Reports

Tritium-Helium Dating in the Sargasso Sea: A Measurement of Oxygen Utilization Rates

Abstract. *The newly developed technique of "tritium-helium dating" has been used to investigate in situ rates of oceanic oxygen utilization. As an example, an apparent oxygen utilization rate of 0.20 ± 0.02 milliliter per liter of water per year has been obtained for the Subtropical Mode water (18°C water) in the Sargasso Sea.*

Using a recently developed technique for measuring gas residence times (*1*), I have determined an "apparent oxygen utilization rate" for the 18°C water in the Sargasso Sea. Mass spectrometric measurements of the isotopic ratio of He extracted from seawater have shown that the concentration of the lighter isotope, ^{3}He, is generally in excess of that expected from solution from the atmosphere (*1*). This excess ^{3}He consists of two components: (i) primordial ^{3}He injected into the deep oceans from the seafloor spreading center and (ii) ^{3}He produced by the in situ radioactive decay of tritium (^{3}H). The former component exists solely in the deep and bottom waters, whereas the latter exists primarily in the upper waters (*1*). This "tritiugenic" ^{3}He can be used in conjunction with ^{3}H to deduce gas residence times (*1*) and hence oxygen utilization rates.

In a parcel of water at the sea surface, ^{3}He is continually being produced by the in situ decay of ^{3}H; but, because the parcel is at the sea surface and in gaseous equilibrium with the atmosphere, this tritiugenic ^{3}He escapes. At some time ($t = 0$) this parcel sinks, losing contact with the atmosphere, and tritiugenic ^{3}He begins to accumulate. By measuring the ^{3}H and tritiugenic ^{3}He content at the time of sampling, it is possible to compute the time that has elapsed since gas equilibration with the atmosphere (τ) according to

$$\tau = 17.8 \log \left(1 + \frac{[^3\mathrm{He}]}{[^3\mathrm{H}]} \right) \qquad (1)$$

where [^{3}H] and [^{3}He] are the concentrations of ^{3}H and tritiugenic ^{3}He, respectively, and τ is in years. With Sargasso Sea surface ^{3}H concentrations and present mass spectrometric precision, elapsed times as short as 2 months may be detected.

The ^{3}H-^{3}He age thus calculated, however, is an average age due to mixing, and some caution must be exercised in the interpretation of this age since the average is weighted according to the [^{3}H] of the mixing end members (*1*). Furthermore, it must be shown that the "^{3}H-^{3}He clock" is "set," or that the parcel was indeed at equilibrium with the atmosphere prior to sinking. Within this framework, it is possible to estimate the net in situ production or consumption rate of any chemical species that is renewed at the sea surface.

I obtained seawater samples to a depth of 1 km from three stations in the Sargasso Sea, using 1.3-liter Nansen bottles; I transferred the samples to He-leakproof containers on shipboard, using a simple gravity feed technique (*2*). Oxygen, temperature, and salinity measurements were made for each Nansen sample. The He was extracted from the seawater in a high-vacuum line, and simultaneously the seawater was degassed in preparation for the measurement of ^{3}H by the "grow-in technique" (*3*). The ratio of [^{3}He] to [^{4}He] and the total He contents were measured to ± 0.2 percent and ± 1.2 percent respectively, on a dual-collection mass spectrometer. The ^{3}H was determined to ± 0.08 tritium unit, ± 4 percent, by reextraction and mass spectrometric measurement of ^{3}He that had grown in over a storage period of about 1 year and was decay-corrected to the time of sampling.

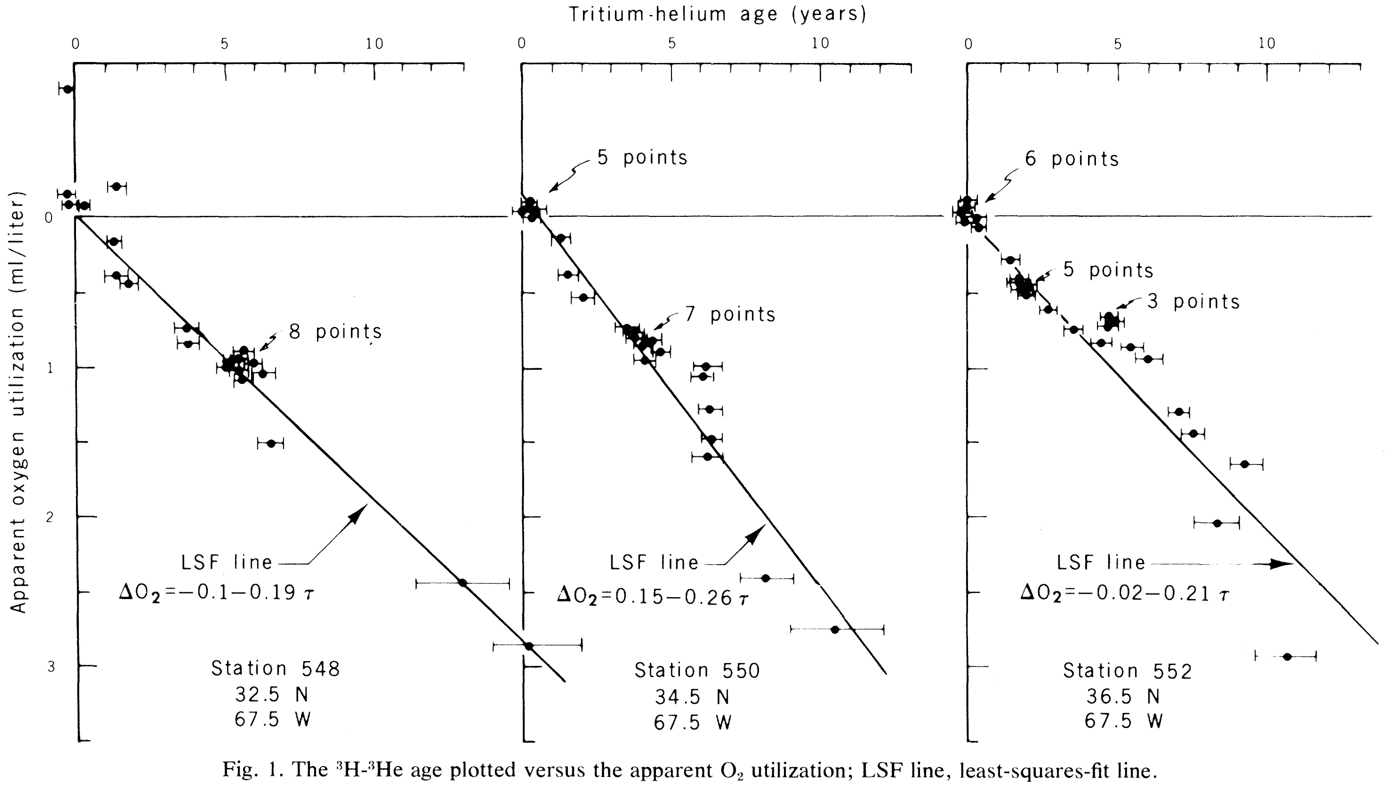

Fig. 1. The ^{3}H-^{3}He age plotted versus the apparent O_2 utilization; LSF line, least-squares-fit line.

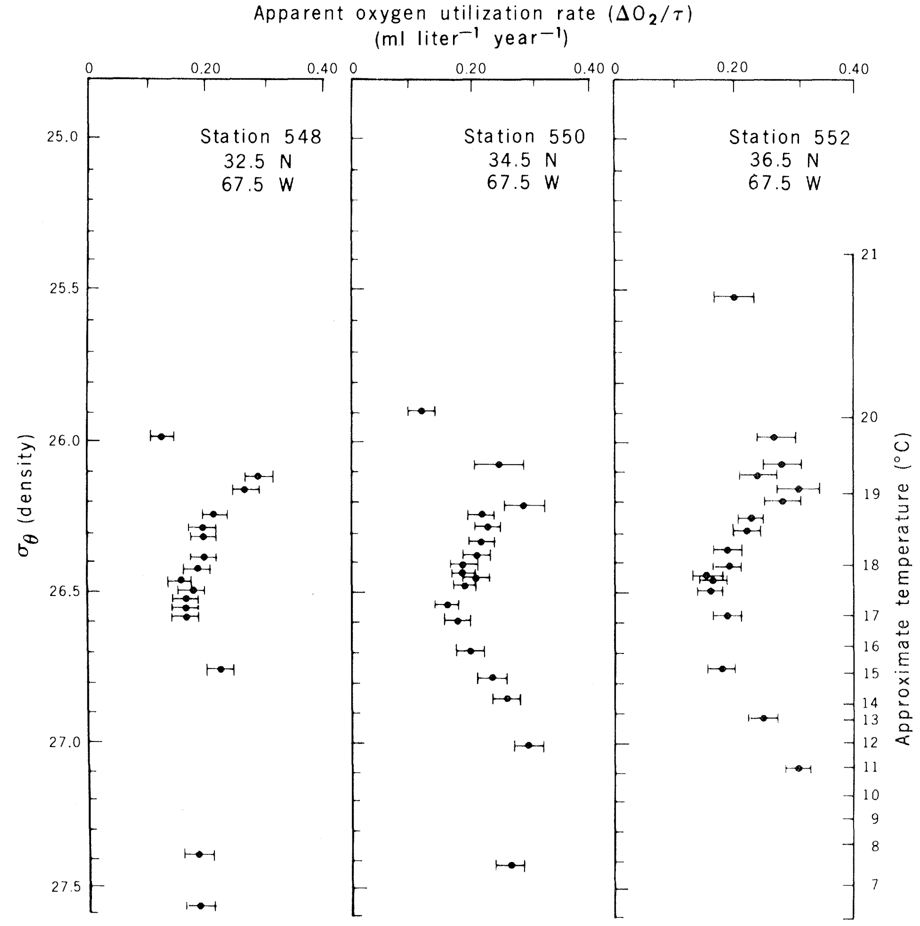

Fig. 2. The apparent O_2 utilization rate as a function of density.

I calculated the tritiugenic $[^3\text{He}]$ from the isotopic ratio of ^{3}He to ^{4}He and the He concentration, using a value of 1.398×10^{-6} for the atmospheric He isotopic ratio (*3*, *4*), the equilibrium solubility data obtained by Weiss (*5*), a He isotope effect in solution of 0.9886 ± 0.0006 (*6*), and a correction for air injection. The apparent O_2 utilization (ΔO_2) was computed as the difference between the O_2 concentration observed and that calculated from solubility (*7*).

The data obtained were characterized by a strong correspondence between the ^{3}H-^{3}He age, O_2, and hydrographic properties (*8*). Figure 1 shows the relationship between ΔO_2 and τ (the ^{3}H-^{3}He age) for the three stations. The linear regression line shown for a particular station does not imply any specific functional relationship, as there are significant and consistent excursions from the curve; the line is simply a reference point from which to examine the grosser aspects of the ΔO_2 rate, R. What is striking is the similarity of the slopes obtained for the three sites and the essentially zero ΔO_2 intercept. This latter phenomenon, combined with the clustering of surface values around $\tau = 0$, strongly supports the hypothesis that the ^{3}H-^{3}He clock is properly set.

The systematic deviations from the linear regression line in Fig. 1 suggest hydrographic variations in R. It is possible to compute R for each sample by dividing ΔO_2 by the ^{3}H-^{3}He age. This has been done in Fig. 2 for all samples except the mixed layer samples (which would have large relative uncertainties due to the low ^{3}H-^{3}He ages). Certain structural features are immediately apparent, corresponding to features in the temperature-salinity relations (*8*). A pronounced maximum in R occurs at the density $\sigma_\theta \sim 26.1$ (19°C), which corresponds to the base of the "winter water" (winter mixed layer remnant) below the seasonal thermocline. At $\sigma_\theta \sim 26.5$, which corresponds to the 18°C water (*9*), there occurs a minimum in R, below this minimum R increases to what may be a deeper maximum at $\sigma_\theta \sim 27.2$ to 27.5 (7° to 10°C).

The shallow maximum in R is most probably located at the site of the "crossover" of decreasing O_2 consumption and decreasing O_2 production with depth. The interpretation that the deeper maximum is probably an artifact of the mixing history of this water mass follows from the fact that the back-corrected (decay-corrected) $[^3\text{H}]$ at time $\tau = 0$ does not correspond to the expected surface $[^3\text{H}]$ for that time (*8*). Consequently, the R values obtained for this water mass represent an upper limit to the true O_2 utilization rate.

For the 18°C water ($\sigma_\theta = 26.5$) mixing nonlinearity is not a large effect, since the mixing half-life for this water mass [about 3 years (*8*)] is short relative to the rate of change of surface $[^3\text{H}]$. That is, $[^3\text{H}]$ in the 18°C water tends to follow quite closely the surface $[^3\text{H}]$ [as seen in recent measurements (*8*)] so that the average ^{3}H-^{3}He age approaches quite closely the true mixed age of the water mass. The mean R for the 18°C water ($26.4 < \sigma_\theta < 26.6$) is thus 0.198 ± 0.004 ml liter^{-1} year^{-1} with an estimated uncertainty of 0.02 ml liter^{-1} year^{-1} due to mixing nonlinearity and the possible effects of air injection. For this same density stratum, Riley (*10*) using an advective-diffusive model, obtained an R of 0.19 ± 0.05 ml liter^{-1} year^{-1}, in good agreement with the results obtained here.

In summary, I have developed a new technique for making in situ measurements of oceanic O_2 utilization rates which is inherently more precise and has greater spatial resolution than earlier methods. When coupled with other biological and chemical measurements, this technique could lead to the first determinations of quantitative causal relations between the rates of chemical (and biochemical) reactions in the sea and the biological and chemical environments in which they occur.

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References and Notes

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