A Method for Oxygen Isotope Analysis of Milligram Quantities of Water and Some of Its Applications[1]

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A method has been developed by which bromine pentafluoride and small amounts of water are reacted in a nickel vessel at 80°C to liberate oxygen in 100% yield. The oxygen is converted to CO_2, which is analyzed on an isotope ratio mass spectrometer. The oxidation reaction takes place instantaneously, and the conversion of the liberated O to CO_2 requires approximately 15 minutes. There are no measurable memory effects in the method and the reproducibility is $\pm 0.1\permil$. A value of 1.0407 was determined for the CO_2-H_2O fractionation factor at 25°C, a number necessary for relating standards in use by various workers. This value is in exact agreement with that obtained by Compston and Epstein in the same laboratory using a reduction technique but is in serious disagreement with values determined by other workers. An application of this technique has been made to the study of a meteorological problem.

INTRODUCTION

There are many problems of chemical, geochemical, biological, and meteorological interest in which only milligram quantities of water are available for oxygen isotope analysis. A few methods of O^{18} analysis of small amounts of water have been reported [e g., *Boyer et al.,* 1961], but they are applicable only to tracer studies involving O^{18}-enriched material. In many studies involving waters of normal isotopic abundance it is desirable to determine differences to better than $\pm 0.2\permil$. Differences in O^{18}/O^{16} ratio of water samples can be determined very precisely by equilibrating CO_2 with the waters at some temperature and analyzing the equilibrated CO_2 mass spectrometrically [e.g., *Epstein and Mayeda,* 1953]. Between 0.5 and 30 ml of liquid water has been used in these equilibrations. In addition to the inability to analyze milligram amounts of water, the CO_2 equilibration technique suffers from the fact that a large CO_2-H_2O fractionation factor (which is not accurately known) must be applied to the O^{18}/O^{16} ratio determined in this way when comparing it with another O^{16}/O^{16} ratio of a non-water phase.

Compston and Epstein [1958] developed a technique in which water vapor was introduced to a furnace charged with a graphite-iron powder mixture. At 500°C the iron reacted with the water, forming iron oxide and hydrogen gas. After removal of the hydrogen the temperature was raised to 950°C, which resulted in the production of CO. The CO was then converted to CO_2 over a nickel catalyst. Time-consuming problems of degassing and recycling and the kinetics of some of the reactions make this technique impractical for routine analyses of large numbers of water samples. There is also a rather large memory effect in the method. By memory we mean that the isotopic composition of a sample reflects a contamination (of the order of a few per cent) from the sample previously run in the apparatus. Consequently, a sample has to be run two or more times for an accurate analysis or a comparatively large sample has to be run to overcome this effect.

Majzoub [1966] used the more direct water-gas reaction in analyzing milligram quantities of water for O^{18} content. In this method water vapor is reacted with graphite at a temperature of between 1100°C and 1200°C to obtain CO and H. Hydrogen is removed by diffusion through a palladium tube and the CO is converted to CO_2 over a nickel catalyst. A complete conversion of a 4-mg sample of water to CO_2 takes only 45 minutes. Although repro-
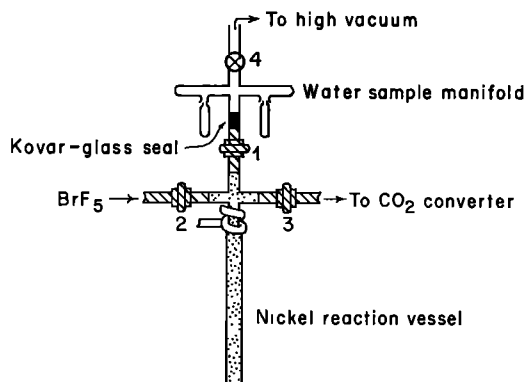
Fig. 1. Apparatus for reacting BrF_5 and small amounts of H_2O.

ducibility is good and reaction times are short, the method has a large memory effect associated with the catalytic conversion to CO_2, and three analyses are often necessary to obtain the correct value.

EXPERIMENTAL PROCEDURE

In the method reported here, water vapor is reacted with bromine pentafluoride[3] according to the reaction

$$BrF_5 + H_2O \rightarrow BrF_3 + 2HF + \tfrac{1}{2}O_2$$

Hoekstra and Katz [1953] developed a method of determining total oxygen in metal and metalloid oxides by reaction with BrF_3, and BrF_5 has been used in the liberation of oxygen from minerals for isotopic analysis [*Clayton and Mayeda*, 1963]. When the reactants are brought together in a translucent Kel-F reaction vessel, the reaction is seen to take place explosively with the production of a red liquid, presumably bromine. With time the bromine is oxidized to bromine trifluoride by the excess bromine pentafluoride. Although reaction takes place at room temperature, erratic yields and isotopic compositions are obtained. At higher temperatures (a minimum has not been established) these problems are eliminated. Most likely such things as metastable oxy-halogen compounds, ozone, and hydrogen peroxide are formed at

room temperature which cannot exist at higher temperatures. More than 200 samples were analyzed in a furnace arbitrarily set at 150°C; however, it was later discovered that flaming the reaction vessel for a couple of minutes was sufficient to produce oxygen in 100% yield.

One of the most difficult aspects of these analyses is bringing the reactants together without altering the amount and isotopic composition of the water sample. Figure 1 illustrates the apparatus used in this study. Valves 1, 2, and 3 are ball valves (Whitey Corp.) made of stainless steel with a Teflon packing. Valve 4 is an ordinary 4-mm high-vacuum glass stopcock. All metal parts are joined together with Swagelock fittings. After evacuation of the system, valves 2, 3, and 4 are closed, and a Dewar flask containing liquid nitrogen is placed around the nickel reaction tube so as to bring the liquid level about half-way up the tube. The water sample is then transferred (see below) to the nickel tube. Five to ten minutes is usually allowed for transfer. The system is then pumped (by opening valve 4) to remove any air contained in the water sample. The liquid nitrogen level is raised and, with valves 1 and 3 closed, a measured amount (3 to 4 times stoichiometric) of BrF_5 is condensed in the higher part of the reaction vessel on opening valve 2. When transfer is complete valve 2 is closed and the reaction vessel is gas-flamed (to a temperature of around 80–100°C) for a few minutes. After cooling, the products are taken out of the reaction zone through valve 3 and passed over liquid nitrogen traps where everything but the oxygen is trapped. The oxygen is then converted to CO_2 over a heated carbon rod.
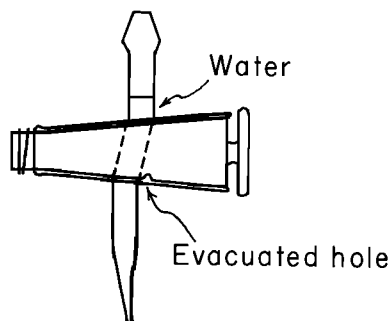
Fig. 2. Modified high-pressure stopcock used to deliver water samples into the reaction zone.

Particular attention should be paid to valve 1. If ever it should be opened in the presence of BrF₅ the metal parts which normally are not in the reaction zone will be fluorinated. The metal fluoride is quite hygroscopic, and some water vapor would be removed on transfer and not be reacted. This would be a serious problem if very small samples were being analyzed.

Two different methods for introducing water have been used. In one method use is made of a modified high-pressure glass stopcock (Figure 2) which has been used in this laboratory in sampling small amounts of water for hydrogen isotope analysis. A tiny hole (approximately 0.02 cm^3 volume) has been drilled in the solid plug at such a position that it can be evacuated through the portion connected to the standard taper but sealed at all other positions. After evacuation the stopcock is removed from the vacuum line and water is drawn into it to the position shown in Figure 2. The stopcock is then turned so that the hole is filled with a sample of the water. The stopcock is then drained, air dried, and attached to the manifold shown in Figure 1. The hole can be made in a number of sizes, and, although somewhat time consuming, this method of securing small amounts of water eliminates the possibility of altering the water in any way.

Another method commonly used in determining D/H ratios of small amounts of water is to seal off the water samples in capillary tubing. The tubing can then be broken in a variety of ways to release the water into the vacuum system. Care must be taken to prevent loss of water by evaporation during the

TABLE 1. Tests for Memory Effects in the Method

Sample	δ Value	Average δ Values	
95–Water–4	−35.85		
96–Water–7	+5.75	Water–2	+1.20 (7)*
97–Water–4	−36.15		
98–Water–4	−36.25	Water–3	−11.96 (6)
99–Water–3	−12.06		
100–Water–3	−12.08	Water–4	−36.02 (9)
101–Water–2	+1.16		
102–Water–2	+1.18	Water–7	+5.62 (6)
103–Water–7	+5.69		
104–Water–7	+5.57		

* Number of preparations.

TABLE 2. Results of Test on the Reproducibility of the Method

δNBS–1*	δWater–4†
−32.11	−36.02
−31.99	−35.95
−31.99	−35.85
−31.89	−36.15
−32.11	−36.15
	−36.25
Average −32.01 ± 0.07	−35.82
	−36.07
	−35.95
	Average −36.02 ± 0.12

* Analyses completed within a 2-day period. The corrected δ values are relative to the Caltech working standard.

† Analyses made at various times during a period of several months.

sealing of the tube because the consequent isotopic fractionation on volatilization will result in a faulty analysis.

The stopcock arrangement has been used for most of the analyses; however, it was necessary to use capillaries to demonstrate stoichiometry. Water samples of from 5 to 30 mg were put into weighed capillaries. The exact weight of the sample was then determined by weighing the capillary after sealing. CO_2 yields of 99 ± 2% were obtained.

To demonstrate that no fractionation effects were inherent in the method, a large sample of water of known isotopic composition was prepared. Eighteen grams of water was obtained from the reduction of a weighed sample of CuO with excess hydrogen gas in a Pyrex vessel heated to 300°C. The water yield was good (not measured accurately), and the effect of possible exchange with the glass walls was minimal owing to the large amount of water prepared. Five analyses of the CuO using both F₂ and BrF₅ to liberate the oxygen gave an average δ value[4] of −6.5 ± 0.2‰. The CuO was quite unreactive to fluorination because of armoring of the grains by CuF_2, and, although the oxygen yields varied from 30 to 87%, the isotopic composition was constant. Two analyses of the water with BrF₅ gave a δ value of

$$\text{4} \quad \delta_x = \left[\frac{(O^{18}/O^{16})_x}{(O^{18}/O^{16})_{std}} - 1 \right] 10^3$$

−6.7 ± 0.1‰. Analyses of the two National Bureau of Standards waters by *Craig* [1961] using the CO_2-equilibration technique showed NBS-1 to be 16.8‰ relative to NBS-1A. The same difference determined with the BrF_5 reaction is 16.7‰.

Memory effects were tested by analyzing, consecutively, water samples differing in O^{18}/O^{16} ratio by more than 40‰. In Table 1 the δ values of ten consecutive runs are listed. Samples 95 to 97 indicate that there is no measurable memory effect. It is seen that the analysis of Water-7 run after Water-2 (4.4‰ different) agrees with the analysis of Water-7 run after Water-4 (41.6‰ different). Further, from sample 97 on, each sample was run twice, in order, and the second analysis (which would have a negligible memory in any case) agrees with the first. This lack of memory gives this method a considerable advantage over the others described. Although it is always preferable to analyze a sample more than once, occasionally only enough material for one analysis is available; in those cases the BrF_5 reaction will give the more reliable result. The reproducibility of the method is ±0.1‰ (Table 2).

THE CO_2-H_2O FRACTIONATION FACTOR AT 25°C AND THE SMOW STANDARD

Most analyses of the oxygen isotopic composition of waters reported in the literature have been made using the CO_2-equilibration technique. Because of the extreme precision and ease of the method, it will undoubtedly continue to be the method of choice when large enough samples are available. To relate these analyses to analyses of other oxygen-containing phases, the CO_2-H_2O fractionation factor at 25°C (the usual equilibration temperature) must be applied. An accurate determination of this fractionation factor also allows a relationship to be made between standards in use by various workers (see *Clayton and Mayeda* [1963] for discussion).

The 'average ocean water' of *Epstein and Mayeda* [1953] has been proposed as a standard for reporting variations in the O^{18} content of meteoric waters [*Craig*, 1961]. This same standard is the logical one to use in reporting the oxygen isotope variations of rocks and minerals. Although there is no sample of standard

TABLE 3. Determination of the CO_2-H_2O Fractionation Factor at 25°C

Sample	δCO_2	δH_2O	α
Water–2	+41.62	+0.87	1.04071
NBS-1	+7.49	−32.01	1.04081
Water-4	+3.14	−36.02	1.04066
NBS-1A	−9.07	−47.78	1.04073

Note. Average α = 1.04073 ± 0.00005.

mean ocean water (SMOW) in existence, Craig has defined its O^{18} content in terms of a National Bureau of Standards water sample:

$$O^{18}/O^{16} \text{ (SMOW)} = 1.008 \ O^{18}/O^{16} \text{ (NBS-1)}$$

To relate his analyses to the SMOW standard by this definition, a worker has either to analyze NBS-1 directly by a method such as described in this paper or to equilibrate it with CO_2 and apply the CO_2-H_2O fractionation factor. Also, with a knowledge of this fractionation factor, many substandards now in use can be related to the ocean water standard.

Taylor and Epstein have reported analyses of rocks and minerals relative to Hawaiian ocean water by defining a sample of Potsdam sandstone to be +15.5‰ on the basis of analyses by *Silverman* [1951]. With the direct analysis of NBS-1 water now possible, the Potsdam sandstone substandard can be related to SMOW. This value is +15.6, a value so close to the defined value that the δ values previously reported relative to this standard are essentially the same relative to the SMOW standard.

A determination of the CO_2-H_2O fractionation factor at 25°C was made during the course of this work (Table 3). The δ values listed are relative to the Caltech working standard and corrected for valve mixing, background, tail, and C^{13} content according to the equations of *Craig* [1957]. Several waters over a large range of isotopic composition were equilibrated with CO_2, and the same water samples used in the equilibrations were then analyzed directly with BrF_5. The CO_2 sample and H_2O sample of each set were run consecutively on the mass spectrometer to obviate any machine changes that might occur with time. In terms of δ values the CO_2-H_2O fractionation factor is

$$\alpha = \frac{1 + \delta CO_2/1000}{1 + \delta H_2O/1000} = \frac{(O^{18}/O^{16})CO_2}{(O^{18}/O^{16})H_2O}$$

In addition to the data presented in Table 3, five H_2O samples prepared and analyzed at the California Institute of Technology were reanalyzed in the laboratory of H. Craig at the University of California at San Diego as an independent check of this fractionation factor. Three of the samples were standards for which Craig had analyses of equilibrated CO_2, and the remaining two equilibrated CO_2 samples were prepared at the California Institute of Technology. At this time the BrF_5 reactions were not run under optimum conditions; however, the value of the fractionation factor determined under these conditions was 1.0406 ± 0.0002, which is in agreement with the result listed in Table 3.

The high precision of the experimental results does not necessarily mean that the equilibrium fractionation is known with the same accuracy. It has been shown repeatedly by many workers that the *Nier* [1947] mass spectrometer as modified by *McKinney et al.* [1950] is capable of determining δ values routinely to a precision of ±0.1‰ or better for small absolute values of δ. However, when measurements of δ values of 40‰ are involved, the ±0.1‰ precision can no longer be a certainty because

any changes in the 46/44 ratio which are not related to the correct 46/44 ratio by a factor will cause changes in the δ values. Additive changes, such as those that can be caused by background impurities and by secondary electrons entering the ion beam collectors, will alter the δ value. Thus a 1% error in the 46/44 ratio can cause a maximum error in δ of ±1%. In this case, where the difference in δ values between CO_2 and H_2O is approximately 40‰, the error is best given as ±0.4‰ or ±0.0004 for the fractionation factor.

There are now four determinations of this constant in the literature: (1) 1.0407 [*Compston and Epstein*, 1958], (2) 1.0424 [*Staschewski*, 1964], (3) 1.0417 [*Majzoub*, 1965], and (4) 1.0407 (this work). Staschewski did not analyze water directly but prepared a sample from oxygen gas of known isotopic composition and equilibrated CO_2 with it. The isotopic composition of the oxygen gas was determined after converting it to CO_2 over graphite in a quartz glass vessel heated to 700°C. Exchange of either O_2 or CO_2 with the glass under these conditions is probable, and his value for the water may be in error. Compston and Epstein used the same mass spectrometer as was used in this work. The fact that these two agree and yet are in serious disagreement with the others suggests that the differences can be due at least

TABLE 4. Oxygen Isotopic Compositions of Water Vapor and CO_2 at Pasadena during Passage of a Cold Front Storm

Date	Time	Air Temperature, °C	δH₂O (vapor)	δH₂O (liquid)	δCO₂
		Prestorm			
Oct. 23	0000	18.0	−14.3		+37.6
Oct. 26	1630	16.7	−14.6		+36.2
Oct. 30	1650	20.5	−14.6		+37.0
		Storm			
Nov. 16	2200	9.0	−16.7		
Nov. 17	1530	8.5	−20.7	−9.2	
Nov. 18	0000	5.0	−23.3		+37.7
		Poststorm			
Nov. 19	1500	17.5	−23.2		+37.7
Nov. 19	1500	17.5	−23.5		
Nov. 20	2000	12.0	−21.2		+36.4
Nov. 21	2200	15.0	−19.5		+36.5
Nov. 26	1400	16.0	−14.6		

Note. δ values are relative to SMOW.

in part to the mass spectrometers. Until absolute standards are available to calibrate the mass spectrometers properly, these discrepancies cannot be resolved.

O^{18} VARIATIONS DURING PASSAGE OF A METEOROLOGICAL FRONT

The method of analysis was applied to the study of the O^{18} variations in water vapor, rain, and CO_2 during the passage of a cold front over Pasadena, California, beginning November 16, 1964. Samples of air were collected by opening evacuated flasks which were at the air temperature. Flasks of either 1-, 2-, or 5-liter size were chosen in accordance with the relative humidity at the time of sampling in an attempt to secure between 10 to 20 mg of water vapor. CO_2 and water vapor were removed from the air by slowly passing the sample over a large trap held at liquid nitrogen temperature. The CO_2 was then separated from the water vapor by replacing the liquid nitrogen trap with a dry-ice trap. The CO_2 was run on the mass spectrometer without further purification, and the water vapor was reacted with BrF_5 and converted to CO_2 for mass spectrometric analysis. As a reproducibility check, a 1-liter and a 5-liter flask were opened simultaneously on November 19, 1964. The CO_2 yields were 98 and 485 μmoles, respectively, and the δ values agreed to within 0.3‰ (see Table 4).

The data in Table 4 indicate a rather constant value for the isotopic composition of atmospheric water vapor before the cold front arrived. During the passage of the storm the atmospheric vapor became progressively lighter in O^{18} up to a value of -23.5‰, which appears to be the value for the vapor in the cold air mass. Subsequent samples showed that the cold air mass was swept away and replaced by an air mass with vapor isotopically similar to that of the prestorm water vapor. There is little doubt that the isotopic composition of the vapor in the warm air mass was markedly different from that of the cold air mass, but it is possible that the cold air vapor was simply re-evaporated rainwater and not at all characteristic of arctic air.

The mechanisms involved in determining the isotopic composition of atmospheric vapor over an area cannot be elucidated by a single series of samples, and many of the questions raised could be answered by studying atmospheric vapor in several areas. It is clear that the isotopic composition is quite variable, and it should be possible to obtain a considerable amount of information concerning air mass movements and the relationships between factors which determine the δ values of water vapor in the atmosphere. Further conjectures based on such limited data would be fruitless.

Throughout the entire passage of the storm, the O^{18} content of atmospheric CO_2 did not vary more than 1.5‰. The average δ value of 37‰ indicates that the CO_2 is nearly the value expected for isotopic equilibrium with ocean water. The δ value for CO_2 did not vary sympathetically with the δ value of the water vapor. Rain collected on November 17, 1964, was 11.5‰ heavier than the vapor when the air temperature at the time of sampling was 8.5°C. Therefore the equilibrium between water vapor and liquid water seems to be established very rapidly. More samples of simultaneously collected water vapor and rain would have to be analyzed before this statement could be considered certain.

It is not our intention at this time to correlate the isotopic effects observed with the various meteorological parameters in operation. We merely show here that a simple technique is available for obtaining meaningful oxygen isotope data in a meteorological system.

SUMMARY

A rapid and precise technique has been developed to analyze milligram amounts of water for oxygen isotopic content by reaction with BrF_5. Because there is no measurable memory effect, the method is more reliable than those proposed by others if only enough material for one analysis is available. The CO_2-H_2O fractionation factor at 25°C was determined to be 1.0407 ± 0.0004. If the CO_2-equilibration technique is used in analyzing water samples, this number is necessary in relating O^{18} analyses of rocks and minerals to the ocean water standard (SMOW). Atmospheric water vapor can easily be sampled for O^{18} content by opening small evacuated flasks, separating the vapor by trapping at liquid nitrogen temperature, and reacting it with BrF_5.

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