tracers used. Again, the transient tracers prove ideal for the task. Finally, the distributions of the short-lived natural tracers and of the anthropogenic tracers allow upper limits to be placed on the rates of vertical (diapycnal) mixing.

## 15.6 Ventilation of the Deep Sea

Although a number of estimates of the mean ventilation time for the deep sea have been proposed, that of about 1400 years, based on radiocarbon, is the most widely quoted. In the three-box model the ventilation time T of the deep sea is given by the following equation:

$$T \equiv \frac{V_{\rm D}}{R} = \left[\frac{({}^{14}{\rm C}/{\rm C})_{\rm S}}{({}^{14}{\rm C}/{\rm C})_{\rm D}} - 1\right]T_{{}^{14}{\rm C}},$$

where  $V_D$  is the volume of the deep sea, R the ventilation rate of the deep sea,  $({}^{14}C/C)_{s}$  and  $({}^{14}C/C)_{D}$  the carbon isotope ratios for the mean surface and mean deep ocean (prior to the industrial revolution), and  $T_{14C}$ the mean life of <sup>14</sup>C (i.e., 8200 years). Taking  $({}^{14}C/C)_{s}/({}^{14}C/C)_{p}$  to be 1.17 ± 0.03 (i.e.,  $\Delta^{14}C_{s} = -50 \pm$ 10% and  $\Delta^{14}C_D = -190 \pm 20\%$ ), a ventilation time of  $1400 \pm 250$  years is obtained. Among other things this model assumes that the ventilation times for water and carbon are equal. Because the  ${}^{14}C/C$  ratio in newly formed deep water has been shown not to reach that observed for the warm surface ocean, the ventilation time for water is surely less than that given by the box model. If the box model calculations used to obtain this result were repeated using average <sup>14</sup>C/C ratios obtained from the GEOSECS data set, the result would not change significantly. Evolution in geochemical and oceanographic thinking since the heyday of box modeling makes clearer the problems associated with using <sup>14</sup>C data to estimate water residence times in the deep sea. Until means of overcoming these problems are achieved it will not be possible to evaluate properly

the ventilation times derived from <sup>14</sup>C data, nor will it be possible to improve on them.

One problem is related to the fact that while the mixed layer of the ocean can be cooled (through contact with winter air) in a few weeks, equilibration between the <sup>14</sup>C/C ratio in the carbon dissolved in the mixed layer and that in the atmospheric CO<sub>2</sub> requires a decade or more. Harmon Craig recognized this problem long ago but until recently it has received only casual attention. The upshot is that the <sup>14</sup>C residence time in the deep sea must exceed the water residence time. Results from the Weddell Sea (Weiss, Östlund, and Craig, 1979) dramatically illustrate this point, for the new deep water formed there contains nearly the same <sup>14</sup>C/C ratio as ambient circumpolar deep water.

The other problem has to do with the recirculation of old water within the deep sea. Rarely is it possible to isolate the component of <sup>14</sup>C/C change due to in situ aging. Rather, the changes in  ${}^{14}C/C$  ratio within a given deep-sea basin can be accounted for largely by the mixing of end members with different <sup>14</sup>C/C ratios. This greatly complicates the use of <sup>14</sup>C data to obtain the flux of deep water into a given basin.

The trend of  $\Delta^{14}$ C along the 4000-m horizon is shown in figure 15.11. The pattern shows a gradual decrease in <sup>14</sup>C/C "down" the Atlantic and "up" the Pacific (with similar values in the Antarctic segments of the two oceans). The down-Atlantic decrease is about 80% and the up-Pacific decrease is about 70‰. While this might be interpreted as evidence for gradual aging as the water moves by advection slowly around the globe, a close look at the situation reveals that at least in the Atlantic the trend is largely the result of mixing between low 14C/C waters of circumpolar origin and high <sup>14</sup>C/C waters of northern Atlantic origin. When this mixing is taken into account the residence time of water in the Atlantic is considerably decreased and the flux of new North Atlantic deep water necessary to maintain it is correspondingly increased (table 15.5).

Table 15.5 Evolution of Calculations of the Apparent <sup>14</sup>C Age of a NADW Sample with a  $\Delta^{14}$ C of -105%

	$\Delta^{14}$ C values							
	Warm surface water	New no. comp. water	New AABW	Δ due to mixing with AABW	Δ due to <i>in situ</i> aging	Apparent <sup>a</sup> age		
Broecker et al. 1960	-28	(-28)	-155	0	-77	675		
Broecker and Li 1970	-40	(-40)	-155	-12	-53	470		
Stuiver (GEOSECS) 1976	—	-70	-160	-10	-25	225		
Broecker (GEOSECS) 1979		-70	-160	-26	-9	80		

a.  $t = 8200 \ln \frac{1 - (\Delta^{14} C_{initial}) \times 10^{-3}}{1 - (\Delta^{14} C_{initial} + \Delta_{aging}) \times 10^{-3}}$ .

450 W. S. Broecker



(15.11A)

Figure 15.11 Maps showing the distribution of <sup>14</sup>C along the 4000-m horizon in the Atlantic (A) and Pacific (B) Oceans. The analyses were made by Östlund at the University of Miami and Stuiver at the University of Washington as part of the GEOSECS program.



(15.11B)

Before going into this matter further, it is appropriate to review the evidence leading to the conclusion that the back mixing of Antarctic deep water is the major cause for the  ${}^{14}C/C$  gradient observed in the Atlantic. Confusion on this point has arisen because of the ambiguity in estimates based on conventional temperature-salinity  $(\theta - S)$  analysis of the fractions of various contributing water types. There are three such northern water types: deep water formed by winter cooling in the Labrador Sea (LSW); water spilling over the sill connecting Iceland to Greenland (DSW); and water which ultimately comes from overflow across the sill connecting Iceland with the British Isles but enters the western basin through the Gibbs Fracture Zone. As shown in table 15.6, the traditional  $\theta$ -S approach is not particularly sensitive, because the  $\theta$  and S ranges for the three contributing northern water types are large compared to the differences from the dominant southern type, i.e., the Antarctic Bottom Water (AABW). Temperature and salinity could be used only if the relative proportions of the northern-source waters one to another were known. They are not (see chapters 1 and 2).

By contrast the SiO<sub>2</sub> and the "NO" contents of the three northern water types are almost identical and are very different from that for AABW (see figure 15.12). Thus, were either of these properties conservative, we would have a means of determining the fractions of high-<sup>14</sup>C northern and low-<sup>14</sup>C southern waters in any given sample from within the mixing zone. One test of conservation is a plot of SiO<sub>2</sub> versus "NO". Linearity would require either conservation of both properties or a fortuitous correlation between the true "NO" coefficient and the amount of SiO<sub>2</sub> added to any given sample through the dissolution particles. As shown in figure 15.12 the relationship is remarkably linear except for waters in the southern eastern basin. If this linearity is (as I believe it can convincingly be shown to be) a demonstration of near conservancy of "NO" and SiO<sub>2</sub>, then the fraction of southern component in each sample of deep Atlantic water collected by the GEOSECS program can be determined either from its SiO<sub>2</sub> or "NO" content (these two independent estimates generally agree to  $\pm 0.03$ ). The plot of  $\Delta^{14}$ C versus fraction of southern component so obtained is given in figure 15.13. The dominance of mixing is clearly demonstrated. The deviation attributable to radiodecay averages only 9‰ (the measurement error on a given sample averages 4‰).

The geographic and depth patterns of the residual anomalies (i.e., those produced by radiodecay within the Atlantic) are shown in figure 15.14. The only pronounced feature is the larger anomaly for the eastern than for the western basin. As shown in table 15.5, estimates of the residence time of waters in the deep western Atlantic have dramatically decreased with time. Part of this decrease is accounted for by the realization that water descending in the deep northern Atlantic has a lower <sup>14</sup>C/C ratio than ambient Atlantic surface water. The rest is due to the increase in the estimates for the role of AABW back mixing.

As I have shown in a separate publication (Broecker, 1979), if an advective model is used to reproduce both the distribution of northern and southern components in the western Atlantic and the distribution of the residual (i.e., *in situ* decay) anomalies, then a flux of  $20 \times 10^6$  m<sup>3</sup>s<sup>-1</sup> of northern component (some mixture of LSW, GFZW and DSW) and  $10 \times 10^6$  m<sup>3</sup>s<sup>-1</sup> of southern component (AABW) are needed. As the deep portions of the eastern basin are known to be ventilated from the western basin (via fracture zones), no extra flux of northern component water is needed for its ventilation (part of the water exiting the western basin does so through the Romanche and possibly other frac-

Water type	θ (°C)	S (%00)	"NO" (μM kg <sup>-1</sup> )	$SiO_2 (\mu M kg^{-1})$	Δ <sup>14</sup> C (‰)
Labrador Sea Deep Water	3.3	34.94	430	12	-69
Denmark Straits Overflow Water	1.5	34.91	427	10	-69
Gibbs Fracture Zone Water	2.8	35.00	429	13	-63
Mediterranean Sea Overflow Water	12	36.4	300	8	~-60
Circumpolar Bottom Water	0.0	34.70	511	125	-163
Circumpolar Intermediate Water	2.2	34.63	472	85	-147

Table 15.6 Characteristics of the Contributors of the NADW Complex





Figure 15.12 Plots of "NO" versus  $SiO_2$  for all the samples taken by the GEOSECS program below 1500 m in the Atlantic Ocean. In the western basin (A) the entire range of compositions between northern (DSW, LSW, and GFZW) and southern (AABW) component water is seen consistent with the twoend-member hypothesis. No change in slope is seen at the Two Degree Discontinuity (Broecker, Takahashi, and Li, 1976). In the northeastern basin (B) those stations nearest to the Straits of Gibraltar show a deviation toward low "NO" value for any given  $SiO_2$  content caused by the admixing of low "NO" Mediterranean water (see table 15.6). Deep waters in the southeastern basin (C) show a deviation toward high silica at any given "NO" value. This presumably reflects *in situ* production of silica through the dissolution of particulate matter.



Figure 15.13  $\Delta^{14}$ C for western basin deep waters as a function of the fraction of southern component (F.S.C., as estimated from the "NO"-SiO<sub>2</sub> relationship). Were mixing alone responsible for the trend, then the points should lie along the line joining  $\Delta^{14}$ C = -160‰, F.S.C. = 1.0, and  $\Delta^{14}$ C = -70‰, F.S.C. = 0.0. Deviations below this line are presumably a measure of the loss of radiocarbon within the mixing zone by radioactive decay. The radiocarbon measurements were made by Stuiver of the University of Washington and Östlund of the University of Miami.

454 W. S. Broecker



Figure 15.14 Four sections showing the geographic and depth distribution of the <sup>14</sup>C anomalies attributable to radioactive decay within the deep Atlantic. The contours show the fraction of southern component (i.e., AABW) within the deep Atlantic.

ture zones which cut the Mid-Atlantic Ridge). The question how much more water is needed to ventilate the eastern basin above the ridge crest is not so easily answered. I guessed that  $10 \times 10^6 \text{ m}^3 \text{ s}^{-1}$  more of northern component is required. If so, then the total flux of northern component is  $30 \times 10^6 \text{ m}^3 \text{ s}^{-1}$ .

The volume of the deep sea (below 1500 m) divided by  $30 \times 10^6$  m<sup>3</sup> s<sup>-1</sup> gives 900 years. Thus, were North Atlantic Deep Water the only source of *carbon* isotope ventilation, the mean age of deep-sea carbon with respect to that entering with new deep water formed in the northern Atlantic would be 900 years. Starting with  $\Delta^{14}$ C values of  $-70\%_0$ , this would give a mean  $\Delta^{14}$ C for deep-sea carbon of  $-167\%_0$  (a value close to the observed mean).

This does not imply that ventilation of the deep sea by waters descending around the continent of Antarctica is negligible. Rather, as shown by Weiss et al. (1979), these waters exhaust heat without substantially changing their <sup>14</sup>C value. Thus if, as commonly estimated, the flux of new deep waters formed around the perimeter of Antarctic is in the range 10 to 40 ×  $10^{6}$  m<sup>3</sup>s<sup>-1</sup> (Gordon, 1975b; Gill, 1973; Killworth, 1974, 1977; Carmack, 1977), then the water ventilation time of the deep sea is probably considerably less than 900 years.

While these calculations are preliminary and subject to many criticisms, they do serve to indicate that derivation of water fluxes from <sup>14</sup>C data is far from a straightforward exercise. The conventional <sup>14</sup>C-residence time (based on box models) provides only an upper limit on the water-residence time. As temperature is probably the property most rapidly equilibrated with the atmosphere and carbon isotopes the most slowly equilibrated, the renewal time for other substances (CO<sub>2</sub>, NO<sub>3</sub>, SiO<sub>2</sub>, . . .) will lie in between the water and carbon-isotope renewal times.

## 15.7 Ventilation of the Main Oceanic Thermocline

The GEOSECS program has provided for the first time a reasonably detailed coverage of the distribution in the ocean of the <sup>14</sup>C and <sup>3</sup>H produced by nuclear testing. These distributions emphasize the importance of two phenomena evident but perhaps not fully appreciated through more conventional oceanographic observations. First they suggest an upwelling flux in the equatorial ocean comparable on a global scale to the flux of newly formed deep water (Broecker, Peng, and Stuiver, 1978). Second, they illustrate the importance of thermocline fronts located near lats. 15°N and 15°S (Broecker and Östlund, 1979).

Strong upwelling in the equatorial ocean (or in the eastern boundary regions feeding into the equatorial zone) is suggested by the distribution of bomb-produced <sup>14</sup>C. The equatorial zone is characterized by low

surface-water bomb <sup>14</sup>C/C ratios and shallow penetration of bomb <sup>14</sup>C (relative to the adjacent temperate gyres). If the gas-invasion rate (from the atmosphere) into equatorial waters is comparable to that into temperate waters (as I believe it must be), then the low inventory of bomb <sup>14</sup>C in the equatorial zone can only be maintained by the input to the equatorial zone of water deficient in bomb 14C. The only source of such water is upwelling from depths of at least 500 m. As the bomb <sup>14</sup>C distribution within the equatorial zone is quite homogeneous along isopycnal surfaces (figure 15.15), this isotope is not a sensitive indicator of the place at which upwelling occurs. However, by combining <sup>14</sup>C data with data for tracers like  $P_{CO_{2'}}$   $P_{N_{2}O_{1}}$  NO<sub>3</sub>, NO<sub>2</sub>, which have shorter surface-water response times than does <sup>14</sup>C, it may be possible to get at the entry pattern of upwelled water. Furthermore, time series of <sup>14</sup>C (as measured directly on water samples and as reconstructed through measurements of coral-growth rings) may reveal fluctuations in the rate of upwelling.

The distributions of <sup>90</sup>Sr and <sup>3</sup>H in the Atlantic demonstrate a front near 15°N, because the water-column inventory of these isotopes drops by an order of magnitude near that latitude. As shown in figure 15.16, the concentration of tritium along any given isopycnal also drops by an order of magnitude from north to south across this front (Broecker and Östlund, 1979). One reason for this difference is that the bulk of the <sup>90</sup>Sr and <sup>3</sup>H "fallout" occurred to the north of the equator. This asymmetry between hemispheres does not explain, however, why the boundary is so abrupt and why it lies near 15°N.

An answer to this dilemma comes from the equatorial upwelling inferred in the zone over which the thermocline is thin and shallow (i.e., 15°N to 15°S). As this upwelling is driven by the poleward divergence of equatorial surface water, any <sup>3</sup>H or <sup>90</sup>Sr reaching the equatorial zone by fallout or by leakage across the 15°N front will be pulled back to the surface and carried poleward across the front. Thus upwelling accounts for both the location of the fallout front and its sharpness.

As shown by Broecker et al. (1978), the distribution of <sup>14</sup>C in the equatorial zone yields a ratio of the flux of upwelled water to the invasion rate of CO<sub>2</sub>. Since the latter has been independently determined, the upwelling flux can be obtained. Using this approach we obtained a flux of about  $15 \times 10^6$  m<sup>3</sup>s<sup>-1</sup> for the Atlantic equatorial zone. A preliminary analysis of the Pacific Ocean <sup>14</sup>C data suggests that the upwelling flux there is about  $30 \times 10^6$  m<sup>3</sup>s<sup>-1</sup>. As mentioned above, no firm statement can yet be made as to where this upwelling occurs, for a high rate of lateral mixing obscures its origin.

456 W. S. Broecker



## **15.8 Formation of Deep Waters**

As pointed out, there are serious difficulties in using the distribution of natural radiocarbon to obtain deepwater formation rates. In the Antarctic this stems from the fact that the <sup>14</sup>C clock is not reset during the formation process. In the deep Atlantic the anomaly due to radiodecay is small compared to the anomaly due to mixing. Also, there is no simple way to separate the contributions of the three (or possibly more) northern water types contributing to North Atlantic Deep Water. It behooves us therefore to seek other geochemical methods to gauge these fluxes. One obvious approach is to use the substances added to the ocean as a by-product of man's activities to trace recently formed deep water. The GEOSECS 3H section along the western basin in the Atlantic (figure 15.17) shows that the pathway followed by the newly formed water was in 1972 clearly "stained" with fallout products. So the potential is there. At a minimum, surveys spaced at decade intervals would clearly demonstrate the manner and rate at which the front of tritiated water is pushing its way into the western basin of the Atlantic.

The problem of inverting distributions of these transient tracers into fluxes is a difficult one. The geometry of the system is complex. Simple box-model representations are bound to give misleading answers. I do not mean to imply by this that the situation is hopeless. Rather the job will be a long one, requiring imagination, diligence, and excellent measurements.

It will be helpful, moreover, to explore what limitations the relationships among these tracers place on the types of dynamic models that might be employed. An example drawn from the GEOSECS observations will serve to illustrate this point. Despite quite differ-



Figure 15.15 Plots of tritium (A) and of radiocarbon (B) v. potential temperature in the equatorial thermocline of the Atlantic Ocean. The tritium data give the impression that tritium-bearing surface water is being mixed down into tritium-free water of potential temperature about 8°C. If 8°C water is taken to be the source for upwelling, then the <sup>14</sup>C data can be interpreted as a mixture of surface water of  $\Delta^{14}C =$ 100% and 8°C water with a  $\Delta^{14}C$  value of about -90%.



Figure 15.16 Tritium distribution along the isopycnal of  $\sigma_{\theta} = 26.80$  in the Atlantic Ocean. The 15°N thermocline front constitutes a very pronounced boundary between high-tritium waters to the north and low-tritium waters to the south.

ent input mechanisms, bomb-produced <sup>14</sup>C and <sup>3</sup>H show a very high degree of covariance in the northern Atlantic (figure 15.18). The samples included in this diagram cover the entire range of depth, geographical location, and water type. Modeling shows that different combinations of advection (away from the source region) and diffusion predict a great variety of <sup>14</sup>C-<sup>3</sup>H trends. Thus the combined tracer fields can perhaps tell us not only the pathways followed but also something of the dynamics of the water movement.

## **15.9 Vertical Mixing Rates**

Although there is no way to demonstrate how the isotopes we study penetrate into the interior of the ocean, we can still use their distributions to place upper limits on the rate of vertical mixing in the sea. This can be done by matching any given depth profile to a onedimensional model, as has been carried out for profiles of <sup>222</sup>Rn and <sup>228</sup>Ra in the deep sea, and for profiles of bomb <sup>3</sup>H and <sup>14</sup>C in the main oceanic thermocline, as shown in figure 15.19. The apparent vertical diffusivities obtained in this way show an inverse correlation with density gradient (Sarmiento et al., 1976; Hoffert and Broecker, 1978). Quay, Broecker, Hesslein, and Schindler (1980), using tritium injections into two small lakes in Canada, were able to obtain vertical diffusivities for much higher density gradients. As the tracers were allowed to spread laterally over the entire breadth of each lake, these results are true rather than apparent vertical diffusivities. As shown in figure 15.19, the tracer results from the lakes fall close to the extension of the oceanic curve.

It is difficult, however, to assess the significance of these results. Sarmiento and Rooth (1980) have shown that the bottom <sup>222</sup>Rn results could be explained entirely by mixing along isopycnals. Sarmiento (1978) has shown this to be the case for <sup>228</sup>Ra in the deep sea as well. It has long been suspected by oceanographers that the main thermocline of the ocean



Figure 15.17 Tritium section along the western basin of the North Atlantic, prepared by Östlund of the University of

Miami, who made all the tritium measurements for the GEO-SECS program.



Figure 15.18 Tritium (in T.U.) vs. radiocarbon (in  $\Delta^{14}$ C) for water samples (from all depths) in the Norwegian Sea (A) and northern Atlantic (B). The solid curves show the results predicted by a one-dimensional diffusion model (the diffusion coefficients are in the units cm<sup>2</sup> s<sup>-1</sup>).



Figure 15.19 Apparent eddy diffusion coefficients for vertical mixing as measured by  $^{222}$ Rn and  $^{228}$ Ra in the deep sea (Sarmiento et al., 1976), <sup>3</sup>H in the pycnocline of the Norwegian Sea (Hoffert and Broecker, 1978) and bomb  $^{14}$ C in the Sargasso Sea (Broecker et al., 1978) as a function of density gradient. Also shown are the results of Quay et al. (1980), obtained by tritium injections into small lakes.

is ventilated mainly along isopycnal surfaces. Certainly the distributions of bomb-produced <sup>3</sup>H and <sup>14</sup>C in the main oceanic thermocline could be explained by this process. The <sup>7</sup>Be profile shown above could be interpreted as an artifact of winter convection. Perhaps an argument relating to the angle between isopycnal surfaces and the tracer source (sea surface or floor) can be made as an alternative to the correlation between apparent vertical diffusivity and density gradient.

In my estimation the only way in which the relative importance of vertical and horizontal mixing can be established is to perform tracer injections at various points in the ocean interior. Such experiments (using <sup>3</sup>He as a tracer) would be comparable in cost to that for the large ocean science projects currently underway. The technology needed is available. By following a <sup>3</sup>He or tritium addition to an isopycnal horizon for several years, it would surely be possible to obtain a better estimate than we now have for the relative magnitudes of mixing along and perpendicular to isopycnal horizons. A knowledge of the relative importance of these processes is critical to the development of adequate models for the interpretation of radioisotope tracer data.

460 W. S. Broecker