URANIUM-THORIUM SERIES ISOTOPES IN OCEAN PROFILES

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Natural radioactivity in the environment originates from two sources. First, primordial radionuclides which were incorporated into the Earth at the time of its formation are still present in it because of their long half-lives. ^{238}U, ^{235}U, ^{232}Th and their decay series (**Figure 1**), ^{40}K, ^{87}Rb and ^{187}Re are examples of this category. Second, cosmic ray-produced isotopes which are generated continuously in the atmosphere and earth's crust through interactions of cosmic rays with their constituents. ^{3}H, ^{14}C and ^{10}Be are some of the isotopes belonging to this group. The distribution of all these isotopes in the oceans is governed by their supply, radioactive decay, water mixing and their biogeochemical reactivity (the tendency to participate in biological and chemical processes) in sea water. Water circulation plays a dominant role in the dispersion of isotopes which are biogeochemically 'passive' (e.g. ^{3}H, Rn), whereas biological uptake and release, solute–particle interactions and chemical scavenging exert major control in the distribution of biogeochemically 'active' elements (e.g. C, Si, Th, Pb, Po). Systematic study of the isotopes of these two groups in the sea can yield important information on the physical and biogeochemical processes occurring in sea water.

Supply of U/Th Isotopes to the Sea

These nuclides enter the oceans through three principal pathways.

Fluvial Transport

This is the main supply route for ^{238}U, ^{235}U, ^{234}U and ^{232}Th to the sea. These isotopes are transported both in soluble and suspended phases. Their dissolved concentrations in rivers depend on water chemistry and their geochemical behavior. In rivers, uranium is quite soluble and is transported mainly as uranyl carbonate, $UO_2(CO_3)_3^{-4}$, complex. The dissolved uranium concentration in rivers is generally in the range of $0.1–1.0\,\mu g\,l^{-1}$. During chemical weathering ^{235}U is also released to rivers in the same $^{235}U/^{238}U$ ratio as their natural abundance (1/137.8). This is unlike that of ^{234}U, a progeny of ^{238}U (**Figure 1**) which is released preferentially to solution due to α-recoil effects. As a result, the $^{234}U/^{238}U$ activity ratios of river waters are generally in excess of that in the host rock and the secular equilibrium value of 1.0 and often fall in the range of 1.1–1.5.

The concentration of dissolved ^{232}Th in rivers, $\sim 0.01\,\mu g\,l^{-1}$ is significantly lower than that of ^{238}U, although their abundances in the upper continental crust are comparable. This is because ^{232}Th (and other Th isotopes) is more resistant to weathering and is highly particle-reactive (the property to be associated with particles) in natural waters and hence is rapidly adsorbed from solution to particles. It is likely that even the reported dissolved ^{232}Th concentrations are upper limits, as recent results, based on smaller volume samples and high sensitivity mass-spectrometric measurements seem to show that dissolved ^{232}Th in rivers is associated with smaller particles ($< 0.45\,\mu m$ size). Similar to ^{232}Th, the bulk of ^{230}Th and ^{210}Pb is also associated with particles in rivers and hence is transported mainly in particulate form from continents.

^{226}Ra and ^{228}Ra are two other members of the U-Th series (**Figure 1**) for which dissolved concentration data are available for several rivers, these show that they are present at levels of $\sim 0.1\,d.p.m.\,l^{-1}$. The available data show that there are significant differences between the abundances of U, Ra isotopes and ^{232}Th in the host rocks and in river waters. The various physicochemical processes occurring during the mobilization and transport of these nuclides contribute to these differences.

Rivers also transport U/Th series nuclides in particulate phase to the sea. These nuclides exist in two forms in the particulate phase, one as a part of their lattice structure and the other as surface coating resulting from their adsorption from solution. Analysis of suspended particulate matter from rivers shows the existence of radioactive disequilibria among the members of the same radioactive decay chain. In general, particulate phases are characterized by $^{234}U/^{238}U$, $^{226}Ra/^{230}Th$ activity ratios < 1 and $^{230}Th/^{234}U$ and $^{210}Pb/^{226}Ra > 1$, caused by preferential mobilization of U and Ra over Th and Pb isotopes.

Soluble and suspended materials from rivers enter the open ocean through estuaries. The interactions of sea water with the riverine materials can modify

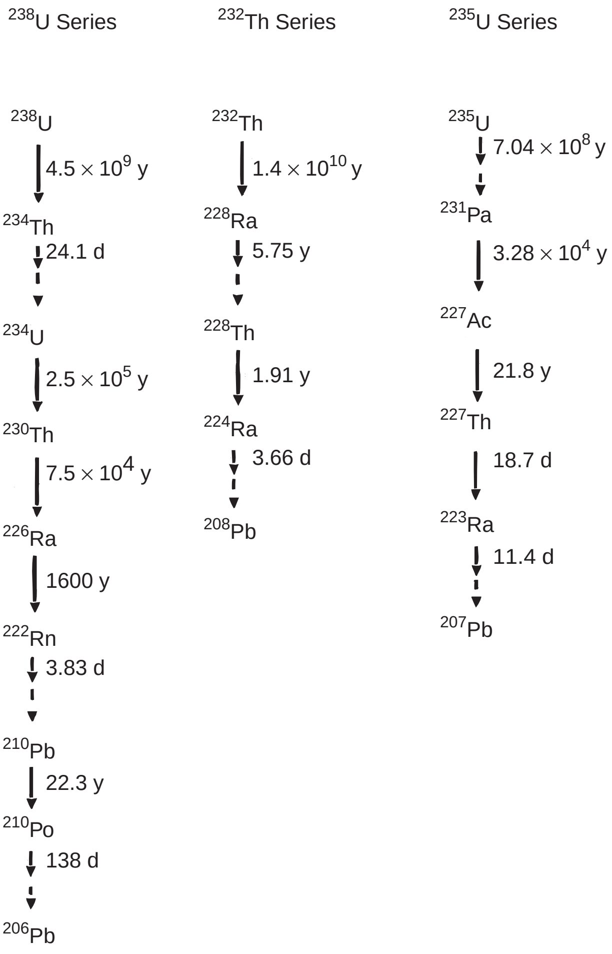

Figure 1 ^{238}U, ^{232}Th and ^{235}U decay series: Only the isotopes of interest in water column process studies are shown.

the dissolved concentrations of many nuclides and hence their fluxes to the open sea. Studies of U/Th series isotopes in estuaries show that in many cases their distribution is governed by processes in addition to simple mixing of river and sea water. For example, in the case of U there is evidence for both its addition and removal during transit through estuaries. Similarly, many estuaries have ^{226}Ra concentration higher than that expected from water mixing considerations resulting from its desorption from riverine particles and/or its diffusion from estuarine sediments. Estuaries also seem to act as a filter for riverine ^{232}Th.

The behavior of radionuclides in estuaries could be influenced by their association with colloids. Recent studies of uranium in Kalix River show that a significant part is bound to colloids which is removed in the estuaries through flocculation. Similarly, colloids seem to have a significant control on the ^{230}Th–^{232}Th distribution in estuarine waters.

In situ Production

Radioactive decay of dissolved radionuclides in the water column is an important supply mechanism for several U/Th series nuclides. This is the dominant mode of supply for ^{234}Th, ^{228}Th, ^{230}Th, ^{210}Po, ^{210}Pb, and ^{231}Pa. The supply rates of these nuclides to sea water can be precisely determined by measuring the concentrations of their parents. This is unlike the case of nuclides supplied via rivers whose fluxes are relatively more difficult to ascertain because of large spatial and temporal variations in their riverine concentrations and their modifications in estuaries.

Supply at Air–Sea and Sediment–Water Interfaces

A few of the U/Th nuclides are supplied to the sea via atmospheric deposition and diffusion through sediment pore waters. Decay of ^{222}Rn in the atmosphere to ^{210}Pb and its subsequent removal by wet and dry deposition is an important source of dissolved ^{210}Pb to the sea. As the bulk of the ^{222}Rn in the atmosphere is of continental origin, the flux of ^{210}Pb via this route depends on factors such as distance from land and aerosol residence times. ^{210}Po is also deposited on the sea surface through this source, but its flux is $<10\%$ of that of ^{210}Pb. Leaching of atmospheric dust by sea water can also contribute to nuclide fluxes near the air–sea interface, this mechanism has been suggested as a source for dissolved ^{232}Th.

Diffusion out of sediments forms a significant input for Ra isotopes, ^{227}Ac and ^{222}Rn into overlying water. All these nuclides are produced in sediments through α-decay (**Figure 1**). The recoil associated with their production enhances their mobility from sediments to pore waters from where they diffuse to overlying sea water. Their diffusive fluxes depend on the nature of sediments, their accumulation rates, and the parent concentrations in them. ^{234}U is another isotope for which supply through diffusion from sediments may be important for its oceanic budget.

In addition to diffusion out of sediments, ^{226}Ra and ^{222}Rn are also introduced into bottom waters through vent waters associated with hydrothermal circulation along the spreading ridges. The flux of ^{226}Ra from this source though is comparable to that from rivers; its contribution to the overall ^{226}Ra budget of the oceans is small. This flux, however, can overwhelm ^{226}Ra diffusing out of sediments along the ridges on a local scale.

Distribution in the Oceans

Uranium

^{238}U and ^{235}U are progenitors of a number of particle-reactive nuclides in sea water which find applications in the study of several water column and sedimentary processes. The study of uranium distribution in the sea is therefore essential to a better understanding of the radioactive disequilibrium between ^{238}U–^{234}Th, ^{234}U–^{230}Th, ^{238}U–^{234}U, and ^{235}U–^{231}Pa in sea water. Uranium in sea water is almost entirely in solution as $UO_2(CO_3)_3^{-4}$. Considerable data on its concentration and ^{234}U/^{238}U activity ratios are available in the literature, most of which are based on α-spectrometry. These results show that uranium concentration in salinity normalized open ocean sea water (35‰) are the same within experimental uncertainties, $3.3 \pm 0.2\,\mu g\,l^{-1}$. Measurements with highly sensitive mass-spectrometric techniques also yield quite similar values, but with a much better precision ($\sim 0.2\%$) and narrower range, 3.162–3.282 ng g^{-1} 35‰ salinity water (**Figure 2**). The $\sim 3.8\%$ spread even in the recent data is intriguing and is difficult to account for as uranium is expected to be uniformly distributed in the oceans because of its long residence time, $\sim (2\text{–}4) \times 10^5$ years. More controlled sampling and analysis of uranium in sea water are needed to address this issue better. The mass-spectrometric measurements of uranium have also provided data showing that the ^{238}U/^{235}U atomic ratio in sea water is 137.17–138.60, identical within errors to the natural abundance ratio of 137.88.

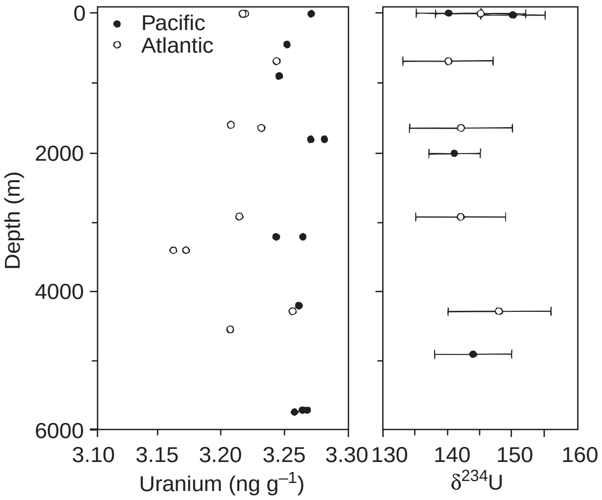

Figure 2 ^{238}U concentration (ng g^{-1} 35‰ salinity water) and $\delta(^{234}U)$ in the Pacific (●) and the Atlantic (○) waters. Data from Chen *et al.* (1986).

Studies of uranium distribution in anoxic marine basins (e.g., the Black Sea and the Saanich Inlet) have been a topic of interest as sediments of such basins are known to be depositories for authigenic uranium. These measurements show that even in these basins, where H_2S is abundant, uranium exists predominantly in $+6$ state and its scavenging removal from the water column forms only a minor component of its depositional flux in sediments.

The preferential mobilization of ^{234}U during weathering and its supply by diffusion from deep-sea sediments causes its activity in sea water to be in excess of that of ^{238}U. The ^{234}U/^{238}U activity ratio of sea water, determined by α-spectrometry, indicates that it is quite homogenous in open ocean waters with a mean value of 1.14 ± 0.02. Mass-spectrometric measurements have confirmed the above observations of ^{234}U excess with a much better precision and have also led to the use of 'δ notation' to describe ^{234}U–^{238}U radioactive disequilibrium.

$$\delta(^{234}U)‰ = [(R_s/R_e) - 1] \times 10^3 \qquad [1]$$

where R_s and R_e are ^{234}U/^{238}U atomic ratios in sample and at radioactive equilibrium respectively. The $\delta(^{234}U)$ in the major oceans (**Figure 2**) are same within analytical precision and average 144 ± 2. Coralline $CaCO_3$ and ferromanganese deposits forming from sea water incorporate ^{234}U/^{238}U in the ratio of 1.144, the same as that in seawater. The decay of excess ^{234}U in these deposits has been used as a chronometer to determine their ages and growth rates.

Th Isotopes

Among the U/Th series nuclides, the Th isotopes (^{232}Th, ^{230}Th, ^{228}Th, and ^{234}Th), because of their property to attach themselves to particles, are the most extensively used nuclides to investigate particle cycling and deposition in the oceans, processes which have direct relevance to carbon export, solute-particle interactions and particle dynamics. ^{232}Th, ^{230}Th and ^{228}Th are generally measured by α-spectrometry and ^{234}Th by β or γ counting. Highly sensitive mass-spectrometric techniques have now become available for precise measurements of ^{232}Th and ^{230}Th in sea water.

Dissolved ^{232}Th concentration in sea water centers around a few tens of picograms per liter. It is uncertain if the measured ^{232}Th is truly dissolved or is associated with small particles/colloids. Some ^{232}Th profiles show a surface maximum which has been attributed to its release from atmospheric dust.

^{234}Th is continuously produced in sea water from the decay of ^{238}U at a nearly uniform rate of ~ 2.4 atoms $\mathrm{l^{-1}\,min^{-1}}$. It has been observed that ^{234}Th activity in the surface ~ 200 m is generally deficient relative to its parent ^{238}U suggesting its removal by particles, the mechanism of how this is accomplished, however, is not well understood. This result has been attested by several studies (**Figure 3**). The residence time of Th in the upper layers of the ocean is determined based on ^{234}Th–^{238}U disequilibrium and the relation;

$$\tau = \left[\frac{R}{(1-R)}\right]\tau_{\lambda} \qquad [2]$$

where R is the ^{234}Th/^{238}U activity ratio and τ_{λ} is the radioactive mean life of ^{234}Th (36.8 days). More complex models considering reversible Th exchange, particle remineralization, aggregation and breakup have also been used to treat the ^{234}Th data which allow better understanding of processes regulating both particle and Th cycling. All these studies demonstrate that Th removal by particle scavenging is ubiquitous in surface water and occurs very rapidly, on timescales of a few days to a few months. Much of this variability in the residence time of Th appears to be dictated by particle concentration, short residence times are typical of coastal and biologically productive areas where particles are generally more abundant. These observations have prompted the use of the ^{234}Th–^{238}U pair as a survey tool to determine the export fluxes of carbon from the euphotic zone. The results, though encouraging, suggest the need for a more rigorous validation of the assumptions and parameters used.

^{228}Th activity in the sea exhibits significant lateral and depth variations with higher concentration in the surface and bottom waters and low values in the ocean interior (**Figure 4**). This pattern is governed by the distribution of its parent ^{228}Ra, which determines its production (see section on Ra isotopes). Analogous to ^{234}Th, the distribution of ^{228}Th in the upper layers of the sea is also determined by particle scavenging which causes the ^{228}Th/^{228}Ra activity ratio to be < 1, the disequilibrium being more pronounced near coasts where particles are more abundant. The residence time of Th in surface waters calculated from ^{234}Th–^{228}U and ^{228}Th–^{228}Ra pairs yields similar values. Profiles of ^{228}Th activity in bottom waters show a decreasing trend with height above the sediment–water interface. In many of these profiles ^{228}Th is in radioactive equilibrium with ^{228}Ra and in a few others it is deficient. Some of these profile data have been used as a proxy for ^{228}Ra to derive eddy diffusion rates in bottom waters.

Systematic measurements of ^{230}Th activity–depth profiles in soluble and suspended phases of sea water have become available only during the past two decades. ^{230}Th is produced from ^{234}U at a nearly uniform rate of ~ 2.7 atoms $\mathrm{l^{-1}\,min^{-1}}$. The dissolved ^{230}Th activity in deep waters of the North Atlantic is $\sim (5\text{–}10) \times 10^{-4}$ d.p.m. $\mathrm{l^{-1}}$ and in the North Pacific it is ~ 2 times higher. In comparison, the particle ^{230}Th concentrations are about an order of magnitude lower (**Figure 5**). These values are

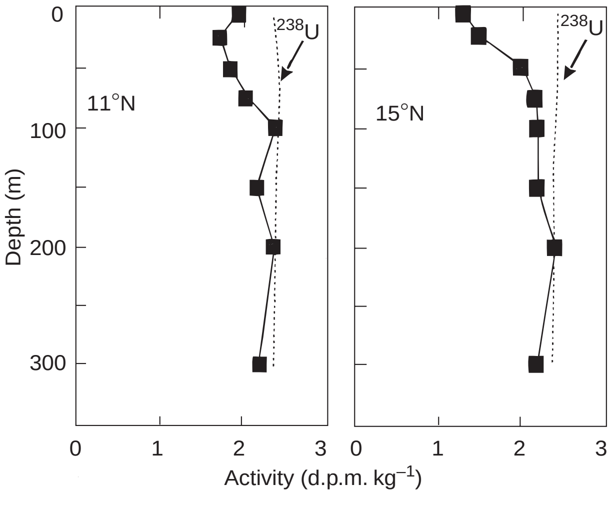

Figure 3 ^{234}Th –^{238}U profiles from the Arabian Sea. Note the clear deficiency of ^{234}Th in the upper layers relative to ^{238}U. (Modified from Sarin *et al.*, 1996.)

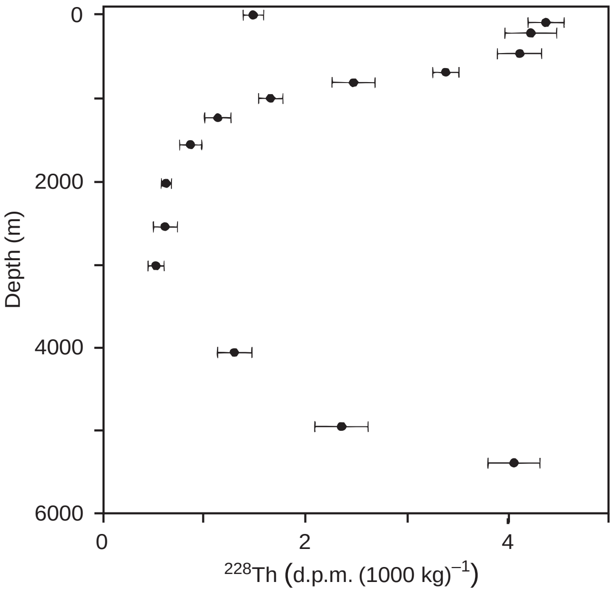

Figure 4 ^{228}Th distribution in the Pacific. The higher activity levels of ^{228}Th in near-surface and near-bottom waters reflect that of its parent ^{228}Ra. Data from Nozaki *et al.* (1981).

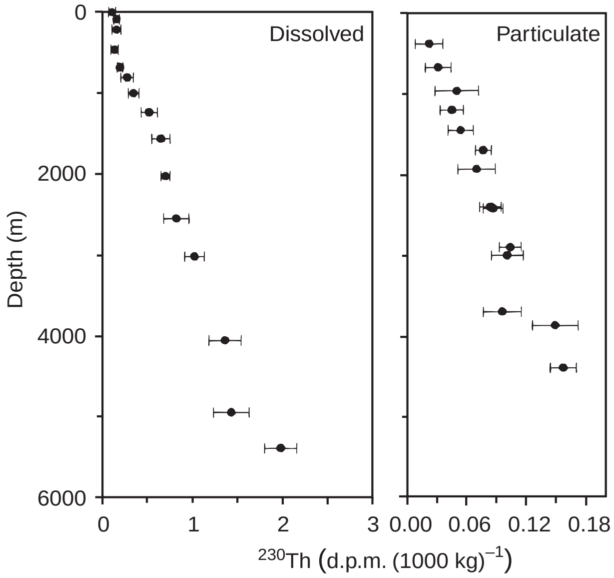

Figure 5 Water-column distributions of dissolved and particulate ^{230}Th. Dissolved ^{230}Th data from the North Pacific (Nozaki *et al.* 1981) and particulate ^{230}Th from the Indian Ocean (Krishnaswami *et al.* 1981). The steady increase in the ^{230}Th activities in both the phases is evident.

far less than would be expected if ^{230}Th were in radioactive equilibrium with ^{234}U, $\sim 2.7\,\mathrm{d.p.m.\,l^{-1}}$, reinforcing the intense particle-reactive nature of Th isotopes and the occurrence of particle scavenging throughout the seawater column. More importantly, these studies showed that both the soluble and particulate ^{230}Th activities increase steadily with depth (**Figure 5**), an observation which led to the hypothesis of reversible exchange of Th between soluble and suspended pools to explain its distribution. In this model the equations governing the distribution of Th in the two phases are:

Suspended Th:

$$k_1 C = (\lambda + k_2)\bar{C} \qquad [3]$$

$$S\frac{\mathrm{d}\bar{C}}{\mathrm{d}z} + k_1 C - (\lambda + k_2)\bar{C} = 0 \qquad [4]$$

Soluble Th:

$$P + k_2\bar{C} = (\lambda + k_1)C \qquad [5]$$

where P is the production rate of ^{230}Th, C and $\bar{C}$ are the ^{230}Th concentrations in soluble and suspended phases, k_1 and k_2 are the first order adsorption and desorption rate constants, respectively, and S is the settling velocity of particles. Analysis of Th isotope data using this model suggests that adsorption of Th occurs on timescales of a year or so, whereas its release from particles to solution is much faster, i.e. a few months, and that the particles in sea are at equilibrium with Th in solution. Modified versions of the above model include processes such as particle aggregation and breakup, remineralization and release of Th to solution. The timescales of some of these processes also have been derived from the Th isotope data.

^{231}Pa, ^{210}Po, and ^{210}Pb

These three isotopes share a property with Th, in that all of them are particle reactive. ^{231}Pa is a member of the ^{235}U series (**Figure 1**) and is produced in sea water at a rate of ~ 0.11 atoms $\mathrm{l^{-1}\,min^{-1}}$. Analogous to ^{230}Th, ^{231}Pa is also removed from sea water by adsorption onto particles, causing its activity to be quite low and deficient relative to ^{235}U (**Figure 6**). The ^{231}Pa/^{235}U activity ratio in deep waters of the western Pacific is $\sim 5\times10^{-3}$. Measurements of ^{230}Th/^{231}Pa ratios in dissolved, suspended, and settling particles have led to a better understanding of the role of their scavenging by vertically settling particles in the open ocean in relation to their removal on continental margins. The dissolved ^{230}Th/^{231}Pa in sea water is ~ 5, less than the production ratio of ~ 10.8 and those in suspended and settling particles of ~ 20, indicating that ^{230}Th is preferentially sequestered onto settling particles. This, coupled with the longer residence time of ^{231}Pa (a few hundred years) compared to ^{230}Th (a few tens of years), has led to the suggestion

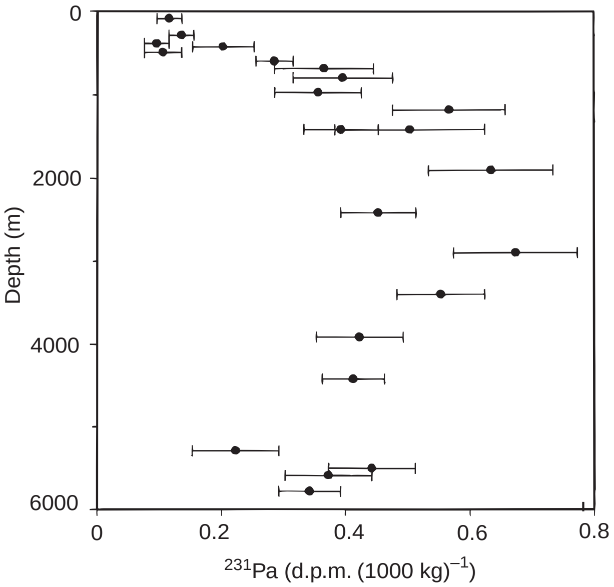

Figure 6 ^{231}Pa distribution in the north-west Pacific. Data from Nozaki and Nakanishi (1985).

that ^{231}Pa is laterally transported from open ocean areas to more intense scavenging regimes such as the continental margins, where it is removed. The measurements of settling fluxes of ^{230}Th and ^{231}Pa using sediment traps and ^{230}Th/^{231}Pa ratios in sediments from various oceanic regions support this connection.

^{210}Po is supplied to sea almost entirely through its *in situ* production from the decay of ^{210}Pb (**Figure 1**), a minor contribution comes from its atmospheric deposition at the air–sea interface. ^{210}Po is deficient relative to ^{210}Pb in surface waters (^{210}Po/^{210}Pb ~ 0.5, **Figure 7**), the deficiency being more pronounced in biologically productive regimes. The residence time of ^{210}Po in surface waters of the world oceans is in the range of 1 ± 0.5 years. The ^{210}Po/^{210}Pb ratio at the base of the euphotic zone falls between 1.0 and 2.0 and often exceeds the secular equilibrium value of unity (**Figure 7**), below ~ 200 m ^{210}Po and ^{210}Pb are in equilibrium. The ^{210}Po profiles in the upper thermocline have been modeled to obtain eddy diffusion coefficients and derive fluxes of nutrients into the euphotic zone from its base. The nature of ^{210}Po profiles in the thermocline and the observation that it is enriched in phyto- and zooplankton indicates that it is a 'nutrient like' element in its behavior and organic matter cycling significantly influences its distribution in the sea. The strong dependence of ^{210}Po removal rate on chlorophyll *a* abundance in various oceans (**Figure 8**) is another proof for the coupling between ^{210}Po and biological activity. In deep and bottom waters, ^{210}Po and ^{210}Pb are generally in equilibrium except in areas of hydrothermal activity where Fe/Mn oxides cause preferential removal of ^{210}Po resulting in ^{210}Po/^{210}Pb activity ratio < 1.

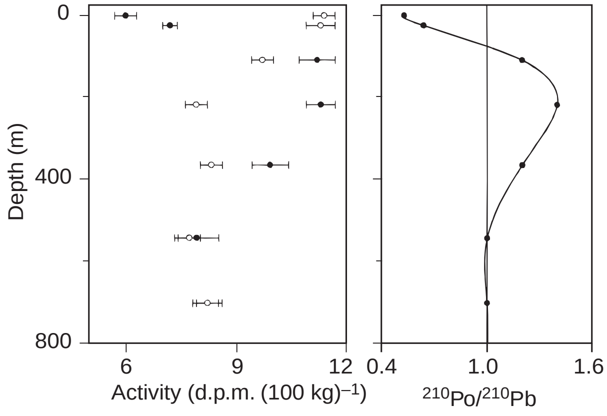

Figure 7 ^{210}Po–^{210}Pb disequilibrium in the Indian Ocean. ^{210}Po (●) is deficient relative to ^{210}Pb (○) near the surface and is in excess at 100–200 m. Data from Cochran *et al.* (1983).

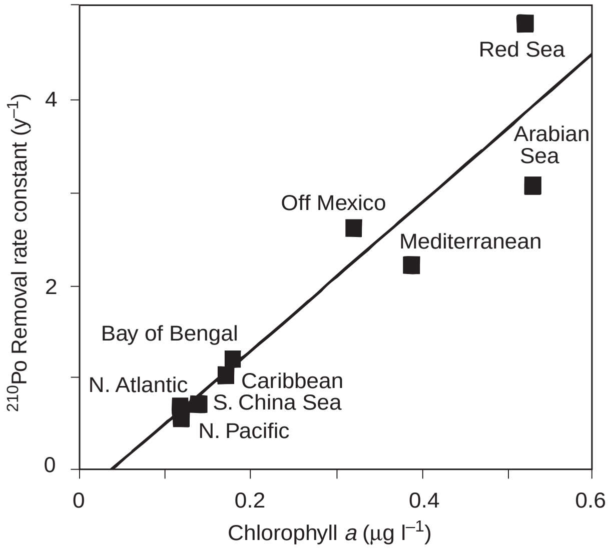

Figure 8 Interrelation between ^{210}Po scavenging rate and chlorophyll *a* concentrations in various oceanic regions. (Modified from Nozaki *et al.*, 1998.)

The studies of ^{210}Pb–^{226}Ra systematics in the oceans have considerably enhanced our understanding of scavenging processes, particularly in the deep sea and the marine geochemistries of lead and its chemical homologues. ^{210}Pb occurs in excess over ^{226}Ra in surface water (**Figure 9**) resulting from its supply from the atmosphere. This excess, however, is less than that would be expected from the known supply rate of ^{210}Pb from the atmosphere if it is removed only through its radioactive decay. This led to the proposal that ^{210}Pb is scavenged from surface to deep waters on timescales of a few years. In many profiles, excess ^{210}Pb shows exponential decrease with depth (**Figure 9**), which has been modeled to derive apparent eddy diffusion coefficients. Measurements of ^{210}Pb–^{226}Ra in the deep sea produced a surprise result in that ^{210}Pb was found to be deficient relative to ^{226}Ra with ^{210}Pb/^{226}Ra of ~ 0.5 (**Figure 10**). This was unexpected from the available estimates of the residence time of lead in the deep sea, i.e., a few thousands of years, orders of magnitude more than ^{210}Pb mean-life. Numerous subsequent studies have confirmed this deficiency of ^{210}Pb, though with significant variability in its extent and has led to the conclusion that ^{210}Pb is rapidly and continuously removed from the deep sea on timescales of $\sim$ 50–200 years. The residence time is much shorter, $\sim$ 2–5 years, in anoxic basins such as the Cariaco Trench and the Black Sea. Two other important findings of these studies are that the extent of ^{210}Pb–^{226}Ra disequilibrium increases from open ocean regimes to continental margins and topographic highs and that there is a significant concentration gradient in ^{210}Pb activity from ocean interior to ocean margins. These results coupled

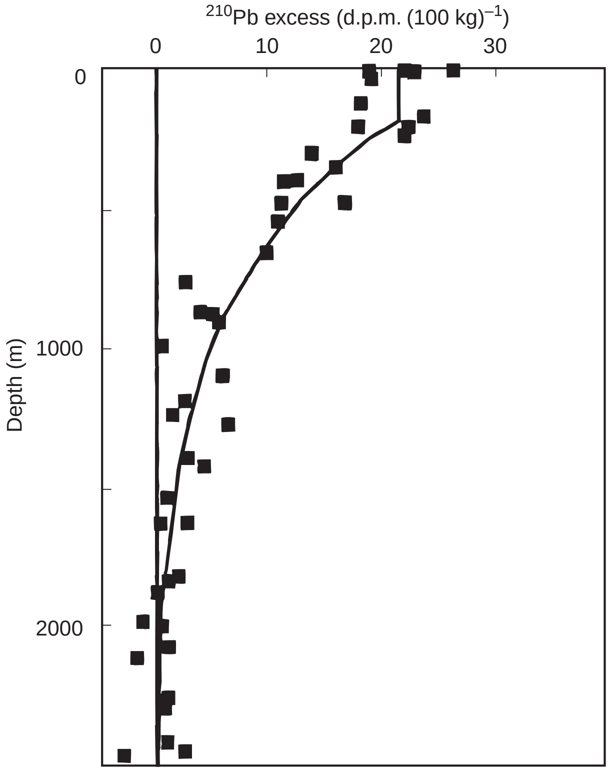

Figure 9 ^{210}Pb excess over ^{226}Ra in the upper thermocline from several stations of the Pacific. This excess results from its atmospheric deposition. (Modified from Nozaki *et al*., 1980.)

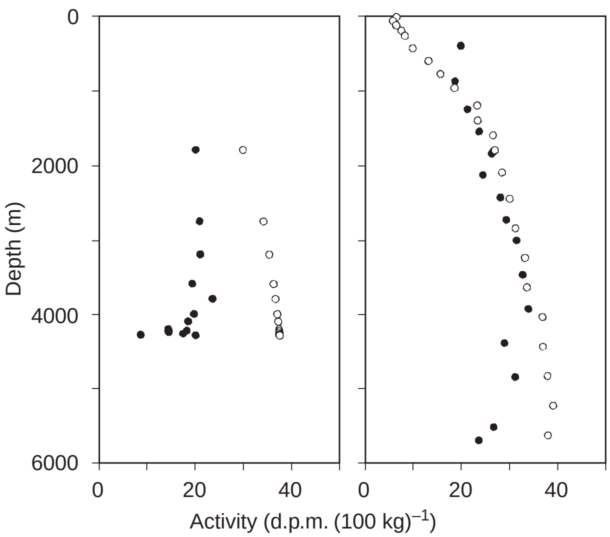

Figure 10 ^{210}Pb (●)–^{226}Ra (○) disequilibrium in sea water. The deficiency of ^{210}Pb in the ocean interior is attributed to its removal by vertically settling particles and at the ocean margins. Data from Craig *et al.* (1973), Chung and Craig (1980) and Nozaki *et al.* (1980).

with ^{210}Pb data in suspended and settling particles form the basis for the proposal that ^{210}Pb is removed from deep sea both by vertically settling particles and by lateral transport to margins and subsequent uptake at the sediment–water interface. Processes contributing to enhanced uptake in continental margins are still being debated; adsorption on Fe/Mn oxides formed due to their redox cycling in sediments and the effect of higher particle fluxes, both biogenic and continental, have been suggested. It is the ^{210}Pb studies which brought to light the role of continental margins in sequestering particle-reactive species from the sea, a sink which is now known to be important for other nuclides such as ^{231}Pa and ^{10}Be.

^{222}Rn

The decay of ^{226}Ra in water generates the noble gas ^{222}Rn; both these are in equilibrium in the water column, except near the air–sea and sea–sediment interfaces. ^{222}Rn escapes from sea water to the atmosphere near the air–sea boundary, causing it to be deficient relative to ^{226}Ra, whereas close to the sediment–water interface ^{222}Rn is in excess over ^{226}Ra due to its diffusion out of bottom sediments (**Figure 11**). These disequilibria serve as tracers for mixing rate studies in these boundary layers. In addition, the surface water data have been used to derive ^{222}Rn emanation rates and parameters pertaining to air–sea gas exchange.

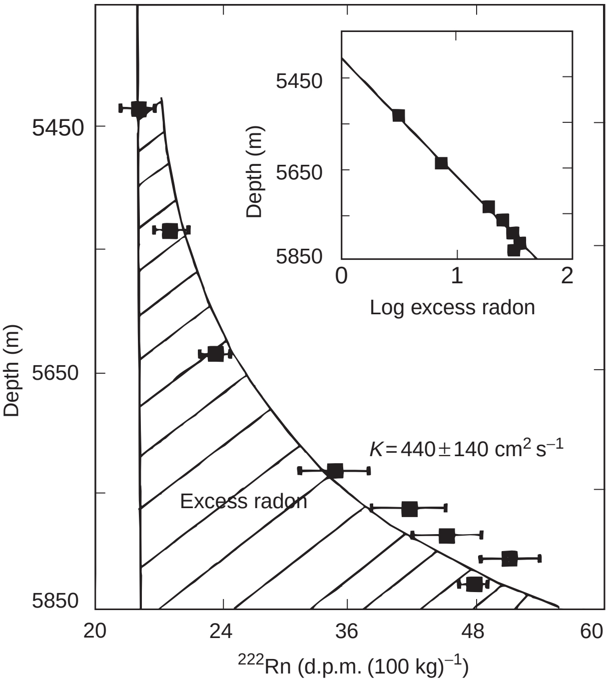

Figure 11 Example of bottom water ^{222}Rn profile in the Atlantic. The calculated vertical eddy diffusion coefficient is also given. (Modified from Sarmiento *et al*., 1976.)

^{222}Rn excess in bottom waters decreases with height above the interface, however, the ^{222}Rn activity profiles show distinct variations. Commonly the ^{222}Rn activity decreases exponentially with height above bottom (**Figure 11**) which allows the determination of eddy diffusion coefficient in these waters. In these cases the ^{222}Rn distribution is assumed to be governed by the equation:

$$K\frac{d^2C}{dz^2} - \lambda C = 0 \qquad [6]$$

where K is the eddy diffusion coefficient and z height above bottom with ^{222}Rn activity C. The values of K calculated from the ^{222}Rn data span about two orders of magnitude, 1–100 cm^2 s^{-1}. Other types of ^{222}Rn profiles include those with a two-layer structure and those without specific trend suggesting that its transport via advection and eddy diffusion along isopycnals and non-steady-state condition also need to be considered while describing its distribution. These studies also demonstrated a strong dependence between ^{222}Rn-based eddy diffusion and the stability of bottom water column.

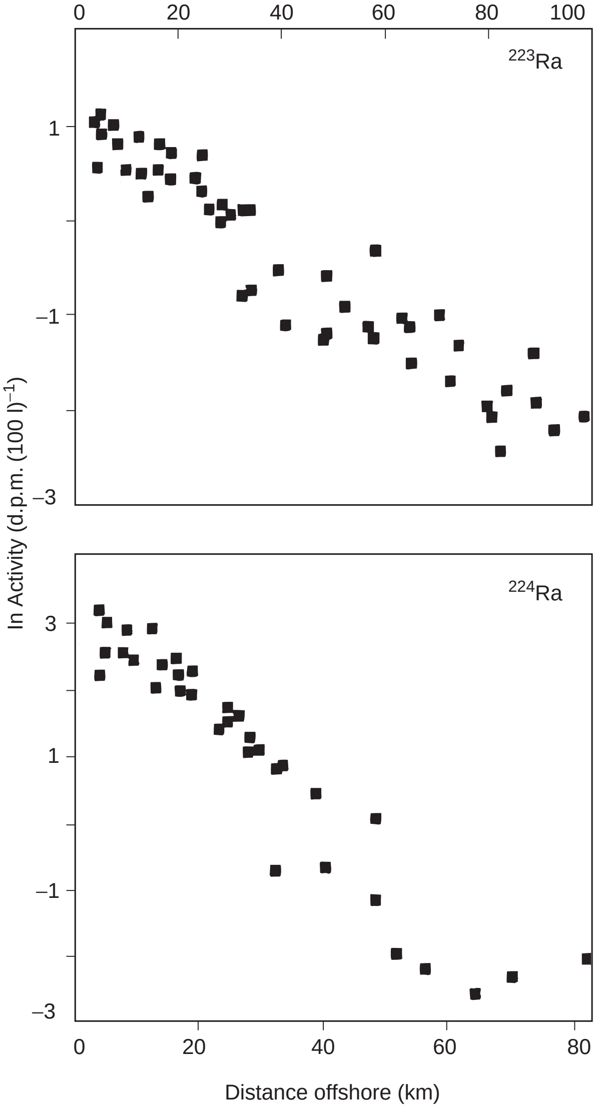

Figure 12 Distributions of ^{223}Ra and ^{224}Ra activities as a function of distance off-shore from Winyah Bay off Carolina Coast, USA. These profiles have been modeled to yield horizontal eddy diffusion coefficients. (Modified from Moore, 1999.)

Ra Isotopes

Ra isotopes, particularly, ^{226}Ra and ^{228}Ra have found extensive applications in water circulation studies. All the Ra isotopes, ^{224}Ra, ^{223}Ra, ^{228}Ra, and ^{226}Ra enter the oceans mainly through diffusion from sediments and by desorption from river particulates and are commonly measured by α and γ counting techniques. ^{224}Ra and ^{223}Ra, because of their very short half-lives (**Figure 1**), are useful for studying mixing processes occurring on timescales of a few days to a few weeks which restricts their utility to regions close to their point of injection such as coastal and estuarine waters (**Figure 12**). The half-life of ^{228}Ra is also short, 5.7 years, and hence its concentration decreases with increasing

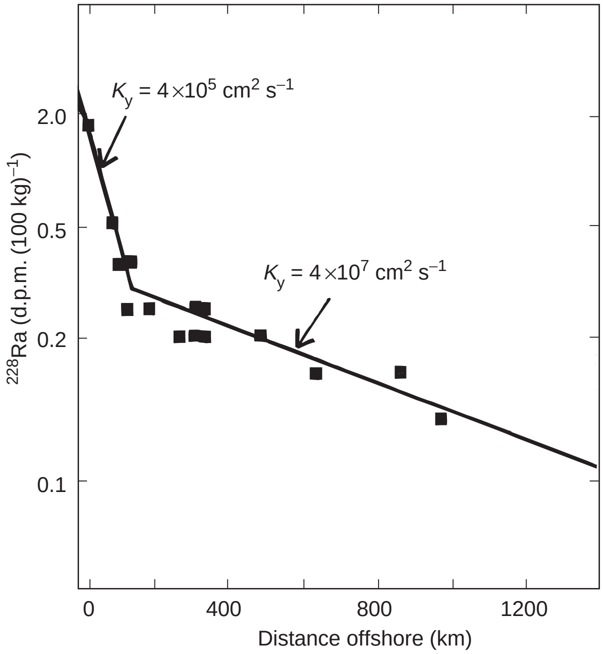

Figure 13 ^{228}Ra distribution as a function of distance from the coast off California. Values of horizontal eddy diffusion coefficient can be derived from these profiles. Note that ^{228}Ra mixes farther into the open sea than ^{223}Ra and ^{224}Ra (**Figure 12**) because of its longer half-life. (Modified from Cochran, 1992.)

distance from its source, the sediment–water interface, e.g., from coast to open sea (**Figure 13**) surface waters to ocean interior and height above the ocean floor (**Figure 14**). These distributions have been modeled, by treating them as a balance between eddy diffusion and radioactive decay (eqn [6]), to determine the rates of lateral and vertical mixing occurring on timescales of 1–30 years in the thermocline and near bottom waters.

^{226}Ra is the longest lived among the Ra isotopes, with a half-life comparable to that of deep ocean mixing times. The potential of ^{226}Ra as a tracer to study large-scale ocean mixing was exploited using a one-dimensional vertical advection–diffusion model to describe its distribution in the water column. Subsequent studies brought to light the importance of biological uptake and cycling in influencing ^{226}Ra distribution, processes which were later included in the ^{226}Ra model.

Figure 15 shows typical profiles of ^{226}Ra in the oceans. Its concentration in surface waters falls in the range of $0.07 \pm 0.01\,\text{d.p.m.}\,l^{-1}$ which steadily increases with depth such that its abundance in the deep waters of the Pacific > Indian > Atlantic (**Figure 15**). ^{226}Ra concentration in the North Pacific bottom water is $\sim 0.4\,\text{d.p.m.}\,l^{-1}$, some of the highest in the world's oceans.

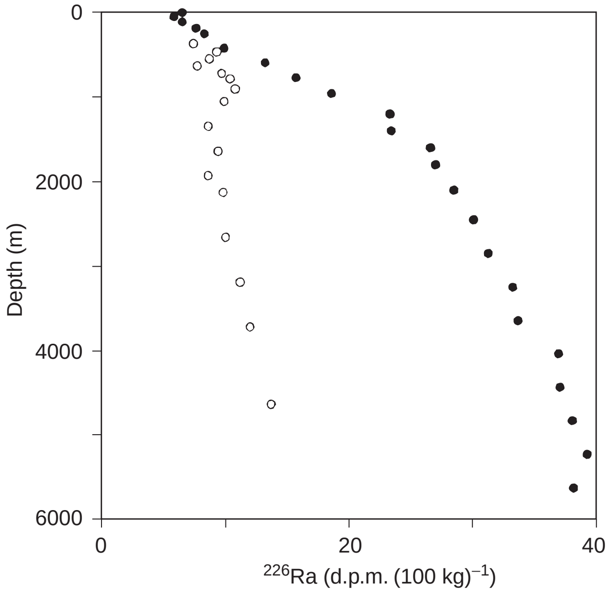

Figure 15 Typical distributions of ^{226}Ra in the water column of the Pacific (●) and Atlantic (○) oceans. Data from Broecker *et al.* (1976) and Chung and Craig (1980).

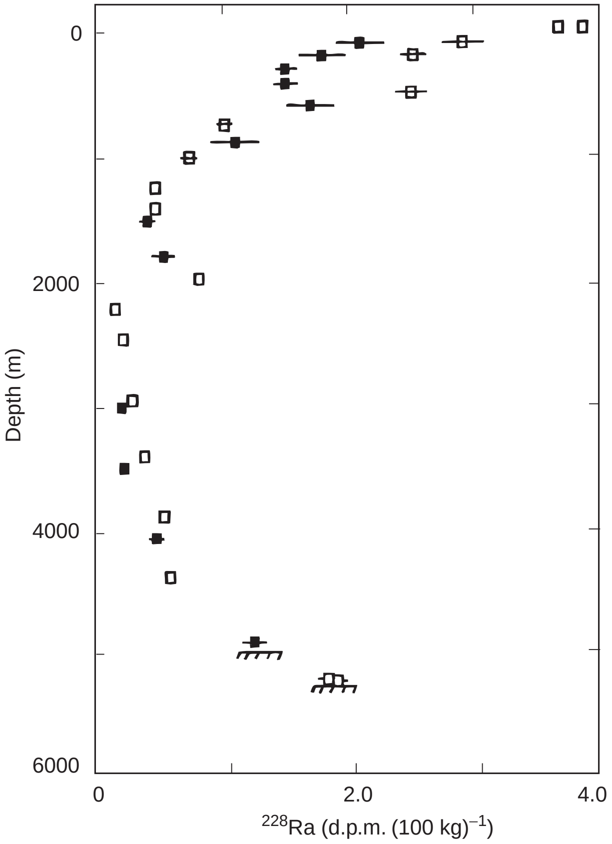

Figure 14 Example of ^{228}Ra depth profile in the North Atlantic. The high concentrations near the surface and near the sediment–water interface is due to its supply by diffusion from sediments. Lateral transport also plays an important role in determining surface water concentrations. (Modified from Cochran, 1992.)

^{226}Ra distribution in the ocean has been modeled to derive eddy diffusivities and advection rates taking into consideration its input by diffusion from sediments, loss by radioactive decay, and dispersion through water mixing, particulate scavenging and regeneration. It has been shown that particulate scavenging and regeneration plays a crucial role in contributing to the progressive increase in ^{226}Ra deep water concentration from the Atlantic to the Pacific. Attempts to learn more about particulate transport processes in influencing ^{226}Ra distribution using Ba as its stable analogue and Ra–Ba and Ra–Si correlations have met with limited success and have clearly brought out the presence of more ^{226}Ra in deep waters than expected from their Ba content (**Figure 16**). This 'excess' is the nascent ^{226}Ra diffusing out of deep sea sediments and which is yet to take part in particulate scavenging and recycling. Such excesses are quite significant and are easily discernible in the bottom waters of the eastern Pacific.

^{227}Ac

The first measurement of ^{227}Ac in sea water was only reported in the mid-1980s. These results showed that its concentration increases steadily

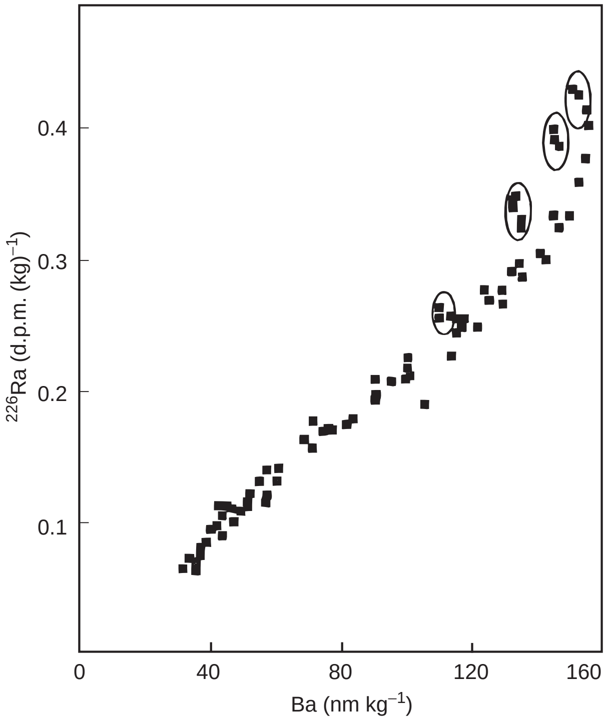

Figure 16 Ra–Ba correlation in the north-east Pacific. The presence of 'excess Ra' (enclosed in ellipses) is clearly discernible in bottom waters. (Modified from Ku *et al.*, 1980.)

from surface to bottom water (**Figure 17**) and that its activity in ocean interior and deep waters is considerably in excess of its parent ^{231}Pa (**Figure 17**). The diffusion of ^{227}Ac out of bottom sediments is the source of its excess in bottom waters, analogous to those of Ra isotopes. Measurements of ^{227}Ac in pore waters have confirmed this hypothesis. ^{227}Ac distribution can serve as an additional tracer in studies of water mixing processes occurring on decadal timescales, thus complementing the ^{228}Ra applications.

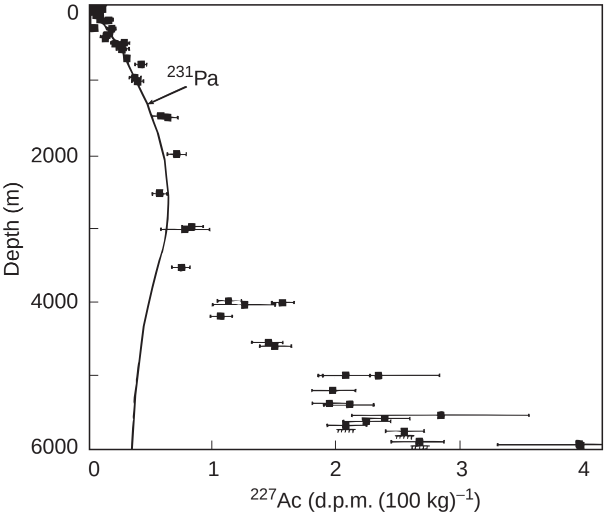

Figure 17 ^{227}Ac profile in the Pacific Ocean. Its large excess over ^{231}Pa is due to its diffusion out of sediments. (Modified from Nozaki, 1984.)

Summary

The distribution of U/Th series nuclides in the sea is regulated by physical and biogeochemical processes occurring in the water column and at the air–sea and sea–sediment interfaces. These processes often create radioactive disequilibria among the members of the U/Th decay chains. These disequilibria serve as powerful 'tools' to examine and quantify several processes in the sea, such as water circulation on various timescales (days to thousands of years), particle-scavenging, solute–particle interactions, particle dynamics and transformation and air–sea gas exchange. The understanding of these processes and elucidation of their timescales have direct relevance to studies such as dispersal of chemical species in the sea, contaminant transport and sites of their removal and particulate carbon fluxes through the water column. Recent advances in sampling and measurements of U/Th series nuclides have considerably enhanced the scope of their application in the study of water column processes.

See also

Estuarine Circulation. River Inputs. Uranium–Thorium Decay Series in the Oceans Overview.

Further Reading

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