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Helium, neon, and tritium in the Black Sea

by Z. Top[1,2] and W. B. Clarke[1]

ABSTRACT

Measurements of the ^{3}He/^{4}He ratio, and concentrations of helium, neon, and tritium have been made in samples collected at station 1355 in the Black Sea during the 1975 cruise of R/V *Chain*. Helium concentrations increase rapidly from 400 m to about 1000 m and then less rapidly below 1000 m. The maximum He concentration excess is about 16% above solubility equilibrium. Neon concentrations are constant, within a few percent of solubility equilibrium, below 400 m. The He-Ne data thus clearly indicate a large component of radiogenic ^{4}He in the deep water from decay of U and Th in the bottom sediments. Tritium concentrations decrease from 67.2 T.U. at the surface to near-zero values at 726 m, 968 m, and 1358 m. Two deeper samples at 1745 m and 1939 m contain some tritium—0.6 ± 0.3 T.U. and 0.7 ± 0.2 T.U. respectively, which shows that a small amount of high-tritium surface water has descended to the bottom during the past twenty years. A one-dimensional three-box model using our tritium concentrations and the geothermal heat flux values measured by Erickson and Simmons (1974) gives vertical exchange times of 440 ± 180 years between the deep water (1000 m-2000 m) and the middle water (400 m-1000 m), and 125 ± 75 years between the middle water and a layer above from 200 m to 400 m in the salinity interval 21.50‰-22.00‰. The fluxes of radiogenic ^{4}He and primordial ^{3}He into the deep water are found to be $1.3 \pm 0.5 \times 10^6$ atoms cm^{-2} sec^{-1} and 1.1 ± 0.6 atoms cm^{-2} sec^{-1} respectively which may be compared with world-ocean estimates of Craig *et al.* (1975)—$3 \pm 1.5 \times 10^5$ atoms cm^{-2} sec^{-1} and 4 ± 1 atoms cm^{-2} sec^{-1}.

1. Introduction

The Black Sea is an oval basin located between the Caucasus-Crimea mountain range to the north and the Pontic mountains to the south. The sole communication

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with the Mediterranean is through the Bosporus at a sill depth of only 50 m. The salinity varies from about 16‰ near the surface to about 22‰ near the bottom, and the waters below about 200 m are anoxic. A compilation of recent studies on the Black Sea using modern methods of geophysics and geochemistry can be found in a Memoir of the American Association of Petroleum Geologists (Degens and Ross, 1974).

^{3}He and ^{4}He are conservative tracers in the ocean. Although the major source of both isotopes is the atmosphere, two additional components of ^{3}He have been identified—a primordial component released from the mantle at various locations of tectonic activity, and a component from decay of nuclear-era tritium. The primordial component is usually observed in the deep water, and the component from tritium is usually observed in the upper 1 km. ^{4}He of atmospheric origin is augmented in some locations by addition of radiogenic ^{4}He from U and Th decay. Recent examples of these studies can be found in Top *et al.* (1980) and Jenkins (1980).

Most of the tritium in the world oceans is in the upper 1 km and has been introduced by atmospheric testing of nuclear weapons. Tritium is attached to the water molecule as HTO, and thus it serves as a useful oceanographic tracer. When tritium measurements are combined with measurements of ^{3}He, the time since equilibration with the atmosphere can be determined in some instances (Jenkins and Clarke, 1976; Jenkins, 1980).

There is no known significant source of neon in the oceans apart from the atmosphere. Although excess ^{20}Ne, thought to be of primordial origin, has been detected in oceanic basalts (Craig and Lupton, 1976) the addition of ^{20}Ne to ocean water, or of ^{21}Ne and ^{22}Ne produced by nuclear reactions, is certainly too small to be detected by present neon isotope measurement techniques. The possible addition of primordial Ne to ocean water by interaction with basalt has been discussed in detail by Dymond and Hogan (1973, 1974). Neon concentration measurements thus provide a means to estimate the amounts of helium of atmospheric and radiogenic origin.

Samples for the present study were collected during cruise 120 of R/V *Chain* during April 1975 at station 1355 in the Black Sea (42°50′N, 33°00′E). A location map is shown in Figure 1. ^{3}He/^{4}He, helium, neon, and tritium measurements were made at McMaster University. Potential temperatures, and salinity measurements were furnished by R. B. Gagosian (private communication, 1978).

2. Experimental methods

Seawater samples were collected in 40 in. lengths of 3/8 in. copper tubes clamped at each end with steel pinch clamps. The laboratory procedure consisted of extraction of the dissolved helium and neon into two separate sample tubes by means of
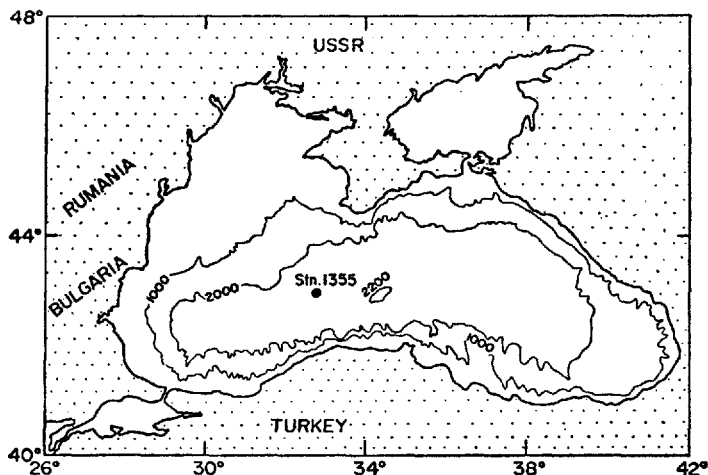
Figure 1. Location of station 1355 in the Black Sea. Depth contours are in meters.

a precisely calibrated "splitter." One tube was used for ^{3}He/^{4}He measurements and the other for He-Ne concentration measurements by isotope dilution. After gas extraction was complete, the degassed water samples were stored in sealed bulbs made of Corning 1720 glass for subsequent mass spectrometric determination of ^{3}He produced from *in situ* decay of tritium. Detailed accounts of the measurement techniques and errors can be found in Jenkins and Clarke (1976), and Clarke *et al.* (1976).

3. Results and discussion

The results of the inert gas isotope measurements are given in Table 1, along with potential temperatures and salinity values. ^{3}He/^{4}He ratios are expressed in the following way:

$$\delta(^3\text{He}) = \left[\frac{(^3\text{He}/^4\text{He})_{\text{sample}}}{(^3\text{He}/^4\text{He})_{\text{atmos.}}} - 1 \right] \times 100\% .$$

Excess helium and neon percentages are calculated using the equilibrium solubility measurements of Weiss (1971):

$$\Delta C = \left[\frac{C}{C_{\text{sol.}}} - 1 \right] \times 100\%$$

where C and $C_{\text{sol.}}$ are observed and equilibrium solubility concentrations of helium or neon. ΔHe values are corrected for air injection using the relation given by Beg (1971).

$$\Delta'\text{He} = \Delta\text{He} - f\Delta\text{Ne}$$

Table 1. Helium, Neon, and Tritium in the Black Sea, April 1975.

Depth (m)	T_p (°C)	S (‰)	$\delta(^3He)$ (%)	He (10⁻⁸ cc STP/g)	Ne (10⁻⁸ cc STP/g)	ΔHe (%)	ΔNe (%)	Δ³He (%)	Tritium	³H-³He Age (years)
10	10.3	18.3	−2.5	4.48	19.16	7.0	6.6	−1.2	67.2 ± 0.4	—
69	7.98	19.65	43.5	4.67	20.11	11.5	10.6	−1.8	42.5 ± 0.4	3.8 ± 0.1
89	8.30	20.24	38.7	4.57	19.46	9.6	7.7	0.1	27.6 ± 0.3	4.9 ± 0.2
95	8.42	20.60	27.7	4.53	19.05	8.7	5.8	1.5	25.1 ± 0.2	3.9 ± 0.2
105	8.46	20.73	31.6	4.38	18.77	5.4	4.4	0.1	18.6 ± 0.3	5.3 ± 0.3
114	8.58	20.85	30.1	4.39	18.77	5.6	4.5	0.1	16.4 ± 0.2	5.7 ± 0.3
119	8.53	20.91	24.7	4.42	18.86	6.4	5.0	0.2	16.3 ± 0.2	4.8 ± 0.3
134	8.58	21.09	21.1	4.45	18.98	7.2	5.9	−0.1	12.1 ± 0.2	5.2 ± 0.3
214	8.69	21.51	7.2	4.57	19.03	10.4	6.5	2.2	9.6 ± 0.3	2.1 ± 0.2
283	8.84	21.74	6.8	4.49	18.64	8.8	4.6	3.0	3.4 ± 0.3	5.4 ± 0.8
322	8.81	21.84	3.1	4.69	19.34	13.5	8.6	2.8	2.8 ± 0.5	1.2 ± 0.2
387	8.83	21.95	1.9	4.52	18.52	9.5	4.1	4.3	1.7 ± 0.2	2.3 ± 0.5
482	8.82	22.05	0.7	4.58	18.48	11.2	3.9	6.3	0.6 ± 0.2	—
726	8.82	22.22	−2.3	4.74	18.49	15.0	4.1	10.0	0.2 ± 0.4	—
968	8.84	22.23	−2.8	4.90	18.54	19.0	4.3	13.6	−0.3 ± 0.3	—
1358	8.88	22.34	−4.3	4.93	18.44	19.7	3.8	14.9	−0.1 ± 0.4	—
1745	8.88	22.34	−5.0	4.99	18.55	21.2	4.1	16.0	0.6 ± 0.3	—
1939	8.89	22.34	−5.5	4.96	18.42	20.4	3.8	15.6	0.7 ± 0.2	—
Errors*	± 0.01	± 0.03	± 0.3	± 0.01	± 0.04	± 0.2	± 0.2	± 0.5	± 0.2	

* Quoted errors for measurements of inert gases and tritium are 1σ analytical errors. Errors for T_p and S were estimated from the scatter of results at similar depths. The T_p and S data were furnished by R. B. Gagosian (private communication, 1978).
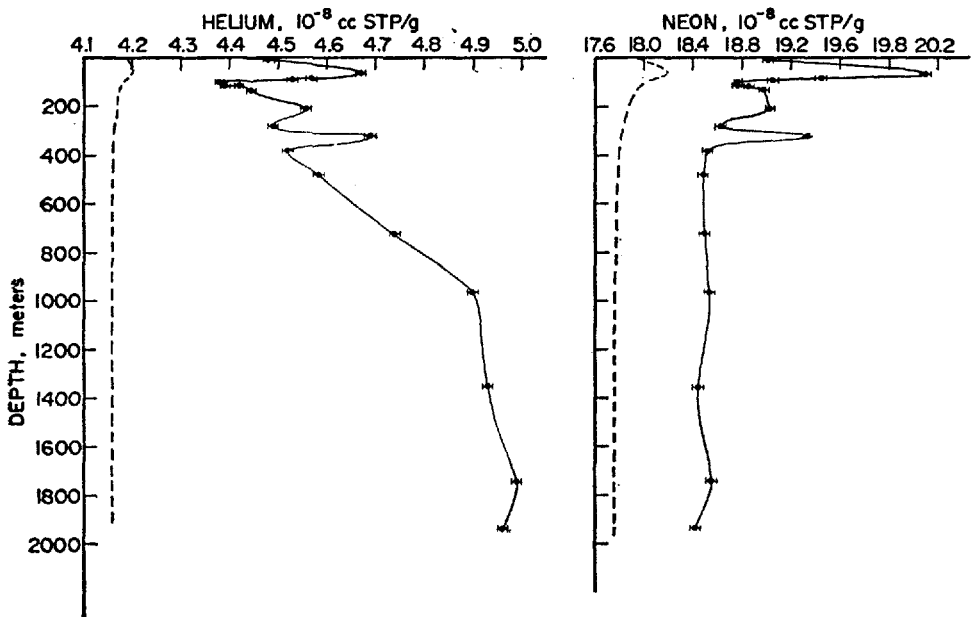
Figure 2. Helium and Neon concentration profiles, station 1355. The dashed curves represent equilibrium solubility values measured by Weiss (1971).

where

$$f = \frac{(Ne/He)_{sol.}}{(Ne/He)_{atmos.}}$$

at the potential temperature and salinity of the sample.

Examination of depth profiles of the various properties reveals several interesting features.

a. Helium and neon. Three maxima at 69 m, 214 m, and 322 m are observed for both helium and neon as shown in Figure 2. The He and Ne variations above 400 m are well correlated and at first sight suggest the addition of air to some samples either by leakage during storage or during the gas extraction process. We believe that such an explanation is unlikely, and that the observed variations are real. The He-Ne maxima at 60 m are accompanied by a maximum in $\delta(^3He)$ and a minimum in temperature, and these features may be related to ground water input at the margins of the Black Sea. The He-Ne maxima at 214 m and 322 m do not appear to be related to other hydrographic features apart from a hint of a tritium maximum at 214 m. Seasonal variations in the Mediterranean input which settle at different density horizons may provide an explanation, but for a detailed understanding further tracer measurements are needed.

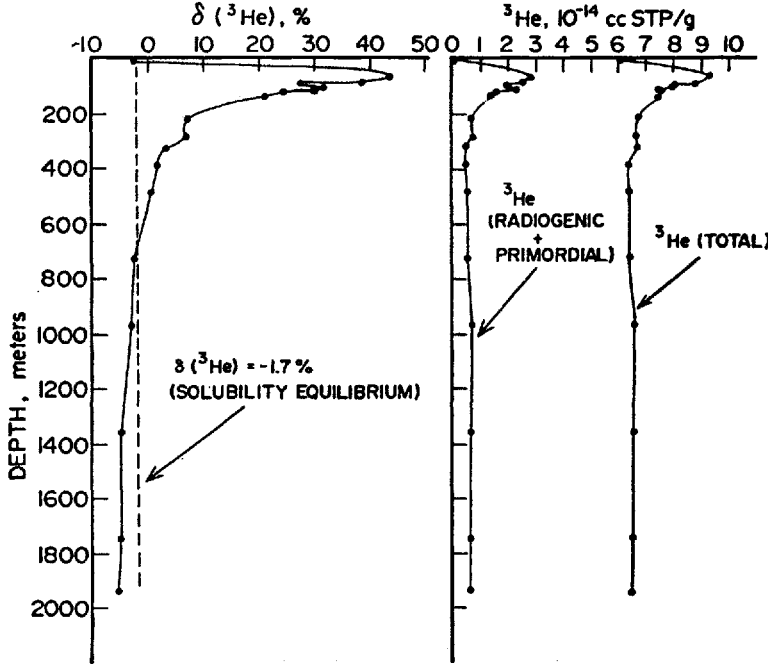Below the 322 m maximum, helium follows a linear trend with a gradient of

Figure 3. Profiles of δ(^{3}He), total observed ^{3}He, and ^{3}He rad. + prim. calculated by subtracting from ^{3}He tot. the amounts due to equilibrium solubility and air injection.

0.7×10^{-8} cc STP/g per km from 400 m to 1000 m and from 1000 m to the bottom the gradient decreases to about 0.07×10^{-8} cc STP/g per km. Neon concentrations below 400 m are nearly constant within experimental error, $4.0 \pm 0.2\%$ above the equilibrium solubility values of Weiss (1971). The He-Ne comparison below 400 m clearly reveals the presence of radiogenic ^{4}He, amounting to as much as 16% of dissolved He in the bottom 1 km—see Table 1.

b. ^{3}He/^{4}He and ^{3}He. The profile of δ(^{3}He) (Fig. 3) shows a sharp maximum at 69 m. Negative values observed below 700 m indicate the addition of radiogenic ^{4}He. Figure 3 also shows profiles of observed ^{3}He, and excess ^{3}He attributed to decay of tritium and of primordial origin. Excess ^{3}He was calculated in the following manner: the observed neon excess above solubility was used to calculate air injected helium as described previously. Air injected ^{3}He was then calculated assuming that δ(^{3}He) = 0 for this component. The above amount plus the equilibrium solubility concentration of ^{3}He, assuming δ(^{3}He) = -1.7% (Top and Clarke, in preparation), was then subtracted from the observed ^{3}He concentration

$$^3He_{r+p} = He\left(1 + \frac{\delta}{100}\right) R_A - (Ne-Ne_{sol.})\left(\frac{He}{Ne}\right)_{atm.} R_A - HeR_S$$

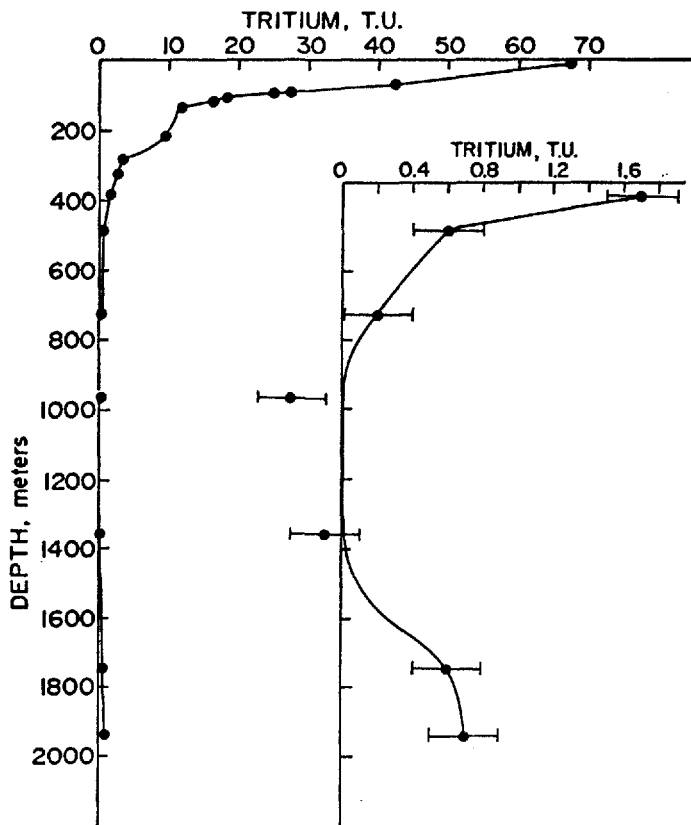where He and Ne are observed concentrations.

Figure 4. Tritium profile at station 1355. Error bars on inset diagram (387 m-1939 m) are 1σ analytical errors.

δ is the observed value of $\delta(^3He)$ corrected for decay of tritium during sample storage

$R_A = 1.384 \times 10^{-6}$ (Clarke *et al.*, 1976)

$R_B = 1.360 \times 10^{-6} = 1.384 \times 10^{-6}\ (1-0.017)$.

In the upper 200 m, it seems certain that the excess ^{3}He arises mainly from decay of nuclear-era tritium. Below 200 m, the excess ^{3}He is from tritium decay and from primordial ^{3}He in the mantle. The separation of these two components is addressed in a later section.

c. Tritium. A strong negative gradient is observed from the surface to 400 m with a hint of a maximum at 214 m which coincides with the maxima in He and Ne at this depth. The tritium concentration appears to reach zero at about 900 m (see Fig. 4) and then increase above zero for the two deepest samples at 1745 m and 1939 m. Although it is possible that these two samples were contaminated either
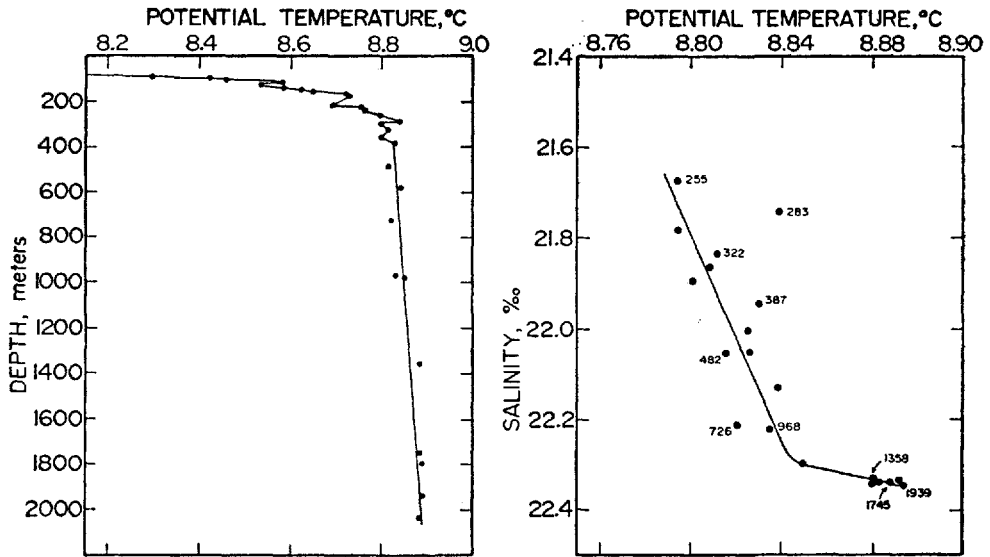
Figure 5. T_p vs. depth and T_p-S diagrams, station 1355. Numbers in the T_p-S diagram are depths in meters at which samples were collected for inert gas and tritium measurements.

during sampling or prior to gas extraction, we have no evidence for such contamination. It should also be noted that a nonzero tritium measurement of 0.30 ± 0.08 T.U. was made by Östlund (1969) at 2123 m depth, in the Black Sea at station 168 (Odysseus Expedition 65), 42° 45′N, 35° 36′E. Possible sources of tritium in the deep water are discussed in section g.

d. Tritium-³He ages. These ages were calculated from the δ(³He), He, and tritium data as outlined by Jenkins and Clarke (1976) and Top *et al.* (1980). A correction was applied for the presence of an air-injected component with ³He/⁴He assumed to be identical to ³He/⁴He in atmospheric helium. Tritium-³He ages range from 1.2 to 5.7 years in the upper 400 m—see Table 1. The ages should represent isolation times since equilibration with the atmosphere provided that water parcels have not mixed with other water parcels of different tritium and/or excess ³He contents. Below 400 m, tritium-³He ages will be seriously in error both because of mixing, and because of the presence of primordial ³He. An additional component due to the ⁶Li (n,α) ³H reaction in the sediments should also be considered. Estimates of the magnitudes of tritium and ³He derived from the ⁶Li reaction are given in sections g and h. It should also be noted that the tritium-³He ages do not have the same meaning as the vertical exchange times estimated later in this paper.

e. Temperature and salinity. Figure 5 shows plots of T_p vs. depth and T_p vs. *S*. An unusual feature of the T_p-depth curve is the positive gradient observed below 400 m.

The T_p-S relationship is approximately linear from 255 m to 1000 m, and data for deeper samples depart from linearity as if because of a temperature excess in the deep water, or because of a lower salinity than expected. We believe that a temperature excess caused by heat input from the sea bottom provides a reasonable explanation for both the T_p-depth gradient and the deep water T_p-S data. It should be noted however that in this simple analysis we ignore the possible presence of lateral fluxes, and the effects of long term climatic changes.

f. Calculation of exchange times. Exchange times between "boxes" may be estimated from the tracer concentration balance in a one dimensional box model. The helium profile shown in Figure 2 indicates two depths at which the slope changes abruptly—400 m and 1000 m. Thus in terms of "boxes" in communication we can represent the basin as consisting of three boxes: a bottom box from 1000 m to 2000 m, a middle box from 400 m to 1000 m, and a top box above 400 m. The whole upper 400 m is clearly not a suitable choice for the top box because of the difficulty of defining tracer concentration evolution functions. A more specific layer can be defined by the study of tritium variation in the shallow waters of the Black Sea. Figure 6 shows plots of tritium vs. salinity for samples collected in 1965 and 1969 (Östlund, 1969; Östlund *et al.*, 1974) and in 1975 (this study). Assuming that the tritium-salinity relationships are smooth and continuous, a family of tritium vs. time relationships can be constructed as shown in Figure 7. A single function for tritium evolution for the box model calculations can be used as a reasonable approximation only in the bottom portion of the upper 400 m. We will choose the salinity range 21.50‰-22.00‰ which represents a layer approximately between 200 m and 400 m. Figure 8 illustrates the depth and salinity boundaries chosen for box model calculations.

The concentrations of tritium and ³He can be used simultaneously in the following box model equations (Peterson and Rooth, 1976).

$$\frac{dX_2}{dt} = \lambda X_2 + \mu_1(X_1 - X_2) + \mu_2(X_3 - X_2) \tag{1}$$

$$\frac{dY_2}{dt} = \lambda Y_2 + \mu_1(Y_1 - Y_2) + \mu_2(Y_3 - Y_2) \tag{2}$$

where λ is the decay constant of tritium, 0.0563 y^{-1}

μ_1, μ_2 are exchange coefficients in y^{-1}

$X_{1,2,3}$ and $Y_{1,2,3}$ are concentrations of tritium and ³He in the bottom, middle and top boxes, respectively.

A major difficulty arises in that the solution for Y_2 is rather insensitive to μ_1 and μ_2. In other words, it is possible to obtain the observed ³He concentration in the middle box for a great range of combinations of μ_1 and μ_2, implying exchange times between a few years and thousands of years. In view of this difficulty we set aside
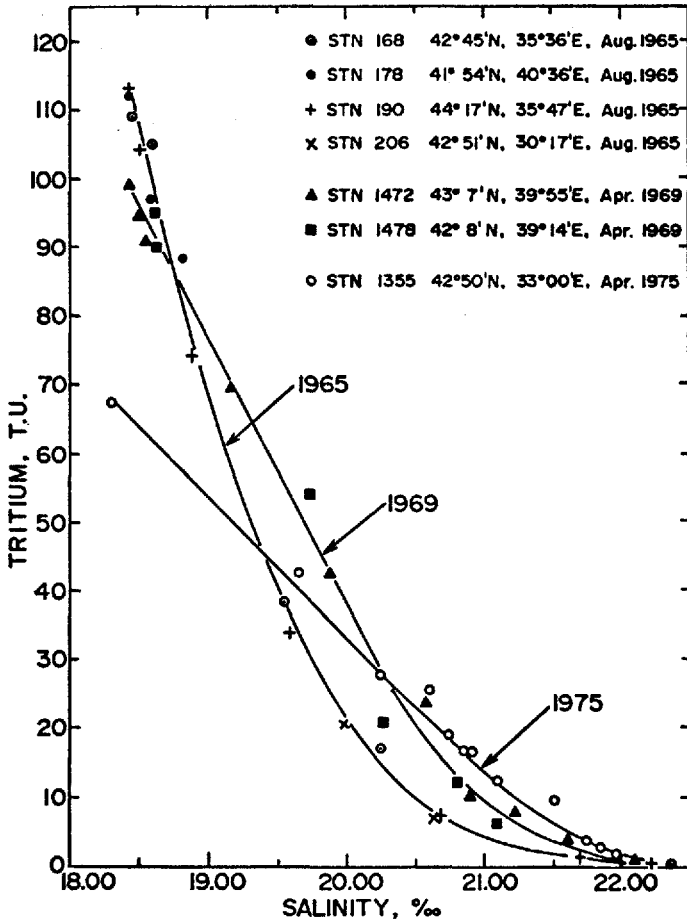
Figure 6. Tritium-salinity data for selected stations in the Black Sea sampled in 1965 and 1969 (Östlund, 1969; Östlund *et al.*, 1974) and for station 1355 sampled in 1975.

the simultaneous system in favor of the tritium concentration balance alone. In this case the model equation is the same as Equation (1), where X_3, as determined by a polynomial fit to the tritium evolution data in the 200 m-400 m layer with the constraint that the tritium concentration was zero in 1962, is given by

$$X_3 = 0.3t + 0.0016t^2 + 0.0037t^3 - 0.00018t^4 \tag{3}$$

where t is time elapsed since 1962, in years, and X_3 is the tritium concentration in tritium units (T.U.)*. In addition, we assume that the tritium concentration in the bottom box has increased linearly with time since 1962 when the concentration was zero, to 0.30 T.U. in 1975, i.e., $X_1 = 0.02t$. The solutions that match the 1975
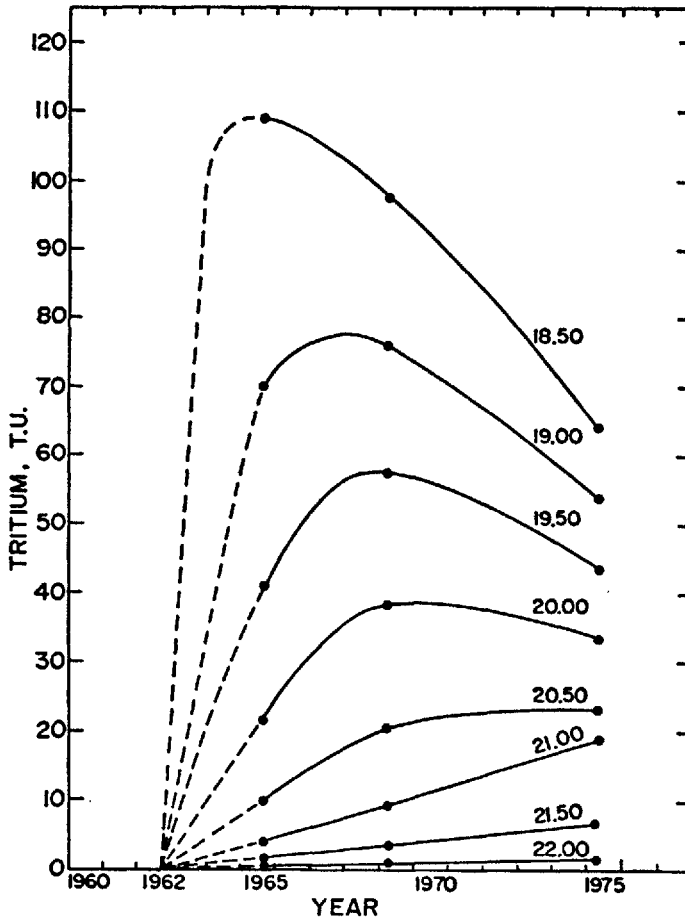
* 1 T.U. = 1 $^3H/10^{18}H$.

Figure 7. Tritium vs. time curves constructed from the data shown in Figure 6. The salinity interval 21.50‰-22.00‰ was chosen to represent the box above the middle box—see the text.

tritium concentrations in the middle box (integral average $= 0.25 \pm 0.15$ T.U.) give a relatively narrow range for μ_2, but an unfortunately large range for μ_1. For example even if the tritium concentration in the middle box is taken to be precisely 0.25 T.U., the integral average from 400 m to 1000 m, μ_2 falls in the range 0.007 y^{-1} to 0.008 y^{-1}, and μ_1 falls in the range 0.001 y^{-1} to 1 y^{-1}. The result for μ_1 can be understood when we consider the very small tritium concentration gradient between the bottom and middle boxes (integral averages of 0.30 T.U. and 0.25 T.U. respectively), and the fact that the main source for tritium in the middle box must be in the top box.

An alternative way of obtaining an estimate of μ_1 is to use the observed temperature gradient below 400 m and heat flow measurements. In this approach we assume
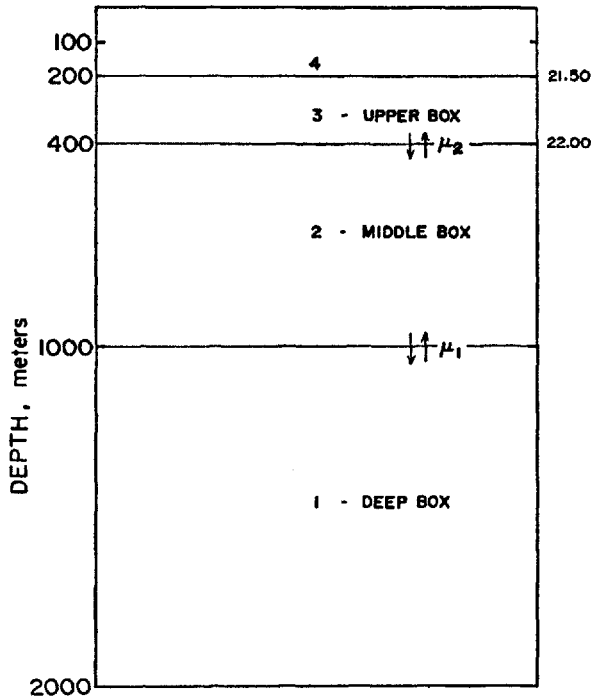
Figure 8. Depth intervals used in box-model calculations. Numbers at right of diagram are salinities in permil.

that the temperature gradient is maintained by the geothermal flux and that a steady state exists for exchange between the lower boxes. The possible effects of long term (few thousand years) climatic changes are considered to be small. The average heat flow determination of Erickson and Simmons (1974) based on 16 individual measurements, is $0.92 \pm 0.23 \, \mu$ cal cm^{-2} sec^{-1} for the Black Sea basin. The average of the three measurements of Zolotarev *et al.* (1979) closest to station 1355 is $0.90 \pm 0.09 \, \mu$ cal cm^{-2} sec^{-1}. The *in situ* temperature difference between the middle and bottom boxes is $\Delta T = 0.154 \pm 0.018°C$ using the measurements of R. Gagosian (private communication, 1978) at station 1355 and station 1356 (42°41′N, 30°37′E). The time required to establish the observed temperature difference is given by

$$t_1 = \frac{C\rho\Delta Z\Delta T}{\rho} . \tag{4}$$

If we use the following values
$$C = 1.0049 \text{ cal g}^{-1} \, °C^{-1}$$
$$\rho = 1.02 \text{ g cm}^{-3}$$

$\Delta Z = 8.0 \times 10^4$ cm

$\Delta T = 0.154$ °C

$\phi = 0.92 \times 10^{-6}$ cal cm^{-1} sec^{-1} (Erickson and Simmons, 1974)

we obtain $t_1 = 440$ y or $\mu_1 = 0.0023$ y^{-1} with an uncertainty of about ± 40%. If we assume that the time scales for heat and tritium exchange are identical, and if we take the 1975 tritium concentration in the middle box to be 0.25 ± 0.10 T.U., we obtain $\mu_2 = 0.008$ y^{-1}; i.e., $t_2 = 125$ y with an estimated error of about ± 60%. This value for t_2 can be compared with a bathtub flushing time of 500 y for the 400 m-1000 m layer using an inflow rate of 176 km^3 y^{-1} through the Bosporus (Shimkus and Trimonis, 1974). Thus it would appear that the evolution of tritium in the middle layer is governed mainly by vertical exchange with the source in the upper 400 m, rather than by horizontal transport from the Mediterranean.

An additional observation is that t_1 is significantly smaller than measured radiocarbon ages of Black Sea bottom water (Östlund, 1974). It seems possible that the high radiocarbon ages are due to introduction of "dead" carbon by redissolution of carbonate from sediments, and a re-evaluation of the radiocarbon ages in this context may resolve the discrepancy.

g. Tritium in the deep water. The observation of nonzero tritium concentrations at 1745 m and 1939 m, and practically zero concentrations at 968 m and 1358 m suggests at first sight a source of tritium in the sediments produced by the reaction ^{6}Li (n,α) ^{3}H. We have calculated the production of tritium by this reaction following the method of Morrison and Pine (1955), using the uranium data of Rona and Joensu (1974), the lithium data of Hirst (1974), and the specific gravity of Black Sea sediments (Keller, 1974). The production rate of tritium in a 10 km layer of sediments is at least three orders of magnitude smaller than necessary to account for the observed concentration of about 0.65 T.U. in the deep water. An alternative explanation for the nonzero tritium values in the deep water might be provided by considering the Mediterranean input as a sinking "plume." The situation pictured qualitatively is as follows: the Mediterranean input sinks because of its higher density, probably entraining some surface water. Eventually the mixture settles at an appropriate density horizon which appears to lie between 400 m and 1000 m according to the helium concentration data. However, the Mediterranean input is not a steady flow but varies seasonally. These seasonal changes may affect the dynamics of the process allowing the plume, at times, to sink until it reaches the bottom. The bottom 300 m where nonzero tritium concentrations are observed has a volume of about $5 \times 10^{13} \times$ m^3. A tritium concentration of 0.6 T.U. could be produced by injection of say 6×10^{11} m^3 of 50 T.U. water into zero tritium water. This volume corresponds to the *total* Mediterranean input for six years. Because the Mediterranean input is much lower in tritium concentration than 50 T.U. it appears that the plume must entrain Black Sea surface water which is relatively high in

tritium—for example values of approximately 150 T.U. have been measured for 1965 samples (Östlund, 1969).

h. ^{4}He and ^{3}He fluxes into the deep water. The ^{4}He flux into the deep water can be readily calculated using the Δ^4He data for the bottom box (see Table 1) and taking $t_1 = 440$ y. We obtain a value of $\phi(4) = 1.3 \pm 0.5 \times 10^6$ atoms cm^{-2} sec^{-1}, which appears to be significantly higher than the global average ^{4}He flux of $3 \pm 1.5 \times 10^5$ atoms cm^{-2} sec^{-1} determined by Craig *et al.* (1975). Assuming that the ^{4}He flux is equal to the steady state production in a 10 km layer of sediments containing 3 ppm U and 10 ppm Th according to Rona and Joensu (1974) we calculate a flux of 1.7×10^6 atoms cm^{-2} sec^{-1}. Thus the observed ^{4}He flux can be accounted for by U and Th decay in the sediments under the Black Sea.

The origin of the ^{3}He flux is more complex. Below about 100 m which is an approximate boundary based on the observation of practically zero radiogenic ^{4}He above that depth, we must consider three possible sources: (1) the reaction ^{6}Li (n,α) ^{3}H in the sediments, (2) *in situ* decay of nuclear-era tritium, and (3) primordial ^{3}He from the mantle beneath the sediments. Production from the ^{6}Li reaction in the sediments would appear to be negligible from the following considerations. Taking values of Li = 67 ppm, U = 3 ppm, Th = 10 ppm (Hirst, 1974; Rona and Joensu, 1974), we calculate a ^{3}He/^{4}He production ratio of 2×10^{-8}, using the method of Morrison and Pine (1955) and more recently measured cross sections for (α,n) reactions (Friedlander *et al.*, 1964). The observed excess ^{4}He in the deep water attributed to radiogenic He in the sediments is 0.65×10^{-8} cc STP g^{-1}. Thus the excess ^{3}He in the deep water arising from ^{6}Li in the sediments should be 1.3×10^{-16} cc STP g^{-1}, which is only about 2% of the observed ^{3}He excess of $0.6\text{-}0.7 \times 10^{-14}$ cc STPg^{-1} in the water below 1000 m—see Figure 9.

Tritium concentrations at 1745 m and 1939 m are 0.6 T.U. and 0.7 T.U. respectively. As discussed previously, production of tritium via the ^{6}Li (n,α) ^{3}H reaction in the sediments appears to be negligible. We conclude that almost all the observed tritium in the deep water is injected via buoyancy plumes or some other mechanism from high tritium nuclear-era surface water. If it is assumed that tritium in the deep water increased linearly with time from zero in 1962 to 0.65 T.U. in 1975, then the amount of ^{3}He produced is 6×10^{-16} cc STP g^{-1}, which is approximately 10% of the observed excess ^{3}He. Although a linear increase of tritium is probably a reasonable assumption, it is possible to imagine a single event tritium injection of as much as twice the 1975 value at the beginning of the 1962-1975 period, in which case the amount of ^{3}He produced would be 17×10^{-16} cc STP g^{-1}, or 25% of the observed excess ^{3}He as a high upper limit.

From the above considerations we conclude that at least 75%, and probably 90% of the observed excess ^{3}He in the deep water is of primordial origin from the mantle. Below 100 m, we would expect that the ratio of primordial ^{3}He to radio-
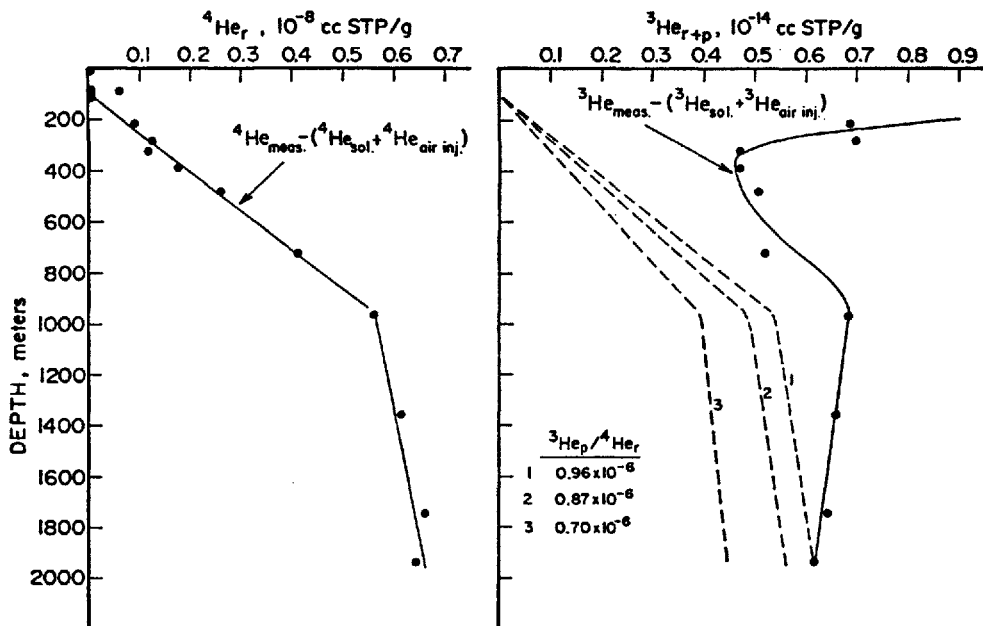
Figure 9. Profiles of radiogenic ⁴He and ³He of radiogenic and primordial origin. Dashed lines represent profiles of primordial ³He calculated assuming different concentrations of radiogenic ³He in the deep water—see the text.

genic $^4\text{He} = \dfrac{^3\text{He}_p}{^4\text{He}_r}$ is independent of depth. In other words we suppose that primordial ^3He and radiogenic ^4He leak into the deep water from the same locations on the sea floor. Because the $^4\text{He}_r$ profile is well defined—see Figure 9, we can construct profiles of $^3\text{He}_p$ with the condition that $\dfrac{^3\text{He}_p}{^4\text{He}_r}$ is a constant. An upper limit for $^3\text{He}_p$ can be found by taking $^3\text{He}_r = 0$ for the deepest sample. The profile for $^3\text{He}_p$ is shown as a dashed line labelled 1 in Figure 9. A lower limit $^3\text{He}_p$ profile labelled 3 is constructed by taking $^3\text{He}_r$ to be 25% of observed excess ^3He in the deepest sample. A more reasonable $^3\text{He}_p$ profile labelled 2 in Figure 9 is based on 10% for $^3\text{He}_r$, and corresponds to $\dfrac{^3\text{He}_p}{^4\text{He}_r} = 0.87 \times 10^{-8}$, which is assumed to be equal to the flux ratio $\phi(3)/\phi(4)$. If we now use the value $\phi(4) = 1.3 \pm 0.5 \times 10^6$ atoms cm^{-2} sec^{-1}, we obtain $\phi(3) = 1.1 \pm 0.6$ atoms cm^{-2} sec^{-1}. This value seems significantly smaller than the world ocean estimate of 4 ± 1 atoms cm^{-2} sec^{-1} (Craig *et al.*, 1975), and the difference may be due to lack of recent tectonic activity underneath the Black Sea and/or partial blocking of the primordial ^3He flux by the 10 km sediment layer. In this connection it should be mentioned that very similar results were obtained for Baffin Bay deep water where the upper limit for $\phi(3)$ was

0.5 atoms cm^{-2} sec^{-1} and $\phi(4)$ was about twice the world ocean estimate (Top *et al.*, 1980).

A puzzling feature of the excess ^{3}He profiles is the apparent maximum in ^{3}He$_r$ at 968 m. ^{3}He$_r$ profiles can be constructed by subtracting ^{3}He$_p$ profiles (dashed lines in Fig. 9) from the measured profile of excess ^{3}He above solubility plus air-injection. The maximum is less pronounced, but still seems real, even if profile 3 is taken to be correct for ^{3}He$_p$ rather than profiles 2 or 1. We would expect to see a *minimum* in ^{3}He$_r$ based on the observation of practically zero tritium concentrations at 726 m, 968 m and 1358 m. If the buoyancy plume model is used to explain nonzero tritium values at greater depths then it is difficult to see how a tritium minimum could accompany a ^{3}He$_r$ maximum. Clearly, more detailed measurements and modelling should be carried out in order to shed some light on this problem. The present measurements and discussion should be regarded only as preliminary attempts which have revealed several interesting features. Some of these features can be explained reasonably well and others defy explanation.

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