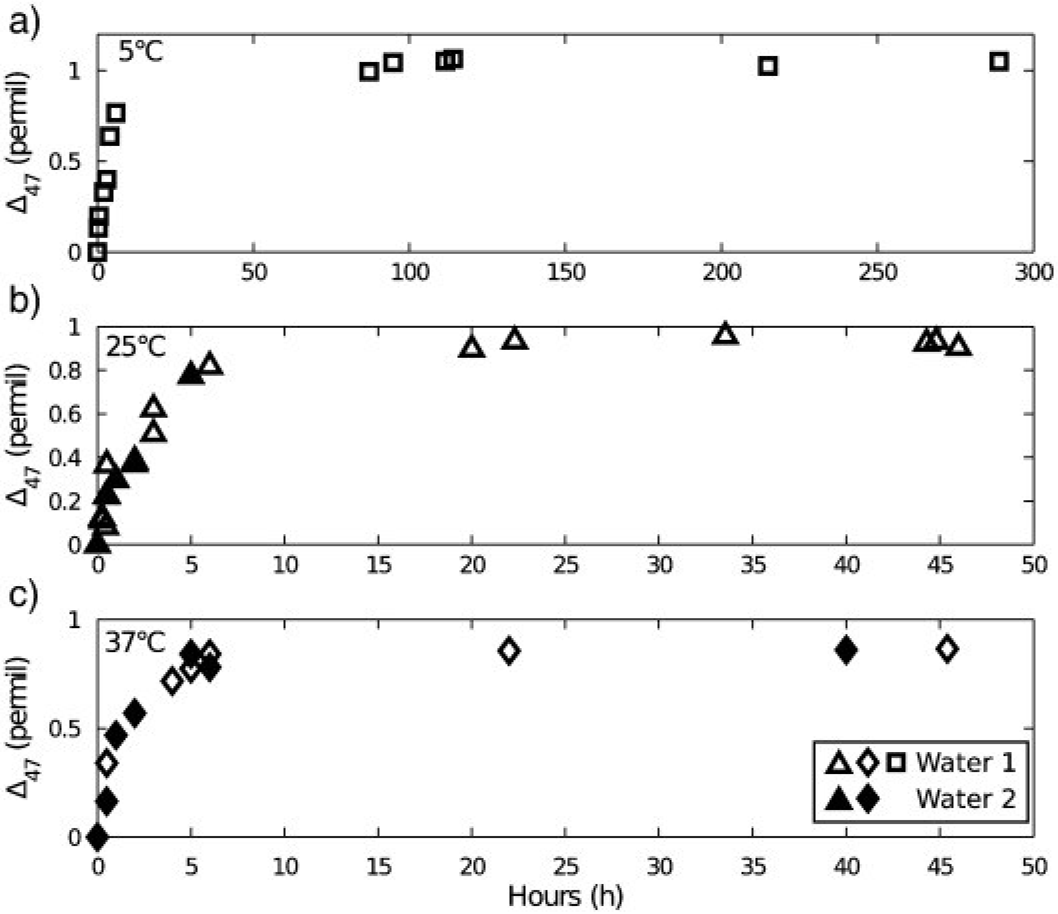

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Fig. 2. Δ_{47} versus time for the experiments: a) 5 °C; b) 25 °C; c) 37 °C. In b) and c), runs done with water 1 are represented by empty symbols, those done with water 2 with solid symbols. They do not define significantly different trends in those diagrams.

$\delta^{13}C_{PDB}$ values of CO_2 recovered at the end of the water-exchange experiments averaged − 10.6 ± 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 ± 0.01‰). 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 ± 0.11‰ — 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 ± 0.06‰, 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 Δ_{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 Δ_{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 Δ_{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) Δ_{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 Δ_{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 Δ_{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 Δ_{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 CO_2 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 $\delta^{18}O$ and Δ_{47} 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 CO_2. I.e., these two rates should differ only if there is a measurable difference between $^{13}CO_2$ and $^{12}CO_2$ 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 CO_2 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 $^{13}C^{18}O^{16}O$ will approach its equilibrium value at a rate indistinguishable from that for $^{12}C^{18}O^{16}O$. Thus, it would be reasonable to assume that the rate of change of $\delta^{18}O$ should equal that for Δ_{47} in a sample of CO_2 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 $^{12}C^{18}O^{16}O$ 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 $\delta^{18}O$

The evolution in $\delta^{18}O$ of CO_2 having natural isotopic abundances should closely track the evolution in the concentration of $^{12}C^{18}O^{16}O$ (i.e., because the concentrations of other relevant species – $^{12}C^{16}O_2$, $H_2{}^{16}O$ and $H_2{}^{18}O$ – 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:

$$\frac{d\left[{}^{12}C^{18}O^{16}O\right]}{dt} = -k_1\left[{}^{12}C^{18}O^{16}O\right] \qquad (3)$$

Moreover, if the concentration of $^{12}C^{16}O_2$ is treated as a constant, the $\delta^{18}O$ of the gas will change with time according to the following equation:

$$\delta^{18}O_{CO_2}(t) \simeq \delta^{18}O_{CO_2,\mathrm{equ}} + \left(\delta^{18}O_{CO_2,\mathrm{ini}} - \delta^{18}O_{CO_2,\mathrm{equ}}\right) \times exp(-k_1 . t) \qquad (4)$$

where t is time and k_1 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 $\delta^{18}O$ in our CO_2 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 δ^{18}O 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 δ^{18}O were known (though with a significant associated error in the case of the initial δ^{18}O). 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 1σlevel).

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.

T (C)	kδ18O **(h^{-1})**	kΔ47 **(h^{-1})**	**Shaking**	**Source**
5	0.17	0.22	Yes	This study
25	0.41	0.35	Yes	This study
37	0.64	0.66	Yes	This study
25	0.38	0.34	Yes	Affek (2013)
42	0.62	0.51	Yes	Affek (2013)
22	0.15	0.12	No	Affek (2013)

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 Δ_{47}

The evolution of Δ_{47} 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, Δ_{47} has a complex definition (Eq. (1)) that makes it even less suitable than δ^{18}O 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 Δ_{47}). In particular, the evolution of $^{13}C^{18}O^{16}O$ is responsible for 97% of mass 47 signal, and thus its variations are most important to controlling the Δ_{47} value. Its concentration is controlled by the following equation:

$$^{13}C^{18}O^{16}O\left(t\right)={}^{13}C^{18}O^{16}O(t)_{equ} + \left({}^{13}C^{18}O^{16}O(t)_{ini} - {}^{13}C^{18}O^{16}O(t)_{equ}\right) \times exp(-k_2 . t) \qquad (5)$$

where k_2 is the rate constant for the equilibration of this isotopologue.

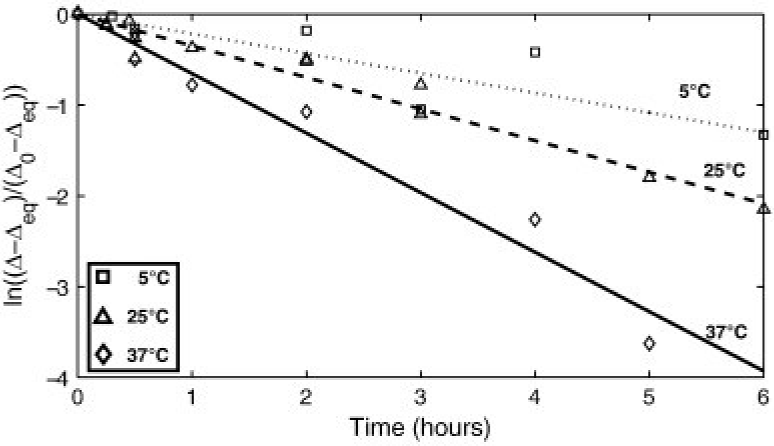

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Fig. 3. Illustration of the early progress of equilibration of the clumped species. Symbols as in 1. In this figure it is assumed that Δ_{47} evolution is governed by a first-order function, see text for details and limits of this approach.

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

(6)Δ47≃103.13C18O16O2.13R.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)Δ47≃10313C18O16Oequ+([13C18O16O]ini−13C18O16Oequ).exp−k2.t2.13R.(18Requ+18Rini−18Requ.exp−k1.t)−1

where k_2 is the rate constant for the evolution of the clumped isotopologue, and k_1 the rate constant for the evolution of bulk δ^{18}O.

Thus the time evolution of Δ_{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 δ^{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 Δ_{47} as we treated that of δ^{18}O, i.e., to use the following expression:

$$\Delta_{47}(t) = \Delta_{47\text{equ}} + \left(\Delta_{47_{\text{ini}}} - \Delta_{47_{\text{equ}}}\right) \times exp(-k_2 . t). \qquad (8)$$

This expression is more straightforward to fit to the experimental results than it was for the analogous expression describing the evolution of δ^{18}O. This is because all experiments began with closely similar initial Δ_{47} values, and all evolved strongly to their final Δ_{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 δ^{18}O and Δ_{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 δ^{18}O and Δ_{47} are indistinguishable within uncertainties, as did Affek (2013).

During our derivation, we assumed that the differences between the starting and the initial δ^{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 Δ_{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 δ^{18}O ranged from 0 to + 10000‰. When the final δ^{18}O is enriched compared to the starting values, a transient positive anomaly in Δ_{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 δ^{18} 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.

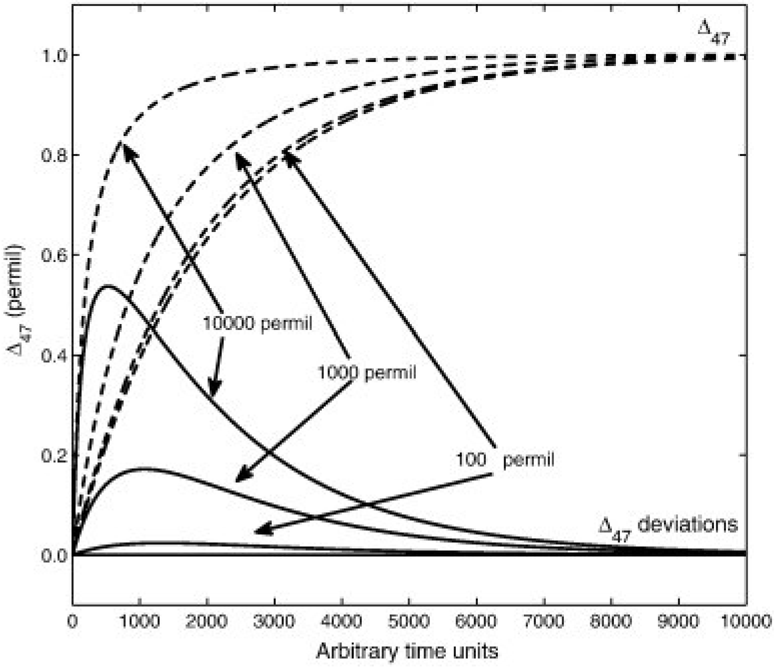

Fig. 4. Comparison of Δ_{47} calculated from Eq. (7) at different contrasts between initial and final bulk δ^{18}O, indicated by the numbers on the figure. Dashed lines: Δ_{47}calculated from Eq. (7), continuous lines: differences between calculations from Eqs. (7), (8). Although we show only curves for large contrasts in δ^{18}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 Δ_{47} must depend on the rate of exchange of ^{18}O and the effect of ^{13}C substitution on the ^{18}O exchange rate. Our data suggest that the rate constants for $^{12}C^{18}O^{16}O$ and $^{13}C^{18}O^{16}O$ 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}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 δ^{18}O and Δ_{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 Δ_{47} is equal to + 1 permil). We assumed, for simplicity, that δ^{13}C was constant, that the water isotopic composition stayed constant with a Δ^{17}O equal to 0 and that very low abundance isotopologues (e.g., $^{12}C^{17}O^{18}O$) 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.

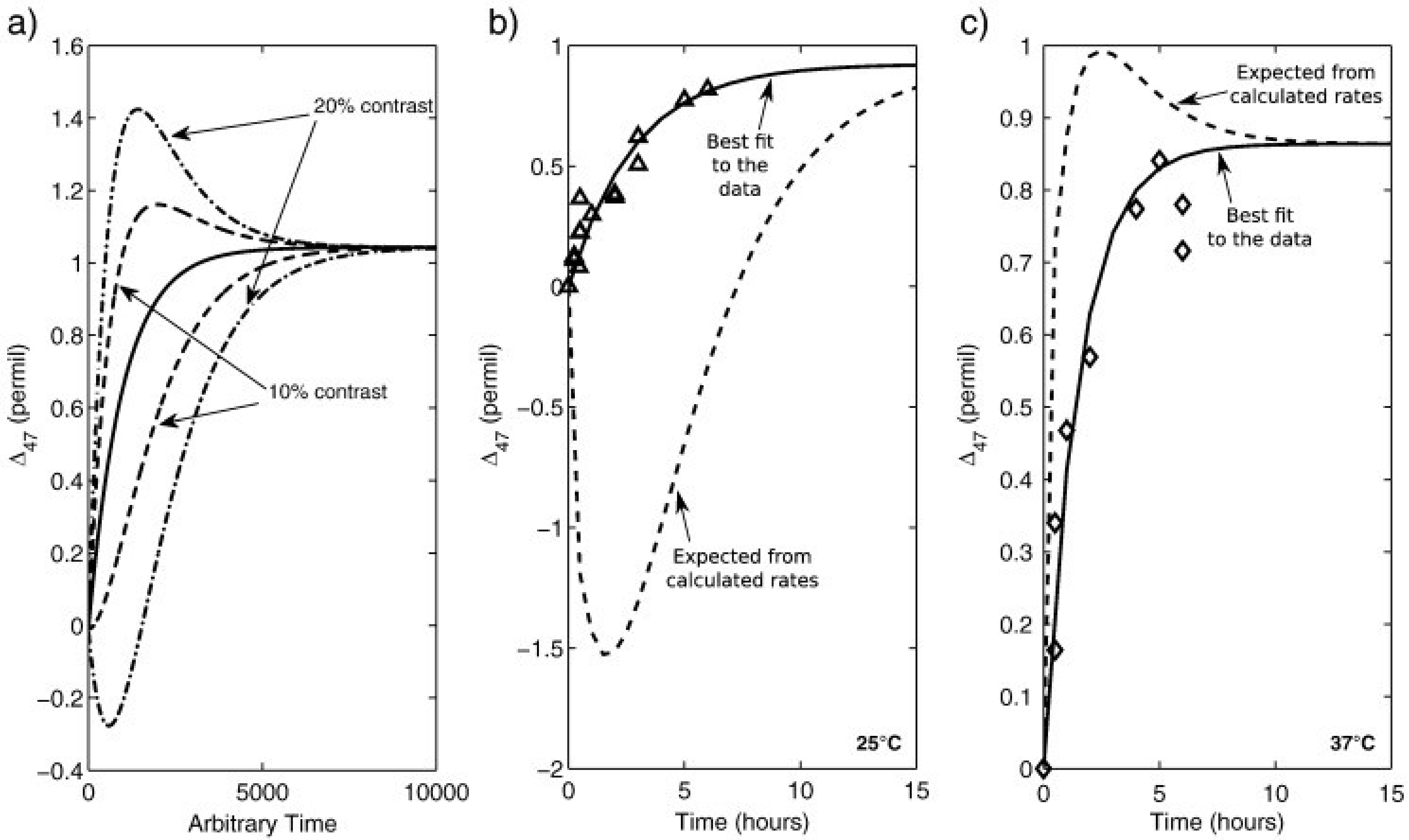

Fig. 5. Modeled results of Δ_{47} evolution with time when the rates for of reactions 3a and 3b are not equal. a) Model with arbitrary time and reaction rates and a 10‰ bulk $\delta^{18}O$ contrast. Continuous line: equal rates, dashed lines: one of the rates is 10% higher than the other, dotted line: 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 (≈ 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, Δ_{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, Δ_{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 Δ_{47}: the Δ_{47} value measures (mostly) the difference between the actual $^{13}C^{18}O^{16}O$ abundance and the abundance of $^{13}C^{18}O^{16}O$ expected for a sample where ^{18}O atoms are randomly distributed between ^{12}C and ^{13}C bearing molecules. Thus, if $^{12}C^{18}O^{16}O$ increases when $^{13}C^{18}O^{16}C$ remains fixed, Δ_{47} must decrease. And, conversely, if $^{13}C^{18}O^{16}C$ rises when $^{12}C^{18}O^{16}O$

remains fixed, Δ_{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 Δ_{47} evolution depend both on the strength of the carbon isotope effect we assume and the amplitude of change in δ^{18}O of CO_2 between its initial and final equilibrium states. When the δ^{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 ^{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 δ^{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 δ^{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 δ^{18}O contrast between initial and final composition varied from 8 to 13‰. As their evolution of Δ_{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:

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

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 δ^{18}O and Δ_{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 δ^{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 Δ_{47} data, which are within 2σ of our results. The similarity of our results with those of Affek

(2013) 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.

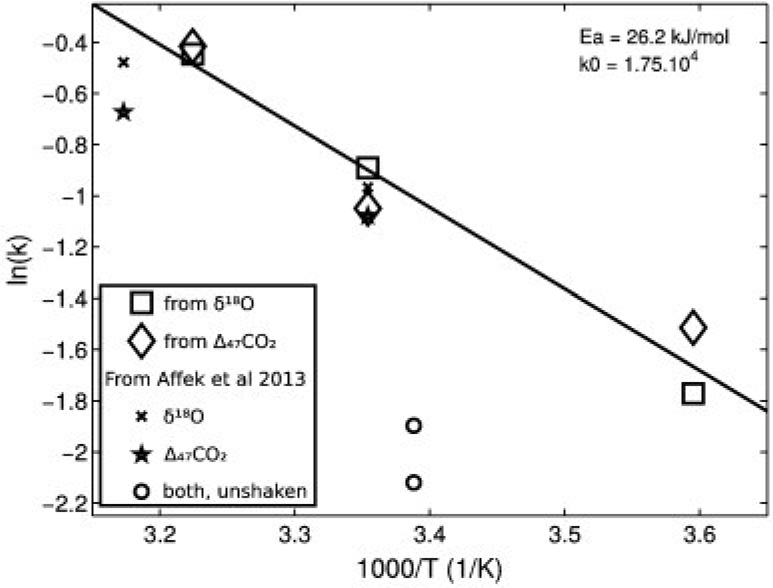

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Fig. 6. Arrhenius plot, showing the rate constants calculated from the experiments from this study (squares, values derived from oxygen isotopes data, diamonds from Δ_{47}measurements), and least-squares fit line through the 6 rate constants calculated. See text for details. Also plotted are rate constants from [2] (small crosses from $\delta^{18}O$ data, stars from Δ_{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, ≈ 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 Δ_{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 Δ_{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, 1994, Zeebe and Wolf-Gladrow, 2001, Lécuyer et al., 2009, Affek, 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_2 budget. Clumped isotope signatures (i.e., Δ_{47} values) of atmospheric CO_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 Δ_{47} value of atmospheric CO_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_2through air) can be used to define the residence time of CO_2 with respect to exchange processes of interest. For example, in models of air–sea exchange, atmospheric CO_2 is assumed to equilibrate with CO_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_2. However, these experiments constrain the exchange between dissolved CO_2 and water, which, according to our data, does not appear to be the rate limiting step in exchange between gaseous CO_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_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_2.

The oxygen isotope composition of CO_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_2 being ≈ 2 years, Farquhar et al., 1993). This time scale is however not relevant, as although the average residence time of CO_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_2 and leaf water (Keeling, 1995, Cuntz et al., 2003).

One could also imagine using the data presented here to interpret values of Δ_{47} and $\delta^{18}O$ for CO_2 in environments other than the atmosphere. For example, Affek and Eiler (2006) showed that the Δ_{47} of CO_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 $CO_2(v)$–$H_2O(l)$ exchange to place limits on the physical conditions of this re-equilibration (surface area of water aerosol, etc.). There are other ‘microenvironments' of this type where similar observations and interpretations could be made, including CO_2emitted 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 CO_2(v)–H_2O(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 CO_2 in the polar stratosphere can have Δ_{47} value up to 1.5‰ (the highest known for a natural material, Yeung et al., 2009). The two leading hypothesis to explain the high Δ_{47} values are either a not yet identified photochemical fractionation of CO_2 in the stratosphere, or temperature-dependent isotopic exchange on polar stratospheric clouds. The measured Δ_{47} are consistent with CO_2 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 $\delta^{18}O$ of stratospheric CO_2 should be in equilibrium with the $\delta^{18}O$ 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 CO_2 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 CO_2 and water (Fortier, 1994, Lécuyer et al., 2009).

Finally, the clumped isotope geochemistry of respired sources of CO_2 (e.g., from soil; in human breath) are little understood but the few observations that are available suggest their Δ_{47} 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 CO_2(v)–H_2O(l) exchange may allow one to use clumped isotope observations to place constraints on the mechanisms of respiration. As is the case with stratospheric CO_2, it would be key for soil respiration to recover the water that exchange with the CO_2 and measure its $\delta^{18}O$, as a disequilibrium in Δ_{47} 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), Δ_{47} value did not reflect the body temperature while the difference in $\delta^{18}O$ between body water and exhaled CO_2 did. This seems contradictory with the results of our experiments, and more work on the isotopic composition of CO_2 in exhaled air is necessary, especially regarding Δ_{47}.

6. Summary and conclusions

We investigated the kinetics of isotopic exchange between liquid water and gaseous carbon dioxide, including $\delta^{18}O$ and mass 47 isotopologues, at 5, 25 and 37 °C. We found that equilibrium between gaseous CO_2 and liquid water was reached after durations of a few hours (for 37 °C series) to tens of hours (for the 5 °C series). $\delta^{18}O$ values at equilibrium were consistent with known fractionation factors for the CO_2-H_2O system. Rate constants were calculated and are equal for the evolution of $\delta^{18}O$ and Δ_{47} 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 ^{18}O exchange between CO_2(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 CO_2 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 $^{13}CO_2$ and $^{12}CO_2$, otherwise the evolution of Δ_{47}during exchange would exhibit peculiar rises or dips that violate first-order kinetics and differ from the evolution in $\delta^{18}O$.

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