Reports

Atmospheric Oxygen: Isotopic Composition and Solubility Fractionation

Abstract. *Atmospheric oxygen has been found to be enriched in oxygen-18 by 23.5 ± 0.3 per mil relative to average ocean water (SMOW). Oxygen dissolved in seawater is further enriched in oxygen-18 by 0.85 per mil at 0°C. The temperature dependence of the solubility enrichment is given by* ε *(per mil) = 0.85−0.010* t *(°C). This result is in good agreement with earlier measurements of the solubility effect in distilled water.*

The horizontal and vertical distribution of ^{18}O in atmospheric oxygen was studied by Dole *et al.* (*1*). They found no differences in the percentage of ^{18}O in air up to altitudes of 51 km, nor in any surface locality, including such diverse locations as an Arctic ice island, Australia, and inland U.S. cities. The individual data and the experimental details of the work are given by Lane (*2*). The stated precision was ± 0.5 per mil, but due to various estimated corrections that had to be applied it was probably not that good. Lane found that atmospheric oxygen had a $\delta^{18}O$ = 20 per mil relative to "ocean water," which was not well defined (*3*). The correct $\delta^{18}O$ of atmospheric oxygen relative to the SMOW international isotopic standard (*4*) has never been established, although this datum on the natural oxygen isotope scale is important for many geochemical and biological problems. An accurate determination of this quantity by means of modern mass spectrometric methods was accordingly undertaken.

Table 1. Isotopic composition of atmospheric oxygen gas relative to SMOW. All samples were collected near the ocean on the campus of Scripps Institution of Oceanography.

Date collected	Time collected (hour)	$\delta^{18}O$ (per mil)
4 March 1970	1500	23.47
10 March 1970	1700	23.49
10 March 1970	1700	23.58
10 March 1970	1700	23.18
10 March 1970	1700	23.41
10 March 1970	1700	23.47
10 March 1970	1700	23.35
14 March 1970	1200	23.41
15 May 1970	1000	23.65
13 June 1970	1200	23.65
15 June 1970	2100	23.59
29 November 1970		23.53
1 December 1970	1530	23.51
1 December 1970	1530	23.48
18 January 1971	1600	23.39
25 January 1971	1645	23.79
25 January 1971	1830	23.70
26 January 1971	1200	23.40
Mean of all data (per mil) =		23.50
σ =		0.14
σ_m =		0.03

The experimental procedure is fully described elsewhere (*5*). Briefly, oxygen is converted to CO_2 by circulating air over a carbon rod heated to 800° to 900°C and surrounded by a liquid nitrogen–cooled trap which condenses the CO_2. The kinetics of the conversion in the presence of large concentrations of nitrogen were studied in detail, since incomplete conversion results in serious isotopic fractionation. The conversion process with air was monitored by means of a gas chromatograph attached to the vacuum system. Argon was used as a carrier gas and $O_2 : N_2$ and $CO : N_2$ ratios were measured. The process is first order in O_2 concentration with half times of 4.0 and 1.8 minutes at 800° and 900°C, respectively, in our conversion system. No detectable CO or O_2 remained in the system at these temperatures [detection limits 10^{-3} and 4×10^{-4} cm³ (STP), respectively]. Air samples containing about 2 cm³ of O_2 were cycled over the carbon rod for 20 minutes to insure yields of at least 99.98 percent. The isotopic fractionation factor for preferential production of $C^{16}O_2$ increases from 1.024 at 51 percent conversion to 1.035 at 96 percent conversion (*5*), so that yields of this magnitude are necessary to avoid errors greater than 0.1 per mil in the isotopic composition of the product CO_2.

The mass spectrometric procedure is described by Craig (*6*). The converted CO_2 samples were measured directly against standards produced by oxygen isotope equilibration of CO_2 with SMOW water at 25°C, and the results are expressed as $\delta^{18}O$ values on the SMOW isotopic scale (*4*). The first O_2 conversion on a new carbon rod produces CO_2 about 0.4 per mil enriched in ^{18}O relative to subsequent conversions, and these samples are discarded. The precision of the isotopic analyses of atmospheric O_2, established by replicate conversions of single air samples, is ± 0.1 per mil (*5*, p. 46).

Table 1 shows the results of 18 analyses of air collected at the Scripps Institution of Oceanography over the 10-month period from March 1970 to January 1971. The samples were collected on a cliff located about 10 m above the sea surface and upwind from any exhaust or ventilating equipment. The average value for atmospheric oxygen relative to SMOW is $\delta^{18}O$ = 23.50 per mil. This delta value on the SMOW scale depends directly on the isotopic fractionation factor between CO_2 and water (*7*), which is here taken to be the Bottinga and Craig value of 1.0409 (*8*). This value is almost certainly correct to ± 0.3 per mil, which is thus the absolute accuracy of the $\delta^{18}O$ of atmospheric oxygen relative to SMOW: 23.5 ± 0.3 per mil.

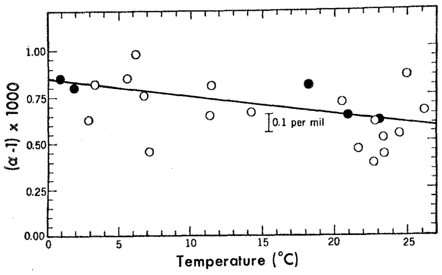

Fig. 1. Isotopic fractionation of oxygen dissolved in seawater (this work, solid circles) and in distilled water [Klots and Benson (*10*), open circles].

Table 2. Oxygen isotope fractionation in solution of air at various temperatures and equilibration times.

Temperature (°C)	Time (hours)	$\delta^{18}O$ (per mil)	ε (per mil)
1	5	24.39	0.86
2	2	24.34	0.81
18	11.5	24.35	0.82
21	1	24.18	0.65
23	4.3	24.14	0.62

In the course of the investigation of ^{18}O variations in dissolved oxygen in seawater (*9*), it became apparent that the dissolved oxygen was enriched in ^{18}O relative to atmospheric oxygen (*5*). This result was not unexpected, since Klots and Benson (*10*) had previously reported this effect in the solution of oxygen and nitrogen in distilled water. We report here measurements of the solubility fractionation in seawater (average salinity 34.6 per mil).

Seawater was collected in 1-liter reagent bottles, poisoned with $HgCl_2$, and stripped of its dissolved gases with CO_2. Air was then bubbled into the bottles of deoxygenated water in order to equilibrate the water with oxygen. The equilibrations were carried out at several temperatures, and the air was sampled periodically for isotopic analysis. The air samples all had $\delta^{18}O$ values within ± 0.05 per mil of the mean value for atmospheric oxygen. After equilibration, the dissolved oxygen was stripped from the solution into a vacuum line. The stripping gas (CO_2) was removed by a trap maintained at liquid-nitrogen temperature that was shown to trap only the condensable gases. The oxygen and nitrogen are then adsorbed onto a type 5A molecular sieve (*11*), and the oxygen is converted to CO_2 for isotopic analysis as described above.

Isotopic fractionation effects are reported in terms of the isotopic fractionation factor α, defined as $\alpha = R_{aq}/R_{gas}$, where the subscripts aq and gas refer to the aqueous phase and the gas phase, respectively. The single-stage enrichment in per mil, ε, is given by $(\alpha - 1) \times 1000$. The measured $\delta^{18}O$ values for the dissolved oxygen and the calculated enrichment factors relative to atmospheric oxygen are given in Table 2. Figure 1 shows the enrichment factors for solution in sea water and the earlier measurements by Klots and Benson (*10*) for distilled water. The linear least squares fit was calculated for the four points measured in this work, excluding the measurement at 18°C, and yielded for the temperature variation of the enrichment factor:

$$\varepsilon(\text{per mil}) = 0.85 - 0.010\, t\ (^\circ\text{C})$$

Klots and Benson's extrapolated value at 0°C is 0.80 ± 0.15 per mil, in excellent agreement with the regression value found here of 0.85 ± 0.05 per mil.

Within the above precision, there is no salinity dependence of the solubility of ^{18}O relative to ^{16}O (salting-out effect). Weiss (*12*) has similarly detected no salinity effect on the solubility of ^3He relative to ^4He. In both cases, the heavier isotope ^{18}O or ^4He is the more soluble.

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References and Notes

1. M. Dole, G. A. Lane, D. P. Rudd, D. A. Zaukelies, *Geochim. Cosmochim. Acta* **6**, 65 (1954).
2. G. A. Lane, thesis, Northwestern University (1955).
3. The delta (δ) units are defined by: $\delta = [(R/R_{std}) - 1] \times 1000$, where R is the ratio $^{18}O:^{16}O$ in a sample, and R_{std} is the ratio in the standard.
4. The acronym SMOW stands for the defined standard mean ocean water isotopic standard [H. Craig, *Science* **133**, 1833 (1961)], which is very close to the true oceanic mean. Samples of SMOW are provided by the International Atomic Energy Agency, Vienna.
5. P. M. Kroopnick, thesis, University of California, San Diego (1971).

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7. Water samples, such as SMOW, are analyzed by equilibrating CO_2 with the water and analyzing the CO_2. Thus, atmospheric O_2 is analyzed relative to CO_2 in isotopic equilibrium with liquid SMOW, and the isotopic fractionation factor for CO_2 and water is required to express the results relative to SMOW.

→ Y. Bottinga and H. Craig, *Earth Planet. Sci. Lett.* **5**, 285 (1969). J. O'Neil and S. Epstein [*J. Geophys. Res.* **71**, 4955 (1966)] reported a value of 1.0407 from their study, and Bottinga and Craig averaged all data from the two laboratories to obtain a factor of 1.04075. However, O'Neil (personal communication) now believes his value may be as large as 1.0412. The Bottinga and Craig value has been adopted here. Other measurements of this factor are reviewed by Bottinga and Craig.

9. H. Craig and P. M. Kroopnick, *Trans. Amer. Geophys. Union* **51**, 325 (1970); P. M. Kroopnick and H. Craig, *ibid.* **52**, 255 (1971) (abstracts).
10. C. E. Klots and B. B. Benson, *J. Chem. Phys.* **38**, 890 (1961).
11. Details of this procedure are given by Kroopnick (*5*). No detectable isotopic fractionation occurs during the adsorption and desorption of oxygen gas on type 5A molecular sieve. The molecular sieve material was obtained from the Linde Division, Union Carbide Corporation, New York.
12. R. Weiss, *Science* **168**, 247 (1970).

13. Supported by grants from the National Science Foundation and the Office of Naval Research to the Isotope Laboratory of the Scripps Institution of Oceanography. We thank Mrs. K. Podvin for performing the mass spectrometer analyses and Dr. J. O'Neill for extensive discussions on the conversion process and the fractionation factor.

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Moon: Possible Nature of the Body That Produced the Imbrian Basin, from the Composition of Apollo 14 Samples

Abstract. *Soils from the Apollo 14 site contain nearly three times as much meteoritic material as soils from the Apollo 11, Apollo 12, and Luna 16 sites. Part of this material consists of the ubiquitous micrometeorite component, of primitive (carbonaceous–chondrite-like) composition. The remainder, seen most conspicuously in coarse glass and norite fragments, has a decidedly fractionated composition, with volatile elements less than one-tenth as abundant as siderophiles. This material seems to be debris of the Cyprus-sized planetesimal that produced the Imbrian basin. Compositionally this planetesimal has no exact counterpart among known meteorite classes, though group IVA irons come close. It also resembles the initial composition of the earth as postulated by the two-component model. Apparently the Imbrian planetesimal was an Earth satellite swept up by the moon during tidal recession or capture, or an asteroid deflected by Mars into terrestrial space.*

Lunar surface rocks are strikingly depleted in siderophile elements (such as Au, Ir, Ni, and Re) and volatile elements (such as Ag, Bi, Br, Sb, and Te). This has made it possible to recognize even a small meteoritic component in those lunar materials that were affected by meteorite impacts: soils, breccias, and glasses (*1, 2*). Both the amount and type of meteoritic material can be estimated from the abundance pattern (usually normalized to cosmic or to Cl chondrite abundances). When the pattern shows siderophile and volatile elements in comparable abundance, a "primitive" meteorite is indicated (for example, carbonaceous chondrites). When volatiles are less abundant than siderophiles, a "fractionated" meteorite is indicated (ordinary chondrites, irons).

We have analyzed eight Apollo 14 samples by our radiochemical neutron activation procedure (*1*), modified to include two more elements, Re and Sb (Table 1). The first two of these samples were bulk soils, collected at two locations. The next five were petrographically distinct separates, handpicked by J. A. Wood and U. B. Marvin from the 1- to 2-mm fraction of four soils. They were cleaned ultrasonically in double-distilled acetone to remove adhering