COSMOGENIC ISOTOPES

D. Lal, Scripps Institute of Oceanography, University of California San Diego, La Jolla, CA, USA

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Introduction

In different settings, spanning from the extraterrestrial to the terrestrial, naturally occurring nuclides offer unique possibilities for being deployed as tracers for studying a great variety of physical, chemical, and biological processes, occurring over a wide range of timescales. This article discusses the continuous production of several stable and radioactive isotopes as a result of nuclear reactions of cosmic ray particles in the Earth's atmosphere and the hydrosphere, and their potential usefulness as tracers for studying oceanic processes. The great merit of cosmic ray produced (cosmogenic) isotopes as tracers lies in the fact that their source functions in the different geospheres can be determined, and that several nuclides with a wide range of half-lives and chemical properties are available.

Cosmic radiation, which consists of energetic H, He and heavier nuclei, with kinetic energies much greater than tens of mega electronvolts (MeV), (with particles of energies much beyond 10^{10} MeV), produce a great variety of nuclides by their interactions with target nuclei in the atmosphere, hydrosphere and the lithosphere. The predominant cosmic ray interaction is fragmentation of the target nuclei by primary and secondary particles of the cosmic radiation. Some nuclides are produced following the capture of thermal (very slowly moving) neutrons by target nuclei, which are abundant in the secondary cosmic radiation as a result of slowing down of fast neutrons emitted in energetic cosmic ray-produced nuclear reactions.

Radiocarbon, ^{14}C, was the first cosmic ray-produced isotope to be discovered in 1947 in sewage methane. Soon thereafter it was applied for archaeological/anthropological dating. This discovery was a milestone in the use of cosmic ray-produced (cosmogenic) isotopic changes as a tool for learning about planetary sciences. It laid the foundations of the field of cosmic ray geophysics/geochemistry. Subsequently, in the early 1960s, about 25 cosmogenic radionuclides produced in the earth's atmosphere, with half-lives ranging from ~ 1 h to millions of years were detected. The driving force for the studies of cosmic ray-produced nuclides was the realization that if they could be detected in different dynamic reservoirs of the geospheres, they could be used as tracers to obtain important information about the timescales involved in the transport of materials through the atmosphere to the hydrosphere, oceans, and the cryosphere, and that in some cases they could be used as clocks to introduce timescales into the diverse proxy records of earth's climate. Oceans are central to the dynamic interplay between the dynamic reservoirs, and therefore considerable emphasis has been placed on understanding the nature of the principal mixing/transfer processes, of the marine biogeochemical cycles, and of the large-scale ocean circulation. All oceanic investigations, in one way or the other, are linked to the central question of what processes control the earth's climate. Geochemical tracers serve as tools to understand these processes and their rates.

As mentioned above, the field of cosmic ray produced (cosmogenic) tracers caught roots in 1947, with the discovery of ^{14}C. It grew rapidly thereafter in the late 1950s/early 1960s, and to date it is still one of the frontier areas in modern geochemistry. There are two reasons for this sustained hold and value of the cosmogenic tracers: continued development of new and powerful techniques for measuring their distribution in natural settings at very low concentrations, and the emergence of new biogeochemical questions which crop up as our understanding of the terrestrial climate system improves. However, there are often no other (suitable) tracers available to study the short- and long-term behavior of oceans on large space scales. This article considers the essentials of the cosmogenic tracers, their potentials, and how new advances continue to keep this field growing.

Terrestrial Cosmogenic Isotopes and Their Production Rates

Most of the cosmic ray energy ($>98\%$) is dissipated in the earth's atmosphere in the nuclear reactions they produce. The atmospheric column represents about 13 mean free paths for nuclear interactions of fast protons and neutrons. After traversal through the atmosphere, the secondary particles of the cosmic radiation continue to produce nuclear reactions with the surficial terrestrial reservoirs: the hydrosphere, the cryosphere, and the lithosphere, but at a much lower rate. The techniques of the 1950s for studying the cosmogenic nuclides were barely adequate to study the isotopes produced in the atmosphere. However, because of their value in understanding geophysical and geochemical processes, they were studied fairly extensively until the 1970s. A number of technical developments in the 1970s have made it easier to study the 'atmospheric' cosmogenic isotopes in the ocean environs, and even the cosmogenic isotopes produced *in situ* in terrestrial materials, including the hydrosphere and the cryosphere.

The cosmogenic tracer-based information obtained from studies of the lithosphere and the cryosphere is of great value in interpreting the oceanic records. **Table 1** lists a suite of isotopes, which serve (or should serve) as useful tracers in geophysical and geochemical studies. This list includes nominally potentially useful 20 nuclides, having half-lives exceeding two weeks, which are produced in the atmosphere, hydrosphere and in the lithosphere. The target elements from which they are produced in the earth's atmosphere, and from principal elements in surficial matter are also listed in **Table 1**.

This article is concerned primarily with nuclides that are useful as tracers in oceanography, and therefore shorter-lived nuclides have been excluded from **Table 1**. Since cosmic ray intensity is appreciably reduced at sea level due to nuclear interactions in the atmosphere isotope production rates (per gram target element per second), in surficial materials, are appreciably smaller than in the atmosphere. Therefore, nuclides, which can be produced in nuclear interactions with the major elements present in the atmosphere, N and O, have their principal source in the atmosphere. The next most abundant element, Ar, in the atmosphere occurs at an abundance of only 0.93% (v/v) in the atmosphere. Nuclear interactions with surficial materials can therefore be an important source of some of the nuclides produced from Ar, and for those isotopes which have mass numbers greater than 40, since ^{40}Ar is the most abundant nuclear isotope in the atmosphere. Permanent constituent gases heavier than Ar have very low abundances in the atmosphere. The abundances of the next heavier gases, Kr and Xe, are ~1 and 0.1 ppm (v/v), respectively.

The production rates of several cosmogenic isotopes in the earth's atmosphere are given in **Table 2**, along with their estimated global inventories. Some of the cosmogenic isotopes are also produced directly, *in situ*, in the upper layers of the oceans. The source strengths of cosmic ray-produced nuclei in the oceans, due to their production in the atmosphere, and direct production in the ocean water, are given in **Table 3**. Atmospheric production is the dominant source of all nuclides in **Table 3**, except for ^{36}Cl, where its *in situ* oceanic production exceeds the atmospheric production by about 50%. In the case of ^{37}Ar the two source strengths are comparable, and in the cases of ^{32}P and ^{33}P *in situ* production in the oceans is an order of magnitude lower.

Table 1 Potentially useful cosmogenic nuclides (arranged in order of mass numbers) with half-lives exceeding 2 weeks, produced in the Earth's atmosphere and in surficial materials

Nuclide(s)	*Half-life*	*Main targets*[a]
^{3}H	12.3 y	O, Mg, Si, Fe (N, O)
^{3}He, ^{4}He	s	O, Mg, Si, Fe (N, O)
^{7}Be	53 d	O, Mg, Si, Fe (N, O)
^{10}Be	1.5×10^{6} y	O, Mg, Si, Fe (N, O)
^{14}C	5730 y	O, Mg, Si, Fe (N)
^{20}Ne, ^{21}Ne, ^{22}Ne	s	Mg, Al, Si, Fe
^{22}Na	2.6 y	Mg, Al, Si, Fe (Ar)
^{26}Al	7.1×10^{5} y	Si, Al, Fe (Ar)
^{32}Si	~150 y	(Ar)
^{32}P	14.3 d	(Ar)
^{33}P	25.3 d	(Ar)
^{35}S	87 d	Fe, Ca, K, Cl (Ar)
^{36}Cl	3.0×10^{5} y	Fe, Ca, K, Cl (Ar)
^{37}Ar	35 d	Fe, Ca, K (Ar)
^{39}Ar	268 y	Fe, Ca, K (Ar)
^{41}Ca	1.0×10^{5} y	Ca, Fe (Kr)
^{53}Mn	3.7×10^{6} y	Fe (Kr)
^{54}Mn	312 d	Fe (Kr)
^{59}Ni	7.6×10^{4} y	Ni, Fe (Kr)
^{60}Fe	1.5×10^{6} y	Ni (Kr)
^{81}Kr	2.3×10^{5} y	Rb, Sr, Zr (Kr)
^{129}I	1.6×10^{7} y	Te, Ba, La, Ce (Xe)

[a] Elements from which most production occurs; those in parentheses give the main targets from which they are produced in the Earth's atmosphere.
s, stable.

Isotopes produced in the earth's atmosphere (**Table 2**), are introduced in the upper ocean:

1. in wet precipitation, in the case of isotopes which are removed directly (^{3}H), or as attached to aerosols (^{7}Be, ^{10}Be, ^{22}Na, ^{26}Al, ^{32,33}P, ^{32}Si, ^{35}S, ^{36}Cl);
2. by air–sea exchange of ^{14}C (as $^{14}CO_2$), and of isotopes of rare gases (^{3}He, ^{37}Ar, ^{39}Ar and ^{81}Kr).

Besides direct *in situ* production of isotopes in the ocean waters (**Table 2**), some isotopes are also introduced to the oceans with river runoff as a result of weathering of the crustal materials in which they are produced, e.g., ^{10}Be, ^{26}Al, ^{41}Ca, and ^{53}Mn (**Table 2**). To date, those introduced by weathering of crustal materials have not been either studied or identified as important, and estimates of the strength of this source, are not presented here.

Table 2 Production rates of several isotopes in the Earth's atmosphere; arranged in order of decreasing half-lives[a]

Isotope	*Half-life*	*Production rate (atoms cm^{-2} s^{-1})*		*Global inventory*
		Troposphere	*Total atmosphere*	
^{3}He	Stable	6.7×10^{-2}	0.2	3.2×10^{3} tons[b]
^{10}Be	1.5×10^{6} y	1.5×10^{-2}	4.5×10^{-2}	260 tons
^{26}Al	7.1×10^{5} y	3.8×10^{-5}	1.4×10^{-4}	1.1 tons
^{81}Kr[c]	2.3×10^{5} y	5.2×10^{-7}	1.2×10^{-6}	8.5 kg
^{36}Cl	3.0×10^{5} y	4×10^{-4}	1.1×10^{-3}	15 tons[e]
^{14}C	5730 y	1.1	2.5	75 tons
^{39}Ar[d]	268 y	4.5×10^{-3}	1.3×10^{-2}	52 kg
^{32}Si	~ 150 y	5.4×10^{-5}	1.6×10^{-4}	0.3 kg
^{3}H	12.3 y	8.4×10^{-2}	0.25	3.5 kg
^{22}Na	2.6 y	2.4×10^{-5}	8.6×10^{-5}	1.9 g
^{35}S	87 d	4.9×10^{-4}	1.4×10^{-3}	4.5 g
^{7}Be	53 d	2.7×10^{-2}	8.1×10^{-2}	3.2 g
^{37}Ar	35 d	2.8×10^{-4}	8.3×10^{-4}	1.1 g
^{33}P	25.3 d	2.2×10^{-4}	6.8×10^{-4}	0.6 g
^{32}P	14.3 d	2.7×10^{-4}	8.1×10^{-4}	0.4 g

[a] Based on Lal and Peters (1967).

[b] The inventory of this stable nuclide is based on its atmospheric inventory, which includes an appreciable contribution from crustal degassing of ^{3}He.

[c] Based on atmospheric ^{81}Kr/Kr ratio of $(5.2 \pm 0.4)\times10^{-13}$.

[d] Based on atmospheric ^{39}Ar/Ar ratio of (0.107 ± 0.004) d.p.m. l^{-1} Ar (STP).

[e] Includes a rough estimate of ^{36}Cl produced by the capture of neutrons at the earth's surface.

Table 3 Source functions of cosmogenic nuclides in the oceans, for nuclides of half-lives >10 days, arranged in order of increasing half-lives

		Principal target element (s)		*Global average surface injection rate*[a]	*Integrated* in situ *oceanic production rate*
Nuclide	*Half-life*	*Atmosphere*	*In ocean water*	*(atoms cm^{-2} min^{-1})*	*(atoms cm^{-2} min^{-1})*
^{32}P	14.3 d	Ar	Cl, S, K	5.82×10^{-3}	7.6×10^{-4}
^{33}P	25.3 d	Ar	Cl, S, K	6.93×10^{-3}	2.9×10^{-4}
^{37}Ar	35.0 d	Ar	K, Ca	9.10×10^{-6}	8.1×10^{-6}
^{7}Be	53.3 d	N,O	O	1.27	6.0×10^{-3}
^{35}S	87.4 d	Ar	Cl, Ca, K	2.84×10^{-2}	5.1×10^{-4}
^{22}Na	2.6 y	Ar	Na	3.75×10^{-3}	3.9×10^{-4}
^{3}H	12.3 y	N,O	O, ^{2}H	1.39×10^{1}	1.2×10^{-2}
^{32}Si	~ 150 y	Ar	S, Ca	9.60×10^{-3}	2.5×10^{-5}
^{39}Ar	269 y	Ar	K, Ca	2.00×10^{-1}	1.2×10^{-5}
^{14}C	5,730 y	N,O	O	1.20×10^{2}	9.0×10^{-3}
^{41}Ca[a]	1.0×10^{5} y	—	Ca	—	2.4×10^{-5} (*n*)[a]
^{81}Kr	2.1×10^{5} y	Kr	Sr	2.30×10^{-5}	1.9×10^{-8} (*n*)[c]
^{36}Cl[b]	3.0×10^{5} y	Ar	Cl	6.60×10^{-2}	1.06×10^{-1} (*n*)[c]
^{26}Al	7.2×10^{5} y	Ar	S, K, Ca	8.40×10^{-3}	6.8×10^{-6}
^{10}Be	1.6×10^{6} y	N,O	O	2.70	1.8×10^{-3}

[a] Flux to oceans from rivers should be included to take into account production in rocks and soil by ^{40}Ca(n, γ) ^{41}Ca reaction; this estimate is not given here because of large uncertainties in these calculations.

[b] As above, due to ^{35}Cl(n, γ) ^{36}Cl reaction.

[c] (*n*), The *in situ* production of ^{41}Ca, ^{81}Kr and ^{36}Cl in the oceans is primarily due to the relevant thermal neutron capture reaction. Note the 50% greater *in situ* production of ^{36}Cl in the oceans compared to its atmospheric source.

Table 4 Approximate steady-state fractional inventories of cosmic ray produced radioisotopes in exchange reservoirs[a]

Exchange reservoir	Radioisotope													
	^{10}Be	^{26}Al	^{36}Cl	^{81}Kr	^{14}C	^{32}Si	^{39}Ar	^{3}H	^{22}Na	^{35}S	^{7}Be	^{37}Ar	^{33}P	^{32}P
Atmosphere	2.3×10^{-3}	1.4×10^{-6}	1.1×10^{-6}	0.96	1.9×10^{-2}	2.0×10^{-3}	0.99	7.2×10^{-2}	0.27	0.65	0.71	0.99	0.80	0.84
Land surface	0.29^b	0.29^b	0.29^b	0	4×10^{-2}	0.29^b	0	0.27	0.21	0.1	0.08	0	5.6×10^{-2}	4.7×10^{-2}
Mixed oceanic layer	5.7×10^{-6}	1.4×10^{-5}	1.4×10^{-2}	6×10^{-4}	2.2×10^{-2}	3.5×10^{-3}	0	0.35	0.44	0.24	0.20	0	0.13	0.11
Deep oceanic layer	10^{-4}	7×10^{-5}	0.69	3.5×10^{-2}	0.92	0.68	0.01	0.3	8×10^{-2}	4×10^{-3}	2×10^{-3}	0	7×10^{-4}	10^{-4}
Oceanic sediments	0.71	0.71	0	0	4×10^{-3}	2.8×10^{-2}	0	0	0	0	0	0	0	0
Half-life (y)	1.5×10^{6}	7.1×10^{5}	3.0×10^{5}	2.3×10^{5}	5730	~150	268	12.3	2.6	87 d	53 d	35 d	25.3 d	14.3 d

[a] Approximate calculations based on Lal and Peters (1967). Values given as zero imply very small fractional inventories.

[b] Part of the inventory may in fact be carried as silt or dust to the oceans before decay.

Pathways of Isotopes to the Oceans, and Their Approximate Inventories/Concentrations in the Atmosphere, Hydrosphere and Sediments

The applications of cosmogenic isotopes as tracers depend on three principal factors: (1) their source function; (2) their half-lives; and (3) their chemical properties. These considerations decide how the fractional inventories of different tracers are distributed on the earth in the atmosphere, hydrosphere, and the sediments. The work of Lal and Peters, using simplified models for the pathways of the isotopes considering six mixing/exchange reservoirs is still quite instructive. These estimates of fractional inventories of 14 isotopes amongst these reservoirs are shown in **Table 4**.

Table 4 shows that most of the global inventory of the long-lived isotopes, ^{10}Be and ^{26}Al is in the oceanic sediments whereas that of another long-lived isotope, ^{36}Cl is in the oceans; this is a manifestation of their chemical properties. Analogous to ^{36}Cl, the chemical behavior determines the large fractional inventories of ^{14}C and ^{32}Si in the oceans. The inventories of the long-lived ^{81}Kr, and also of ^{39}Ar (~ 270 y half-life), are primarily in the atmosphere primarily because of the low abundances of Kr and Ar in the atmosphere. It should be noted that generally the applications of an isotope are favored in the reservoir where its inventory is the largest. However, this is not always true. For example, in the cases of ^{39}Ar and ^{33,32}P, in spite of their low inventories in the oceans, they have valuable applications in studies of oceanic processes.

Approximate theoretical estimates of isotope concentrations in the oceans (disintegrations per minute (d.p.m.) per tonne of sea water) are presented in **Table 5**. The values are in the range of 10^{-5}–250 d.p.m. t^{-1}. The corresponding specific elemental concentrations are very low, with isotope/element ratios lying in range of 10^{-19}–10^{-10}.

The concentrations of a large number of naturally occurring radioactive and stable nuclides, those produced in nuclear reactions caused by cosmic radiation, and those produced by energetic particles in radioactive disintegrations and in nuclear decays of naturally occurring long-lived nuclides, have been measured in the past five decades in the marine environment. Dramatic improvements in the radiometric techniques in the past two decades have allowed their measurements to be done fairly reliably. The database on the distribution of the cosmogenic and other tracers in the oceans is therefore growing steadily. Their measurements to date are in

Table 5 Approximate specific radioactivities of cosmic ray produced isotopes in the ocean

Radioisotope	*Half-life (y)*	*Average specific radio activity in oceans*	
		d.p.m. per tonne water	*d.p.m. per g element*
^{10}Be	1.5×10^{6}	10^{-3}	1.6×10^{3}
^{26}Al	7.1×10^{5}	1.2×10^{-5}	1.2×10^{-3}
^{81}Kr^{a}	2.3×10^{5}	7×10^{-6}	2.1×10^{-2}
^{36}Cl	3.0×10^{5}	0.55	3×10^{-5}
^{14}C	5730	260	10
^{32}Si	~ 150	1.5×10^{-2}	2.3×10^{-2}
^{39}Ar^{b}	268	2.9×10^{-3}	5×10^{-3}
^{3}H	12.3	36	3.3×10^{-4}

[a] Based on atmospheric ^{81}Kr/Kr ratio of $(5.2\pm0.4)\times10^{-13}$.

[b] Based on atmospheric ^{39}Ar/Ar ratio of (0.107 ± 0.004) d.p.m. per liter Ar.

Based on Lal and Peters (1967)).

good agreement with the theoretically predicted values of their distribution in the oceans (cf. **Tables 3** and **4**).

In many cases these nuclides serve as tracers for the study of physical, chemical, and biological processes in the oceans. Several radiotracers successfully provide chronology of sediments, corals, and manganese nodules, but learning about large-scale ocean circulation is another matter. The ability merely to make measurements of a tracer in the marine environment is not sufficient to use it as an effective tracer for delineating important oceanic variables. Tracer data must be examined in terms of ocean models. Constructing ocean models is an iterative process between data acquisition and model building, forcing model outputs, to become compatible with the observations. The oceanic processes are very complex, exhibiting significant spatial and temporal variability on a wide range of scales. For the tracer data to be useful in developing meaningful coupled atmosphere–ocean circulation models, which may be considered as the goal of tracer studies, one would require three-dimensional tracer data with sufficient resolution in the horizontal direction. The latter are not available, except for ^{14}C, where a considerable database is growing as a result of recent WOCE (World Ocean Circulation Experiment) expeditions.

Tracers in Oceanography: Why We Need Them and What We Learn From Them?

The oceans represent a large mass of water endowed with a large amount of diverse substances and heat. The dissolved and particulate oceanic 'complex' is in continuous exchange with the land surface and the atmosphere. An appreciable part of the dissolved phases is recycled within the oceans through biogeochemical cycles, which are maintained by the large-scale oceanic circulation. The latter is a manifestation of the continuous exchange of heat between the atmosphere and the ocean. Large-scale oceanic circulation replenishes nutrients in the surface waters, which are rapidly removed by biological productivity. Biological recycling changes the chemical makeup of ocean waters at all depths.

Thus there is a complex cause–effect relationship with significant feedbacks between oceanic circulation, biogeochemical cycling within the oceans, and composition of sea water. Understanding these processes is essential for understanding oceanographic processes, earth's climate, terrestrial biogeochemistry, and the proxy records contained in the oceanic sediments. Success in achieving this goal requires sensitive multidisciplinary techniques in which tracers play an important part.

Chemical and isotopic tracers have been used successfully for the past five decades. Oceanic water masses are conventionally characterized by their chemical and isotopic composition, and temperature. A central problem in oceanography is to understand the origins and the processes which determine the evolution of different water masses. Radioactive isotope tracers provide additional information on timescales, specifically on the rate constants of different processes. The most attractive feature of radioisotopes is that they provide time integrals of evolution of water masses through space, influenced by exchange/mixing processes, and radioactive decay of the tracer, which introduces the element of time in the model(s). In steady-state situations, all losses and gains balance out. By combining with information on stable isotopes, one can then determine effective time required for the water mass to reach equilibrium between gain and loss terms, i.e. get an estimate of the effective equilibration time of the water mass as it evolves.

Tracers fall into two broad categories:

1. Transient tracers which are introduced sporadically in a system, e.g., radionuclides introduced by testing of nuclear weapons, and from discharges from nuclear reactors.
2. Steady tracers which are introduced continuously in a system, e.g., those produced by nuclear interactions of cosmic rays on the earth, and by radioactive decay of dissolved uranium in the oceans.

It is convenient to further designate the tracers according to their chemical behavior in the system:

1. conservative tracers, which follow the motion of the 'fluid' in the system;
2. nonconservative tracers, which do not follow the motion of the 'fluid' in the system.

The first naturally occurring radiotracer to be used in oceanography was ^{226}Ra. The first successful tracer measurements of the cosmogenic ^{14}C with a view to understanding timescales in large-scale water circulation were made in 1960 and demonstrated the great value of this tracer in oceanography. The discovery of cosmogenic ^{32}Si in marine siliceous sponges opened up the possibility of using this as a tracer for studying biogenic silica fluxes to the deep sea, and the nutrient cycle of silicon. As the techniques for the measurement of weak activities of the nuclides became available, additional nuclides were measured in the oceans. To date 12 cosmogenic nuclides have been studied in the oceans, some during the 1960s, several during the 1980s. It is important to realize that all tracers are important because of their particular unique attributes (cf. **Table 4**).

Table 6 lists tracers, which are studied in oceanographic research, together with ^{36}Cl (which is included for its potential usefulness for determining the average source strength of cosmic ray neutrons in the past 0.5–0.7 My (million years)). The usefulness of cosmogenic tracers depends on their half-lives, chemical properties, and their source functions, which can be appreciated from their expected distribution in the geospheres (**Table 4**), and by the ease with which they can be measured. (**Table 4** does not include ^{4}He, ^{20}Ne, ^{21}Ne, ^{22}Ne, ^{22}Na, ^{35}S, ^{36}Cl, ^{37}Ar, ^{41}Ca, ^{53}Mn, ^{52}Ni, ^{60}Fe and ^{81}Kr, which are either not useful as oceanic tracers because of their short half-lives, or very long half-lives, or have very low cosmogenic production rates. However, with technical developments these nuclides may eventually become useful.) The long-lived cosmogenic radionuclide, ^{129}I is not included in **Tables 3** and **4** because (1) its half-life is rather long (15.7 My) to be useful for studying oceanic processes, (2) it is continuously produced in the oceans, and in ocean sediments in the spontaneous fission of ^{238}U, and (3) it has been added to the oceans in appreciable amounts in the last five decades by human activities; such as nuclear weapons' testing and processing of nuclear plants (which have raised the prenuclear age inventory of ^{129}I in the oceans of about 100 kg by more than an order of magnitude.

Several cosmogenic tracers also qualify as transient tracers at the present time, because of an appreciable contribution from anthropogenic sources (**Table 3**). Thus, the nuclides ^{3}H, ^{14}C (produced in appreciable amounts in nuclear weapons testing), tritugenic ^{3}He and ^{129}I (which has also been

Table 6 Important characteristics and principal applications of selected cosmogenic tracers

Isotope	*Half-life*	*Principal applications*
Isotopes which do not form compounds		
^{3}He	Stable	Air–sea exchange; escape of helium from the atmosphere
^{37}Ar	35 d	Air–sea exchange; tropospheric circulation
^{39}Ar	268 y	Air–sea exchange; vertical mixing in oceans
^{81}Kr	2.3×10^5 y	Ground water ages, and constancy of cosmic radiation
Isotopes which label constituent molecules in the atmosphere and the hydrosphere		
^{3}H (H_2O)	12.3 y	Characterizing water molecules in the atmosphere, hydrosphere and cryosphere
^{14}C (CO_2, CO_3, HCO_3)	5730 y	Characterization of the carbon cycle reservoirs
^{32}Si ($HSiO_3$, SiO_2)	~ 150 y	Biogeochemical cycle of silicon
^{32}P, ^{33}P (DIP, DOP)	14.3, 25.3 d	Biogeochemical cycle of phosphorus
Isotopes which attach to aerosols/particles		
^{7}Be	53 d	Atmospheric circulation, vertical mixing in surface ocean waters
^{10}Be	$1.5\,10^6$ y	Role of particle scavenging in the coastal and open oceans; dating of sediments and accretions
^{26}Al	7.1×10^5 y	Role of particle scavenging in the coastal and open oceans; dating of marine sediments and accretions
^{32}Si ($HSiO_3$, SiO_2)	~ 150 y	Labeling the dissolved oceanic silicon pool; atmospheric circulation
^{32}P, ^{33}P	14.3, 25.3 d	Labeling the dissolved oceanic phosphorus pool; tropospheric circulation

Note: Not included here are ^{36}Cl and ^{129}I for reasons discussed in the text.

produced in large amounts by nuclear weapons tests and operation of nuclear power plants), serve as (useful) transient tracers in some geophysical reservoirs.

An important consideration in the use of a transient tracer is knowledge of its source strength. Anthropogenic sources are generally not well defined; however, in the case of ^{14}C, an important advantage is that its contribution to the atmospheric CO_2 reservoir is well known (i.e., the excess ^{14}C amount relative to ^{12}C), and this precisely defines its source function. In the case of anthropogenic ^{3}H, this is not the case, but a great advantage is that one can measure both the ^{3}H and tritugenic ^{3}He in a water sample and defines an 'age' of the water mass. These measurements are by no means easy, however, but a large database of information has been produced which has yielded very useful insights into large-scale ocean circulation in the upper ocean.

There are also two important nonnuclear transient tracers, chlorofluorocarbons CFC-11 and CFC-12, which have also proven very useful in view of their known (changing) relative concentrations in the atmosphere. These behave essentially as conservative tracers; any CFC losses would not be expected to change their ratio in the oceanic water mass. The use of new tracers (F113, CCl_4) has extended the timescales of CFC in both directions.

In practice, one has to work with tracers of different properties, and each of its properties can be taken advantage of, as its special attribute. Even nonconservative tracers, e.g., ^{14}C and ^{32}Si, have their own significance and merit. In fact, in the oceans the only conservative tracers of natural origin are ^{3}H (half-life 12.3 y) and ^{3}He (stable).

New Techniques for Measurements of Tracers in the Oceans in the 1980s and 1990s

By the end of the 1970s, the field of cosmogenic tracers had clearly recognized the usefulness of most of the cosmogenic tracers, with sufficient measurements at hand in each case. After isolated studies of a few tracers, e.g., ^{14}C, ^{10}Be, in individual water samples, it became apparent that oceans can yield their secrets only with multiple tracer attack. In early multiple tracer investigations, detailed information regarding the nature and rate of processes responsible for the formation of the Antarctic Bottom water was obtained by including the tracers ^{3}He and ^{14}C. The field was expanded in the 1980s and 1990s with larger-scale exploitation of several tracers for answering specific questions. This came about due to a fruitful combination of events and discoveries, which gave a tremendous fillip to both chemical oceanography and tracer studies including nuclides belonging to U-Th series. Foremost was the decision to study oceans in a systematic manner, along geochemical sections (GEOSECS), using a suite of tracers. GEOSECS expeditions were successfully carried out to the principal oceans in 1972–78 and resulted in fairly accurate tracer data. The GEOSECS concept was very successful; it rested on the necessity for making more precise measurements of several tracers and ocean properties in addition this integrated study resulted in information about temporal changes in the property profiles at the same stations after an elapse of one to two decades since the site was occupied in the GEOSECS expedition. And finally, it was an artful and timely combination of theory and experiment, which gave a tremendous boost to the field of learning about oceanographic processes.

The 1980s also marked an era of dramatic advance in the techniques of measurements of long-lived cosmogenic radionuclides ^{14}C, ^{10}Be, and ^{26}Al in the oceans, in sediments, and in manganese nodules using AMS (accelerator mass spectrometry). This opened up new windows for observing in detail a host of physical, chemical, and biological processes. The ease with which these nuclides can be measured allowed long series of measurements in space and time to be obtained. Examples of this development are the direct measurements of ^{10}Be and ^{26}Al concentration profiles in sea water in the principal oceans; and profiles of ^{10}Be concentrations in marine sediments and in manganese nodules which opened up a new field of investigation in marine beryllium geochemistry.

A new field, the study of P-biodynamics in surface waters using cosmogenic ^{32}P and ^{33}P surfaced in the late 1980s. This tracer application was not held up for want of a technique. In this case, it was not realized that these short-lived nuclides (half-lives, 14.3 and 25.3 days) in fact had about the appropriate half-lives for studying timescales of exchange of phosphorus between dissolved inorganic P, organic P and plankton. Concurrently, technical advances were also being made to measure short-lived radionuclides in ocean waters, where the AMS technique does not offer any gain in detection sensitivity, e.g. ^{32}P (half-life, 14.3 days), ^{33}P (half-life, 25.3 days) and ^{32}Si (half-life, 150 years). By using a standard liquid scintillation counting system to simultaneously measure both ^{32}P and ^{33}P activities, much higher sensitivity is attainable than by using low-level counters, especially for samples of low specific radioactivity.

Examples of Oceanic Data Derived Using Cosmogenic Tracers

With this foreground what has been learnt about the oceanic processes using cosmogenic tracers is now briefly examined. We are obviously interested in learning about cycles of principal nutrient elements, and processes by which the ocean chemistry evolves (as regulated by aeolian and fluvial fluxes from the land, biogeochemical cycles within the oceans, and large-scale oceanic circulation). This problem can be approached in bits and pieces only, and then the interconnections and feedbacks examined. A comprehensive mosaic of all the interactions and controls may or may not be achieved. The records of present day ocean biogeochemical processes are recorded in the sediments. It is therefore important to study the chronology and the makeup of ocean sediments to get a comprehensive picture of the temporal evolution of ocean chemistry and climate through aeons. The suite of tracers listed in **Table 3** has provided sufficient information on oceanic processes in four broad fields.

1. Biogeochemical cycling of nutrients and trace elements
2. Chronology of marine sediments and manganese nodules
3. Principal features of large-scale oceanic circulation
4. Biogeochemical and ocean circulation controls on climate.

In each of these studies, the task is complemented by the availability of radiotracers belonging to the U-Th series. It should be stressed that tracers each have some particular unique features for studying critical problems in oceanography. All tracers are not created equal: some are more equal than others. This social expression also finds a rightful place in the realm of oceans. This can be illustrated by citing unique features of two of the cosmogenic nuclides, ^{14}C (half-lifem, 5730 years) and ^{10}Be (half-life, 1.5 My), which have a special status among all natural tracers.

The great 'virtues' or attributes of ^{14}C are that (1) it is a carbon isotope, and is introduced in to the carbon cycle reservoirs as carbon dioxide in the earth's atmosphere, and (2) its half-life is well suited to study late Quaternary events and processes, including dating of sediments and timing of deep and bottom water formation.

In the oceans, ^{14}C does not behave as a conservative tracer, since carbon (and its compounds) is not distributed uniformly in the oceans. But this does not present any problems; rather its studies allow determination of carbon fluxes within the ocean. In fact, if ^{14}C was a conservative tracer, it could not have been used to date marine sediments. It has been added in significant amounts to the atmosphere as a result of nuclear weapons tests during the 1950s and 1960s. Consequently, ^{14}C can be used both as a 'steady-state' and as a 'transient' tracer.

The second most attractive ocean tracer is the cosmogenic ^{10}Be, which serves to delineate pathways of particle active elements through the water column, and is useful for dating sediments and in manganese nodules to about 10 My BP. The particle active nature of ^{10}Be leads to its preferential deposition in the coastal regions of the oceans. Recent studies have demonstrated that using special chemical techniques, the activity of cosmogenic ^{26}Al can be measured in the oceanic environment, and it has been suggested that it should be a useful tracer for studying changes in the past biological productivity of the oceans. This application arises from the higher chemical reactivity of ^{26}Al, compared to ^{10}Be. If this suggestion is borne out from future studies, ^{26}Al would constitute an invaluable tracer for studying temporal and spatial variations in biological productivity. Its studies would complement the information obtained using the cosmogenic ^{10}Be.

Recent measurements of cosmogenic ^{32}P (half-life, 14.3 days) and ^{33}P (half-life, 25.3 days) in surface ocean waters have opened up new possibilities of quantifying P-biodynamics with complementary information on eddy diffusivity in the waters, based on the cosmogenic ^{7}Be (**Table 3**). A wealth of new ^{32}P, ^{33}P data have been added on the distribution of cosmogenic ^{32}P and ^{33}P in the surface ocean waters, and in plankton.

Epilogue

A large number of cosmogenic tracers are available for oceanic studies, and the use of these tracers has steadily increased to date. But of course, tracers are not the complete answer to the mysteries of the ocean. It is necessary to learn how to use tracers, how to model them, how to combine them with other tracers, singly and multiply, etc. The usefulness and application of a tracer cannot be discussed on an absolute basis, because such an approach would result in a largely academic discussion. A tracer may have the appropriate physical and chemical attributes, but its source strength may be too weak, or its source function may not be known at the present time. Tracer suitability has therefore to be evaluated periodically as frontiers of knowledge expand. With the freedom in thinking about what type of tracer measurements can be made, a great deal of valuable information will probably be derived from it; however, one has to think about applying it within practical constraints. An important constraint is the number of measurements, which can be made within a reasonable period, and within available financial resources. Today, the principal constraint is the inadequacy of spatial and temporal coverage of the tracer data. With more synoptic data, tracer modeling could also be refined. Any shortcomings in these foil the goal of these studies. We are now in the mode of understanding details of ocean circulation and chemistry; not just the integrated overall features. In the earliest applications of cosmogenic tracers just a few measurements of radiocarbon in the oceans were sufficient to show that the upper ocean had a turnover time of about 600 years. In the case of the atmosphere, the mean time for removal of aerosols was similarly learned very quickly from the observed fallout of nuclear weapons tests-injected radioactivities (^{90}Sr, ^{3}H, etc.) and from the fallout of cosmogenic ^{22}Na, ^{7}Be and ^{32}P. With continued applications of these tracers, it has been shown that oceanic processes are indeed complex, especially at the interfaces (air–sea, mixed layer–intermediate waters–deep waters, and water–sediment), and in the polar oceans, which determine formation of bottom–deep waters. Thus, our hasty perception of these tracers being a panacea quickly changed, even back in the 1970s.

What is the basic nature of large-scale oceanic circulation? The radiochemists used the *Kw* model in its simple one-dimensional form; *K* denotes the eddy diffusivity, and *w* the advection velocity. At this time a stimulating discussion of essential mathematical approaches for treating the tracer data was presented. Simple material balance calculations by Lal showed that an appreciable amount of carbon was added to the dissolved carbon inventory (J-flux) at depths by sinking biogenic particles. This important aspect of resetting the ^{14}C clock in the deep sea by J-flux is now being examined on a global basis under WOCE experiments, and constitutes a critical parameter in climatic feedback processes. Subsequently, tracer data showed that an important transfer of oceanic properties occurred across pycnoclines. Modeling of tracer data in fact reveals model inadequacies and fosters development of more appropriate physical models. There are several very basic issues that are recognized, but not well understand. For example, what are the roles of tides and internal waves in large-scale ocean circulation? These questions have been asked several times, but not yet attacked properly due to our present limitations. Today, we are far from a synthesis of comprehensive models which are capable of providing an interactive atmosphere–ocean coupled model which can respond to changes in climate, or predict climatic changes as the model is run.

There are several academic and technical issues which we are confronting today:

1. complexity of the ocean system; variable response at different time and space scales;
2. lack of three-dimensional tracer data;
3. lack of information on temporal and spatial changes in tracer distribution;
4. lack of understanding of physical, chemical, and biological processes.

However, there are proven methods based on ^{14}C, ^{10}Be, ^{26}Al, ^{39}Ar, ^{32}Si, ^{7}Be, ^{33}P and ^{32}P. Improved tracer modeling will emerge only with further advances in techniques for their measurement, and with a better understanding of the atmospheric and oceanic circulation, mixing, and biogeochemical processes. On the question of ease of measurement, the radionuclide ^{39}Ar is an important case in point here. It is a conservative tracer, ideally suited for studying vertical mixing in the oceans, but to date very few measurements have been made, since they are very time consuming. Another example is that of ^{32}Si. Although it has been measured at several stations in the Atlantic, Pacific and Indian oceans, these measurements are not currently precise enough to make detailed mixing and transport models to define the silica cycle in the oceans. They are, however, useful to determine vertical J-fluxes, one-diemnsional K/ω ratios, and the latitudinal inventories of ^{32}Si in the oceans.

Physical oceanography provides the theoretical basis for oceanic mixing and circulation, but the experimental data necessary to understand the nature of this circulation must be based on present day and proxy observations of chemical composition of sea water in space and time. Directed global scale coordination between scientists to study important oceanic processes, such as physical and biological controls on biological production, and export of carbon, are rapidly providing new insights and accelerated developments of realistic models. An example is the coordinated US Joint Global Ocean Flux Studies (JGOFS) in the Equatorial Pacific Ocean in 1992, during a four-month period which coincided with the maximum intensity of the warm El Niño event, and another three-month period during well-developed cool surface-water conditions. The combined physical/chemical and biological data produced, which included ^{234}Th concentrations of sinking particulates, led to new insights about the roles of dissolved organic carbon, microzooplankton grazing, nutrient and CO_2 fluxes, and highlighted the importance of physical, in contrast to biological, processes in this region, where net carbon fluxes out of the system are very small as a result of highly efficient biological cycling.

This discussion would not be complete without mention of the 'purposeful tracer experiment' carried out as a component of WOCE, using SF_6 released in the open ocean. The results confirmed the earlier estimates of very low diapycnal diffusivity, of the order of $0.1\,\mathrm{cm^2\,s^{-1}}$, implying that heat, salt, and tracers must penetrate the thermocline primary by transport along, rather than across, density surfaces.

Clearly, understanding of the large-scale ocean circulation will come from multiple approaches, with directed research to simultaneously understand transfer and mixing of 'properties' and 'substances' and their relationship to climatic changes. It has taken five decades to develop techniques to make relevant oceanographic measurements, and one should expect rapid advances in our knowledge of oceanic processes as a result of innovative research, and international observational programs such as Tropical Oceans and the Global Atmosphere (TOGA) and WOCE.

It must be realized that a state must be reached where experiments and theory go hand in hand, leading to the development of better (more realistic) models, and acquisition of critical tracer data. In the absence of a knowledge of the processes involved, models employed often yield very erroneous results. Thus, whereas even a few tracer data are quite informative (since a few data points can be treated only with zero order models), any attempts to understand oceanic processes in detail pose a serious challenge. A few examples are considered here, where tracer data have contributed to the development of realistic models. As mentioned earlier, simple one-dimensional models were developed earlier on using two parameters K and w, to consider vertical transfer of tracers through an oceanic column. Even today these are used, in the absence of better alternatives, and in reality, because of a lack of tracer data in the three-dimensional space. The result is that as yet the general validity of the K-w models in space is not known or their dependence on climate. The latter arises because there are experimental tracer data for ocean waters only during the Holocene.

The recent significant developments in oceanic general circulation are a result of transient tracer experiments, and order of magnitude improvements in a number of fields, including orbit dynamics, gravity field estimation and atmospheric variability. High accuracy data on ocean surface elevation by satellite altimetry is leading to hopes of complete theee-dimensional time-evolving estimates of ocean circulation, which would also improve estimates of oceanic heat, and several property fluxes.

There has been prolific growth in the field of tracer oceanography within the last two decades, but there are acute limitations in providing a consistent picture of the interrelationships between physical, chemical, and biological processes, which are needed to develop a coupled atmosphere–ocean model that responds to climate in an interactive manner. It is not clear how this will be achieved in the near future.

Finally, it is gratifying to see that the cosmogenic radiotracer field has evolved highly from an academic curiosity in the 1950s and 1960s to its present-day form, wherein it aims to become an integral part of realistic atmosphere–ocean global atmosphere and ocean circulation models.

See also

Carbon Cycle. Carbon Dioxide (CO_2) Cycle. Phosphorus Cycle. Radiocarbon. Stable Carbon Isotope Variations in the Ocean.

Further Reading

Broecker WS (1981) Geochemical tracers and ocean circulation. In: Warren BA and Wunsch C (eds) *Evolution of Physical Oceanography*, pp. 434–460. Cambridge, MA: MIT Press.

Broecker WS and Peng TH (1982) *Tracers in the Sea*. New York: Lamont-Doherty Geological Observatory.

Jenkins WJ (1992) Tracer based inferences of new primary production in the sea. In: Falkowski PG and Woodhead AD (eds) *Primary Productivity and Biogeochemical Cycles in the Sea*. New York: Plenum Press.

Lal D (1962) Cosmic ray produced radionuclides in the sea. *J. Ocean. Soc.* Japan: 20th Anniv. Vol. 600–614.

Lal D and Peters B (1967) Cosmic ray produced radioactivity on the earth. *Handbuch der Physik* 46(2): 551–612.

Lal D (1999) An overview of five decades of studies of cosmic ray produced nuclides in the oceans. *Science of the Total Environment* 237/238: 3–13.

Ledwell JR, Watson AJ and Law CS (1993) Evidence for slow mixing across the pycnocline from an open ocean tracer-release experiment. *Nature* 364: 701–703.

Libby WF, Anderson EC and Arnold JR (1949) Age determination by radiocarbon content: world-wide assay of natural radiocarbon. *Science* 109: 227–228.

Measures CI and Edmond JM (1982) Beryllium in the water column of the Central Pacific. *Nature* 297: 51–53.

Murray JW, Barber RT, Roman MR, Bacon MP and Feely RA (1994) Physical and biological controls on carbon cycling in the equatorial Pacific. *Science* 266: 58–65.

Raisbeck GM and Yiou F (1999) ^{129}I in the oceans: origins and applications. *Science of the Total Environment* 237/238: 31–41.

Schlosser P and Smethie Jr WM (1995) Transient tracers as a tool to study variability of ocean circulation. In: *Natural Climate Variability on Decade-to-century Time Scales,* pp. 274–289. Washington: National Research Council.

COUPLED SEA ICE–OCEAN MODELS

A. Beckmann and G. Birnbaum, Alfred-Wegener-Institut für Polar und Meeresforschung, Bremerhaven, Germany

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Introduction

Oceans and marginal seas in high latitudes are seasonally or permanently covered by sea ice. The understanding of its growth, movement, and decay is of utmost importance scientifically and logistically, because it affects the physical conditions for air–sea interaction, the large-scale circulation of atmosphere and oceans and ultimately the global climate (e.g., the deep and bottom water formation) as well as human activities in these areas (e.g., ship traffic, offshore technology).

Coupled sea ice–ocean models have become valuable tools in the study of individual processes and the consequences of ice–ocean interaction on regional to global scales. The sea ice component predicts the temporal evolution of the ice cover, thus interactively providing the boundary conditions for the ocean circulation model which computes the resulting water mass distribution and circulation.

A number of important feedback processes between the components of the coupled system can be identified which need to be adequately represented (either resolved or parameterized) in coupled sea ice–ocean models (see **Figure 1**):

- ice growth through freezing of sea water, the related brine release and water mass modification;
- polynya maintenance by continuous oceanic upwelling;
- lead generation by lateral surface current shear and divergence;
- surface buoyancy loss causing oceanic convection; and
- pycnocline stabilization in melting regions.

Not all of these are equally important everywhere, and it is not surprising that numerous variants of coupled sea ice–ocean models exist, which differ in physical detail, parameterizational sophistication, and numerical formulation. Models for studies with higher resolution usually require a higher level of complexity.

The main regions for applying coupled sea ice–ocean models are the Arctic Ocean, the waters surrounding Antarctica, and marginal seas of the Northern Hemisphere (e.g., Baltic Sea, Hudson Bay). A universally applicable model needs to include (either explicitly or by adequate parameterization) the specific mechanisms of each region, e.g., mainly seasonal variations of the ice cover or the presence of thick, ridged multiyear ice.

This article describes the philosophy and design of large- and mesoscale prognostic dynamic–thermodynamic sea ice models which are coupled to primitive equation ocean circulation models (*see* **General Circulation Models**). The conservation principles, the most widely used parameterizations, several numerical and coupling aspects, and model evaluation issues are addressed.

Basics

Sea water and sea ice as geophysical media are quite different; whereas the liquid phase is continuous, three-dimensional, and largely incompressible, the solid phase can be best characterized as granular, two-dimensional and compressible. Both share a high degree of nonlinearity, and many direct feedbacks between oceanic and sea ice processes exist.

Today's coupled sea ice–ocean models are Eulerian; granular Lagrangian models, which consider the floe–floe interaction explicitly, exist but have so far not been fully coupled to ocean circulation models. Originally designed for use with large-scale coarse resolution ocean models, sea ice in state-of-the-art models is treated as a continuous medium. Following the continuum hypothesis only the average effect