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Conversion of O₂ into CO₂ for High-Precision Oxygen Isotope Measurements

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An improved procedure of $^{18}O/^{16}O$ ratio measurements by means of oxygen conversion to CO_2 is developed, which allows one to obtain the true $\delta^{18}O$ values with a precision of ±0.05‰ in oxygen samples down to 7 μmol. The isotopic exchange between quartz glass and oxygen gas was measured in the temperature range of 600−900 °C, and it was found to be less than 0.2%.

The isotopic composition of oxygen (or the $^{18}O/^{16}O$ ratio expressed as $\delta^{18}O$) is one of the most important characteristics of different biogeochemical processes.[1-5] The ratio $^{18}O/^{16}O$ is commonly determined mass spectrometrically in the chemical form CO_2 by measuring the $46/(44 + 45)$ mass ratios.[6] This technique includes the conversion of O_2 into CO_2, which can be a source of considerable errors in obtained results.[7] Some aspects of this process were considered by Taylor and Epstein,[7] Kroopnick,[8] Bender and Grande,[9] and more recently Mattey and Macpherson.[10] An examination of these and other published works as well as our own investigations show that (1) it is practically impossible to reach a 100% CO_2 yield owing to CO production, although this can be usually suppressed by using Pt catalysts and optimizing the operating conditions of the conversion reaction; (2) the errors caused by CO production can reach 0.3‰ and higher; (3) there is not one single accepted opinion about the optimal conditions of the oxygen conversion; and (4) the $\delta^{18}O$ values obtained for the small samples (<20 μmol) are systematically and considerably lower then the values obtained for the large ones, and the smaller the samples the greater are the differences.

At present in more and more cases we need a precision in $\delta^{18}O$ data of 0.1% and better. Moreover, the development of laser ablation techniques allows analysis of small samples of silicates, phosphates, oxide minerals, etc., and therefore a high-precision procedure for conversion of small oxygen samples is necessary. The same problem is faced in the study of oxygen isotope ratios of dissolved oxygen in high-saline waters, where the oxygen content is 20 μmol/L and lower.[11] Therefore, we have investigated in detail the oxygen conversion reaction and the isotope fractionation effects associated with different processes and developed a procedure to obtain high-precision $\delta^{18}O$ data.
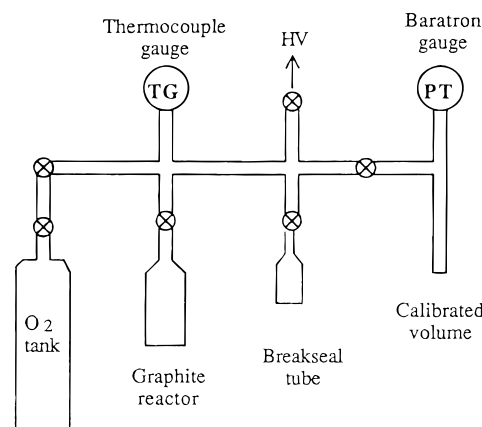
(1) Craig, H. *Stable isotopes in oceanographic studies and paleotemperatures*; Tongiorgi, E., Ed.; Pisa, 1965; pp 161−182.
(2) Kroopnick, P.; Craig, H. *Earth Planet. Sci. Lett.* **1976**, *32*, 375−388.
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(5) Epstein, S.; Zeiri, L. *Proc. Natl. Acad. Sci. U.S.A.* **1988**, *85*, 1727−1731.
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(7) Taylor, H. P.; Epstein, S. *Geol. Soc. Am. Bull.* **1962**, *73*, 461−480.
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(9) Bender, M. L.; Grande, K. D. *Global Biochem. Cycles* **1987**, *1*, 49−59.
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Figure 1. Schematic oxygen conversion line.

EXPERIMENTAL SECTION

Reagents. The oxygen gas used as standard was 99.999% pure (Rivoira, Inc., Italy) with $\delta^{18}O = 8‰$ (vs standard mean ocean water, SMOW). The ^{18}O-enriched oxygen was prepared by electrolysis of water with 10% ^{18}O enrichment (Enritech Ltd., Rehovot, Israel) and then mixing with room air, followed by the separation of oxygen from nitrogen and hydrogen using a procedure similar to that developed by Thiemens and Meagher.[12] The composition of the final product was determined using a residual gas analyzer (RGA) Quadrex 200 (Leybold Inficon, Inc., New York) and was 99.95% O_2 (with $\delta^{18}O = 242‰$) and 0.05% Ar. The content of nitrogen and hydrogen was less then 0.005%.

Apparatus. The conversion system is shown schematically on Figure 1. Construction of the metal line is from $^{1}/_{4}$-in.-o.d. 316 stainless steel with Nupro BKT series valves and Swagelok fittings. The amounts of gaseous oxygen and carbon dioxide were determined manometrically with a MKS Baratron 127A type pressure transducer (PT) with an accuracy of ±0.15%. The system is pumped with an oil diffusion pump (10^{-5} Torr) isolated from the line by a large liquid nitrogen trap. The pressure in the line was measured by a Huntington thermocouple vacuum gauge (Mechanical Laboratories, Inc., Mountain View, CA).

The graphite reactor consists of a 20 × 3 mm rod of spectrographic graphite wound with a Pt wire (30 × 0.25 mm) inside a quartz glass tube (13-mm o.d.) (Figure 2). The size of the graphite rod was optimized so that the O_2−CO_2 conversion proceeds rapidly with minimum adsorption of CO on the graphite rod. The quartz tube is electrically heated with an external oven made from 1-mm-diameter Thermocoax heating element (Philips Electronic Instrument Co., Mahwah, NJ). The voltage is regulated to ±1 V with a Variac. The temperature inside the reactor was measured under vacuum by a chromel−alumel thermocouple, and

(12) Thiemens, M. H.; Meagher, D. *Anal. Chem.* **1984**, *56*, 201−203.

Figure 2. Details of graphite reactor.

Labels in figure:
- 12 mm
- SiO₂ glass tube with 1mm wall thickness
- 195 mm
- Heating wire (1.5m THERMOCOAX[R] heating element, ∅ 1mm) connected to Variac[R]
- 30mm
- 20mm
- Graphite rod (∅ 3mm) wound with 1.2m Pt wire (∅ 0.25mm)

Table 2. Oxygen Isotopic Composition at Different CO_2 Yields

		sample	
7 μmol		48 μmol	
yield, %	$\delta^{18}O$, ‰	yield, %	$\delta^{18}O$, ‰
100	8.107^a	100	8.107^a
98.8	7.93	99.6	8.04
97.8	7.82	98.7	7.92
96.6	7.63	96.8	7.72
94.2	7.35	94.5	7.36
92.7	7.17	92.3	7.10

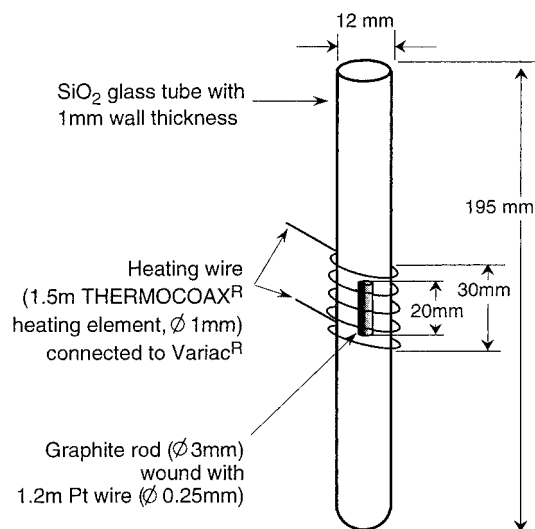^{a} Extrapolated value.

the dependence of temperature on voltage was determined. Clayton and Epstein[13] pointed out that it is important that the gas sample should not come in contact with any hot oxygen-containing compound, because of possible isotopic exchange, resulting in an improper value of the O^{18}/O^{16} ratio. Consequently, in many laboratories the heating of the graphite was carried out by a radio frequency induction furnace[13] or electrically by an internal platinum element,[7] which allows the heating of the graphite only. Because heating with an external furnace is easier, we studied especially the isotopic exchange between oxygen gas and quartz glass at different temperatures. In the next section, we show that this exchange is negligible.

The graphite rod requires conditioning before reproducible results can be obtained. A new rod is heated under vacuum for 16−20 h at 1000 °C. Several O_2 aliquots (usually three to five) are then converted until the $\delta^{13}C$ values of the produced CO_2 become stable. After this treatment, the conversion reactor is ready for routine analyses.

The $\delta^{18}O$ of CO_2 was measured against our laboratory standard using an upgraded VG Micromass 602 isotope ratio mass spectrometer, and the results are given with respect to the SMOW standard. The mass spectrometric precision for both $\delta^{13}C$ and $\delta^{18}O$ is typically ±0.04‰.

Analytical Procedure. The following oxygen conversion procedure was developed during our investigations:

1. Before each conversion reaction the carbon reactor is degassed at 900 °C while being evacuated; the time of degassing depends on the conversion temperature of the previous reaction and is 20−30 min for temperatures above 770 °C and >1 h for 600 °C.

2. The conversion is monitored by a vacuum gauge situated directly above the carbon reactor and is complete when the pressure in the line falls to minimum and does not change. This final pressure can be higher than the pressure observed prior to introduction of oxygen owing to CO production.

3. After the conversion is complete the oven is turned off, and the system is evacuated and cooled for 2 min to prevent the interaction of resultant CO_2 with the still hot graphite and the formation of CO.

4. Following the reaction the amount of CO_2 produced is measured manometrically in order to determine the conversion yield, and the oxygen isotopic composition is determined on the mass spectrometer.

5. The first isotopic measurement at the start of the day always gives a $\delta^{18}O$ value 0.1−0.15‰ higher than the following values. Therefore, in routine work a first pure oxygen aliquot is converted and the produced CO_2 discarded.

6. After 100−120 conversions the CO_2 yield sharply drops by about 1.5% due to changes in the graphite structure (it considerably increased in porosity), and the rod should be replaced.

A CO_2 yield less than 100% and corresponding errors in oxygen isotopic measurements can be caused both by the incomplete oxygen conversion[2] and by the CO production.[7] We investigated the composition of the residual gas at the different conversion conditions using the RGA, and in all cases no less than 99.99% of the oxygen was converted. Thus, the possible errors from incomplete conversion must be less than 0.05‰,[2] and the major source of error in isotopic measurements is connected with isotopic fractionation between CO_2 and CO.

RESULTS AND DISCUSSION

Isotopic Exchange between O_2 Gas and Quartz Glass. The degree of isotopic exchange between gaseous oxygen and quartz glass ($\delta^{18}O = 10.6$‰) at high temperatures was determined by using ^{18}O-enriched oxygen. The heavy oxygen was introduced into the tube and heated for 40 min at 600 °C and for 30 min at 900 °C, and each time its isotopic ratio was measured against a standard oxygen. The very small differences between $\delta^{18}O$ values of the heated and the unheated gases (Table 1) indicate that the isotopic exchange in both cases is small, and for the oxygen of air with natural $\delta^{18}O$ abundance, this effect is less than 0.05‰.

Oxygen Isotopic Fractionation between CO_2 and CO. Although it is well-known that carbon monoxide formation can be a source of serious errors in the determination of $^{18}O/^{16}O$ ratios, some vagueness in this problem still remains. In Table 2 we list

(13) Clayton, R. N.; Epstein, S. *J. Geol.* **1958**, *66*, 352−373.

Table 3. $\delta^{18}O$ Obtained at Different Conversion Temperatures (Sample Size 48 μmol)

| | 600 °C | | | 770 °C | | | 890 °C | | |
run	yield, %	$\delta^{18}O_{mes}$, ‰	$\delta^{18}O_{true}$, ‰	yield, %	$\delta^{18}O_{mes}$, ‰	$\delta^{18}O_{true}$, ‰	yield, %	$\delta^{18}O_{mes}$, ‰	$\delta^{18}O_{true}$, ‰
1	97.2	7.85	8.22	98.8	7.91	8.07	98.2	7.77	8.01
2	96.5	7.83	8.29	98.6	7.94	8.10	98.2	7.82	8.06
3	97.4	7.94	8.28	98.9	7.94	8.08	97.4	7.75	8.09
4	97.4	7.87	8.21	98.7	7.90	8.07	97.4	7.73	8.07
av	97.1	7.87 ± 0.03	8.25 ± 0.03	98.8	7.93 ± 0.02	8.09 ± 0.01	97.8	7.75 ± 0.03	8.06 ± 0.02

Table 4. $\delta^{18}O$ Obtained at Different Conversion Temperatures (Sample Size 7 μmol)

| | 600 °C | | | 770 °C | | | 890 °C | | |
run	yield, %	$\delta^{18}O_{mes}$, ‰	$\delta^{18}O_{true}$, ‰	yield, %	$\delta^{18}O_{mes}$, ‰	$\delta^{18}O_{true}$, ‰	yield, %	$\delta^{18}O_{mes}$, ‰	$\delta^{18}O_{true}$, ‰
1	95.1	7.49	8.14	97.8	7.78	8.08	95.3	7.52	8.15
2	94.8	7.67	8.36	97.8	7.81	8.11	95.6	7.46	8.05
3	95.0	7.63	8.28	97.6	7.70	8.05	95.0	7.46	8.13
4	95.1	7.60	8.25	97.8	7.84	8.13	95.4	7.52	8.13
av	95.0	7.60 ± 0.05	8.26 ± 0.06	97.8	7.78 ± 0.04	8.09 ± 0.03	95.3	7.49 ± 0.03	8.12 ± 0.03

the results of isotopic measurements for different CO_2 yields. As can be seen, it is necessary to obtain a more than 99.2% CO_2 yield for an error of 0.1‰ or less. It is a rather difficult problem, especially for the small samples, and to circumvent it we suggest the following way based on the approach of Northrop and Clayton.[14]

From the data given in Table 2 we noted that the measured $\delta^{18}O$ (δ_{mes}) varies linearly with the CO_2 yield (Y) according to the relation

$$\delta_{mes} = \delta_{true} - 0.1305(100 - Y) \qquad (R = 0.998) \qquad (1)$$

where δ_{true} is the true isotopic value at 100% CO_2 yield and R is the correlation factor. Then the isotopic fractionation coefficient between CO and CO_2 can be easily determined from the slope coefficient and it is equal to 1.013 05. A similar fractionation coefficient (1.0123) can be calculated from the experimental data of Taylor and Epstein,[7] and a close value (1.0128) was determined from the data obtained using our another conversion line. This similarity suggests that the fractionation CO_2–CO is not sensitive to different system geometries or somewhat different conditions during the conversion. Thus, for routine work eq 1 can be written in the form

$$\delta_{true} = \delta_{mes} + 0.1305(100 - Y) \qquad (2)$$

where in the case of the unknown amount of oxygen, Y values are determined beforehand for a given conversion line and sample size from experiments with pure oxygen.

Temperature of the Conversion Reaction. In previous reports the O_2 to CO_2 conversion was made at different temperatures: 600,[13,15,16] 750–770,[9,17] and 900 °C.[2,8] In Tables 3 and 4

are given our results of conversion yields and $\delta^{18}O$ measurements for this temperature range. The highest yield is obtained at 770 °C, while the yields at 600 and 890 °C are equal, but lower. It should be mentioned that at 600 °C most of the CO is adsorbed on the graphite rod, at 890 °C almost all the CO fraction is in the gas phase, while at 770 °C the CO is both adsorbed and gaseous.

At each reaction temperature the precision of measured $\delta^{18}O$ data is high (±0.02–0.06‰); however, the differences between the average values at different temperatures are larger than the combined measurement error. The average corrected values, according to eq 2, at 770 and 900 °C are close, but the values at 600 °C are higher by 0.14–19‰. This enrichment can be explained by cross sample contamination. At 600 °C the formed CO is adsorbed, and it is very difficult to completely degas the graphite reactor. Therefore in each subsequent conversion reaction a small remaining adsorbed CO, which is enriched in ^{18}O, exchanges with the following sample.

Small Samples. As seen from Tables 3 and 4, the uncorrected $\delta^{18}O$ values of the small samples (7 μmol) are lower by about 0.3‰ than the large samples (48 μmol) values. These lower values are explained by the lower CO_2 yields and can be corrected according to eq 2. After the correction is made, the values for both small and large samples agree each with other within 0.05‰. It should be noted, however, that in very small samples (<5 μmol) the measured $\delta^{18}O$ values are considerably lower than expected from eq 2. The cause of this depletion is not understood, but could be due to very low oxygen conversion pressure, which affects the isotopic fractionation. A similar phenomenon was also observed by Mattey and Macpherson[10] and remains to be explained.

Correction for less than 100% CO_2 yield in small samples can be easily done if the initial amount of oxygen is known. If it is not known, the yield can be estimated from the volume of the CO_2 produced (Table 5). This relationship should be obtained for a given conversion line from the experiments with the pure oxygen.

(14) Northrop, D. A.; Clayton, R. N. *J. Geol.* **1966**, *74*, 174−196.
(15) Clayton, R. N.; Mayeda, T. K. *Geochim. Cosmochim. Acta* **1963**, *27*, 43−52.
(16) Horibe, Y.; Shigehara, K.; Takakuwa, Y. *J. Geophys. Res.* **1973**, *78*, 2625−2629.
(17) Crowson, R. A.; Showers, W. J.; Wright, E. K.; Hoering, T. C. *Anal. Chem.* **1991**, *63*, 2397−2399.

CONCLUSIONS

1. The developed procedure of $^{18}O/^{16}O$ ratio measurements by means of oxygen conversion to CO_2 allows one to obtain the

Table 5. Dependence of Conversion Yield on Sample Size (at 770 °C)

sample, μmol	yield,[a] %	sample, μmol	yield,[a] %
48	98.9	15	98.3
26	98.8	12	98.0
20	98.5	7	97.8

[a] Each value is an average of eight duplicates with a aprecision of ±0.1%.

true $\delta^{18}O$ values with a precision of ±0.05‰ in oxygen samples down to 7 μmol.

2. The optimal temperature of conversion reaction is 750−770 °C.

3. Isotopic exchange between quartz glass and oxygen gas is negligible in the temperature range of 600−900 °C.