WOODS HOLE OCEANOGRAPHIC INSTITUION
NSR-22-014-001

CARBON ISOTOPE FRACTIONATION IN THE SYSTEM CO_2(gas)-CO_2(aqueous)-HCO_3^-(aqueous)

FACILITY FORM 602

N67 27703 (ACCESSION NUMBER)
(THRU)
13 (PAGES)
1 (CODE)
CR-84428 (NASA CR OR TMX OR AD NUMBER)
06 (CATEGORY)

GPO PRICE $
CFSTI PRICE(S) $
Hard copy (HC) $3.00
Microfiche (MF) .65

ff 653 July 65

Abstract. Carbon isotope fractionation between gaseous carbon dioxide and aqueous bicarbonate decreases from 9.2 to 6.8‰ over the temperature range 0 to 30°C. This fractionation occurs in the hydration stage, not in the passage of atmospheric CO_2 through the air-water interface.

It has long been recognized that atmospheric carbon dioxide is depleted in C^{13} relative to the inorganic carbon pool of the oceans. Reid and Urey (1) first measured the equilibrium fractionation in the exchange $C^{13}O_2$ + $HC^{12}O_3^- \rightleftharpoons C^{12}O_2 + HC^{13}O_3^-$ and arrived at a value of 1.0120 ± 0.0025 at 25° C. Craig (2) found a C^{13} depletion of some 7‰ in atmospheric carbon dioxide relative to oceanic bicarbonate and Abelson and Hoering (3) redetermined a value of 1.0083 for the fractionation in the above equilibrium at 25°C. This latter value is apparently the only one derived from laboratory experiments using improved analytical techniques that have become available since the early work of Reid and Urey (1). No experimental data at all seem to exist on the change of this fractionation over the temperature range 0 to 30°C which is the most important one with regard to natural conditions involving the atmosphere and the oceans. Data are also lacking on carbon isotope fractionation between oceanic bicarbonate and molecular carbon dioxide dissolved in the water. Both fractionation effects are of geochemical as well as biological interest. Knowledge of their magnitude may aid, for example, in determining whether certain marine plants utilize dissolved carbon dioxide or bicarbonate or possibly both species during photosynthesis. We therefore decided to perform several laboratory experiments to determine the size of these fractionations under equilibrium conditions.

Round-bottom, three-neck distilling flasks of 300 ml capacity were used as reaction vessels. Attached were a gas sample tube, a liquid-sampling pipette consisting of two stopcocks in series with a 3-ml volume between them, a modified stopcock whose bulb contained H_3PO_4 and a main stopcock for isolating the whole system. All stopcocks and joints were lubricated with a minimum of silicone grease in order to avoid contact between solution and grease. Preparation of a run proceeded as follows: The gas sample tube was filled with the desired amount of CO_2 and the pipette and the stopcock containing H_3PO_4 were evacuated and closed after the acid was thoroughly degassed. A 50 ml aliquot of the sample solution was then pipetted into the flask and frozen by applying a mixture of dry ice and acetone around the flask. When the solution was completely frozen the flask was evacuated to a pressure of about 10^{-3} torr and closed. After thawing of the solution, the same cycle was repeated so as to remove most of the gases dissolved in the solution. After the second thawing the CO_2 in the gas sample tube was released into the flask and the entire reaction vessel with attachments was immersed in a water bath whose temperature was controlled to $\pm$ 0.5°C. A minimum of 18 hours was allowed for equilibration during which time the vessel was shaken periodically.

At the end of a run, a portion of the solution was drawn into the pipette for later pH measurement and the gaseous CO_2 was condensed back into the gas sample tube. Both these steps as well as the pH measurement were carried out at the particular temperature of the experiment. Following the isolation of the gas phase, the solution was acidified by opening and draining the stopcock containing the phosphoric acid. The evolved CO_2 was extracted and purified by two passes through a trap cooled with dry ice and acetone. The CO_2 constituting the equilibrium gas phase was subjected to the same purification before transfer to the mass spectrometer. The spectrometer used for the isotope ratio measurements is a conventional 6-inch, 60° instrument with dual inlet system and double collector, manufactured by Nuclide Corporation.

In the first set of experiments 10^{-4} mole of CO_2 with a δC^{13} of -27.0‰

(4) was equilibrated with a solution of 10^{-4} mole of $NaHCO_3$ with a δC^{13} of -6.0‰. The pH of the solution was 8.4, ensuring that roughly 98% of the carbon was present in bicarbonate (5). The δC^{13} measured on the CO_2 derived by acidifying the solution after the run, therefore, closely represented the value for the bicarbonate in equilibrium with the CO_2 atmosphere above the solution. Fig. 1 shows the data obtained at 0 and 30°C equilibration temperatures. The reproducibility in all experiments described here is of the order of ± 0.2 to 0.4‰ for Δ, i.e. the difference between the δ-values of the equilibrated phases. As the error in Δ depends on two separate sample preparations and analyses in addition to the errors inherent in the equilibration and separation stages, this level of precision seems quite acceptable. Fig. 1 also includes the data obtained in a separate experiment, similar to the one above, where the initial carbon dioxide was isotopically heavier (δC^{13} = + 3.6‰) than the bicarbonate (δC^{13} = -6.0‰). This experiment was performed in order to approach equilibrium from the opposite direction. As is evident from Fig. 1, a switchover was achieved and after the run the CO_2 above the solution was 9.6 ‰ lighter than the bicarbonate. Within the limitations of these experiments, this value can be considered identical to the others obtained at the same temperature, viz. 9.3, 8.8, 9.1‰. The C^{13}/C^{12} difference between atmospheric carbon dioxide and aqueous bicarbonate at 0°C may thus be taken to be 9.2 ± 0.4‰. Table 1 lists the experimentally determined differences and their mean values for 0°, 10°, 20°, and 30°C. The last column of the Table gives the fractionation factors α, defined as

$$\alpha = \frac{(C^{13}/C^{12})_{HCO_3^-}}{(C^{13}/C^{12})_{CO_2}}$$

for each temperature. These values were calculated from the best fit to all the data in a plot of 1000 $\ln\alpha$ vs. $10^6\ T^{-2}$ where T is the absolute temperature.

Another series of experiments was aimed at determining the isotopic composition of dissolved CO_2 in equilibrium with aqueous bicarbonate and atmospheric CO_2. To this end buffered solutions of pH values ranging from 6.20 to 6.53 were allowed to equilibrate with carbon dioxide gas. The buffers used were mixtures of KH_2PO_4 and Na_2HPO_4 dissolved in distilled water. Equilibration temperature was 0°C in order to maximize fractionation effects. Preparation procedure was identical to the one described above except that in these runs all the carbon was initially in the form of CO_2 gas. Upon bringing the gas and solution into contact some of the CO_2 entered the solution and partly hydrated and dissociated to H^+ and HCO_3^-. The molar ratio of free CO_2 (this includes roughly 0.1% undissociated H_2CO_3) in the solution to the bicarbonate is dependent upon the pH and the temperature and can be obtained from tables of values calculated by Saruhashi (5). To determine the isotopic composition of the dissolved CO_2, it was then only necessary to measure the pH of the solution at the end of the experiment and the δC^{13} values of the gaseous CO_2 and of the total carbon in the solution ($\delta_{\Sigma C(aq)}$). The δC^{13} of the bicarbonate and of the aqueous CO_2 were then calculated from the following equations

$$\delta_{HCO_3^-} = \delta_{CO_2(gas)} + \Delta \qquad (1)$$

$$\delta_{CO_2(aq)} = \delta_{\Sigma C(aq)} - Q\left(\delta_{HCO_3^-} - \delta_{\Sigma C(aq)}\right) \qquad (2)$$

where Δ is the previously determined difference between the δ's of CO_2 and bicarbonate in equilibrium (9.2‰ at 0^oC) and Q is the molar ratio of HCO_3^- to CO_2 in the solution, a value obtained from Saruhashi's tables for the pH and temperature of the experiment.

Table 2 shows the data obtained in three runs in which Q varied from 0.41 to 0.89. In all three cases the calculated $\delta_{CO_2(aq)}$ is identical to the measured $\delta_{CO_2(gas)}$ to within $\pm$ 0.5‰ or better, an excellent agreement considering the fact that the errors associated with Δ, Q and two independent sample preparations and analyses entered into the calculation.

To obtain a further check on the data presented in Table 2, one additional experiment was performed in which the pH of the solution was lowered to 5.2. At this low a pH, 96% of the carbon in solution is in the form of CO_2 and the bicarbonate fraction can be neglected for the purposes of the present experiment. In terms of equation (2) above, Q was 0.04 which made the second term negligible and $\delta_{\Sigma C(aq)} \simeq \delta_{CO_2(aq)}$. As the solubility of CO_2 at a pH of 5.2 is appreciably lower than at the pH values of the other experiments the CO_2 pressure above the solution was raised by allowing 20 cc STP of CO_2 to equilibrate with the solution instead of the usual 2.25 cc. Upon completion of the run great care was taken not to allow any of the dissolved CO_2 to escape the solution. The stopcock of the gas sample tube into which the gaseous CO_2 was being frozen was quickly closed as soon as the first bubbles appeared in the solution due to the sudden pressure drop above the solution. It is conservatively estimated that at least 99% of the gaseous CO_2 were recovered and that no more than 1% of the dissolved CO_2 escaped the solution before closing of the stopcock. The solution was then acidified to liberate the dissolved CO_2. Comparison of the volumes after purification of the gas samples showed that about 16% of the gas had gone into solution. The initial CO_2 of the experiment, comprising the total carbon involved, had a δC^{13} of -27‰. After equilibration the measured values for the gaseous and dissolved CO_2 were -26.5 and -27.1‰ respectively, again identical values within the established precision.

The experiments have shown that (a) the fractionation of carbon isotopes between atmospheric carbon dioxide and aqueous bicarbonate decreases from 9.2 ± 0.4‰ at 0°C to 6.8 ± 0.4‰ at 30°C and (b) there is no measurable fractionation between atmospheric carbon dioxide and carbon dioxide dissolved in water. In the absence of complete stagnancy equilibrium appears to be established rather quickly so that the difference in the kinetics of passage through the air-water interface between the two isotopic species $C^{12}O_2$ and $C^{13}O_2$ cannot significantly contribute to the CO_2-HCO_3^- fractionation. It may be assumed that the fractionation occurs in the hydration step where carbon bonds are rearranged and not in the dissociation though this cannot be ascertained experimentally because of the low relative abundance of the undissociated phase. One biological implication of this is that it is possible to distinguish the inorganic carbon source of aquatic plants. If the plants utilize CO_2 only, their carbon should be isotopically identical to that of air breathing plants as long as the utilization proceeds along the same paths and the CO_2 can equilibrate with the atmosphere. If a plant can utilize either CO_2 or bicarbonate depending on their relative availability, the proportion of the two will be reflected in the plant's carbon isotope content. In the extreme case of exclusive bicarbonate uptake, the plant will, depending upon mean growth temperature, be 7 to 9‰ heavier than in the case of pure CO_2 uptake. The apparent ease of equilibration and consequent insignificance of the kinetic effect in the passage of CO_2 molecules through the air-water interface also casts doubt on the reality of the postulated large kinetic effect (6) in the passage of CO_2 from the atmosphere into the plant cytoplasm during photosynthesis.

In the light of these experiments, carbon isotope differences between most fresh waters (light) and marine water (heavy) can no longer be interpreted to be exclusively a result of the large biogenic CO_2 contributions to rivers and lakes. The pH and consequently the ratio of the carbonic acid substances in solution appears to be a principal factor in determining the ultimate δC^{13} in a given water body.

W.G. Deuser

E.T. Degens

Department of Chemistry
Woods Hole Oceanographic Institution
Woods Hole, Massachusetts

1. A.F. Reid and H.C. Urey, J. Chem. Phys. 11, 403 (1943).

2. H. Craig, Geochim. Cosmochim. Acta 3, 53 (1953) and J. Geol. 62, 115 (1954).

3. P.H. Abelson and T.C. Hoering, Proc. Natl. Acad. Sci. 47, 623 (1961).

4. $$\delta C^{13} = \left(\frac{(C^{13}/C^{12})_{\text{sample}}}{(C^{13}/C^{12})_{\text{standard}}} - 1 \right) \times 1000$$

All values reported are relative to the Chicago PDB standard.

5. K. Saruhashi, Pap. Met. Geophys. Tokyo 6, 38 (1955).

6. R. Park and S. Epstein, Geochim. Cosmochim. Acta 21, 110 (1960).

7. This work was supported by NSF Grant GP 4083.

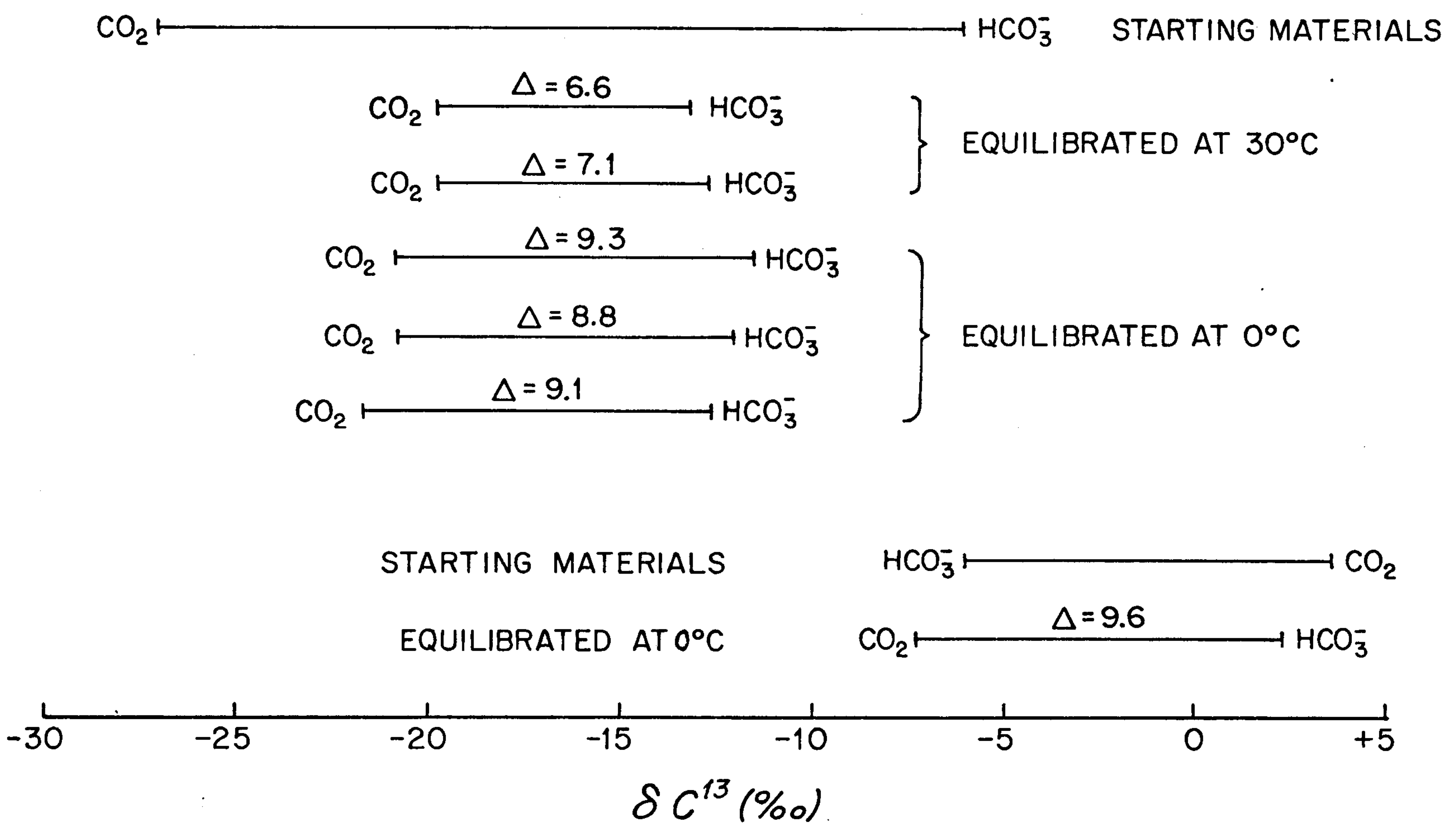

Fig. 1 Comparison of δC^{13} values of CO_2 and HCO_3^- before and after equilibration at 0 and 30°C.

Table 1. Equilibrium fractionation of carbon isotopes between atmospheric carbon dioxide and aqueous bicarbonate.

Temp. (°C)	$\Delta_{CO_2 - HCO_3^-}$ (‰)	$\bar{\Delta}$ (‰)	α (add ± 0.0003)
0	9.3	9.2	1.0093
0	8.8		
0	9.1		
0	9.6		
10	8.1	8.1	1.0084
10	8.1		
20	7.6	7.3	1.0076
20	7.0		
30	6.6	6.8	1.0069
30	7.1		

Table 2. Comparison of δC^{13} values (‰) of CO_2(gas) and CO_2(aq) in equilibrium at $0^{o}C$.

pH	Q	$^{\delta}\Sigma C$(aq) (measured)	$^{\delta}CO_2$(gas) (measured)	$^{\delta}CO_2$(aq) (calculated)	Diff.
6.53	0.89	5.7	1.6	1.2	+0.4
6.27	0.48	5.5	2.8	2.4	+0.4
6.20	0.41	5.7	2.7	3.2	-0.5