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Carbon isotope fractionation during gas-water exchange and dissolution of CO_2

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Abstract—The kinetic and equilibrium fractionation effects for ^{13}C during CO_2 gas transfer (ϵ_k and ϵ_{aq-g}) have been measured in acidified distilled water. The equilibrium fractionation effects between bicarbonate and carbonate and gaseous CO_2 (ϵ_{HCO_3-g} and ϵ_{CO_3-g}) have been measured in $NaHCO_3$ and $NaHCO_3$ + Na_2CO_3 solutions, respectively, from 5° to 25°C. The measured fractionations, except ϵ_{CO_3-g}, agreed with earlier work to within 0.2‰. ϵ_{CO_3-g} was about 2‰ smaller than most values previously reported. The temperature dependence of the fractionation for ^{13}C between bicarbonate and carbonate and gaseous CO_2 was found to be $\epsilon_{HCO_3-g} = -(0.141 \pm 0.003)T(°C) + (10.78 \pm 0.05)‰$ and $\epsilon_{CO_3-g} = -(0.052 \pm 0.03)T(°C) + (7.22 \pm 0.46)‰$, respectively. The fractionation during gas dissolution was $\epsilon_{aq-g} = -(0.0049 \pm 0.003)T(°C) - (1.31 \pm 0.06)‰$ and the kinetic effect during gas transfer, ϵ_k, was $-0.81 \pm 0.16‰$ at 21°C and $-0.95 \pm 0.20‰$ at 5°C.

The equilibrium fractionation between total DIC in seawater and CO_2 in air (ϵ_{DIC-g}) was measured and compared with that calculated from the concentration of aqueous CO_2, HCO_3^-, and $CO_3^=$ and individual fractionations between the three C species and CO_2 gas. The measured and calculated results showed a significant difference of up to 0.2‰. We hypothesize that carbonate ion complexes likely complicate the calculation of ϵ_{DIC-g} from individual C species. We obtain the following empirical function of ϵ_{DIC-g} in seawater vs. temperature and the carbonate fraction (f_{CO_3}), $\epsilon_{DIC-g} = (0.014 \pm 0.01)Tf_{CO_3} - (0.105 \pm 0.002)T + (10.53 \pm 0.05)‰$, when $0.05 < f_{CO_3} < 0.20$ and $5°C < T < 25°C$.

INTRODUCTION

Stable isotopic composition of C has been widely used as a tracer of C flow between natural reservoirs. Since the ocean is a major sink for anthropogenically produced CO_2, $\delta^{13}C$ has been incorporated into ocean-atmosphere coupling models to study the oceanic uptake of anthropogenic CO_2 (Siegenthaler and Münnich, 1981; Keeling et al., 1989). Because of the addition of ^{13}C depleted CO_2 ($\sim -27‰$ vs. PDB) released from fossil fuel combustion, the $\delta^{13}C$ of atmospheric CO_2 has decreased from pre-industrial level of $-6.4‰$ to $-7.6‰$ in 1980 (Friedli et al., 1986). The $\delta^{13}C$ of the ocean C has been affected by this anthropogenic CO_2 perturbation as indicated by the 0.4‰ decrease during the last 20 years in $\delta^{13}C$ of mixed layer dissolved inorganic C in the Pacific ocean (Quay et al., 1992).

Gas exchange of $^{12}CO_2$ and $^{13}CO_2$ can be described by the following general flux equations,

for CO_2:

$$d[CO_2(aq)]/dt = -k\gamma(P^s - P^a), \quad (1)$$

for $^{13}CO_2$:

$$d[^{13}CO_2(aq)]/dt = -k^{13}\gamma^{13}(P^sR_g^s - P^aR_g^a), \quad (2)$$

where aq represents aqueous CO_2 concentration, t is time, k is the air-water exchange coefficient (also referred to as transfer velocity or piston velocity), γ is the CO_2 solubility, P denotes the partial pressure of CO_2, and R the $^{13}C/^{12}C$ ratio, where ^{12}C is assumed to be equal to total C since ^{12}C composes of 98.9% of total C. The superscripts a and s refer to the air and solution, respectively, and the subscript g represents gas. The $^{13}C/^{12}C$ ratio of CO_2 dissolved in seawater can not be directly measured. Instead, the $^{13}C/^{12}C$ ratio of total

dissolved inorganic C (DIC = CO_2(aq) + HCO_3^- + $CO_3^=$) is measured. To make the gas transfer of $^{13}CO_2$ comparable to $^{12}CO_2$, we define the kinetic fractionation factor (α_k) as the ratio of the $^{13}CO_2$ and CO_2 gas transfer rates, i.e.,

$$\alpha_k = k^{13}/k \quad (3)$$

and equilibrium solubility ratio of $^{13}CO_2$ and $^{12}CO_2$ as

$$\alpha_{aq-g} = \gamma^{13}/\gamma. \quad (4)$$

At equilibrium,

$$\alpha_{aq-g} = R_{aq}/R_g. \quad (5)$$

Equation 2 can be rewritten as

$d[^{13}CO_2(aq)]/dt$

$$= -k\alpha_k\alpha_{aq-g}\gamma(P^sR_{DIC}/\alpha_{DIC-g} - P^aR_g^a), \quad (6)$$

where $\alpha_{DIC-g} = R_{DIC}/R_g$. We assume that the C system in the water is in chemical and isotopic equilibrium since the rate of CO_2 hydration and reaction with carbonate ion is on the order of 20–200 seconds (Johnson, 1982; Usdowski, 1982), much faster than the CO_2 diffusive transfer across the interface which is on the order of at least hours for the experimental conditions reported here.

The equilibrium fractionation factor between DIC and gaseous CO_2, α_{DIC-g}, depends on the carbon speciation of the solution, i.e., the proportion of the CO_2(aq), HCO_3^-, and $CO_3^=$, and the individual fractionation factor of each species with respect to gaseous CO_2 ($\alpha_{i-g} = R_i/R_g$). Therefore,

$$\epsilon_{DIC-g} = \sum f_i\epsilon_{i-g}, \quad (7)$$

where f is the proportion of each species (i) and ϵ is the permil fractionation which is

$$\epsilon = (\alpha - 1)*1000. \qquad (8)$$

The proportion of $CO_2(aq)$, HCO_3^-, and CO_3^- are usually obtained from the measured pH and DIC concentration of the solution.

The kinetic isotope fractionation during CO_2 gas exchange (ϵ_k) in seawater has been measured in the laboratory to be ca. -1 to [as $-1\sim$] $-$ 4‰, but with a large uncertainty of 2–5‰, by Wanninkhof (1985) and Inoue and Sugimura (1985). The equilibrium fractionations, ϵ_{i-g}, are known from the earlier work of many researchers. ϵ_{aq-g} was measured as $-1.09‰$ at 25°C by Vogel et al. (1970). Previous determinations of ϵ_{HCO_3-g} ranged between 10.3‰ and 6.7‰ over 5° to 40°C, but with significant discrepancies of about 0.2 $\sim$ 0.3‰ at 25°C between different groups (Deuser and Degens, 1967; Wendt, 1968; Emrich et al., 1970; Mook et al., 1974; Lesniak and Sakai, 1989). Notably, the fractionation between carbonate ion and gaseous CO_2, ϵ_{CO_3-g}, has not been established accurately because of the difficulties in extracting a sufficient amount of CO_2 in the presence of CO_3^-. For example, individual measurements of ϵ_{CO_3-g} ranged from 6.5‰ (Turner, 1982) to 8.3‰ (Lesniak and Sakai, 1989) at 25°C. Since all previous equilibrium fractionation factors were measured in sodium bicarbonate solutions, the applicability of these factors to seawater needs to be tested.

Model predictions of the gas transfer of $^{13}CO_2$ are very sensitive to the equilibrium fractionation between DIC and gaseous CO_2. For example, Tans et al. (1993) found that oceanic CO_2 uptake rates showed an uncertainty of ± 1 Gigaton/yr per 0.2‰ uncertainty in the air-sea ^{13}C fractionation. This sensitivity results because of the small ($<1‰$) disequilibrium fractionation of ^{13}C between the atmospheric CO_2 and surface DIC. Results of Tans et al. (1993) underscore the need to accurately determine, i.e., to better than $\pm 0.1‰$, the isotopic fractionation effects during CO_2 gas transfer. In this work, we have redetermined all four fractionations during CO_2 gas transfer and dissolution in freshwater and directly measured the ϵ_{DIC-g} in seawater.

METHODS

All the experiments were conducted in closed-systems of pure CO_2 gas or air over a solution of distilled water or seawater.

Kinetic Experiments

The system for kinetic experiments is similar to that used for measurements of kinetic isotopic fractionations of O_2 and N_2 by Knox et al. (1992). It consists of a 4-L flask which was open to the atmosphere through a water manometer and an attached sampling port (Fig. 1a). The 4-L flask was prefilled with degassed, acidified distilled water which was made by adding 1 mL 50% H_3PO_4 per liter (pH $\sim$ 2) and boiling for half an hour. An amount of pure CO_2 gas was then admitted into the flask and the exact volume of this input was determined by the amount of water displaced into the manometer (Fig. 1a). The pressure of the headspace during the experiment was kept constant at atmospheric pressure by the inflow of degassed water as CO_2 gas dissolved. The water volume change was recorded about every 10 minutes and $\delta^{13}C$ of the gaseous CO_2 was measured every hour by taking ~ 1 cc of CO_2 from the headspace through the sampling port which was connected to a vacuum extraction line. The sample was purified and collected by pumping through two dry ice-isopropanol slush traps and two liquid nitrogen traps. The amount of CO_2 collected was determined by measuring the pressure (Baratron Model #222BA, MKS Instruments Inc.) of the CO_2 gas expanded
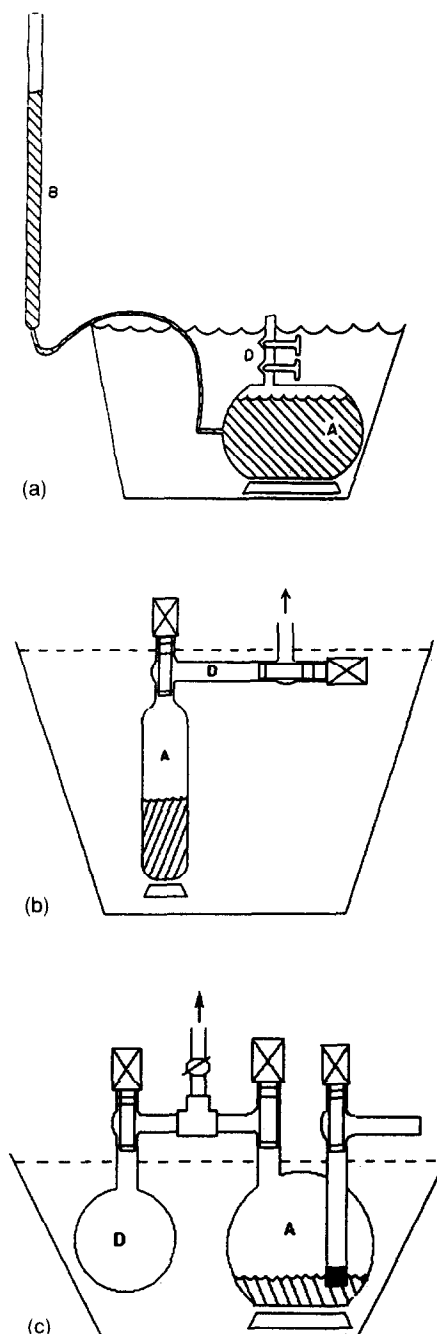

FIG. 1. Schematic representation of the experimental systems. (a) The kinetic system. Gas transfer takes place in the 4-L flask (A) which is open to the atmosphere via a water manometer (B). Sampling is done through the expansion port (D). (b) The equilibrium system for fresh water experiments. The 200 mL flask for equilibrium (A). Gas samples are taken from the expansion arm (D), which is about $^1/_{10}$ of the total headspace. (c) The equilibrium system for sea water experiments. In the 1000 mL equilibrium flask (A) clean air with ~ 350 ppm CO_2 is in contact with ~ 200 mL sea water sample. The finger extended to the bottom of the flask with fritted end is used for stripping. The expansion volume D is ~ 500 mL. Water phase represented by hatching. (See text for details).

into a known volume of the extraction line. The efficiency of the extraction was 100 $\pm$ 0.5% based on Na_2CO_3 standards. The overall precision on measured volumes of extracted CO_2 was better than 1%. $\delta^{13}C$ of CO_2, measured on a Finnigan 251 mass spectrometer, is

reported relative to PDB, based on working standards calibrated against NBS-19. The overall precision of $\delta^{13}C$ of CO₂ from headspace, including 0.02‰ for the mass spectrometer, was 0.03‰. Three kinetic experiments have been done, two at 21°C and one at 5°C.

Equilibrium Experiments in Fresh Water

Equilibrium fractionations between each C species and CO₂ gas were measured in a closed-system (Fig. 1b) consisting of a 200 mL flask with a side arm of about 10 mL attached through two o-ring stopcocks (Louwers Hapert Right-Angle O-Ring Stopcock). The arm can be connected to the extraction line as in the kinetic experiment.

Three separate experiments were performed in freshwater. In the first experiment, pure CO₂ was allowed to equilibrate with degassed, acidified distilled water. The bottle was evacuated first and then CO₂ gas was frozen in. The water was degassed as in the kinetic experiments and drawn into the bottle through a siphon while boiling. In the second and third experiments, a NaHCO₃ (~0.5 M) and NaHCO₃ + Na₂CO₃ (~0.5 M) solution, respectively, was equilibrated with pure CO₂ gas. Solid NaHCO₃ or NaHCO₃ + Na₂CO₃ was admitted through a weighing paper tube into the bottom of the bottle before it was evacuated. The $\delta^{13}C$ of the pure CO₂ gas (-36.45 ± 0.02‰) and the solid NaHCO₃ (-22.04 ± 0.03‰) and Na₂CO₃ (-1.84 ± 0.04‰) was measured previously. In all three experiments, the total amount of C input was determined to ±0.2%. Four or five flasks were equilibrated simultaneously at each temperature, using a water bath, for 7–10 days. The minimum time to reach equilibrium was determined, in the stirred flasks, by sampling one of the bottles at 4, 6, and 10 days; there was no significant difference in the $\delta^{13}C$ values (i.e., all were less than 0.05‰) for the three aliquots. After equilibrium was established, an aliquot of CO₂ in the headspace was removed and measured for $\delta^{13}C$. The partial pressure of CO₂ in the headspace was obtained by knowing the amount of CO₂ collected from the side arm and the volume ratio of the arm to the main part of the flask. Then the system was closed and readied for the next equilibrium experiment at another temperature. No detectable leaks occurred, as would have been indicated by a pressure of noncondensable gas, during any of the equilibrium experiments.

At the end of the final run in the second and third experiments, the concentration and $\delta^{13}C$ of total DIC and the total alkalinity (ALK) of the solution in each flask were measured. A 2 mL aliquot of the solution was extracted and weighed using a syringe. This aliquot was injected into a 15 mL pre-evacuated flask, with 2 mL 50% H₃PO₄, connected to the extraction line to collect CO₂. A separate 20 mL aliquot of the solution was diluted and measured for the total alkalinity by Gran titration (Stumm and Morgan, 1981).

The C distribution between the gas phase and the solution was determined from measured partial pressure of CO₂ and the total C added to the flask by using CO₂ equilibrium dissociation equations. Solubility of CO₂ gas from Weiss (1974), dissociation constants of carbonic acid from Harned and Davis (1943) and Harned and Scholes (1941) and activity coefficients of bicarbonate and carbonate from Walker et al. (1927) were used. The bicarbonate species composed 97% of total DIC in the 0.5 M NaHCO₃ solution, whereas the carbonate proportion was 18% of total DIC in the 0.5 M NaHCO₃ + Na₂CO₃ solution. We calculated, using Eqn. 7, the isotope fractionations between CO₂ gas and CO₂(aq), HCO₃⁻, and CO₃²⁻ from the results of the three independent experiments that used acidified degassed distilled water, a NaHCO₃ solution and a NaHCO₃ + Na₂CO₃ solution, respectively.

Equilibrium Experiments in Seawater

A 1000 mL flat-bottom flask with two o-ring stopcocks was used (Fig. 1c). A finger extending to the bottom of the flask with a fritted glass termination was used for bubbling. The flask was prepurged with clean air having pCO_2 of ~350 ppm and $\delta^{13}C$ ~ -8.7‰. Then about 200 mL seawater, collected from the North Pacific during spring 1991, was admitted into the flask through a glass tube by exerting higher than atmospheric pressure on the seawater with air described above. pH was adjusted by using NaOH or HCl when necessary. Two flasks containing seawater were simultaneously sub-

merged in a circulation water bath to equilibrate for 1 week while stirring. After equilibration, the headspace gas was expanded into a 500 mL flask connected through a Ultra-Torr® fitting and then isolated (Fig. 1c). CO₂ gas in the expanded volume was purified from air and water vapor and collected for $\delta^{13}C$ measurement. The flask containing the seawater was connected to the extraction line, acidified and stripped of gas using He flow for half an hour; CO₂ was collected for total C and $\delta^{13}C$ measurements. The $\delta^{13}C$ of the DIC in seawater was obtained by correcting for the CO₂ remaining in the headspace. pH and C speciation were calculated from CO₂ partial pressure in the headspace and the total DIC concentration of the solution using the dissociation constants of seawater given by Goyet and Poisson (1989).

We have done several tests to see if there was any carbon isotopic fractionation effect during the expansion of the gas from the 1000 mL flask to the 500 mL flask. We conclude there was none since results showed that the $\delta^{13}C$ difference for CO₂ in the two flasks after expansion was less than 0.02‰.

RESULTS AND DISCUSSION

The isotopic fractionation between C species and CO₂ gas is a function of temperature (Vogel et al., 1970; Mook et al., 1974). It can be approximated as a linear function of T (°C) within the range of ocean temperature (-2°C to 30°C) to within ±0.03‰. All the results of this work have been presented using Celsius temperature.

Equilibrium Fractionation during CO₂ Gas Dissolution (ϵ_{aq-g})

In an acidified solution (pH ~ 2), the measured fractionation between total DIC and gaseous CO₂ at equilibrium directly represents the fractionation between aqueous and gaseous CO₂ (ϵ_{aq-g}). Mean values for ϵ_{aq-g} were measured to be -1.29‰ to -1.19‰ from 5°C to 25°C, respectively, (Fig. 2) with a standard deviation of ±0.05‰ based on five simultaneous runs at each temperature. The temperature dependence of ϵ_{aq-g} is clear, despite the uncertainties of ϵ_{aq-g} at each temperature, with a slope of 0.01‰/°C. Compared to the Vogel et al. (1970) data, our results of ϵ_{aq-g} are about 0.1‰ more negative but with a similar slope. The discrepancy is unlikely
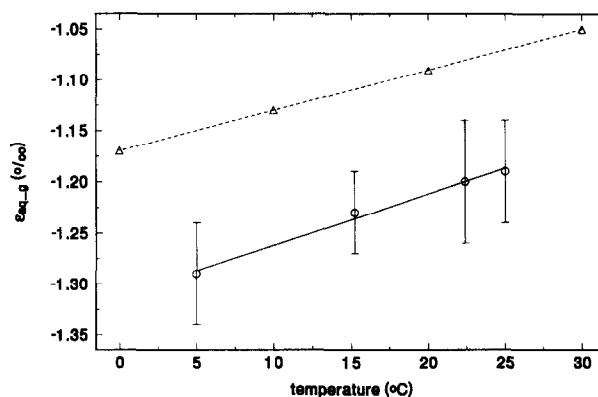

FIG. 2. The ^{13}C equilibrium fractionation between dissolved and gaseous CO₂ (ϵ_{aq-g}) measured using acidified distilled water equilibrated with pure CO₂ from 5° to 25°C. The open circles are the average values of five bottles at each temperature. The solid line is the linear regression of the average values, $\epsilon_{aq-g} = (0.0049 ± 0.0015)T(°C) - (1.31 ± 0.05)‰$. The dashed line and the open triangles are the results reported by Vogel et al. (1970).

to be an interlaboratory offset, since ϵ_{aq-g} depends on relative $\delta^{13}C$ measurements, and more likely is caused by a difference between the two experimental methods.

Kinetic Fractionation during CO_2 Gas Transfer (ϵ_k)

Combining Eqns. 1 and 6, we obtained

$$d[CO_2(aq)R_{aq}]/d[CO_2(aq)]$$

$$= \alpha_k \alpha_{aq-g}(P^s R_{aq}/\alpha_{aq-g} - P^a R_g^a)/(P^s - P^a). \quad (9)$$

For the calculation convenience, we used the volume change of the CO_2 in the headspace (V) to determine the time rate of aqueous CO_2 change and defined the saturation degree of CO_2 as the ratio of $CO_2(aq)$ concentration to the saturated value under atmospheric pressure, i.e., $S = P^s/P^a$. Equation 9 is rewritten to get the kinetic fraction factor as

$$\alpha_k = [\Delta(VR_g)/\Delta V][(S - 1)/(SR_{aq} - R_g \alpha_{aq-g})], \quad (10)$$

where V and R_g were directly measured. Values for S and R_{aq} were obtained, from V and $\delta^{13}C_g$ measurements, based on the C balance in a closed-system. The saturation degree as a function of time and $\delta^{13}C_g$ vs. saturation level are shown in Fig. 3a and 3b, respectively. Due to the high solubility of CO_2, the saturation degree only reached about 50% before the CO_2 headspace disappeared. Values for ϵ_k were directly calculated for each interval between measurements of $\delta^{13}C_g$ based on Eqns. 8 and 10. The calculated values of ϵ_k depended on the value of ϵ_{aq-g} but were independent of the absolute gas exchange rate.

The overall range in ϵ_k values was from -0.3 to $-1.5\%o$, excluding one data point, as discussed below using ϵ_{aq-g} of this work (Fig. 3c). The total error in the ϵ_k calculation depends on the errors in measurements of the volume change and $\delta^{13}C$ of CO_2 extracted from the headspace. The error was largest, up to $0.7\%o$, at the beginning of the experiment when CO_2 gas started to dissolve and at the end when the headspace of CO_2 almost disappeared. The large difference of total amount of CO_2 between the headspace and solution resulted in large uncertainty on the calculation of $\delta^{13}C_{aq}$ in these two extreme situations. The error for the rest of the ϵ_k values was no greater than $\pm 0.2\%o$. The mean ϵ_k values (± 1 SD), excluding the first and last points for each experiment, were $-0.81 \pm 0.16\%o$ at $21°C$ and $-0.95 \pm 0.20\%o$ at $5°C$. The mean ϵ_k values were $-0.99 \pm 0.16\%o$ and $-1.11 \pm 0.20\%o$ at $21°C$ and $5°C$, respectively, if ϵ_{aq-g} values from Vogel et al. (1970) were used. A significant temperature dependence for ϵ_k was not detected within the measurement uncertainty. Siegenthaler and Münnich (1981) reported a value of $-0.5\%o$ for ϵ_k from a theoretical calculation of the ratio of $^{13}CO_2$ and $^{12}CO_2$ gas transfer rates based on the measured molecular diffusion rates of these species. Their ϵ_k calculation depends on the choice of the gas exchange model relating gas transfer rates to diffusion rates, i.e., they assumed a square root dependence. Due to the uncertainties caused by this choice and the unknown isotope fractionation effect of up to $-0.5\%o$ during CO_2 hydration (Siegenthaler and Münnich, 1981), the range of a theoretical ϵ_k value is estimated to be from -0.5 to $-1.4\%o$, which is confirmed by our results of $-0.81 \pm 0.2\%o$ at $21°C$ and $-0.95 \pm 0.2\%o$ at $5°C$.

(a)

(b)

(c)
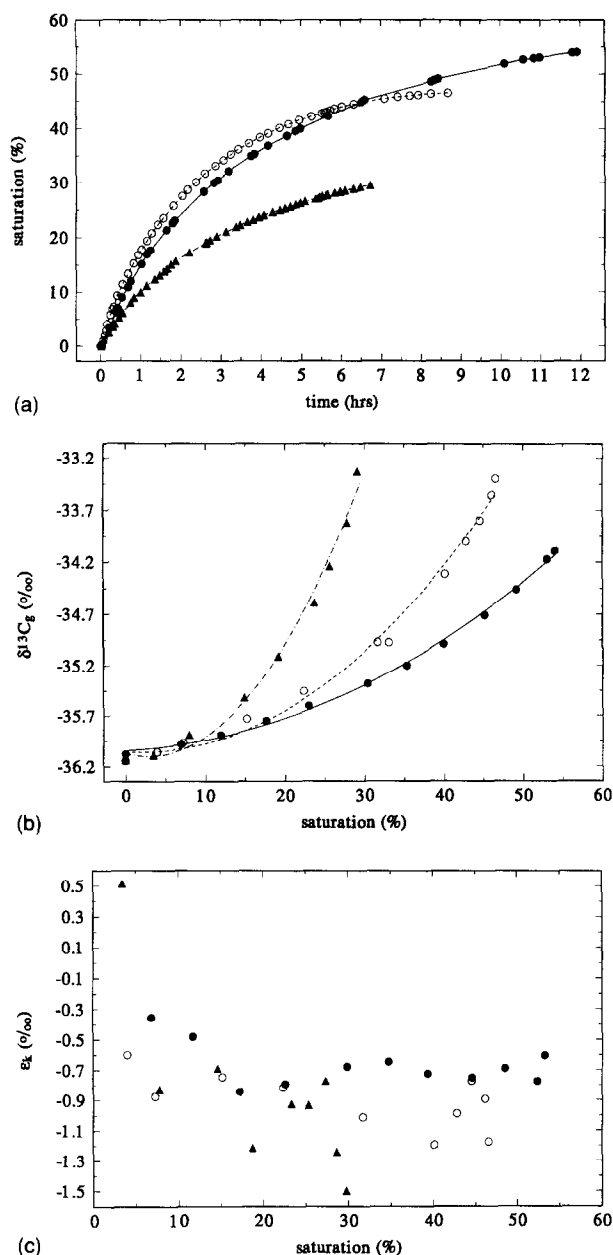
FIG. 3. The kinetic fractionation for ^{13}C during CO_2 gas transfer between pure CO_2 and distilled water (ϵ_k). Filled circles are data for experiment #1 and open circles for #2 both at $21°C$ and filled triangles at $5°C$. (a) The saturation degree of dissolved CO_2 in the solution vs. time. (b) The $\delta^{13}C$ (vs. PDB) of the gaseous CO_2 in the headspace vs. saturation degree. The lines are a polynomial fit of the data. (c) The ϵ_k vs. CO_2 saturation degree in the solution, calculated, based on Eqn. 8 and 10, using ϵ_{aq-g} of this work. The average value is $-0.81 \pm 0.16\%o$ at $21°C$ and $-0.95 \pm 0.20\%o$ at $5°C$, excluding the first and last points for each experiment (see text).

The total fractionation during CO_2 invasion, i.e., ϵ_{as} $= (\alpha_k \alpha_{aq-g} - 1)*1000$, was calculated to be $-2.02\%o$ to $-2.23\%o$ and $-2.08\%o$ to $-2.26\%o$ from $21°C$ to $5°C$ with ϵ_{aq-g} values from this work and Vogel et al. (1970), respectively (Table 1). The choice of ϵ_{aq-g} has less influence on results of ϵ_{as} than ϵ_k. In order to compare our results to those made in seawater, the above ϵ_{as} values should be corrected by $-0.2\%o$ to account for the fractionation during the reaction of CO_2

Table 1 Kinetic and equilibrium fractionations for ^{13}C during CO_2 gas exchange process.

Exp#	T(°C)	ε_{aq_g}(‰)	ε_k(‰)[b]	ε_{as}(‰)
1	21	-1.09[a]	-0.89±0.11	-1.98±0.13[b]
2	21	-1.09[a]	-1.08±0.15	-2.18±0.16[b]
3	5	-1.16[a]	-1.11±0.20	-2.26±0.21[b]
1	21	-1.21[b]	-0.71±0.10	-1.92±0.13[b]
2	21	-1.21[b]	-0.91±0.14	-2.12±0.15[b]
3	5	-1.28[b]	-0.95±0.20	-2.23±0.21[b]
	15			-2.0±3.0[c]
	23			-4.0±5.0[c]
	30			-5.0±7.0[c]
	3.5-20			-2.4±2.0[d]

ε_{aq_g}: the equilibrium fractionation factor between aqueous and gaseous CO_2.
ε_k: the kinetic fractionation factor during gas exchange calculated from the experiment data and ε_{aq_g}.
ε_{as}: the total fractionation during CO_2 invasion, obtained from $\varepsilon_{as} = (\alpha_k \alpha_{aq\_g} -1)*1000$.
[a]Vogel et al. (1970)
[b]This work
[c]Inoue and Sugimura (1985) in seawater
[d]Wanninkhof (1985) in seawater

with hydroxide (Siegenthaler and Münnich, 1981). Our ε_{as} values are well within the range of $-2.4 \pm 2‰$ and $-3 \pm 4‰$ measured in seawater by Wanninkhof (1985) and Inoue and Sugimura (1985), respectively, and the uncertainty has been reduced by a factor of 10.

Equilibrium Fractionation between HCO_3^- and CO_2 Gas (ε_{HCO_3-g})

The equilibrium fractionation between HCO_3^- and CO_2 gas (ε_{HCO_3-g}) varied from 7.9‰ to 10.2‰ over the temperature range of 25°C to 5°C, respectively (Fig. 4). Linear regression of the mean values for ε_{HCO_3-g} at each temperature yields:
$\varepsilon_{HCO_3-g} = -(0.1141 \pm 0.0028)T(°C) + (10.78 \pm 0.04)‰$.
The four simultaneous measurements made at each temperature yield a consistent precision of $\pm 0.04‰$ (Fig. 4). Our values of ε_{HCO_3-g} are very close to those measured by Mook et al. (1974) with the same slope of temperature dependence, but about 0.05‰ lower. If the results of ε_{HCO_3-g} measured in this work were used, as discussed below, instead of those from Thode et al. (1965) which are 2 ~ 3‰ higher, the Mook et al.'s (1974) calculated values for ε_{HCO_3-g} would decrease by 0.03‰ and agree with our values within the experimental uncertainty of $\pm 0.04‰$. In contrast to our results and those from Mook et al. (1974), ε_{CO_3-g} values determined by Lesniak and Sakai (1989) using an open flask experimental procedure were higher by about 0.4‰.

Equilibrium Fractionation between $CO_3^=$ and CO_2 Gas (ε_{CO_3-g})

The fractionation between $CO_3^=$ and CO_2 gas (ε_{CO_3-g}) ranged from 6.0‰ to 7.0‰ at 25° to 5°C, respectively (Fig. 5). The temperature dependent function of $\varepsilon_{CO_3\_g}$ is ε_{CO_3-g} $= -(0.052 \pm 0.021)T(°C) + (7.22 \pm 0.38)‰$. The average standard deviation of ε_{CO_3-g} based on five simultaneous measurements at each temperature was $\pm 0.4‰$, which is consistent with the uncertainty ($\pm 0.04‰$) of the ε_{HCO_3-g} calculation and the 4:1 ratio of HCO_3^- to $CO_3^=$ in solution. The 2 to 3‰ offset of ε_{CO_3-g} from the theoretical values given by Thode et al. (1965), however, is significant at all temperatures. ε_{CO_3-g} reported by Turner (1982) falls within the uncertainty of our results. Lesniak and Sakai (1989) reported values that are 2.3‰ higher than ours at 25°C (Fig. 5).
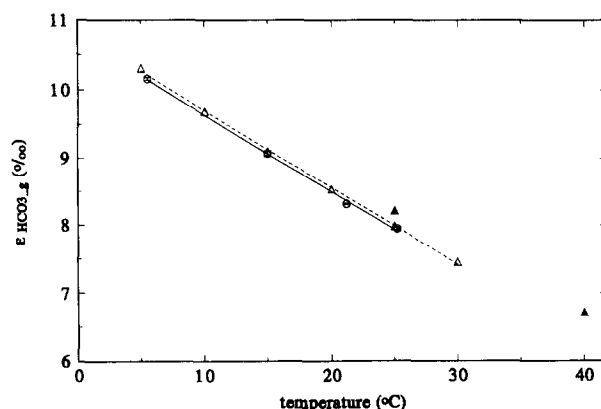

Fig. 4. The ^{13}C fractionation between HCO_3^- and gaseous CO_2 (ε_{HCO_3-g}) measured using a $NaHCO_3$ solution equilibrated with pure CO_2 gas from 5°C to 25°C. The open circles are the average values of four bottles equilibrated at each temperature. The error bars, average $\pm 0.04‰$, are within the size of the symbols. The linear regression of the average values gives (solid line): $\varepsilon_{HCO_3-g} = -(0.114 \pm 0.003)T(°C) + (10.78 \pm 0.04)‰$, which is an average of 0.05‰ lower than Mook et al.'s (1974) (open triangles and dashed line) values. The filled triangles are from Lesniak and Sakai (1989).

The DIC concentration, total alkalinity, and the $\delta^{13}C$ of the solution measured at the end of the experiments agreed well with the values calculated from the total C and CO_2 headspace pressure measurements (Table 2). The average ratio of the measured value to the expected value from initial input was 99.5 $\pm$ 0.7% for DIC and 100.0 $\pm$ 0.7% for alkalinity. The average difference between the measured and calculated $\delta^{13}C$ of the solution is 0.00 $\pm$ 0.06‰. This indicates that the mass balance for C we used in the calculations is valid within the measurement error range.

The difference between our ε_{CO_2-g} results and previously published values is significant. In average seawater aqueous CO_2 is <1%, HCO_3 is 87-93%, and carbonate is 7-13% of
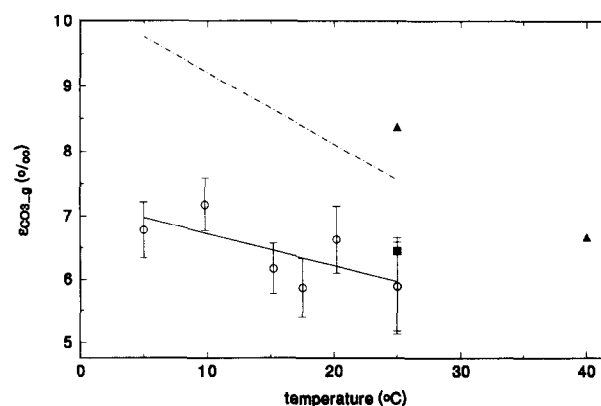

Fig. 5. The ^{13}C fractionation between $CO_3^=$ and gaseous CO_2 (ε_{CO_3-g}) measured using a $NaHCO_3 + Na_2CO_3$ solution equilibrated with pure CO_2 gas from 5°C to 25°C. The open circles are the average values of five bottles equilibrated at each temperature. The errors range from 0.3-0.5‰ based on five measurements at each temperature. A regression yields (solid line) $\varepsilon_{CO_3-g} = -(0.052 \pm 0.021)T(°C) + (7.22 \pm 0.38)‰$ which is about 1.5 to 2.8‰ lower than the Thode et al. (1965) theoretical results (dashed line). The filled triangles are from Lesniak and Sakai (1989) and the solid square from Turner (1982).

Table 2 Comparison of the carbon system and $\delta^{13}C$ parameters measured at the end of the ε_{CO3_g} experiment at 25°C and the expected values calculated from a CO_2 mass balance.

Bot#	¹ALK (%)	¹DIC (%)	²ΔpH	$\delta^{13}C_{DIC}$cm (‰)	$\delta^{13}C_{DIC}$c (‰)	²Δ$\delta^{13}C$ (‰)
1	99.32	99.82	0.00	-19.59	-19.59	-0.00
2	99.38	99.05	0.02	-19.50	-19.41	0.09
3	100.72	100.36	0.02	-19.69	-19.75	-0.06
4	100.52	98.68	0.04	-20.34	-20.29	0.05
5	99.88	100.47	0.04	-18.20	-18.29	-0.08
AVG	99.96	99.68	0.03			0.00
SD	0.58	0.71	0.02			0.07

1. ALK and DIC represent the ratios of the measured alkalinity and total DIC concentration values to the expected values calculated at equilibrium from the initial inputs of pure CO_2, solid $NaHCO_3$ and Na_2CO_3 (see text).
2. Δ refers to the difference of measured value minus the expected value.
m and *c* represent measured and calculated values respectively.

total DIC (5°–30°C). The fractionation between DIC of seawater and CO_2 gas would be about 0.2–0.3‰ less than the value previously assumed (Mook, 1986; Keeling et al., 1989; Siegenthaler and Münnich, 1981; Tans et al., 1993) if the ε_{HCO_3-g} and ε_{CO_3-g} values we measured in freshwater are applicable to seawater. In contrast, our remeasurements of ε_{aq-g} and ε_{HCO_3-g}, when compared to previous measurements, yield a decrease in ε_{DIC-g} of only 0.05‰. We will see below, however, that extrapolation to seawater of ε_{CO_3-g} measurements made in a Na_2CO_3 solution likely is not justified.

Direct Measurements of Fractionation between Seawater DIC and CO_2 in Air

ε_{DIC-g} has been measured directly in seawater samples at different temperatures and pH (Table 3). The measured ε_{DIC-g} was ~0.2‰ higher at 23°C than the value calculated from the C speciation in seawater and ε_{i-g} values determined in this work (Fig. 6), and within 0.07‰ of this value at 5°C. In contrast, the measured ε_{DIC-g} was within 0.06‰ of the value calculated using ε_{i-g} values from Vogel et al. (1970), Mook et al. (1974), and Thode et al. (1965) at 23°C and lower by ~0.2‰ at 5°C. The slope of the measured ε_{DIC-g} vs. temper-

Table 3 The measured equilibrium fractionations between DIC in seawater and CO_2 in air (ε_{DIC_g}).

a. ε_{DIC_g} (‰) measured over a range in pH at t=23.0±0.2(°C).

EXP#	pH¹	%CO₂	%HCO₃	%CO₃	²ε_{DIC_g}	³ε_{DIC_g}c	⁴ε_{DIC_g}c
19	8.33	0.28	81.02	18.70	8.17	7.77	8.12
19	8.30	0.31	81.96	17.73	8.09	7.79	8.12
18	8.11	0.50	87.15	12.35	8.09	7.84	8.08
17	8.11	0.51	87.25	12.24	8.04	7.86	8.10
18	7.99	0.67	89.55	9.78	8.13	7.88	8.07
20	7.72	1.33	93.34	5.33	8.03	7.94	8.06
20	7.69	1.40	93.53	5.07	8.08	7.94	8.05

b. ε_{DIC_g} (‰) measured over a range of temperatures at pH=8.15±0.1

EXP#	t(°C)	%CO₂	%HCO₃	%CO₃	²ε_{DIC_g}	³ε_{DIC_g}c	⁴ε_{DIC_g}c
18	23.2	0.50	87.15	12.35	8.09	7.84	8.08
18	23.2	0.67	89.55	9.78	8.13	7.88	8.07
17	23.0	0.51	87.25	12.24	8.04	7.86	8.10
7	22.0	0.48	87.03	12.49	8.18	7.97	8.21
9	21.0	0.47	86.93	12.60	8.34	8.07	8.32
8	21.0	0.52	87.77	11.71	8.32	8.09	8.32
21	14.9	0.54	89.12	10.34	8.96	8.77	9.01
21	14.9	0.57	89.57	9.86	8.91	8.78	9.01
23	9.8	0.68	92.04	7.28	9.51	9.41	9.63
23	9.8	0.73	92.39	6.88	9.50	9.42	9.63
24	7.6	0.54	90.28	9.18	9.80	9.59	9.87
24	7.6	0.59	90.83	8.58	9.76	9.60	9.87
22	5.3	0.55	90.70	8.75	9.92	9.85	10.15
22	5.3	0.56	90.77	8.67	9.86	9.85	10.15

¹pH adjusted using HCl and NaOH.
²Directly measured in seawater.
³Calculated from the fractionations measured for fresh water (this work) and proportion of individual species in seawater (equation 7).
⁴Calculated as above, but using the fractionations from Vogel et al. (1970), Mook et al. (1974) and Thode et al. (1965).
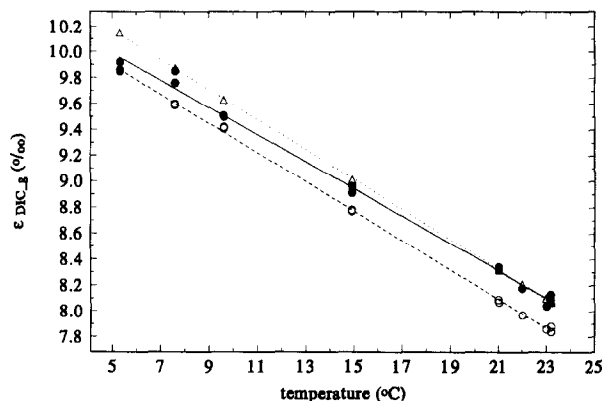

FIG. 6. The ^{13}C fractionation between DIC in seawater and CO_2 in air (ε_{DIC-g}) from 5°C to 25°C. The filled circles are data directly measured, corrected for the carbonate fraction, and the solid line a regression yielding, ε_{DIC-g} = -(0.105 ± 0.002)T(°C) + (10.51 ± 0.05)‰ at f_{CO_2} = 0.12 or pH ~ 8.15. The open circles and dashed line are ε_{DIC-g} predicted from the corresponding carbon speciation in seawater and the ε values for CO_2aq, HCO_3^- and $CO_3^=$ measured in fresh water shown in Fig. 2, 4, and 5. The open triangles and dotted line are the calculated ε_{DIC-g} using ε values for CO_2aq, HCO_3^- and $CO_3^=$ previously reported by Vogel et al. (1970), Mook et al. (1974), and Thode et al. (1965).

ature is slightly lower than that resulting from using ε_{i-g} values (Fig. 6).

We hypothesize that ion complexes in seawater might have significant effects on ε_{HCO_3-g} and ε_{CO_3-g}. A comparison of the measured and predicted ε_{DIC-g} at 23°C indicates that the magnitude of the discrepancy depends on the proportion of total carbonate, where total means free and complexed $CO_3^=$ ions (Fig. 7). That the discrepancy becomes larger as the proportion of carbonate increases suggests that the carbonate complexes, e.g., $MgCO_3$ and $CaCO_3$, might significantly affect the fractionation between total carbonate and gaseous CO_2. The effect of sodium complexes on ε_{HCO_3-g} and ε_{CO_3-g} has
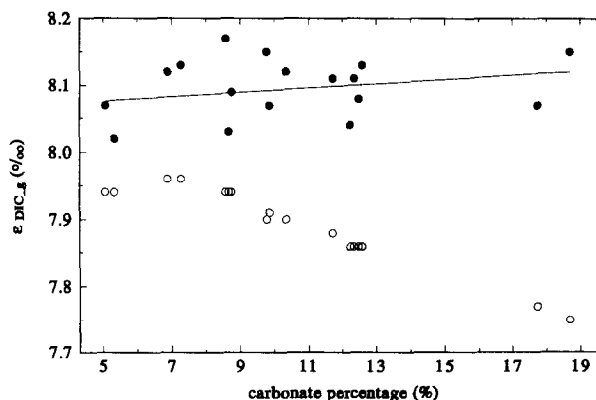

FIG. 7. The ^{13}C fractionation between DIC in seawater and CO_2 in air (ε_{DIC-g}) vs. the carbonate fraction at 23°C. The filled circles are data measured for seawater and the solid line is the regression vs. the carbonate fraction, ε_{DIC-g} = (0.33 ± 0.3)f_{CO_3} + (8.06 ± 0.04)‰ at t = 23°C. The open circles are calculated ε_{DIC-g} values based on the ε values for CO_2aq, HCO_3^- and $CO_3^=$ measured in distilled water, $NaHCO_3$, and Na_2CO_3 solutions (this work) at the corresponding carbonate fraction.

already been included in the reported values of ϵ_{CO_3-g} and ϵ_{CO_3-g} measured in sodium bicarbonate solutions. In seawater free carbonate ion plus $NaCO_3^-$ account for only 25–29% of total carbonate species while $MgCO_3$ plus $CaCO_3$ account for up to 70% (Stumm and Morgan, 1981). The fractionation between solid $CaCO_3$ and CO_2 gas during $CaCO_3$ precipitation has been reported to be around 9.0 to 10‰ at 25°C (Turner, 1982; Emrich et al., 1970). Assuming that the ion pairs of $MgCO_3$ and $CaCO_3$ are 70% of total carbonate and have an average ϵ value of 9.0‰ with respect to gaseous CO_2 and that free carbonate and $NaCO_3$ are 30% of total carbonate with an average ϵ of 6.0‰ (Fig. 5), the fractionation between total carbonate species and CO_2 gas would be 8.1‰ at 23°C. A correction of this magnitude explains the observed discrepancy between the measured and calculated ϵ_{DIC-g} results (Fig. 7). In addition, $MgHCO_3$, as the most prevalent bicarbonate species other than free HCO_3 ion, might also have effects on ϵ_{HCO_3-g}. Thode et al. (1965) measured an ϵ_{DIC-g} increase from 7.1–12‰ when the Mg^{2+} concentration in a $NaHCO_3$ solution was increased from 0–0.5 M.

The hypothesized carbonate ion complex effect, however, can't explain the slope difference of the temperature dependence between measured and predicted ϵ_{DIC-g} values (Fig. 6). The expected difference between the observed and predicted ϵ_{DIC-g} would be larger at low temperature based on this hypothesis. Further investigation needs to be done on this point.

We have obtained an empirical function of ϵ_{DIC-g} vs. temperature (5° to 25°C) and the proportion of total carbonate species in total DIC: $\epsilon_{DIC-g} = (0.0144 \pm 0.01)T(°C)$ f_{CO_3} $- (0.107 \pm 0.002)T(°C) + (10.53 \pm 0.05)‰$. We use carbonate fraction instead of pH because the carbonic acid dissociation constants vary with temperature and, therefore, calculated pH depends on temperature. Although the theoretical relationship between ϵ_{DIC-g} and carbonate fraction is not a linear function, it can be linearly approximated in the narrow pH range of 7.7–8.5 used in the experiments. The total error in ϵ_{DIC-g} is estimated at 0.05‰ based on regression curves vs. temperature and $CO_3^=$ fraction.

CONCLUSIONS

Results from the experiments have yielded new estimates for carbon isotope fractionation effects during CO_2 gas transfer, gas dissolution, and chemical equilibrium between HCO_3^-, $CO_3^=$, and aqueous CO_2. We have confirmed the kinetic fractionation factor measured previously by Wanninkhof (1985) and Inoue and Sugimura (1985), while reducing the uncertainty by ten times. The equilibrium fractionation measurements in sodium bicarbonate solution and seawater

indicate that the fractionation factor between total DIC and gaseous CO_2 can't be simply calculated from the fractionation factors measured for three C species, as has been done previously. An empirical function of ϵ_{DIC-g} in seawater has been obtained with an average error of 0.05‰ in the temperature range of 5° to 25°C and carbonate fraction of 0.05–0.20 (Table 4).

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Table 4 Summary of the ^{13}C fractionations between gaseous CO_2 and dissolved CO_2, HCO_3^- and $CO_3^=$ in fresh water and seawater as functions of temperature and $CO_3^=$ fraction. The uncertainties in the slopes and intercepts account for the uncertainties in the mean ϵ values measured at each temperature (Bevington and Robinson, 1992).

1) $y = a \times T + b$ in fresh water at $5°C < T < 25°C$
2) $y = a \times T + b + d \times T \times f_{CO_3}$ in sea water at $5°C < T < 25°C$; $0.05 < f_{CO_3} < 0.20$ or $7.5 < pH < 8.5$

Y	a(‰/°C)	b(‰)	d(‰/°C)	solution
1) ϵ_{as}	0.013±0.016[a]	-2.30±0.27[a]		distilled water
1) ϵ_{aq-g}	0.0049±0.003	-1.31±0.06		distilled water
1) ϵ_{HCO3-g}	-0.114±0.003	10.78±0.05		NaHCO3
1) ϵ_{CO3-g}	-0.052±0.03	7.22±0.46		Na2CO3+NaHCO3
2) ϵ_{DIC-g}	-0.107±0.002	10.53±0.05	0.014±0.01	seawater

[a] Obtained from measurements at two temperatures only, *i.e.*, 21°C and 5°C.

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