Kinetic fractionation of the carbon isotopes ^{13}C and ^{12}C during transfer of CO_2 from air to seawater

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ABSTRACT

Laboratory experiments have been performed to determine the kinetic fractionation between $^{13}CO_2$ and $^{12}CO_2$ as CO_2 invades seawater. Knowledge of this fractionation, which is regulated by physical and chemical processes in the ocean boundary layer, is important for ocean–atmosphere models which use $^{13}CO_2$ as a tracer. Until now, only theoretical calculations have been performed to determine this fractionation. The experimental results give a fractionation of $-2.4 \pm 2.0 \%_0$ while the calculated value for invasion is $-2.1 \pm 0.3 \%_0$ (i.e. $^{13}CO_2$ invading slower). The results show that the fractionation of CO_2 during invasion into a hydroxide solution ($-14 \%_0$) is clearly too high as a value for invasion into seawater and should no longer be used as an upper limit in CO_2 models.

1. Introduction

The fractionation of $^{13}CO_2$ and $^{12}CO_2$ when CO_2 crosses the air–seawater interface has not been determined experimentally. Knowledge of the magnitude of this fractionation is of importance to models which use $^{13}CO_2$ as a tracer for anthropogenic CO_2 since the ocean is a major sink for CO_2 (Bacastow and Keeling, 1981; Broecker et al., 1979). The determination of this fractionation also enhances our understanding of boundary layer processes.

$^{13}CO_2$ can be used as a tracer since the primary sources of CO_2, the biosphere and fossil fuel CO_2, have distinctly different $\delta^{13}C$ values from the ocean and the atmosphere. The $\delta^{13}C$ values of fossil fuel CO_2 and of CO_2 released from decay of biomatter is about $-26\%_0$ (Peng et al., 1983) while the average surface ocean ΣCO_2 value is $1.5\%_0$ (Broecker and Peng, 1982) and the atmospheric value is about $-7.7\%_0$ (Mook et al., 1984). Thus, release of CO_2 from these sources will decrease the atmospheric $\delta^{13}C$ value. From a $\delta^{13}C$ record through time, the release pattern of biosphere and anthropogenic CO_2 should be able to be determined. The $\delta^{13}C$ record in tree rings can be utilized to determine the change of atmospheric $\delta^{13}C$ with

time (Peng et al., 1983). This change of atmospheric $\delta^{13}C$ with time is dependent on the fractionation of CO_2 as it enters the ocean. A box model of Keeling et al. (1980) shows a difference in $\delta^{13}C$ change in the atmosphere from 1956 to 1978 of $0.15\%_0$, depending on whether an air–seawater fractionation constant of $-14\%_0$ or $0\%_0$ is used. This is quite significant if we consider that the total $\delta^{13}C$ change in the atmosphere for the past 100 years is about $-1\%_0$ based on tree ring data (Peng et al., 1983).

The fractionation constants of -2.1 or $0\%_0$ and $-14\%_0$ are often used as endmembers in models. The value of $-2.1\%_0$ was determined by Siegenthaler and Münnich (1981) and is based on theoretical calculations assuming that most of the CO_2 invades into the ocean by molecular diffusion through the boundary layer. The fractionation constant of $-14\%_0$ was obtained from experiments of Baertschi (1952) and Craig (1953) in which CO_2 invaded a hydroxide solution. Although the primary mechanism of CO_2 invasion into a hydroxide solution is chemical reaction at the interface while in natural waters with pH <8, it is diffusion, the hydroxide fractionation constant has often been applied for invasion into ocean water.

If the invasion rate of CO_2 is controlled by

molecular diffusion through the boundary layer, the flux can be written as:

$$F = F_{as} - F_{sa}$$
$$= \omega(C_o - C_s)$$
$$= \omega(\beta C_a - C_s), \qquad (1)$$

where

F = net flux of CO_2;
F_{as} = one way flux of CO_2 from air to seawater;
F_{sa} = one way flux of CO_2 from seawater to air;
C_s = concentration of CO_2 in solution;
C_o = concentration of CO_2 in water if at equilibrium with air;
C_a = concentration of CO_2 in air;
ω = gas exchange coefficient;
β = solubility.

We can write a similar equation for the flux of $^{13}CO_2$:

$$^{13}F = {}^{13}F_{as} - {}^{13}F_{sa}$$
$$= {}^{13}\omega(^{13}\beta\, {}^{13}C_a - {}^{13}C_s)$$
$$= {}^{13}\omega/\omega(\alpha_s R_a \omega\beta C_a - R_s\, \omega C_s).$$

The superscript ^{13} refers to ^{13}C.

$\alpha_s = {}^{13}\beta/\beta =$ ratio of solubilities of ^{13}C and ^{12}C which is the equilibrium fractionation between aqueous CO_2 and gaseous CO_2;

In the above equation, we set $^{12}C = C$ which will cause a very small error as 99% of the carbon is in the form of ^{12}C. If we define $\alpha_{as} = (^{13}\omega/\omega)\alpha_s$ and $\alpha_{sa} = {}^{13}\omega/\omega$ as the air–sea and the sea–air kinetic fractionation factors we get as a final equation:

$$^{13}F = \alpha_{as} R_a F_{as} - \alpha_{sa} R_s F_{sa}. \qquad (2)$$

The fractionation constant, ε, is often used to express fractionations. It is related to the fractionation factor, α, by $\varepsilon = (\alpha - 1)1000$.

The equilibrium fractionation factor, α_s, between $CO_2(aq)$ and $CO_2(gas)$ is 0·9989 at 20 °C (Vogel et al., 1970). The ratio of exchange coefficients, $^{13}\omega/\omega$, is related to the ratio of the molecular diffusivities of $^{13}CO_2$ and $^{12}CO_2$ which is 0.9991 (Schönleber,

1976). If the stagnant film theory of gas exchange is used (Whitman, 1923), the ratio of exchange coefficients is equal to the ratio of diffusivities, and the film replacement model (Danckwerts, 1970) predicts a square root dependence of exchange coefficient with diffusivity. Depending on the model, the predicted kinetic fractionation factors for physical exchange will be $\alpha_{as} = 0.998$ or 0.9984 and $\alpha_{sa} = 0.9991$ or 0.9995.

We cannot measure the $^{13}CO_2/^{12}CO_2(aq)$ $(=R_s)$ ratio directly. The $^{13}C/^{12}C$ ratio of the total carbon $(=R_\Sigma)$ is measured instead. To determine R_s, we have to know the equilibrium fractionation factors between $CO_2(aq) - HCO_3^-$ and $CO_2(aq) - CO_3^{2-}$, and the concentration of $CO_2(aq)$ and ΣCO_2 $(=HCO_3^- + CO_3^{2-} + CO_2(aq))$. We must also assume that the rate of conversion of CO_2 to HCO_3^- and CO_3^{2-} is much faster than the rate of invasion, so that the carbonate system in the water is in equilibrium. The equilibrium fractionation factors have been determined.

At 20 °C:

$CO_2(aq) - HCO_3^-$ $\alpha_1 = 0.9905$ (Mook et al., 1974)

$CO_2(aq) - CO_3^{2-}$ $\alpha_2 = 0.991$ (Thode et al., 1965).

The $^{13}C/^{12}C$ ratio of the dissolved CO_2, R_s, will be:

$$R_s = \frac{\Sigma CO_2 R_\Sigma - (H^{13}CO_3^-/H^{12}CO_3^-)\, HCO_3^- - (^{13}CO_3^{2-}/^{12}CO_3^{2-})\, CO_3^{2-}}{CO_2(aq)}.$$

$R_a, R_s = {}^{13}C/^{12}C$ ratio in gaseous and aqueous CO_2 respectively.

ΣCO_2, R_Σ, and $CO_2(aq)$ are measured. HCO_3^-, CO_3^{2-}, $H^{13}CO_3^-/H^{12}CO_3^-$, $^{13}CO_3^{2-}$ are determined from the dissociation constants and equilibrium fractionation factors.

Unlike many other atmospheric gases, CO_2 can react at the interface. The hydration reactions are:

$$CO_2 + OH^- = HCO_3^- \qquad (3)$$

or

$$CO_2 + H_2O = H_2CO_3. \qquad (4)$$

These reactions can enhance CO_2 uptake as CO_2 is converted into another molecule, thereby bypassing the rate limiting step of gas exchange which is molecular diffusion through the boundary layer. Bolin (1960) showed that reaction (3) is not important for pH < 8 if the hypothetical molecular

boundary layer thickness is equal to or less than that of the average ocean (35 μ). The boundary layer is defined as, $z = D/\omega$, D = diffusion coefficient, ω = exchange coefficient. Reaction (4), which also depends on the boundary layer thickness and pH, contributes about 2 % to the total exchange under average oceanic conditions.

Chemical enhancement will increase the fractionation of the carbon isotopes. Baertschi (1952) and Craig (1953) determined that the fractionation constant for CO_2 invasion into a hydroxide solution is $-14‰$. The fractionation during hydration is unknown but it can be assumed to be less than or equal to the hydroxide fractionation. Siegenthaler and Münnich (1981) calculated the contribution of the hydration reactions to the fractionation for surface ocean water by calculating the residence time of CO_2 molecules at the surface versus the mean life time of CO_2 with respect to reaction with water of hydroxide ions at the surface. They obtained a value of $-0.2‰$ for the reaction with hydroxide and an upper limit of $-0.5‰$ for the reaction with water (if a fractionation constant of $-14‰$ is used). If we include this small chemical effect for the air–seawater and seawater–air fractionation constants, we obtain $\varepsilon_{as} = -1.8‰$ to $-2.9‰$ and $\varepsilon_{sa} = -0.7‰$ to $-1.6‰$. The uncertainty in the values is due to the unknown fractionation during hydration and the influence of choice of gas exchange model.

Enzymes in water can increase the rate of hydration of CO_2. Berger and Libby (1969) proposed that the concentration of the enzyme carbonic anhydrase might be high enough in some surface ocean water to enhance CO_2 uptake. Goldman and Dennet (1983) did laboratory experiments with various natural waters in which they did not find any evidence for rate enhancement. If enhancement of the hydration reaction by enzymes does indeed occur at the ocean boundary, we would expect larger fractionation factors.

2. Experimental procedures

The experiment was run in a closed system. The set-up consisted of a 36 l Pyrex battery jar covered with a plexiglass top (see Fig. 1). A rubber bellows pump (Aircadet model 7530) circulated the air in the tank and through a CO_2 spike flask. The pump was connected to the top of the jar with $\frac{1}{2}''$ Pyrex tubing and Cajon brand fittings. A CO_2 extraction system was connected to the set-up so the air samples could be prepared for mass spectrometric analyses while the experiment was running.

The battery jar was situated in a large constant temperature water bath. A circulator/temperature controller (Polyscience model T50) kept the temperature of the seawater constant to within 0.02 °C. The water was mixed with a large glass paddle with fins at three different levels. The paddle
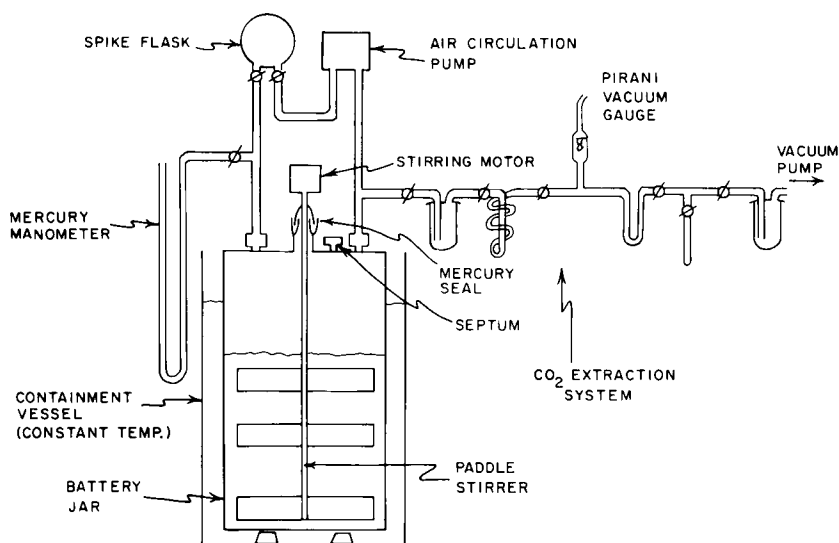

Fig. 1. Diagram of the set-up in which the fractionation experiments were performed.

was connected to a stirring motor (Fisher model Dynamix) with a mercury seal stirring assembly. The stirring rate was about 50 rpm. This was the maximum speed which could be attained without significantly perturbing the smooth water surface.

The system was tested for leaks by putting a slight vacuum on the empty jar and observing the pressure change with time. The pressure remained constant for 5 h. The vacuum leak test was repeated for a shorter period of time before each run. To test for outgassing of the various rubber parts of the system, such as the pump bellows and the O-ring connectors, the empty jar was flushed with nitrogen and the P_{CO_2} (partial pressure of CO_2) rise with time was determined. The P_{CO_2} in the set-up rose 9 μatm over a 17 h time span which is negligible for the experimental objectives.

At the start of the experiment, the jar was $\frac{2}{3}$ filled with seawater which came from 2500 m in the Sargasso Sea and had been poisoned with mercuric chloride. The P_{CO_2} of the water was equilibrated with the atmosphere by bubbling air through it overnight. The air phase was enriched in CO_2 by acidifying about 0.02 g of sodium bicarbonate and releasing the evolved CO_2 into a flask which was connected to the system with O-ring connectors. The air phase was enriched to about 1500 μatm. Before and after each run, a water sample was taken which was analyzed for P_{CO_2}, ΣCO_2, pH, and ^{13}C. The first air samples were taken 15 min after the spike flask was opened and the stirrer and pump were started. Subsequent air sampling occurred every hour. The air samples for P_{CO_2} analyses were taken through a septum with a 50 ml syringe and analyzed on a gas chromatograph. 150 ml CO_2 air samples to be analyzed for $\delta^{13}C$ were isolated in the first stage of the CO_2 extraction system which was evacuated prior to sampling. The water vapour in the samples was extracted with 2 dry ice/iso-propanol traps. The CO_2 was trapped in a U-tube which was cooled with liquid nitrogen. The residual atmospheric gasses were pumped away after which the CO_2 was transferred to a break seal tube. The CO_2 was analyzed on a Micromass model 901 mass spectrometer. The extraction took about 25 min which gave enough time to clean and evacuate the extraction system before the next sample was taken.

The run time for an experiment ranged from 4–6 h. The total quantity of P_{CO_2} and ^{13}C samples

which could be taken was limited by the mercury seal which broke after 6 samples due to the negative pressure in the set-up. Eight runs were performed, two at 20 °C, three at 12.5 °C and three at 3.5 °C. The P_{CO_2}(air) samples were corrected for volume of air extracted. The P_{CO_2}-(water) samples were analyzed at 20 °C but the values were corrected to the temperature of the experiment.

3. Discussion

The results of the experiment confirm that the fractionation of CO_2 across a seawater interface is comparable to the calculated fractionation. The fractionation factors and gas exchange coefficients are obtained by fitting the data points to a model curve derived by using eqs. 1 and 2 and replacing the flux by a finite-step concentration function, $\Delta C / \Delta t$ (see Fig. 2). Taking into account that the experimental system is closed, the change of mass of CO_2 in the gas phase is opposite in sign and equal in magnitude to the change of mass of ΣCO_2 in the water. The change in P_{CO_2}(aq.) during the experiment is determined from the ΣCO_2 and the Revelle factor:

$$\mathrm{Re} = \frac{dP_{CO_2}}{P_{CO_2}} \bigg/ \frac{d\Sigma CO_2}{\Sigma CO_2}.$$

First, the exchange coefficient in the model is adjusted till a least squares fit of the model run and P_{CO_2}(air) data points was obtained. After the exchange coefficient is determined, the ratio of exchange coefficients, $^{13}\omega/^{12}\omega$, is varied to get a least squares fit between model and $\delta^{13}C$ air data points. The other variables, P_{CO_2}(air), P_{CO_2}(aq), volume water, volume air, R_{Σ}, and Re are measured for each run. The constants which are used in the model are given in Table 1.

Eq. (1) which describes the CO_2 exchange by Fickian transport may be used in the model even though there might be some chemical enhancement since CO_2 data is used to calculate the gas exchange coefficient. We must bear in mind though that the calculated exchange coefficient might not relate to other non-reactive gases due to the chemical component of CO_2 exchange. If any chemical enhancement of the CO_2 exchange occurs, it will manifest itself by a larger fractionation between $^{13}CO_2$ and $^{12}CO_2$ during invasion, since
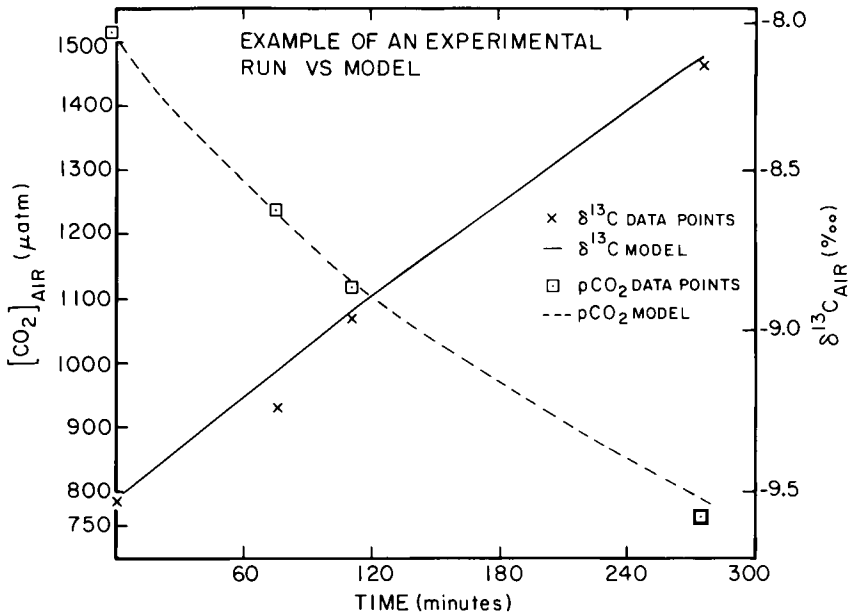
Fig. 2. Graphical representation of the experimental points and least squares fit model curves for run #2.

Table 1. *The temperature dependence of constants used in the model to calculate P_{CO_2} and $\delta^{13}C$*

Temperature (°C)	20.5	12.55	3.5
Henry law constant (M/atm)[a]	0.0339	0.0426	0.0562
Diffusion coefficient[b] (cm^2 s^{-1})	1.65 E-5	1.35 E-5	1.00 E-5
ε_s (‰)	−1.1	−1.1	−1.2
ε_1 (‰)	−8.5	−9.3	−10.4
ε_2 (‰)	−8.1	−8.8	−10

[a] From Stumm and Morgan (1981). The Henry Law constant is a measure of solubility (= CO_2(aq)/CO_2(gaseous)).

[b] From Himmelblau (1964).

ε_s: equilibrium fractionation constant of $^{13}C/^{12}C$ between dissolved and gaseous CO_2 (Vogel et al., 1970).

ε_1: equilibrium fractionation constant between gaseous CO_2 and HCO_3^- (Mook et al., 1974).

ε_2: equilibrium fractionation constant between gaseous CO_2 and CO_3^- (Thode et al., 1975).

reaction of CO_2 with H_2O or OH^- causes a larger fractionation than diffusion of CO_2 across the interface.

The pertinent data of the runs are given in Table 2. The calculated exchange coefficients are a factor of two to three lower than those of the average ocean but they are within the lower limit obtained from ^{222}Rn measurements in the open ocean (Peng et al., 1979). The air–seawater fractionation constants in the second to last column, and depicted graphically in Fig. 3, show a fair amount of scatter. The average for each temperature varies too, but they lie within a standard deviation of each other so we attribute the offset to be experimental and/or computation errors rather than a temperature effect. The offset could be due to incorrect constants used in the model at different temperatures (see Table 1). The variation in ε_{as} between the runs is greater than the deviation of the points from the model curve for each run (see Table 3) so the variation does not seem due to analytical errors in the P_{CO_2} (air) or $\delta^{13}C$ (gas) analyses, although the small number of samples does not preclude this possibility. The $\delta^{13}C$ (of the ΣCO_2) analyses are suspect as a cause for the difference between the runs since an incorrect water value will cause a constant offset. There were some problems with the extraction procedure and there is a strong correlation between the measured $\delta^{13}C$ (water) and the air–seawater fractionation factor. For example, run 3 which has an anomalously low $\delta^{13}C$ (water) also has a large negative fractionation constant. If the $\delta^{13}C$ (water) for this run is changed from the

Table 2. *Summary of data and calculated exchange coefficients and fractionation constants*

Run	Initial P_{CO_2} (gas) (μatm)	Final P_{CO_2} (gas) (μatm)	Temperature water (°C)	Initial pH	Initial ΣCO_2 (water) (mMl⁻¹)	Initial $\delta^{13}C$ (gas) (‰)	Final $\delta^{13}C$ (gas) (‰)	$\delta^{13}C$ (water) (‰)	P_{CO_2} (water) (μatm)	Gas exchange coefficient (cm/s⁻¹)	ε_{as} (‰)	ε_{sa} (‰)
1	1573	844	20.05	8.00	2.4	−7.44	−6.55	0.0	341	1.47×10^{-3}	−2.9	−1.8
2	1516	761	20.05	8.09	2.1	−9.52	−8.16	1.0	356	1.58×10^{-3}	−1.3	−0.2
3	1527	628	12.55	8.00	2.2	−14.6	−10.07	−2.8	358	1.08×10^{-3}	−6.8	−5.7
4	1118	642	12.55	7.88	2.2	−9.97	−8.74	1.0	394	1.25×10^{-3}	−2.2	−1.1
5	933	590	12.55	7.77	2.3	−9.95	−8.84	−1.3	329	1.30×10^{-3}	−3.8	−2.7
6	892	527	3.5	7.76	2.7	−12.16	−11.27	1.6	349	1.06×10^{-3}	0.0	1.2
7	814	598	3.5	7.64	2.8	−11.41	−10.31	0.8	349	1.33×10^{-3}	−1.8	−0.6
8	951	555	3.5	7.60	2.4	−12.58	−10.36	0.8	366	1.1×10^{-3}	−0.8	0.4

TEMPERATURE

20.05°C

12.55°C

3.5°C

AVERAGE OF ALL THE
EXPERIMENTAL RUNS

BAERTSCHI (Na OH sol.)

SIEGENTHALER & MÜNNICH
(Theoretical)

−17 −16 −15 −14 −13 −12 −11 −10 −9 −8 −7 −6 −5 −4 −3 −2 −1 0

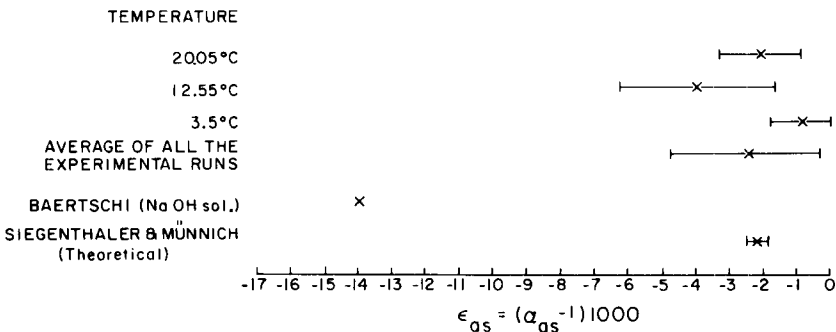$$\varepsilon_{as} = (\alpha_{as}^{-1})1000$$

Fig. 3. Graphical representation of the kinetic fractionation constant, ε_{as}, for the three temperatures at which the experiment was run. The fractionation of CO_2 as it is absorbed by a hydroxide solution as determined by Baertschi (1952) and the calculated fractionation by Siegenthaler and Münnich (1981) are shown for comparison. The error bars on their experimental values are the standard deviations for the runs at the same temperature. The error bar on the theoretical work is the uncertainty due to the unknown fractionation during hydration (see text).

measured −2.88‰ to −1.5‰, ε_{as} will change from −6.8‰ to −5.6‰. There is no correlation between the small differences in pH or exchange coefficients and the calculated α_s values to explain the variation between the runs.

The sensitivity of the model was tested by varying the exchange coefficient, ω, and the fractionation constant, ε_{as}, by 10% from the least squares fit value. After a 4-h model run, the P_{CO_2} differed by 30 μatm and the $\delta^{13}C$ by 0.07‰ from the least squares fit value. Table 3 gives the average and the % deviation of the P_{CO_2} and $\delta^{13}C$ measurements versus the best fit model curve. All the runs show a good agreement between the measured P_{CO_2} and the model. The $\delta^{13}C$ points show greater scatter about the least squares fit curve and thus we have to be more tentative about the exact fractionation constant for each run. In the worst case (run #7), the average $\delta^{13}C$ deviation corresponds to an uncertainty in ε_{as} of 0.8‰.

The experiment should be a good analog for CO_2 invasion into the ocean, although the ΣCO_2 values are slightly higher and the pH values are slightly lower for the water which we used in the experimental set-up than average surface ocean values, and the exchange coefficients in the set-up are lower than observed in the ocean. The results show no influence of the ΣCO_2 ranging from 2.1 to 2.8 mM or the pH changing from 7.6 to 8, so it seems save to assume that the experiments are representative for surface ocean water (which has a pH of 8 and a ΣCO_2 of 2.0 mM). The slower exchange rate will lead to a greater influence of the hydration reactions on the exchange rates. Using the equations presented by Bolin (1960), one can calculate that for the lowest exchange coefficient

Table 3. *Deviation of data points from least squares fit model runs*

Run	Average P_{CO_2} deviation (μatm)	% P_{CO_2} deviation	Average ^{13}C deviation (‰)	% ^{13}C deviation
1	4.3	0.4	0.05	0.6
2	7.6	0.9	0.05	0.5
3	6.3	0.8	0.24	2.1
4	11.8	1.4	0.25	2.8
5	4.8	0.7	0.28	3.2
6	2.6	0.4	0.12	1.1
7	4.4	0.7	0.31	2.9
8	14	2.1	0.03	0.3

average deviation:

$$\frac{\Sigma(\mid \text{experimental point} - \text{model point} \mid)}{\text{no. of data points}}.$$

% deviation:

$$\sum \left(\frac{\mid \text{experimental point} - \text{model point} \mid}{\text{model point}} \right)$$
$$\frac{}{\text{no. of data points}}.$$

(run 3), the hydration reactions will contribute less than 5% to the total exchange. If we use a chemical fractionation constant of −14‰, we would expect the air-sea fractionation constant, ε_{as}, to be 0.7‰ lower for the experiment than over the ocean.

The average value of ε_{as} for all the runs (−2.4‰ ± 2‰) is in good agreement with the calculated value. Although the scatter in the ε_{as} value for the runs precludes giving an exact value under the experimental conditions, the results clearly show that the large fractionation constant (−14%) obtained from CO_2 absorption into a hydroxide solution is too high to apply to oceanic conditions.

4. Acknowledgements

REFERENCES

Bacastow, R. B. and Keeling, C. D. 1981. Atmospheric carbon dioxide concentration and the observed airborne fraction. In *Scope 16, carbon cycle modelling* (ed. B. Bolin). New York: John Wiley, 103–112.

Baertschi, P. 1952. Die fractionierung der Kohlenstoff Isotopen bei der Absorption von Kohlerdioxyd. *Helv. Chim. Acta 35*, 1030–1036.

Berger, R. and Libby, W. F. 1969. Equilibration of atmospheric carbon dioxide with seawater: possible enzymatic control of the rate. *Science 164*, 1395–1397.

Bolin, B. 1960. On the exchange of carbon dioxide between the atmosphere and the sea. *Tellus 12*, 274–281.

Broecker, W. S. and Peng, T.-H. 1982. *Tracers in the sea*. Palisades: Eldigio Press.

Broecker, W. S., Takahashi, T., Simpson, H. J. and Peng, T.-H. 1979. Fate of fossil fuel carbon dioxide and the global carbon budget. *Science 206*, 409–418.

Craig, H. 1953. The geochemistry of stable carbon isotopes. *Geochim. Cosmochim. Acta 3*, 53–92.

Danckwerts, P. V. 1970. *Gas liquid reactions*. New York: McGraw-Hill Book Co., 101–103.

Goldman, J. C. and Dennet, M. R. 1983. Carbon dioxide exchange between air and seawater: no evidence for rate catalysis, *Science 220*, 199–201.

Himmelblau, B. M. 1964. Diffusion of dissolved gases in liquids. *Chem. Rev. 64*, 527–550.

Keeling, C. D., Bacastow, R. B. and Tans, P. P. 1980. Predicted shift in the C-13/C-12 ratio of atmospheric carbon dioxide. *Geophys. Res. Let. 7*, 505–508.

Mook, W. G., Koopmans, M., Carter, A. F. and Keeling, C. D. 1984. Seasonal, latitudinal, and secular variations in the abundance and isotopic ratios of carbon dioxide (I). Results from land stations. *J. Geophys. Res. 88*, 10915–10933.

Mook, W. G., Bommerson, J. C. and Staverman, W. H. 1974. Carbon isotope fractionation between dissolved

bicarbonate and gaseous carbon dioxide. *Earth Planet. Sci. Lett. 22*, 169–176.

Peng, T.-H., Broecker, W. S., Freyer, H. D. and Trumbore, S. 1983. A deconvolution of the tree ring based C-13 record. *J. Geophys. Res. 88*, 3609–3620.

Peng, T.-H., Broecker, W. S., Mathieu, G. G., Li, Y.-H. and Bainbridge, A. E. 1979. Radon evasion rates in the Atlantic and Pacific oceans as determined during the Geosecs Program. *J. Geophys. Res. 84*, 2471–2485.

Schönleber, G. 1976. Messung der Isotopentrennung bei der Diffusion von $^{13}CO_2$ und $^{12}CO_2$ in Wasser. Diploma Thesis, Heidelberg.

Siegenthaler, U. and Münnich, K. O. 1981. C-13/C-12 fractionation during CO_2 transfer from air to sea. In *Carbon cycle modelling* (ed. B. Bolin). Scope 1. New York: John Wiley and Sons, 249–257.

Stumm, W. and Morgan, J. J. 1981. *Aquatic chemistry*, 2nd edition. New York: Wiley and Sons Inc.

Thode, H. G., Shima, M., Rees, C. E. and Krisnamurty, K. V. 1965. Carbon-13 isotope effects in systems containing carbon dioxide, bicarbonate, carbonate and metal ions. *Can. J. of Chem. 43*, 582–595.

Vogel, J. C., Grootes, P. M. and Mook, W. G. 1970. Isotope fractionation between gaseous and dissolved carbon dioxide. *Z. Physik 230*, 225–238.

Whitman, W. G. 1923. The two film theory of gas absorption. *Chem. Met. Eng. 29*, 146–148.