Silicon molecules are exported from the surface layers to the interior of ocean with settling particles as biogenic opal and lithogenic silica. Oceanic biogenic SiO_2 mostly consists of poorly crystallized polymorphs of silica – biogenic opal. Radiolarian tests are a zooplankton counterpart. Globally, the majority of biogenic opal particle export is attained by diatom frustules. Silicoflagellate skeletons often constitute a few percent of the total biogenic opal flux in a low-latitude ocean. In general, about 40–70% of the opal–SiO_2 particles are dissolved before reaching the interior sink. An estimate of global flux of silicon in the ocean interior is 0.72 Gt year^{-1}. The global Ca (in carbonate particles) and Si (in biogenic opal particles) export fluxes at the oceanic interior are 2.9 and 1.4 Gt year^{-1}, respectively.

The density of lithogenic particles, clay and fragments of rock-forming mineral particles, that are brown from dry land, suspended in the air above the oceans differs by several orders of magnitude by locations, depending on global atmospheric advection patterns and distance from the source. Unlike biogenic ocean particles, airborne particles that arrive at the deep seafloor are hardly altered from the time they fall onto the ocean surface, and can therefore be considered a proxy for atmospheric circulation. Lithogenic particles may play critical roles in supplying micronutrients, particularly dissolved iron. Lithogenic particles ballast aggregates to settle and remove organic carbon particles from the upper ocean as coccoliths do.

Current export flux data reveals distinct 'biogeochemical regions' where the biological pump operates in two significantly different modes. In one the export of $CaCO_3$ particles is dominant over opal particles. In the other the export of opal particles is dominant over $CaCO_3$ particles; the mole ratio of Si in biogenic opal particles to the inorganic carbon from $CaCO_3$ particles (Si/C ratio) is higher than 1. The opal export-dominated domain occupies the cold water regions except the polar oceans and covers less than 20% of the present global ocean. The subarctic Pacific – including the area north of 45°N, the Bering Sea, the Sea of Okhotsk and the northern East Sea (Japan Sea) – and the Southern Ocean to the south of the Subantarctic Polar front are opal export-dominated oceans. This difference is caused by the availability of dissolved SiO_2 in the water column, and the mixing and upwelling of the thermohaline circulation. The moderate and tropical basins of the Pacific and Indian Ocean are carbonate-export dominated (the Si/C ratio is smaller than 1) ocean. Most of the North and South Atlantic Ocean including the Nordic Seas are $CaCO_3$-dominated oceans except for the Atlantic Southern Ocean.

In the Pacific Ocean the Subarctic and Subantarctic Front demarcate these two biogeochemical regions; the poleward areas of the fronts are opal-export dominated. Opal export-dominated ocean removes atmospheric CO_2 more efficiently because it is usually associated with higher export of organic carbon with a higher rain ratio. The processes of sequestering opal do not affect the alkalinity. On the other hand, carbonate particles that are exported to the deep ocean floor generate alkalinity by dissolution and contribute alkalinity when deep water is recycled to the surface ocean by global thermohaline circulation in a millennium order of timescale.

See also

Calcium Carbonates. Carbon Cycle. Carbon Dioxide (CO₂) Cycle. Marine Silica Cycle. Marine Snow.

TRITIUM–HELIUM DATING

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Introduction: Tritium in the Oceans

Tritium (^{3}H) is the heaviest isotope of hydrogen. Its nucleus consists of one proton (making it hydrogen) and two neutrons. Inasmuch as it is chemically hydrogen, tritium exists within the global environment primarily as part of the water molecule. Thus it is a potentially useful tracer of the hydrologic cycle, and an ideal tracer of water motions within the ocean. Tritium is radioactive, decaying with a half-life of 12.45 years to the stable, inert daughter isotope ^{3}He. Because of its geologically short half-life, there is very little natural tritium in the environment. Small quantities are created by cosmic ray spallation (i.e. the smashing of atomic nuclei into small fragments by high-energy
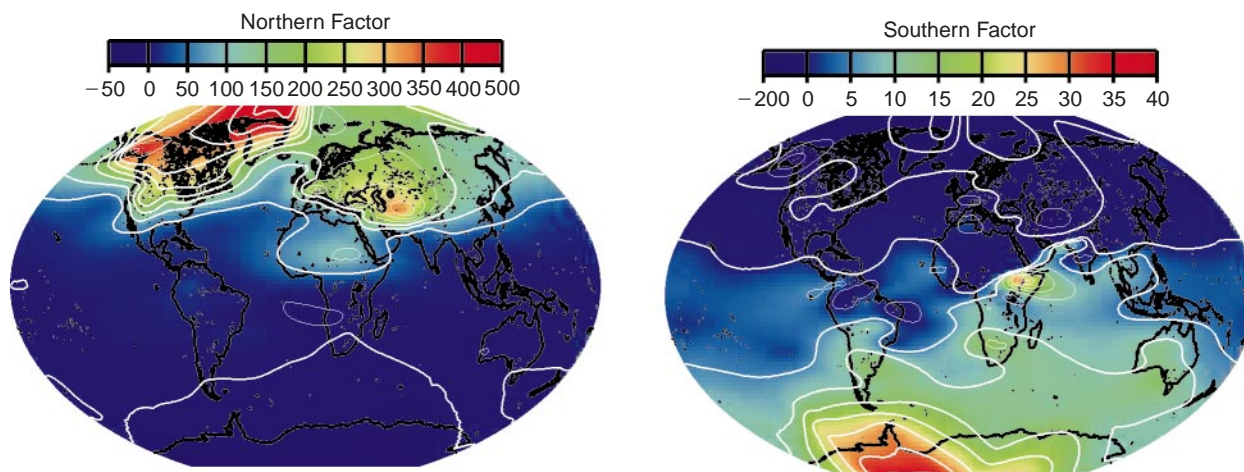
Figure 1 Spatial pattern of the two dominant principal components of bomb tritium in precipitation. These were derived from a statistical analysis of the time variation of bomb tritium in precipitation by S. Doney.

cosmic rays) in the upper atmosphere. The balance between production and radioactive decay leads to a global natural tritium inventory of approximately 4 kg.

This natural inventory was dwarfed by the production of tritium by the atmospheric testing of nuclear fusion weapons during the 1950s and early 1960s. During this period, several hundred kilograms of tritium were released, largely late in the test series, and primarily in the Northern Hemisphere. The detonations generally injected the tritium into the stratosphere, where it was quickly oxidized to form water vapor. Over a period of a few years, the tritiated water vapor was transferred, largely at mid-latitudes, to the troposphere, where it was rapidly 'rained out' to the earth's surface. The delivery of bomb tritium to the earth's surface was monitored by a number of WMO/IAEA (World Meteorological Organization (UN)/International Atomic Energy Authority) precipitation sampling stations. The pattern and timing of this delivery has been shown to consist of two primary components: a dominant northern, spike-like component, and a weaker southern component. Due to the geographic nature of the coupling between the stratosphere and the troposphere, tritium concentrations were elevated in both components toward higher latitudes, and weaker near the equator (**Figure 1**). Tritium levels in precipitation over land also tended to increase with altitude.

The northern component reflects the more immediate injection of bomb tritium into the northern hemispheric hydrologic system because virtually all of the major detonations occurred in the Northern Hemisphere. Prior to the bomb tests, the concentration of natural tritium in rainfall was of the order of
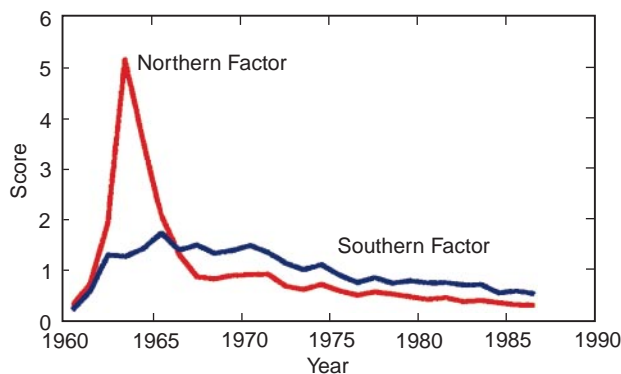
Figure 2 Time history of the two dominant principal components of tritium in precipitation. Note that the northern component (red curve) is more spike-like and the southern component (blue curve) is more 'smeared out' in time.

5–10 tritium units (1 TU = 1 tritium atom per 10^{18} normal hydrogen atoms). During the mid-1960s, tritium concentrations of more than several thousand TU were recorded in higher latitude, mid-continental locales such as Chicago, USA or Ottawa, Canada. The southern component, on the other hand, is much weaker in amplitude and more smeared out in time since it results primarily from the cross-equatorial leakage of northern hemispheric tritium with few local sources (**Figure 2**).
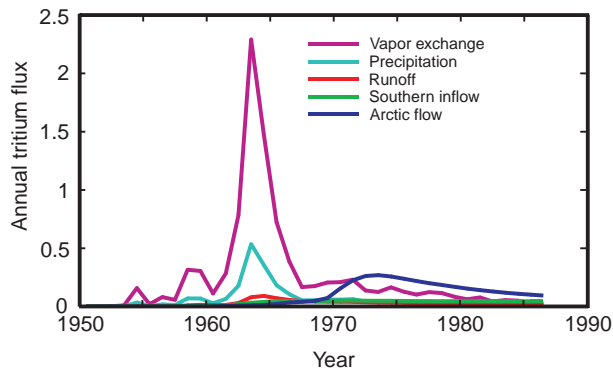
Providing the production of bomb tritium is well known, the patterns and time variations of tritium concentrations in rain, environmental, and ocean waters provide useful insights into the hydrologic cycle and ocean circulation. Unfortunately, direct observation of environmental tritium levels was limited because the development of analytical techniques lagged events. Efforts are ongoing to

reconstruct tritium records in precipitation by analysis of this isotope in tree rings. This has been made possible by the relatively recent development and improvement of high-sensitivity techniques of tritium measurement by ^{3}He regrowth.

The deposition of tritium to the oceans occurs both by direct precipitation and by vapor exchange. Vapor exchange is a two-way process, and in general dominates over the direct precipitation. There are relatively few direct measures of tritium concentration in atmospheric water vapor, but studies indicate that it is closely related to levels in precipitation. This linkage has been exploited in order to construct tritium depositional histories for ocean basins from tritium in precipitation records.

Another pathway whereby tritium enters the ocean is through continental runoff and river flow. Tritium deposited to the continents ultimately flows to the oceans via lakes, rivers and groundwater flow, but is retained within the continental hydrosphere for time-scales of many years, thereby introducing a delayed input to the oceans. Further, when computing the time-evolving tritium inventory within an ocean basin, it is necessary to consider inflow and outflow across the basin's boundaries.

The relative importance of the various inputs to the ocean varied with time. An analysis of the tritium budget for the North Atlantic Ocean, for example, shows that water vapor exchange (the magenta curve in **Figure 3**) and direct precipitation (the cyan curve in **Figure 3**) were the dominant inputs of tritium during the mid-1960s when the tritium 'spike' occurred. By the 1970s, however, the major input became the inflow of low salinity water from the Arctic (the dark blue curve in **Figure 3**). A substantial inventory of bomb tritium had been delivered to and held up within the Arctic freshwater system, to be released more gradually to the subpolar oceans, and subsequently to the North Atlantic.

This input can be seen in the distribution of tritium in surface waters as observed during the early 1980s (**Figure 4**). **Figure 4** shows the intrusion of tritium-labeled waters along the east coast of Greenland and the Labrador Sea (red areas). This is superimposed on a general southward-decreasing trend. In response to the deposition of tritium, North Atlantic surface water concentrations rose rapidly, reaching values approaching 18 TU, or about 40 times greater than natural, prebomb, surface ocean levels. After peaking in 1964, surface water concentrations decreased, in part due to radioactive decay of this isotope, but also due to the dilution of surface waters with older, lower tritium waters from below, and lower concentration Southern Hemisphere waters. Consequently, the surface water decrease observed is significantly faster than the radioactive decay timescale.
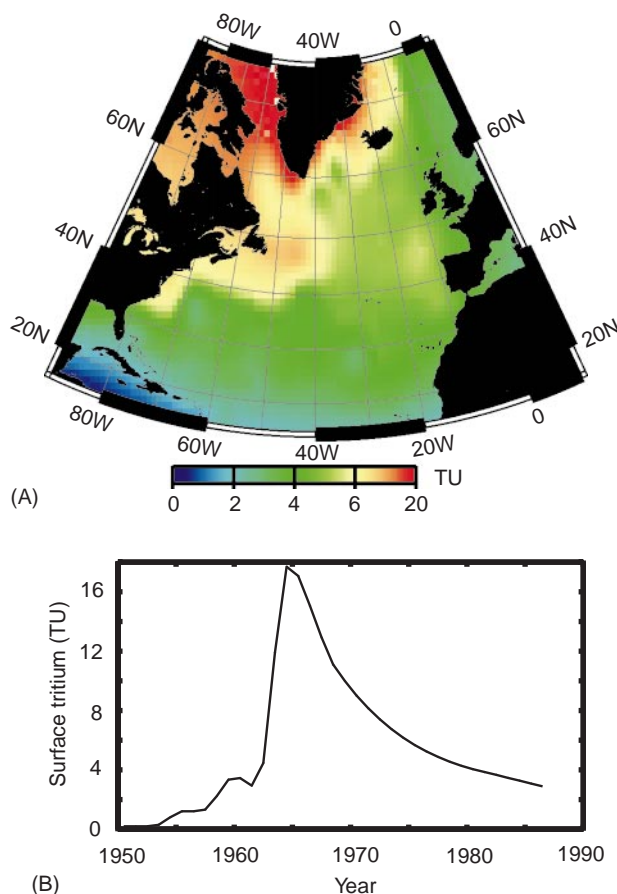
Figure 4 North Atlantic surface water tritium concentrations: (A) geographical distribution in the early 1980s; (B) variation with time in the subtropics.
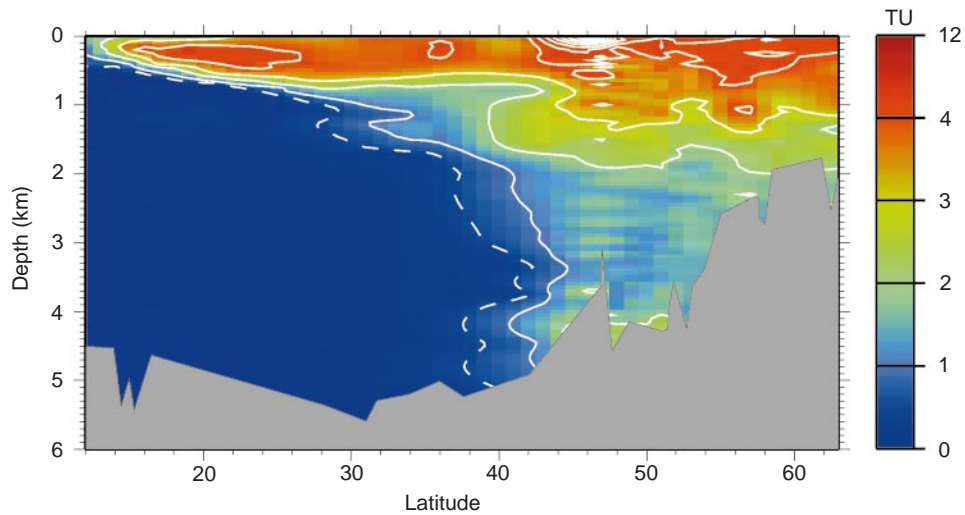

Figure 3 The various modes of tritium deposition to the North Atlantic over time. Note that during the peak of bomb-testing, vapor deposition was dominant, but that after the early 1970s, the influx of fresh water from the Arctic plays a prominent role.

Figure 5 A North Atlantic tritium meridional section taken in the early 1980s.

The penetration of tritium into the oceans provides us with a direct visualization of the large-scale ventilation of the oceans. As a time-dependent dye, it stains water that has been in contact with the surface since the bomb tests in the 1960s. The time evolution of this picture highlights those processes that occur on decade time-scales that are important for climate change. **Figure 5** is a north–south section taken through the western North Atlantic in the early 1980s. The section shows how far the dye has penetrated along the pathway of the planetary-scale overturning circulation ('the global conveyor') and is an important quantitative measure of the rate of this overturning on decade timescales.

The boundary between high- and low-tritium waters at depths of 4–5 km corresponds to the transition region between the subtropical and subpolar gyres. In the subpolar gyre, deep convection injected tritium into deep and intermediate waters. In the subtropical gyre, subsurface penetration occurs from the north, primarily along deep western boundary currents. Otherwise, bomb tritium is restricted to the upper 1 km, tracing the bowl-like structure of the main thermocline, which it penetrates by subduction of fluid by a combination of wind stress convergence (a process called 'Ekman pumping', i.e. convergence of surface waters due to wind forcing effectively pushes water downward) and southward penetration under lighter, warmer waters.

A time series of tritium in the Sargasso Sea near Bermuda shows the penetration of this bomb tritium into the subtropical North Atlantic (**Figure 6**). To compensate for predictable radioactive decay, the concentration of tritium has been decay-corrected to one point in time (arbitrarily chosen here to be 1981, the approximate mid-point of the series). Two relatively sudden increases in tritium concentrations occur in the deep waters. The first appears at a depth of about 1500 m in the late 1970s, whereas the deeper one arrives in the late 1980s. These increases signal the arrival of waters that had been 'ventilated' or exposed to the surface since the bomb tests. The delayed arrival provides a measure of the transit time of properties southward from the outcropping regions, important knowledge for ocean climate models.

The time series, however, is dominated in the upper waters by the downward penetration of bomb tritium into the main thermocline. The tritium 'spike' first appears as a surface-intensified maximum at the beginning of the record, but then subsequently descends into the thermocline at a rate of about $20\,\mathrm{m\,y^{-1}}$. As it descends, its intensity decreases due to dilution (the series has been corrected for radioactive decay). The rate at which this maximum descends into the thermocline is vital information for climate modeling; i.e., this information is important for predicting how the ocean will respond to changes on decade timescales.

Tritium–³He Dating in the Ocean

The penetration of tritium into the oceans, and its subsequent evolution, provides us with valuable information on ocean ventilation and large-scale circulation on multiyear and multidecade timescales. However, it is possible to use this tracer in combination with its stable, inert daughter ³He to extend its utility to much shorter timescales, and

provide a powerful measure of circulation and ventilation, as well as the rates of biological and chemical processing in the oceans. The manner in which this is accomplished can be seen in the following thought experiment.

Imagine a parcel of water at the sea surface (**Figure 7**). Tritium within this fluid parcel is decaying, producing its daughter product ^{3}He. (Half of the tritium decays to ^{3}He in 12.45 years, while in 24.9 years, one-quarter would be left, and in 37.4 years, only one-eighth would remain, etc.) However, because it is at the sea surface, this ^{3}He will be lost to the atmosphere via gas exchange. Thus no excess or 'tritiugenic' ^{3}He would accumulate. However, should this water parcel sink below the surface and lose contact with the atmosphere, tritiugenic ^{3}He would accumulate at a predictable rate. By measur-

ing both the tritium concentration and the accumulated ^{3}He in the fluid parcel, the time that has elapsed since the fluid was last in contact with the surface can be determined according to the equation:

$$\tau = 17.96\ln\left(1 + \frac{[^{3}\text{He}]}{[^{3}\text{H}]}\right)$$

where τ is the tritium–^{3}He age in years, and $[^{3}\text{He}]$ and $[^{3}\text{H}]$ are the concentrations of ^{3}He and tritium in the water, respectively. For typical surface water concentrations of a few tritium units, elapsed times as short as a month or two can be detected, and the upper limit to the dating technique is of the order of 10–20 years (see discussion below). This range of timescales is ideal for studying
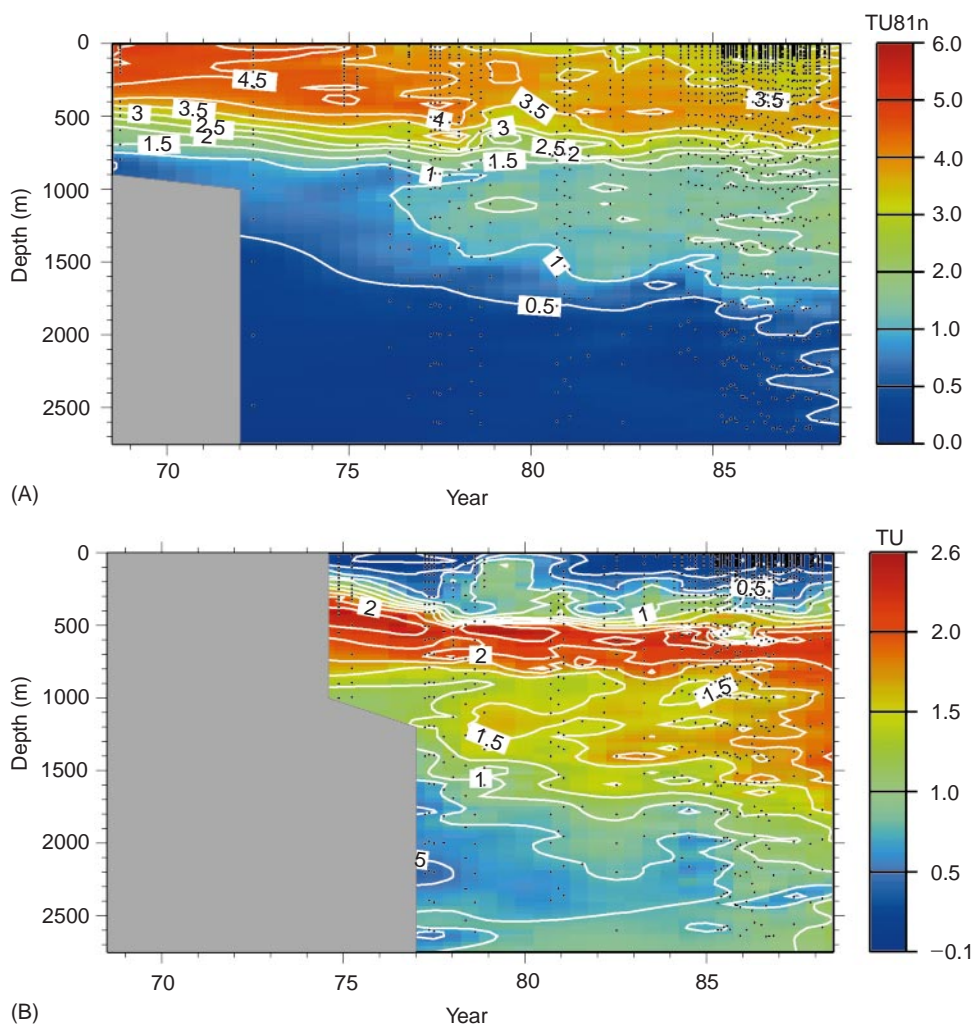
Figure 6 A Bermuda time series of (A) tritium and (B) ^{3}He. The tritium concentrations have been decay-corrected (that is, corrected for the effects of radioactive decay) to a fixed point in time (1981). This allows the effects of dilution and fluid motions to be seen.

shallow-ocean circulation, ventilation, and bio-geochemical processing.

In the subtropics, where wind-stress is convergent, water tends to be forced downward from the surface ocean into the thermocline. This downwell-ing is an important process for ventilation of the thermocline, and for driving the shallow gyre circu-lation. **Figure 8** shows the measured tritium–helium age as measured on a constant density surface $(1024\,\mathrm{kg\,m^{-3}})$ in the eastern subtropical North
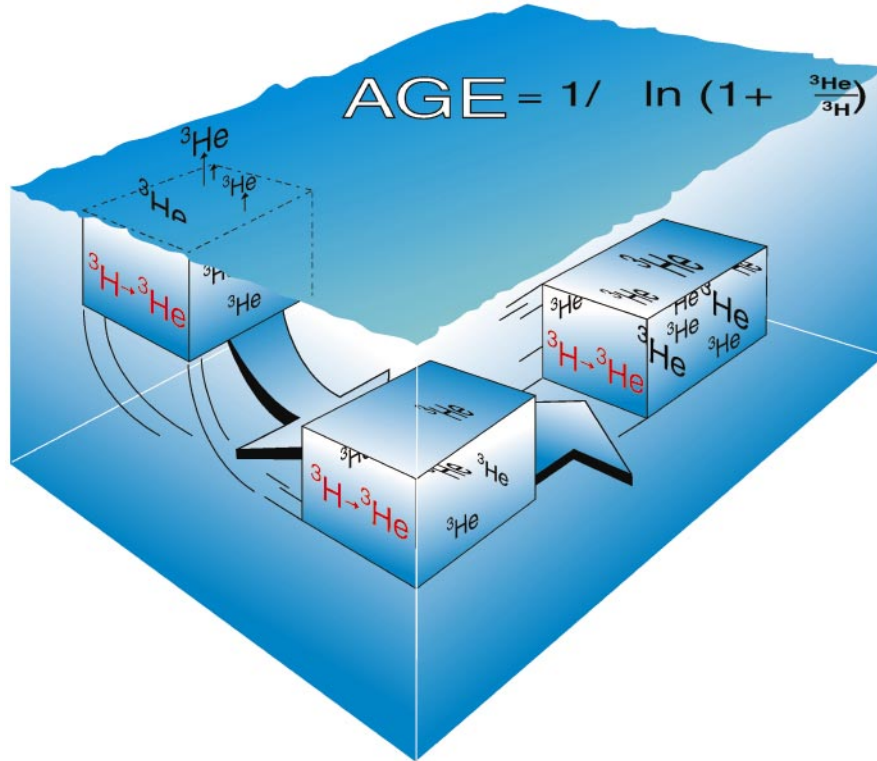

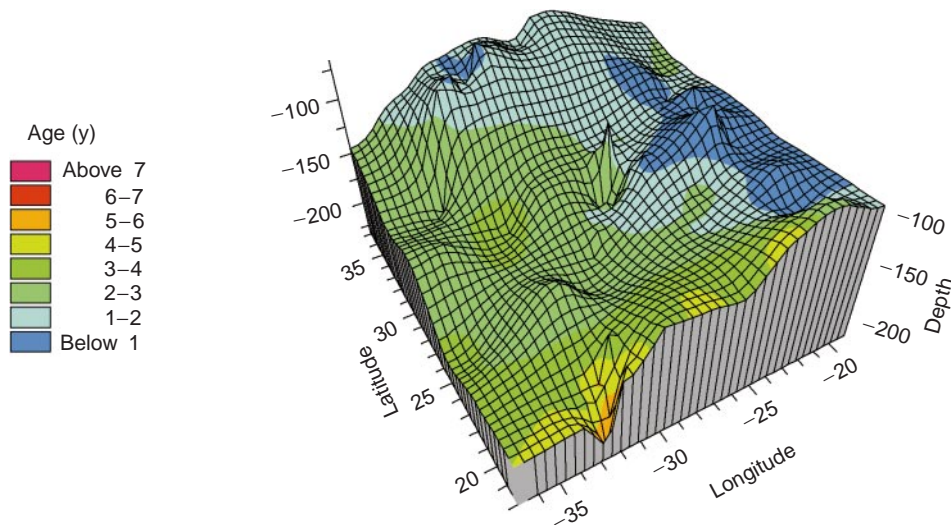**Figure 7** The tritium–helium dating concept.

Figure 8 The distribution of tritium–helium age on a constant density surface ($26.4\,\mathrm{kg\,m^{-3}}$) in the subtropical North Atlantic.

Atlantic in the early 1990s. Water is youngest in the north-east, where the horizon rises toward the ocean surface. In fact, this horizon intercepts the base of the wintertime mixing layer, and the tritium–helium age of the water is less than one year, indicating that it was in active contact with the previous winter's surface mixed layer. The age of the water increases monotonically as the layer deepens to the southwest, consistent with a south-westward flow associated with the large-scale circulation of the gyre. The next logical step would be to use the observed age-gradients to compute fluid velocities.

Before applying this technique quantitatively, however, there are two significant concerns that need to be considered. The first is the possible re-lease of volcanic helium from submarine hydrothermal activity. This injection occurs at active volcanic centers, predominantly along midocean ridges, and to a lesser extent at near-axial seamounts. This helium is a mixture of primordial helium inherited during the earth's formation from the presolar nebula and radiogenic helium produced by the decay of long-lived radioactive U and Th isotopes in the deep earth. The injection of this helium is visible on a very large scale in the deep Pacific Ocean, where plumes of this helium extend across the basin (**Figure 9**). These plumes provide compelling evidence of ocean–crust interaction, terrestrial degassing, and trace deep ocean circulation (*see* **Volcanic Helium**).
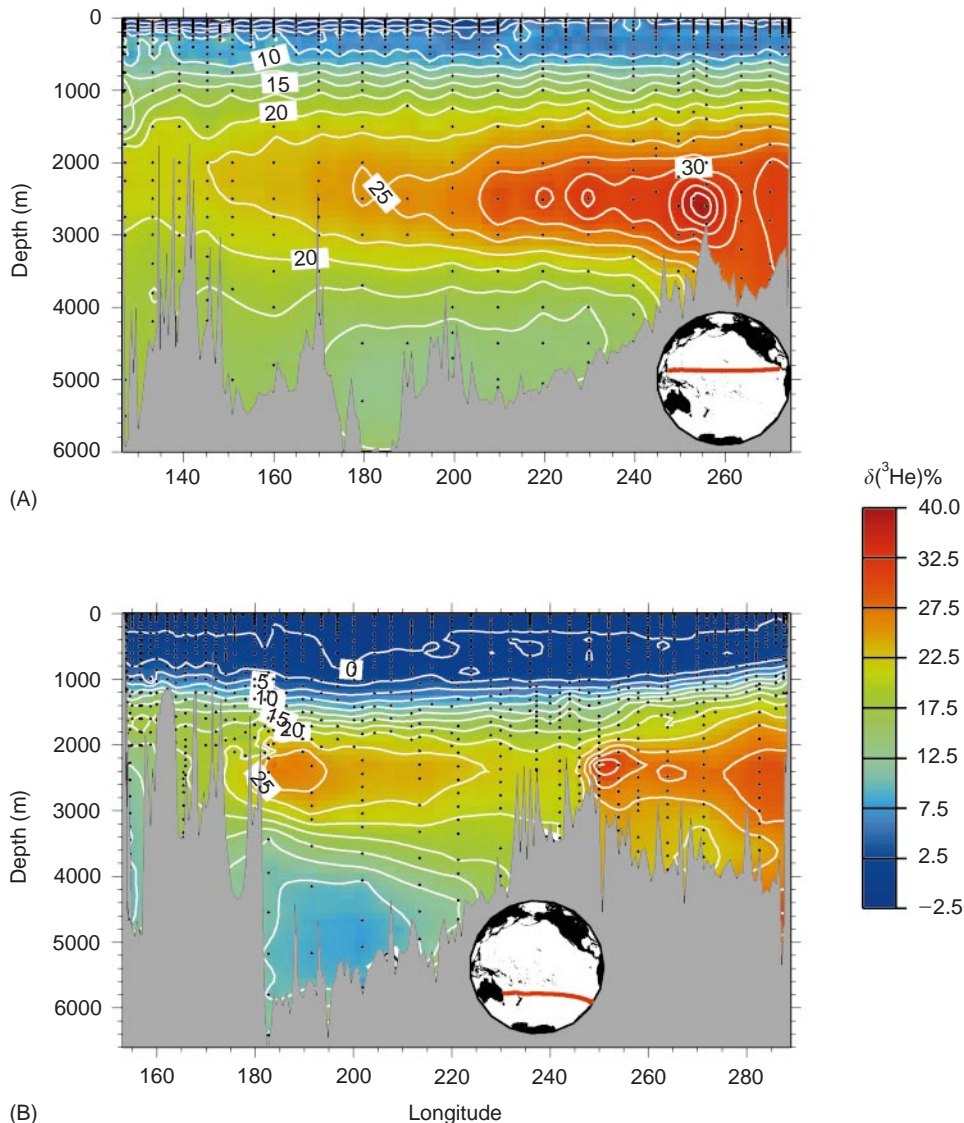
Figure 9 Two deep Pacific zonal sections of ^{3}He. Data are presented as isotope ratio anomaly (%), relative to atmospheric helium. Samples were processed during the WOCE Pacific hydrographic expeditions from 1989 to 1994.

As this helium tends to be enriched in ^{3}He compared to atmospheric helium, it may be confused with tritiugenic ^{3}He. Such injections tend to occur in deeper waters, away from the surface where one would tend to use tritium–^{3}He dating. Moreover, calculations indicate that despite the impressive signature in abyssal waters, the actual flux of volcanic ^{3}He is smaller than the tritiugenic production rate due to bomb tests. Clearly, however, caution should be exercised in areas where the two signals can interfere. The shallow North Atlantic, in particular, is well suited to tritium–^{3}He dating, partly because water masses tend to be younger there, and partly because seafloor spreading rates (and hence the rate of injection of volcanic ^{3}He into the deep water) are low. (One would expect, on average, that volcanic activity would be related to seafloor spreading rates.)

A second concern arises from the behavior of the tritium–^{3}He age in response to mixing. Returning to the model concept discussed earlier, it must be recognized that water does not circulate in discrete 'parcels' but is subjected to mixing. In general, this manifests itself in a 'nonlinear' response in the tritium–^{3}He age. For example, consider two fluid parcels that undergo mixing in equal proportions (**Figure 10**).

We consider, for simplicity, the case where the two are mixed in equal proportions, but the arguments apply equally well for an arbitrary mixture. In general, the tritium–^{3}He age of the mixture would be calculated from its tritium and ^{3}He concentrations, and will be different from the average

**Table 1** Examples of water mass mixing effects on the tritium–helium age

		$[^3H]$	$[^3He]$	Age (y)
Case 1	Watermass A	10	1	1.71
	Watermass B	1	10	43.04
	50:50 Mixture	5.5	5.5	12.45
Case 2	Watermass A	10	100	43.04
	Watermass B	1	0.1	1.71
	50:50 Mixture	5.5	50.05	41.51
Case 3	Watermass A	10	10	17.95
	Watermass B	10	1	1.71
	50:50 Mixture	5	5.5	13.32

of the component ages. That is, the age of the mixture is not equivalent to the mixture of the ages. The results for three example cases are shown in **Table 1**.

In the first case, the average age of the two water masses should be slightly more than 22 years, but the tritium concentration of the mixture is dominated by water mass A, which is the younger water mass. In the second case, the mixture is significantly older than 'average age', again because it is dominated by the higher tritium component. Only when the two components are of equal tritium concentration (case 3) does the mixture age more closely match the average of the components. Even here, there is a deviation due to the logarithmic nature of the age dependence.

Consideration of the scenarios presented in **Table 1** reveals that when water masses mix, the tritium–^{3}He age of the resultant mixture is weighted in favor of the water mass component with the greater tritium concentration. The implication of this is that a small admixture of a young, relatively tritium-rich water mass will depress the tritium–^{3}He age disproportionately. Therefore, there will be a tendency for the tritium–^{3}He age to be an underestimate of the true age in the presence of mixing. Although it seems a serious concern, consideration of real-world oceanographic situations indicates that this is not a significant problem for timescales of less than a decade.

The effects of mixing on the tritium–^{3}He age have been quantified by the development of an advection–diffusion equation for the age. This is accomplished by combining the definition of the tritium–^{3}He age (τ) with the advection–diffusion equations for tritium and ^{3}He.
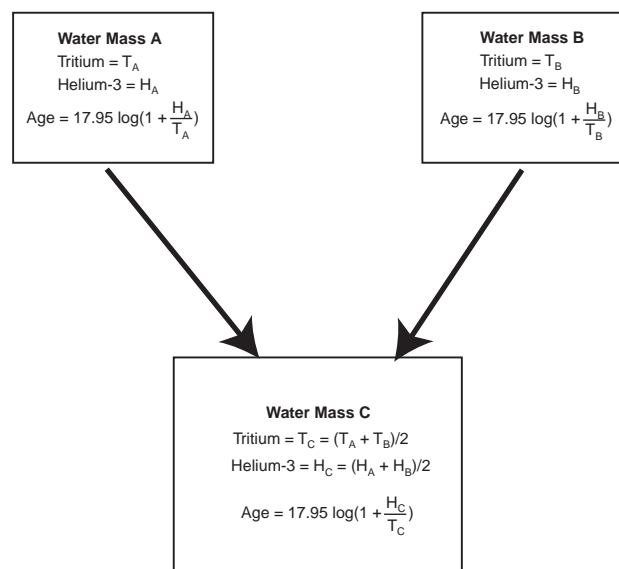
Figure 10 The effect of mixing on the tritium–helium age.

$$\frac{\partial \tau}{\partial t} + \vec{u} \cdot \nabla \tau = \nabla(\kappa \nabla \tau) + 1 - \kappa\left(\frac{\nabla[^3\text{He}]}{[^3\text{He}]} + 2\frac{\nabla[^3\text{H}]}{[^3\text{H}]}\right) \cdot \nabla \tau$$

where κ is the turbulent diffusivity and u is the fluid velocity. The equation appears similar to that of an ideal age tracer (A), governed by

$$\vec{u} \cdot \nabla A = \nabla(\kappa \nabla A) + 1$$

except for the presence of the unsteady (time derivative) term and the last term on the right. The unsteady term arises from the fact that the parent distributions are changing with time, and the age distribution is adjusting accordingly. The last term appears more as a pseudovelocity that is a direct manifestation of the nonlinear mixing behavior exemplified in the two-water-mass thought experiment described earlier. Although the equation appears complex, the key point is that all the terms are observable. That is, given field observations of the tracers, the terms can be computed to within a value of κ. The effects on the shallowest surfaces are small. Analysis of actual distributions within the shallow North Atlantic, for example, shows that deviations from 'ideal' behavior are negligibly small. Moreover, combining the age distributions with other tracers, for example salinity, and with geostrophic constraints, permits the determination of absolute velocities within the main thermocline to a resolution of order $0.1 \, \text{cm s}^{-1}$.

See also

Elemental Distribution: Overview. Ekman Transport and Pumping. Ocean Subduction. Thermohaline Circulation. Water Types and Water Masses.

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TROPHIC LEVELS

TSUNAMIS

Colin McNeil, Academic Press, UK

Tsunamis are long-period waves generated primarily by submarine earthquakes. The name comes from a Japanese word meaning 'harbour wave', however, it is now used in the scientific literature to exclusively describe seismic sea waves.

Tectonic activity in the seafloor creates a vertical movement in the seafloor and a resultant vertical movement across a wide area of the sea's surface. This leads to the formation of a train of long-period waves. Periods of over an hour are not uncommon. These waves can travel very large distances from the earthquake's epicenter and, as they near the coast, their amplitude is increased by local topographic features.

Considerable damage to property and loss of life have been recorded as the result of tsunamis. Warning systems have been developed mainly around the Pacific Ocean, where the risk is greatest. Provided the epicenter and the time of occurrence are known good estimations can be made of the time the tsunami will reach coastal areas.