

NATURAL AND ANTHROPOGENIC RADIONUCLIDES

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Keywords: Actino-uranium decay series, anoxic sediments, anthropogenic nuclides, becquerel, bioaccumulation, cosmic-ray produced nuclides, daughter-parent pair, decay chains, decay mode, decay product, diagenesis, eddy diffusion, fission product, geochemical fractionation, geochronology, half-life, nepheloid layer, new production, nuclide, oozes, particulate scavenging, radioactive disequilibrium, radioactive equilibrium, radioactivity, radionuclide, secondary neutrons, secular equilibrium, sedimentation rate, spallation, stratosphere, thorium decay series, tracer, transuranic elements, tritiated water, tritium, T. U., unreacted fissile material, uranium decay series, varved clays.

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Summary

This article presents some important natural and anthropogenic radionuclides in marine environments and the applications of these radionuclides to marine science studies based on their chemical and nuclear characteristics. The radionuclides that are soluble in seawater are useful tracers for the studies of mixing processes and the large-scale circulation of water masses. These radionuclides include, but are not limited to, radium-226, radium-228, radon-222, strontium-90, cesium-137 and tritium. The radionuclides that are particle-reactive are effectively removed or scavenged by sinking particulates. These nuclides can be used to evaluate the mean residence time of the corresponding elements as well as the mean settling rate of the particulates based on the radioactive disequilibrium observed between a reactive daughter in both the dissolved and particulate phases and its soluble parent in the oceans. Daughter-parent pairs as such include Th-234–U-238, Th-230–U-234, Th-228–Ra-228, Pb-210–Ra-226, etc. Some of the most common applications are described.

Carbon-14 and tritium are two important radionuclides produced by both cosmic radiations and nuclear explosions. The input of these to the oceans resulting from nuclear explosions or weapon testing conducted in the 1950's and 1960's was so enormous that it completely masked the natural distribution of these two nuclides in surface waters. There was evidence of deep water penetration in some parts of the oceans. Using C-14 as an oceanic tracer becomes more complicated due to the air-sea exchanges of CO₂ and the biogeochemical cycles of carbon. The anthropogenic CO₂ contributed by the industrial revolution had diluted the C-14 content of atmospheric CO₂, but bomb-produced C-14 contributed to a maximum C-14 content in atmospheric CO₂ around 1963. The $\Delta^{14}\text{C}$ values were over +750% in the Northern Hemisphere and about +650% in the Southern Hemisphere at that time. Although most of the deep waters are not yet affected by the anthropogenic CO₂ and C-14, the dating of a deep water mass by C-14 requires a thorough understanding of the possible effects arising from any transformation between organic and inorganic carbon in both the dissolved and particulate phases.

Anthropogenic Sr-90, Cs-137 and Pu-239 are commonly found to be widespread but latitude-dependent in surface ocean waters. Sr-90 and Cs-137 are essentially in soluble form, but Pu-239 is particle-reactive and can be removed from surface waters to deep waters by sinking organic and inorganic particulates. Pu-239 behaves like polonium and can be enriched in plankton and other organisms.

1. Introduction

Radioactive nuclides, or radionuclides, in the oceans or marine environments are widely distributed but show substantial variations that may be used as tools for oceanic mixing and circulation studies as well as for the determination of sediment accumulation rates. Because of their chemical characteristics and specific decay constants, radionuclides of various half-lives can provide a wide range of time scales for oceanic and geochemical processes that occur in the oceans or marine environments. Based on their mode of production or sources, radionuclides may be divided into two types, namely natural and anthropogenic. Natural radionuclides include: a) long-lived parents in a pair of simple

parent-daughter decay, such as potassium-40 and rubidium-87; b) the uranium, thorium and actino-uranium decay series with grandparents and their regenerated successive daughters; and c) radionuclides produced by cosmic radiation, such as beryllium-7 and phosphorus-32 which fall out of the atmosphere into the marine environments directly or indirectly. Anthropogenic radionuclides are produced artificially by thermonuclear reactions during the explosion of nuclear weapons or discharges from nuclear installations. These include tritium and carbon-14 which were added to the cosmic-ray produced inventories in huge amounts during the extensive bomb tests in the 1960's, and also many heavier nuclides, such as strontium-90, cesium-137 and plutonium-239.

The concentration of radionuclides in marine environmental samples, such as seawaters, marine particulates and bottom sediments, varies substantially in space and time; the concentrations are often expressed in either of two ways: a) in mass per unit mass or volume of seawater, or mass per unit mass of particulates or sediments; or b) in activity per unit mass or volume of the material in question. The activity of a radionuclide is simply defined as its decay rate which is proportional to its mass (or number of atoms) with a constant, its radioactive decay constant. Using activity to express the quantity or concentration of a radionuclide owes much to its method of determination, which often requires counting the number of atoms decayed in a specified time interval, i.e., its decay rate or activity. Activity as a unit is especially useful in the uranium, thorium and actino-uranium decay series in which a daughter with a short half-life or a large decay constant can reach radioactive equilibrium with its parent with a long half-life in a closed system when steady-state is attained, and their activities are then equal. The activity unit used is the curie (Ci), which is defined as the decay rate at 3.7×10^{10} disintegrations per second (dps or Becquerel, Bq). Since the activities or concentrations of most radionuclides in the marine environments are many orders of magnitude lower than this unit, the picocurie ($1 \text{ pCi} = 10^{-12} \text{ Ci}$) is commonly used. One pCi equals 2.22 disintegrations per minute (dpm). The radionuclides observed in various marine environments are briefly outlined in the following paragraphs. More detailed descriptions and discussion focus on the uranium, thorium and actino-uranium decay series and some radionuclides, which have been demonstrated to have wide applications in marine environments. These radionuclides are covered in the main body of this article. However, the radionuclides discussed are rather limited, and some may be brief while others are in more detail, depending on the extent of their application.

2. Natural Radionuclides

Long-lived natural radionuclides as the parent of a pair of simple parent-daughter decay include potassium-40 and rubidium-87. Both nuclides in the marine environments are of terrestrial origin. Potassium-40, as a radioisotope of potassium, has an isotopic abundance of 0.0118 per cent and a half-life of 1.26×10^9 years. A liter of seawater at salinity 35 contains about 0.4 grams of potassium in which potassium-40 has an activity of about 12.4 Becquerel or about 335 pCi l^{-1} . This activity accounts for more than 90 per cent of the total radioactivity in a unit volume of seawater, and can be calculated directly from the potassium content. The decay of potassium-40 to argon-40 provides an important tool for dating the age of the formation of potassium-bearing minerals. This tool has been applied to date igneous rocks or the rocks solidified from molten magma from seamounts and mid-ocean ridges, but the initial retention and subsequent loss of

argon due to alteration may cause large errors in age dating. To be reliable, it has to be used concurrently with other dating methods to obtain a concordant age. Its application to marine sediment dating is very limited. Rubidium-87 has an isotopic abundance of 27.85 per cent and a half-life of 4.9×10^{10} years. Rubidium concentration in seawater is about 120 ug l^{-1} in which rubidium-87 activity is about 2.9 pCi l^{-1} . This activity is less than one per cent of that due to potassium-40 (335 pCi l^{-1}). Similar to potassium-40, rubidium-87 is useful for dating igneous rocks. It may also be applied to dating metamorphic or sedimentary rocks.

The decay product of rubidium-87 is strontium-87, which also has a non-radiogenic component, strontium-86. Strontium in seawaters has a very uniform Sr-87/Sr-86 ratio, similar to that of marine carbonates. This may suggest that strontium in seawater was mainly derived from marine carbonates since other major strontium sources have quite different Sr-87/Sr-86 ratios. The Sr-87/Sr-86 ratio is in general higher in non-carbonate deep sea sediments than in seawater. Thus, this ratio may serve as a proxy for terrigenous sources of deep sea sediments. The decay chains of uranium, thorium and actino-uranium start with uranium-238, thorium-232 and uranium-235, respectively, as their grandparents of primordial, or primitive, origin. Table 1 shows major and useful daughter radionuclides in the uranium-238, thorium-232 and uranium-235 decay chains together with their principal decay modes and half-lives. Because of their importance in marine environments, each decay chain or series is treated in a separate subsection, including those individual radionuclides that vary in response to various oceanographic or geochemical processes. Certain natural radionuclides are also used in industry (Table 2).

Radionuclide	Decay mode	Half-life	Daughter
Uranium series			
U-238	α	$4.51 \times 10^9 \text{ y}$	Th-234
Th-234	β	24.1 d	U-234
U-234	α	$2.47 \times 10^5 \text{ y}$	Th-230
Th-230	α	$7.52 \times 10^4 \text{ y}$	Ra-226
Ra-226	α	1622 y	Rn-222
Rn-222	α	3.82 d	Pb-210
Pb-210	β	22.3 y	Bi-210
Bi-210	β	5.01 d	Po-210
Po-210	β	138.4 d	Pb-206
Thorium series			
Th-232	α	$1.41 \times 10^{10} \text{ y}$	Ra-228
Ra-228	β	5.75 y	Th-228
Th-228	α	1.91 y	Ra-224
Ra-224	α	3.64 d	Pb-208
Actino-uranium series			
U-235	α	$7.1 \times 10^8 \text{ y}$	Pa-231
Pa-231	α	$3.25 \times 10^4 \text{ y}$	Ac-227
Ac-227	β	21.6 y	Th-227
Th-227	α	18.2 d	Pb-207

Table 1. Decay Chains of Uranium, Thorium and Actino-Uranium Showing Major Decay Modes and Half-lives.

Industry	Feedstock	Waste/byproducts
Phosphate production	Phosphate rock: 1700 Bq kg ⁻¹ U-238	Phosphogypsum solid: Ra-226 Liquid effluent: Po-210
Metal production Tin	Ores: tinstone, stannite ~1000 Bq kg ⁻¹ U-238; 300 Bq kg ⁻¹ Th-232	Volatilization of Po-210 Slags: 1000 Bq kg ⁻¹ U-238 300 Bq kg ⁻¹ Th-232 Lead/bismuth byproducts may also be active
Niobium	Ores: pyrochlore 10,000 Bq kg ⁻¹ U-238; 80,000 Bq kg ⁻¹ Th-232	Slags containing U-238 and Th-232
Rare earths elements	Monazite 10,000 Bq kg ⁻¹ Th-232	Slags containing Th-232 (unless Th separated)
Thorium	Monazite	Product 100,000 Bq kg ⁻¹ Th-232
Titanium	Ores: ilmenite, rutile U-238 and Th-232 70-9000 Bq kg ⁻¹	Volatilisation of Po-210
Refractory materials	Ores: zircon, baddelyite 10,000 Bq kg ⁻¹ U-238 and Th-232	Volatilisation of Po-210
Energy production Coal combustion	Coal (typical): K-40, 50 Bq kg ⁻¹ ; U-238, 20 Bq kg ⁻¹ ; Th-232, 20 Bq kg ⁻¹ . Some coals several times higher. One report of 15,000 Bq kg ⁻¹ U-238 in high uranium area	0.5%-3% released to the atmosphere, remainder in ash
Oil combustion	Oil	During extraction: Ra-226 in the scales formed in the pipework up to 4000 Bq kg ⁻¹
Natural gas combustion	Radon up to 50 Bq l ⁻¹	During extraction: Ra-226 in the scales
Other industries Uranium mining and milling	Ores: 0.2%-20% U ₃ O ₈	Tailings containing daughter radionuclide of U-238 plus up to 0.01% uranium Radon released depends on cover Abandoned tailings 3 Bq m ⁻² s ⁻¹ Ra-226 conc. 100,000 Bq kg ⁻¹ (1% ore) Radon also emitted from mines: 300 GBq t ⁻¹ ore mined
Precious materials – gold, etc		Tailings can contain U-238 500-2000 Bq kg ⁻¹ and/or Th-232 1000-2000 Bq kg ⁻¹

Table 2. Examples of Natural Radionuclides in Industry
(modified from IAEA, 2000).

2.1. Uranium-238 and its Decay Products

Naturally occurring uranium isotopes include uranium-238, uranium-235 and uranium-234 whose abundances are 99.274 per cent, 0.720 per cent and 0.0056 per cent, respectively. Uranium-238 is often referred to as uranium, and its concentration is in mass rather than activity unless parent-daughter relationships are discussed. Uranium is readily dissolved in seawater as a stable complex ionic form $[\text{UO}_2(\text{CO}_3)_3]^{4-}$. Its concentration is quite uniform at about $3.3 \mu\text{g l}^{-1}$ in open ocean waters with only a negligible fraction in the particulate phase, on the order of $0.01 \mu\text{g l}^{-1}$.

Uranium concentrations are more variable in river waters and are in general only about 10 per cent of the ocean water values. In coastal or estuarine waters with significant river input, the uranium concentration may be modified locally by the uranium content of the river. In such waters, both uranium concentration and salinity are lowered by dilution of the river water. In open ocean waters, uranium concentration has been demonstrated to be linearly correlated with salinity in such a way that the former may be accurately estimated from the latter, which is readily available.

U-238 decays with a long half-life, thereby producing Th-234, a short-lived daughter (Table 1). As the ocean is not a closed system and thorium is highly reactive, Th-234 is easily removed by particulates from the surface. Only in deeper layers can they reach secular equilibrium or equal activity. Since U-234 is the next daughter product with a long half-life (2.47×10^5 y) and is a uranium isotope, the activity ratio of U-234 to U-238 in marine environments is a parameter of interest. Although the isotopic abundance of U-234 is very small in terms of mass, the activity of U-234 is comparable to that of U-238 because the half-life of U-234 is much shorter, i.e., it has a much greater decay constant. In ocean waters, the activity ratio is quite uniform at 1.15, indicating an excess of U-234 over U-238. This suggests preferential mobilization of U-234 in seawaters reflecting results of continental weathering processes and input from sediment pore waters. The activity ratio in river waters varies with values somewhat higher than the seawater ratio, implying river waters are not the only uranium source for ocean waters.

Due to its highly soluble nature, uranium has a long mean residence time in the oceans. The estimated values range from 10^5 to 10^7 years. This mean residence time is long enough to allow studies of oceanic or geochemical processes that cause a radioactive disequilibrium between a parent and its daughter, since the daughter production rate can be accurately determined. In the uranium decay series, several radionuclides as well as their parent-daughter pairs in marine environments are described in the following.

2.1.1. Radium-226

Radium-226 is produced from thorium-230 decay in the uranium decay series (Table 1). It decays to radon-222 with a half-life of 1622 years. Investigations of Ra-226 in the oceans reveal that its concentration varies greatly but does generally increase with depth. Ra-226 concentration in river water also varies, making it difficult to assess river contribution. Current wisdom is that Ra-226 in the ocean is released mainly from the bottom sediments via pore water exchange and diffusion due to its high mobility and much higher concentration in the sediments.

Extensive measurements of Ra-226 conducted in the 1970s during the Geochemical Ocean Section Study (GEOSECS) programs have shown that the surface water is fairly uniform in the Atlantic, Indian and Pacific Oceans except in the Antarctic south of the convergence zone, where the concentration or activity may be twice as much. Typical vertical profiles for the three major oceans are illustrated schematically in Figure 1. The trend to increase suggests that Ra-226 is being added from the underlying sediments as the bottom water circulates, and the input rate is greater than the decay rate such that, as the water becomes older, it has higher activity. Because of the large variation in the deep and bottom water, Ra-226 has been used as a tracer for global-scale mixing and circulation studies.

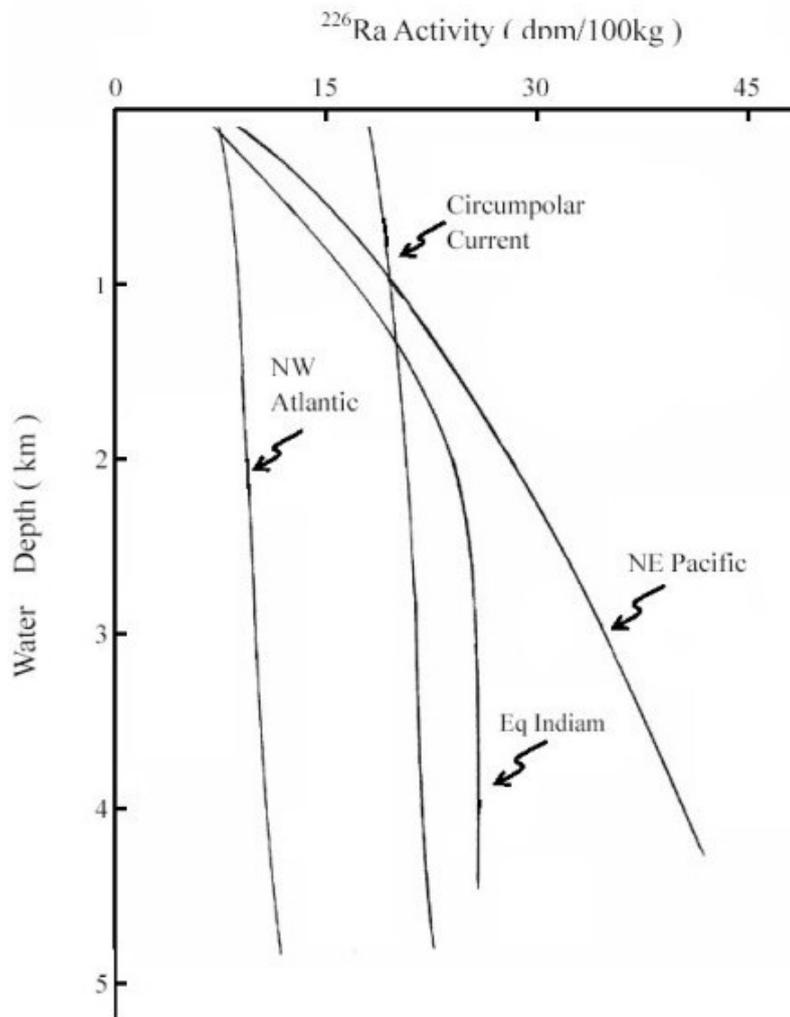


Figure 1. Schematic Radium-226 Profiles Showing a Systematic Increase from the Atlantic to the Pacific in Deep and Bottom Waters (based on GEOSECS data).

Because radium has no stable isotope, barium is often used as a substitute since, chemically, it behaves in a similar way to radium. Vertical concentration profiles are similar for barium and Ra-226 at the same location, both showing a large increase with depth. Ra-226 has a good correlation with silica, in general, suggesting silica as a possible carrier of Ra-226. However, in the northeast Pacific there is an apparent enrichment of Ra-226 over silica and barium due to a strong Ra-226 input from the

bottom sediments in the area. In the circumpolar water, Ra-226 concentration is fairly uniform from surface to bottom due to strong vertical mixing and upwelling. Ra-226 concentration in coastal waters and inland seas varies much more greatly than in the open oceans. In the Dead Sea Ra-226 concentration can be more than two orders of magnitude higher than that in the northeast Pacific deep waters, the highest in deep open ocean waters.

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Biographical Sketch

Dr. Yu-chia Chung is currently a professor of Geochemistry and Oceanography at the Institute of Marine Geology and Chemistry, National Sun Yat-sen University located in Kaohsiung, Taiwan. He has been teaching and conducting research at the Institute since he returned to Taiwan from the U. S. in 1986. His major research interest has been focussing on marine particulates using sediment traps as tools and applications of radionuclides as tracers for studying marine and atmospheric geochemical processes of various time scales including sedimentary geochronology.

Before joining the Institute of Marine Geology and Chemistry, He was associated with the Scripps Institution of Oceanography, University of California, San Diego. He was one of the few scientists who had participate in the GEOSECS (Geochemical Ocean Section Study) program from the very beginning to the end. His major contribution to the GEOSECS program was on radium-226 and lead-210 measurements in the Pacific and Indian oceans. He was also involved in an integrated monitoring and research program on earthquake prediction in southern California based on geochemical methods.

Born in Changhwa, Taiwan, on 22 April 1949, **Prof. Chen-Tung Arthur Chen**, his wife and two daughters are currently residing in Kaohsiung, where he has been Professor at the Institute of Marine Geology and Chemistry since 1986. After receiving his B.Sc. degree in Chemical Engineering from National Taiwan University in 1970, Prof. Chen was awarded his Ph.D. degree in Chemical Oceanography from the University of Miami in 1977. In the same year, he was appointed Assistant Professor in the College of Marine Sciences of Oregon State University, where he was later promoted to Associate Professor in 1981. He served as Visiting Professor at National Sun Yat-Sen University (NSYSU) in Kaohsiung, Taiwan, and as Chargé de Recherche (CNRS), Université Pierre et Marie Curie in Paris during 1984-1985. During this period, he founded the Institute of Marine Geology at NSYSU, and served as its director until 1989 when he was made Dean of the College of Marine Sciences, a position he held until 1992.

Prof. Chen has sat on numerous international committees, including the Scientific Committee on Oceanic Research and the World Ocean Circulation Experiment. He also served as one of the executives of the Scientific Steering Committee of the Joint Global Ocean Flux Study (JGOFS) between 1992-1995. Just prior to that, he had helped to form the Joint JGOFS / LOICZ Marginal Seas Task Team in 1991, and served as its chairman until 1995. Prof. Chen is at present one of the editors of *Oceanography Journal* and associate editor of *Marine Chemistry*. Besides having more than 150 of his own scientific papers published, Professor Chen was awarded the highly-coveted Biowako Prize for Ecology from Japan in 1997.