Respiration, photosynthesis, and oxygen isotope fractionation in oceanic surface water[1]

Peter M. Kroopnick

Department of Oceanography, Hawaii Institute of Geophysics, University of Hawaii, Honolulu 96822

Abstract

Atmospheric oxygen is about 23‰ higher in ^{18}O than ocean surface water, whereas oxygen in isotopic equilibrium with ocean water would be only 6‰ higher in ^{18}O. The fractionation of ^{16}O during respiration has been measured on natural populations in unfiltered marine surface water samples. The decrease of dissolved oxygen concentration and the increase in $\delta^{18}O$ due to respiration was measured as a function of time. An average enrichment factor of 21‰ was calculated for the removal of oxygen in a closed system. The results indicate that the enrichment of ^{18}O in the atmosphere, and possibly the present oxygen concentration, may be controlled by biogenic processes.

Atmospheric oxygen is enriched with its stable isotope (^{18}O) to the extent of about 23‰ with respect to average ocean water. This fact was observed independently by Dole (1935), Morita (1935, and Morita and Titani 1936). Somewhat later, Dole et al. (1954) showed that this enrichment is constant up to an altitude of 51 km. More recent measurements put the enrichment at between 23.5‰ and 23.8‰ versus the SMOW isotopic standard (Kroopnick and Craig 1972; Horibe et al. 1973). These values depend on the fractionation factor for the equilibration of CO_2 with water. Horibe et al. used 1.0414 while Kroopnick and Craig used 1.0409. Urey and Greiff (1935) and Urey (1947) used a statistical mechanical approach to calculate that if equilibrium was obtained between molecular oxygen and liquid water the oxygen gas would be enriched in ^{18}O with respect to the liquid by 6‰ at 25°C. This leaves an unexplained enrichment of about 17‰. Several hypotheses have been advanced to explain this enrichment, known as the Dole-Morita effect (Kamen and Barker 1945). These explanations will be discussed here along with some new data on oxygen isotope fractionation during respiration in stored samples of surface seawater.

It was first thought that green plant photosynthesis might control the $^{18}O : {}^{16}O$ ratio in the atmosphere. Dole and Jenks (1944) confirmed the findings of Ruben et al. (1941) that the oxygen evolved during photosynthesis was derived from the dissociation of water molecules and further determined that the liberated oxygen was enriched in ^{18}O by about 5‰ relative to the water from which it was derived. Thus photosynthetic oxygen has approximately the $^{18}O : {}^{16}O$ ratio expected for thermodynamic equilibrium between liquid water and molecular oxygen. Photosynthesis therefore cannot account for the Dole-Morita effect.

Barker (*cited by* Lane and Dole 1956) and Rabinowitch (1945) suggested independently that the cause of the Dole-Morita effect might be isotopic fractionation caused by the preferential uptake of ^{16}O during cellular respiration. Barker (Dole et al. 1947) proposed that soil bacteria would be mainly repsonsible. However, Rabinowitch (1945) estimated that 85% of photosynthesis and respiration occurs in the oceans. More recent calculations for oceanic vs. land production allow us to estimate that about 60% of the total oxygen consumed per year probably occurs in the oceans (Broecker 1970).

Lane and Dole (1956) found that oxygen isotope enrichment during respiration in

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several plants, bacteria, and in man varied from 7 to 25‰. Dole et al. (1954) discussed the oceanic data presented by Rakestraw et al. (1951), and also several other oceanic profiles, all of which indicated large ^{18}O enrichments near the dissolved oxygen minimum. Rakestraw et al. proposed that the increase in ^{18}O with decreasing oxygen concentration in the water column could be explained by a closed system Rayleigh fractionation model with an enrichment factor of 9‰. This enrichment is too small to account for the Dole-Morita effect. However, a closed system model is not applicable to the oceans because of vertical and horizontal mixing effects (Craig and Kroopnick 1970; Kroopnick and Craig 1971). Craig (1971) has shown that in the deep waters of the Pacific, the time scales for O_2 consumption and advection are comparable. Enrichments in an open system will always be less than in a closed one. At present, calculations including these mixing effects are only possible for the deep ocean and will be reported separately (Kroopnick in prep.).

Roake and Dole (1950) theorized that ^{18}O enhancement in atmospheric oxygen may take place in the stratosphere, where under the influence of ultraviolet radiation a random isotopic exchange between carbon dioxide and oxygen might occur. Their laboratory experiments actually indicated a slight depletion of ^{18}O in the oxygen, but they suggested that in the atmosphere random exchange could produce the needed enrichment. Vinogradov et al. (1959) pointed out that carbon dioxide equilibrated with water becomes highly enriched in ^{18}O and that subsequent exchange of the carbon dioxide with oxygen could possibly account for the Dole-Morita effect. They calculated, however, that for their mechanism to be important the atmospheric carbon dioxide concentrations would have to be three times larger than the present value of 0.032%.

Other processes that could control the O_2 balance in the atmosphere are the oxidation of reduced carbon, sulfides, and ferrous iron during the weathering of rocks and the oxidation of reduced volcanic gases. Holland (1973) estimated that the total amount of oxygen used in the weathering of crustal rocks is on the order of $4 \cdot 10^{14}$ g yr^{-1}. He concluded that the turnover of oxygen through the weathering and sedimentation cycle takes place on a time scale of several millions of years, and that over the last 65 million years atmospheric conditions and biological processes have not changed appreciably.

The rate of production of oxygen by photosynthesis is significantly higher than its consumption by geological processes and is thought to be balanced by respiration and oxidation of organic matter. The atmosphere contains about $5 \cdot 10^{20}$ g of oxygen of which $6 \cdot 10^{16}$ g yr^{-1} are used in biological production and consumption (Broecker 1970). The turnover time for atmospheric oxygen is thus about 10,000 years. This is considerably faster than the weathering cycle of 3,000,000 years. Thus the steady state concentration of the oxygen in the atmosphere must be controlled by the photosynthesis-respiration-oxidation cycle and it is expected that the isotope distribution can be similarly explained.

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Experimental methods

The biological fractionation of oxygen isotopes in closed systems of natural marine populations can be conveniently studied by measuring the consumption of oxygen in bottles of seawater stored under various conditions in the laboratory. Rakestraw (1947) incubated water samples from the surface, from the oxygen minimum layer, and from deep water at temperatures near those at the depths from which they were taken. He found that the rates of consumption decreased with time and effectively ceased after 50 days. Such rates in bottles are almost certain to be higher than those in the open ocean, since the rate of oxygen consumption measured in bottles is proportional to the ratio of surface area to water volume (ZoBell and Anderson 1936). One

of the most important discoveries of ZoBell and Anderson was that the rate of oxygen consumption in filtered seawater is independent of the oxygen concentration within the examined range of 0.3 to 12.7 ml of oxygen per liter (ZoBell 1940).

I have measured both oxygen consumption and oxygen isotopic fractionation under similar conditions in bottled seawater from samples collected at the end of the Scripps Institution of Oceanography pier. Individual 1-liter sterilized reagent bottles were filled by submerging them just below the surface. The ground-glass stoppers for the bottles were greased with silicone vacuum grease and then taped securely to prevent any air leakage. One of the samples was immediately analyzed for dissolved O_2 and ^{18}O; the others were stored in the dark at 19°C and analyzed at various times.

In a second experiment a 20-liter sterilized bottle was filled with surface water from the same location, mixed to ensure a uniform sample, and 1-liter sterilized bottles were then filled from it by siphon. Bacto-peptone was added to these bottles to promote higher rates of bacterial respiration. The samples were then stored in the dark at 19°C until analysis.

Dissolved oxygen was measured by the basic Winkler-Carpenter method, scaled down to accept a 50-ml sample (Carpenter 1965). The procedures for quantitatively extracting the dissolved oxygen from seawater and for mass spectrometer analyses have been described in detail elsewhere (Kroopnick 1971; Kroopnick and Craig 1972). Briefly, the dissolved gases (mostly N_2, O_2, CO_2) were stripped from solution into a vacuum system. The stripping gas (CO_2) was removed by a trap kept at liquid nitrogen temperature. The oxygen and nitrogen were then absorbed onto a type 5A Molecular Sieve cooled with liquid nitrogen. The oxygen was converted to CO_2 by circulating the air over a carbon rod heated to 800°–900°C and surrounded by a liquid nitrogen-cooled trap that condensed the CO_2. The unwanted N_2 was then pumped away and the CO_2 was analyzed by standard mass spectrometric procedures (Craig 1957). Oxygen isotopes are reported as the per mil enrichment relative to the defined ocean water standard (SMOW): $\delta^{18}O = [(R/R_{std}) - 1] \cdot 10^3$ where R is the $^{18}O : {}^{16}O$ ratio (Craig 1957). Surface seawater is enriched about 0.5‰ relative to SMOW. The overall precision for extracting, combusting, and analyzing replicate samples is ±0.1‰.

Table 1. Biological fractionation experiments. (Samples were collected at the end of the S.I.O. pier and stored in the dark at 19°C unless otherwise specified.)

Sample	Comments	Time (days)	O_2 (ml/kg)	$\delta^{18}O$ (‰)	ε (‰)
	1-2 Jan 71				
	water temp = 12.25°C				
II-8	Analyzed immediately	0	5.93	23.60	-
II-14		1.2	5.78	24.19	22.5
II-1		1.3	5.80	23.93	14.5
II-15		3.1	5.63	25.32	32.1
II-12	Peptone added	0.75	0	-	-
II-13	Peptone added	0.8	3.62	31.54	15.6
II-4	Peptone added	1.25	0	-	-
	25 Jan 71				
	water temp = 13.3°C				
III-1	Analyzed immediately	0	5.94	23.33	-
III-4		4.3	5.40	25.40	21.2
III-5	5°C	4.4	5.33	25.18	16.6
III-6		9	5.26	26.19	23.1
III-7		100	2.70	38.66	18.9
	4 Apr 71				
	water temp = 13.3°C				
IV-1	Analyzed immediately	0	5.53	23.73	-
IV-2	Peptone added	0.5	5.31	24.24	12.3
IV-3	Peptone added	0.9	1.57	61.18	28.5
IV-4	Peptone added	0.9	2.51	42.31	22.8
IV-5	Peptone added	1.0	1.67	51.09	22.0
					avg=20.8
					σ_m = 1.7

Results

The data are given in Table 1. Figure 1 shows the dissolved oxygen concentration (C) minus the initial concentration (C_0) plotted as a function of storage time. In all cases oxygen was consumed and the $\delta^{18}O$ of the remaining oxygen dissolved in the water increased as the total concentration of dissolved oxygen decreased. The $\delta^{18}O$ values are listed beside each point.

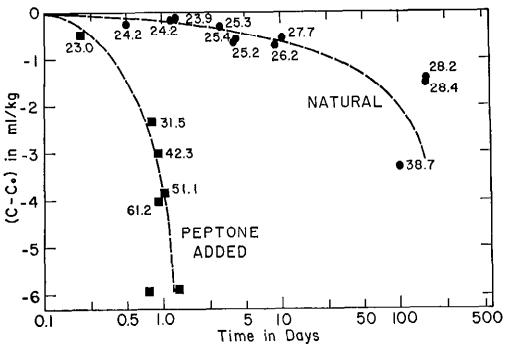

Fig. 1. Dissolved oxygen concentration minus the initial value, plotted versus storage time. The square symbols represent seawater samples to which peptone was added. The circles represent natural, untreated samples. The number beside each point is the $\delta^{18}O$ of the oxygen remaining at that time. The oxygen content of the two unnumbered samples was too low to measure their $\delta^{18}O$. The lines are only to distinguish the two experiments and have no theoretical significance.

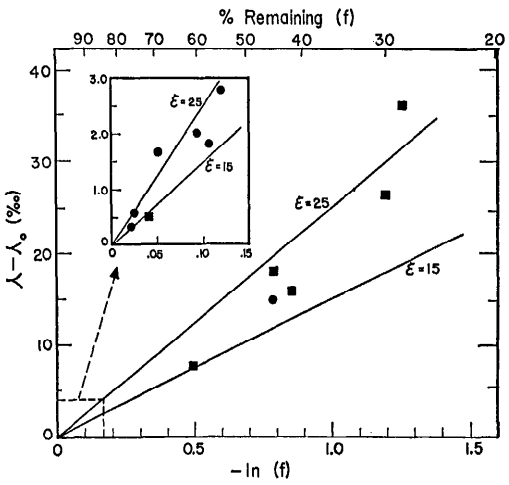

Fig. 2. Isotopic results of closed-system biological fractionation experiments. Symbols as in Fig. 1. $\lambda = \ln(1 + \delta^{18}O)$, and f is the fraction of dissolved oxygen remaining.

The single stage enrichment factor (ϵ) was calculated using the Rayleigh equation

$$R/R_0 = f^{-\epsilon},$$

where R is the ratio $^{18}O : {}^{16}O$ of the dissolved oxygen being removed at any instant, R_0 is the ratio in the remaining material, and f is the fraction of dissolved oxygen remaining. Since $\delta^{18}O$ increased with decreasing oxygen concentration, the enrichment factor ϵ is positive, indicating that during respiration ^{16}O is consumed in preference to ^{18}O, enriching the remaining oxygen in ^{18}O. A more convenient form of this equation is

$$\lambda - \lambda_0 = -\epsilon \ln (f),$$

where $\lambda = \ln(1 + \delta^{18}O)$.

The isotopic results are plotted in Fig. 2 using the above notation. The large scatter in the data may be due to the nonhomogeneity of the samples, since each storage bottle developed its own bacterial community. The samples with peptone added show a much larger oxygen consumption, and isotopic enrichment, than those without it. The calculated enrichment for the samples with peptone agrees with that calculated for natural samples and is more accurate due to the larger changes. Averaging all the above results gives a single-stage enrichment of 21‰ ($\sigma_m = 1.6$).

Discussion

Returning to the problem of why atmospheric oxygen is enriched in ^{18}O by 23.5‰ over seawater, these experiments show that respiration can cause an enrichment of about 21‰. The 2.5‰ discrepancy between these experiments and the observed 23.5‰ enrichment in atmospheric oxygen may be due either to experimental uncertainties or to photosynthesis.

We estimated earlier, on the basis of the work of Ruben et al. (1941) and Dole and Jenks (1944), that photosynthesis could cause an enrichment of about 5‰. The photosynthetic oxygen in their experiments was collected from actively growing *Chlorella* cultures, but although respiration continues in the presence of light, no correction for either consumption or fractionation was applied. The oxygen evolved in their experiments may thus have become enriched in ^{18}O by respiration and may not be representative of pure photosynthesis. The agreement of Dole and Jenk's measured value with that calculated by Urey (1947) may have been fortuitous, and a re-exami-

nation of the photosynthetic fractionation factor using modern mass spectrometric techniques is underway.

The ^{18}O results presented above suggest that both the molecular O_2 and ^{18}O concentrations in the atmosphere are controlled by a steady state balance between photosynthesis and respiration in marine surface water.

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