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Guanidine Hydrochloride Method for Determination of Water Oxygen Isotope Ratios and the Oxygen-18 Fractionation between Carbon Dioxide and Water at 25 °C

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A technique utilizing guanidine hydrochloride has been used to determine $^{18}O/^{16}O$ ratios in water. These O-isotope ratios have been considered in conjunction with $^{18}O/^{16}O$ ratios obtained from equilibration of CO_2 with surplus water to obtain a value for the carbon dioxide–water fractionation factor at 25 °C of 1.04143 ± 0.00032 (99% confidence interval). This determination of $\alpha CO_2\text{-}H_2O$ falls within the range of values cited in the literature.

Advances in the state of gas-source, isotope-ratio mass spectrometry and the need for precise stable isotope data to address problems in geochemistry necessitate the measurement of equilibrium fractionation factors to five significant figures. Values of the $CO_2\text{-}H_2O$ fractionation factor ($\alpha CO_2\text{-}H_2O$) published in the literature span the range from 1.0406 (1) to 1.0424 (2). Other values reported include 1.0407 (3), 1.0409 (4), 1.0412 (5–8), 1.0414 (9, 10), 1.0416 (11), and 1.0417 (12, 13) with a value of 1.04115 discussed by the Advisory Group Meeting on Stable Isotope Reference Samples for Geochemical and Hydrological Investigations convened in September 1983, by the International Atomic Energy Agency, Vienna (14). This value has been questioned by Coplen et al. (15) on the basis that most of the data used to calculate the $\alpha CO_2\text{-}H_2O$ value had not been normalized to the V-SMOW/V-SLAP scale and that controversy remained over the fourth significant figure. Coplen et al. (15) discussed normalization to a per mill (‰) scale in which $\delta^{18}O$ V-SLAP $= -55.5$‰ relative to V-SMOW (0‰).

The fractionation factor $\alpha CO_2\text{-}H_2O$ is defined as

$$\alpha CO_2\text{-}H_2O = \frac{(^{18}O/^{16}O)_{CO_2}}{(^{18}O/^{16}O)_{H_2O}} = \frac{1000 + \delta_{CO_2}}{1000 + \delta_{H_2O}} \quad (1)$$

The 1.8‰ variation reported for $\alpha CO_2\text{-}H_2O$ values (from 1.0406 to 1.0424) has significant consequences to problems where an accuracy of better than 0.2‰ may be required. For example, the exact value of $\alpha CO_2\text{-}H_2O$ has important implications for estimations of fluid isotopic compositions or temperatures in paleoclimate, sedimentary diagenetic, and ore deposit studies. Measurements made at the Southern Methodist University stable isotope laboratory have given a value for $\alpha CO_2\text{-}H_2O$ of 1.04143 ± 0.00032 (99% confidence interval). Water samples were analyzed by the common technique of equilibrating CO_2 with H_2O (16) whose ^{18}O content was first determined by reaction of a separate aliquot with guanidine hydrochloride (17). In previous work, the O-isotopic composition of the water either was assumed or was analyzed directly by reaction with BrF_5, according to the technique developed by O'Neil and Epstein (5). O'Neil, et

al. (7) have obtained a value for $\alpha CO_2\text{-}H_2O$ or 1.0412 using this latter technique.

Suzuoki and Itoh (18) have equilibrated water vapor and CO_2 with a heated platinum wire as a catalyst (19). Kishima and Sakai (20) have improved on the method of Suzuoki and Itoh (18) by the development of the micro CO_2-water equilibration (MCE) technique which is less complex and more adaptable to water samples of variable size. Most recently, Brenninkmeijer et al. (21), expanding on the work of Brenninkmeijer and Mook (22), have obtained a value for $\alpha CO_2\text{-}H_2O$ of 1.04111 ± 0.00007. This method involves the oxygen component of water being converted to CO_2 by reaction with carbon in graphite, polystyrene, or polyethylene in a nickel bomb at 950 °C for a period of 9–14 min.

EXPERIMENTAL SECTION

In this study we have determined the starting isotopic composition of the waters used by the guanidine hydrochloride technique. Samples of water were reacted with guanidine hydrochloride, a process in which the water oxygen is quantitatively converted to CO_2. In this technique, a modified form of which has been described by Viglino et al. (17), borosilicate glass tubes 8 mm in diameter, 1 mm in wall thickness, and 200 mm in length are sealed at one end and annealed at 565 °C to relieve residual stress. A 100-mg quantity of guanidine hydrochloride, NH_2C: $(NH)NH_2 \cdot HCl$, which satisfies the purity standards established by Wong et al. (23), is loaded into each tube. The loaded tubes are then placed in a drying oven at 110 °C until needed.

For a sample analysis, a tube is connected by a vacuum fitting to a capillary tube-cracking assembly containing a 10-μL water sample sealed in a capillary tube. This assembly is attached to a standard vacuum line and evacuated to $<10^{-5}$ mbar pressure. Any residual water or atmospheric contaminants are removed by melting the guanidine hydrochloride reagent while pumping under vacuum. After cooling to room temperature, the lower 10 mm of the reagent tube is immersed in liquid nitrogen, the main vacuum valve is closed, and the capillary is broken releasing the water sample which freezes in the reaction tube at -196 °C. The liquid nitrogen trap is replaced with a dry ice–acetone trap and any noncondensable gases present are pumped away. The loaded reaction tube is then sealed while pumping by carefully heating in a 10 mm area at the top to collapse the glass and yield a sealed tube $\simeq 150$ mm long. The loaded tubes may be stored indefinitely in this condition. The tubes are next heated in an oven at 260 °C for 8–10 h allowing the water to react with the guanidine hydrochloride to produce ammonia and carbon dioxide by the reaction

$$NH_2C\text{:}(NH)NH_2 \cdot HCl + 2H_2O \xrightarrow{260\ °C} 2NH_3 + CO_2 + NH_4Cl \quad (2)$$
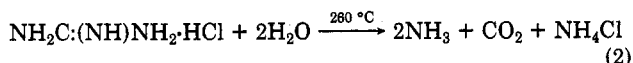
When cooled below 70 °C, the gases combine to produce solid ammonium carbamate by the reaction

$$2NH_3 + CO_2 + NH_4Cl \underset{<70\ °C}{\overset{>70\ °C}{\rightleftharpoons}} NH_4NH_2CO_2 + NH_4Cl \quad (3)$$
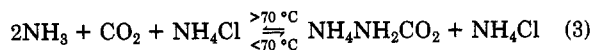
Table I. $\delta^{18}O$ Values Obtained Using the Guanidine Hydrochloride Technique[a]

	V-SMOW	V-SLAP
batch 1	−0.11	−55.59
	+0.05	−55.37
	+0.07	−55.30
batch 2	−0.08	−55.33
	−0.12	−55.51
	−0.02	−55.30
batch 3	+0.20	−55.73
	−0.01	−55.50
	−0.02	−55.48
batch 4	−0.07	−55.60
	+0.11	−55.69
	0.0	−55.53
mean, std dev	−0 ± 0.08	−55.50 ± 0.12

[a] Results expressed in ‰ relative to V-SMOW = 0 and V-SLAP = −55.5.

Table II. Comparison of $\delta^{18}O$ Values of Geothermal Waters from the Guanidine Hydrochloride Technique with Those Obtained from Equilibration[a]

water sample	guanidine hydrochloride technique	equilibration[b] technique 1	equilibration[c] technique 2
1	−22.96	−22.95	
2	−82.66	−82.49	
3	−2.27	−2.02	
4	+2.50	+2.50	
5	+1.28	+1.47	
6	+8.84	+8.83	
7	+2.82	+2.90	
8	+1.00	+1.06	
lab std 1	−3.83	−3.90	
lab std 2	−12.79	−12.80	
9	+2.26		+2.29
10	+2.11		+2.11
11	+3.20		+3.32
12	+2.65		+2.57
13	+2.99		+3.07
14	+3.02		+2.72
15	+2.52		+2.85
16	+3.08		+3.10
17	+2.94		+3.02
18	+2.92		+2.85

[a] Results expressed in ‰ relative to V-SMOW = 0 and V-SLAP = −55.5. [b] 4 mL of H_2O + 13.1 mmol of CO_2, acidified with 100% H_3PO_4, equilibrated at 25 °C for 4 days without shaking. [c] 5 mL of H_2O + 100 mmol of CO_2 acidified with 100% H_3PO_4, equilibrated at 25 °C for 4 days without shaking.

The tubes may also be stored indefinitely in this condition.

Finally, the CO_2 is extracted from the reaction tube by placing the tube, which has been scored to facilitate cracking, together with 0.5 mL of 100% H_3PO_4 in a simple evacuated tube-cracking assembly composed of a 28/12 ball joint and a greaseless "O"-ring stopcock. The main vacuum valve is closed and the ball joint is flexed, breaking the tube. The assembly is removed from the vacuum line and placed in an oven at 80 °C for 1 h. The ammonium carbamate decomposes to NH_3 and CO_2. The NH_3 reacts with the phosphoric acid to produce ammonium phosphate. The reactions occurring during the second stage of the procedure are

$$NH_4NH_2CO_2 + NH_4Cl \xrightarrow[80\,°C]{H_3PO_4} CO_2 + NH_4Cl + (NH_4)_3PO_4$$

(4)
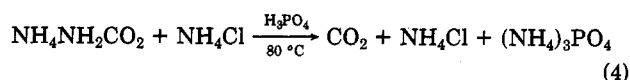
After cooling, the assembly is attached to the vacuum line and the CO_2 purified by passage through two dry ice–acetone traps at −80 °C and collected for mass spectrometric analysis. Residual

Table III. Fractionation Factors for CO_2–H_2O Obtained from Equilibration and Measured δ Values for Each Species (Mass 46)

	δ_{corr}[a]	δ_{PDB-CO_2}[b]	δ_{norm}[c] (V-SMOW/V-SLAP)
Run 1 ($\rho = 548.11$, $\delta_c = 39.794$)			
CO_2 after equilibration (δ_m)	2.71	−1.67	39.74
CO_2 before equilibration (δ_t)	−24.64	−28.90	11.38
H_2O after equilibration	−36.94	−41.15	−1.37
αCO_2–H_2O			1.04116
Run 2 ($\rho = 876.92$, $\delta_c = 37.090$)			
CO_2 after equilibration (δ_m)	0.13	−4.24	37.06
CO_2 before equilibration (δ_t)	−24.62	−28.88	11.40
H_2O after equilibration	−39.72	−43.92	−4.26
αCO_2–H_2O			1.04150
Run 3 ($\rho = 879.82$)			
CO_2 after equilibration (δ_m)	0.212	−4.16	37.15
CO_2 before equilibration (δ_t)	−21.77	−26.04	14.36
δ_c(calcd)	0.24	−4.13	37.17
H_2O before equilibration	−39.64	−43.84	−4.18
αCO_2–H_2O			1.04153
Run 4 ($\rho = 879.82$)			
CO_2 after equilibration (δ_m)	−20.66	−24.94	15.51
CO_2 before equilibration (δ_t)	−21.65	−25.93	14.48
δ_c(calcd	−20.66	−24.94	15.51
H_2O before equilibration	−59.86	−63.97	−25.15
αCO_2–H_2O			1.04170
Run 5 ($\rho = 606.78$)			
CO_2 after equilibration (δ_m)	2.25	−2.13	39.26
CO_2 before equilibration (δ_t)	−21.65	−25.93	14.48
δ_c(calculated)	2.29	−2.09	39.30
H_2O before equilibration	−37.69	−41.89	−2.15
αCO_2–H_2O			1.04154
Run 6 ($\rho = 606.78$)			
CO_2 after equilibration (δ_m)	2.79	−1.59	39.82
CO_2 before equilibration (δ_t)	−21.65	−25.93	14.48
δ_c(calculated)	2.83	−1.55	39.87
H_2O before equilibration	−36.89	−41.10	−1.32
αCO_2–H_2O			1.04124

$$\overline{\alpha}_{CO_2-H_2O} = 1.041\,43 \pm 0.000\,197$$

[a] δ_{corr} is the raw data corrected for machine effects and effects of ^{13}C and ^{17}O. [b] δ_{PDB-CO_2} is the data normalized to Peedee Formation Belemnite carbon dioxide. [c] δ_{norm} is the data normalized to V-SMOW/V-SLAP.

gas pressure after freezing is typically less than 5×10^{-3} mbar.

The equilibration technique, originated by Cohn and Urey (16) and perfected by Epstein and Mayeda (24), was then employed to determine the fractionation factor α between CO_2 and water using the isotopic composition of the starting water obtained by

the above technique. The fractionation is measured in per mill expressed in the δ notation as

$$\delta = \frac{R_{sample} - R_{standard}}{R_{standard}} \times 1000 \qquad (5)$$

where R is the ratio of the heavy to the light isotope. At 25 °C, or any constant temperature, the factor α cancels in the δ notation when expressing the isotopic composition of water samples with respect to a water standard such as SMOW, Craig (25). This is not the case, however, for waters having undergone isotope exchange with minerals. The isotopic composition of standard V-SMOW (Vienna-Standard Mean Ocean Water) is by definition zero (14). The standard V-SLAP (Vienna-Standard Light Antarctic Precipitation) was defined as −55.5‰ by Gonfiantini (26). Both standards are distributed by the International Atomic Energy Agency, Vienna, and the National Bureau of Standards, Washington.

RESULTS AND DISCUSSION

The water samples used were distilled waters. The capillary sample tubes were prepared in four batches. As a check to ensure that the sealing process of the tubes did not cause fractionation of the sample, representatives from each batch were measured for D/H relative to the mass spectrometer working standard. This check yielded δD values with reproducibilities of <1‰, indicating the sealing process did not cause any isotope fractionation of the water.

Accepting that the capillary tubes were properly prepared, we then measured the δ values of distilled water, V-SLAP, and V-SMOW by the guanidine hydrochloride technique. The results of the standards are listed in Table I. The data are grouped by runs and indicate the high reproducibility of results. It is necessary to heat the reaction tube for 8–10 h to ensure reaction. We have adopted a heating time of 16 h as a convenience for laboratory routine. All tubes must be heated for exactly the same time period, removed from the oven while still at 260 °C, and cooled rapidly to prevent the formation of large crystals which may occlude CO_2 and cause problems with incomplete yields. We observe the precision of $^{18}O/^{16}O$ ratios by this technique for uniform heating/cooling cycles to be within ±0.078‰ with a standard deviation of 0.032. The precision of this technique is demonstrated in Table II by a group of 18 geothermal waters analyzed by both the guanidine hydrochloride technique and the equilibration method.

The fractionation factors obtained from the equilibration of ∼1.6 mmol of CO_2 with ∼550 mmol of water are listed in Table III. Two of the water $^{18}O/^{16}O$ ratios after equilibration were determined by the guanidine hydrochloride technique and αCO_2–H_2O calculated from eq 1.

We have corrected for the oxygen in the CO_2 in runs 3–6 by using the formula of Craig (27)

$$\delta_c = \delta_m \left(\frac{\rho + \alpha}{\rho}\right) - \left(\frac{\alpha}{\rho}\right)\delta_t \qquad (6)$$

All quantities are given with respect to the same reference gas and same M/S where δ_m is the measured δ^{18} of CO_2 in equilibration vessel after equilibration, δ_c is δ^{18} of CO_2 in equilibrium with the original H_2O before isotopic exchange,

$\alpha = {}^{18/16}CO_2/{}^{18/16}H_2O$ at 25 °C, $\delta_t = \delta^{18}$ of CO_2 used prior to equilibrium, and ρ is the gram-atom ratio of oxygen in the H_2O to that of the CO_2 (in the equilibration vessel). The fractionation factor is calculated from eq 6

$$\alpha = \frac{\rho(\delta_c - \delta_m)}{(\delta_m - \delta_t)} \qquad (7)$$

The data have been corrected to the line defined by V-SMOW = 0 and V-SLAP = −55.5 as recommended by the IAEA (14).

CONCLUSIONS

A value of 1.041 43 ± 0.000 32 (99% confidence interval) has been determined for the fractionation of oxygen isotopes between CO_2 and H_2O at 25 °C by a technique utilizing guanidine hydrochloride for water oxygen isotope ratio determinations. Measurements of water $^{18/16}O$ ratios made with this method have a precision within ±0.078‰ with a standard deviation of 0.032.

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