

## Chapter 2

# An Overview of Isotope Geochemistry in Environmental Studies

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**Abstract** Isotopes of many elements have been used in terrestrial, atmospheric, and aqueous environmental studies, providing powerful tracers and rate monitors. Short-lived nuclides that can be used to measure time are continuously produced from nuclear reactions involving cosmic rays, both within the atmosphere and exposed surfaces, and from decay of long-lived isotopes. Nuclear activities have produced various isotopes that can be used as atmospheric and ocean circulation tracers. Production of radiogenic nuclides from decay of long-lived nuclides generates widespread distinctive isotopic compositions in rocks and soils that can be used to identify the sources of ores and trace water circulation patterns. Variations in isotope ratios are also generated as isotopes are fractionated between chemical species, and the extent of fractionation can be used to identify the specific chemical processes involved. A number of different techniques are used to separate and measure isotopes of interest depending upon the half-life of the isotopes, the ratios of the stable isotopes of the element, and the overall abundance of the isotopes available for analysis. Future progress in the field will follow developments in analytical instrumentation and in the creative exploitation of isotopic tools to new applications.

## 2.1 Introduction

Isotope geochemistry is a discipline central to environmental studies, providing dating methods, tracers, rate information, and fingerprints for chemical processes in almost every setting. There are 75 elements that have useful isotopes in this respect, and so there is a large array of isotopic methods potentially available. The field has grown dramatically as the technological means have been developed for measuring small variations in the abundance of specific isotopes, and the ratios of isotopes with increasing precision.

Most elements have several naturally occurring isotopes, as the number of neutrons that can form a stable or long-lived nucleus can vary, and the relative abundances of these isotopes can be very different. Every element also has isotopes that contain neutrons in a quantity that render them unstable. While most have exceedingly short half-lives and are only seen under artificial conditions (>80% of the 2,500 nuclides), there are many that are produced by naturally-occurring processes and have sufficiently long half-lives to be present in the environment in measurable quantities. Such production involves nuclear reactions, either the decay of parent isotopes, the interactions of stable nuclides with natural fluxes of subatomic particles in the environment, or the reactions occurring in nuclear reactors or nuclear detonations. The isotopes thus produced provide the basis for most methods for obtaining absolute ages and information on the rates of environmental processes. Their decay follows the well-known radioactive decay law (first-order kinetics), where the fraction of atoms,  $\lambda$  (the decay constant), that decay over a period of time is fixed and an intrinsic characteristic of the isotope:

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<div>H1Hydrogen</div>																	<div>He2Helium</div>						
<div>Li3Lithium</div>	<div>Be4Beryllium</div>																	<div>B5Boron</div>	<div>C6Carbon</div>	<div>N7Nitrogen</div>	<div>O8Oxygen</div>	<div>F9Fluorine</div>	<div>Ne10Neon</div>
<div>Na11Sodium</div>	<div>Mg12Magnesium</div>																	<div>Al13Aluminium</div>	<div>Si14Silicon</div>	<div>P15Phosphorus</div>	<div>S16Sulphur</div>	<div>Cl17Chlorine</div>	<div>Ar18Argon</div>
<div>K19Potassium</div>	<div>Ca20Calcium</div>	<div>Sc21Scandium</div>	<div>Ti22Titanium</div>	<div>V23Vanadium</div>	<div>Cr24Chromium</div>	<div>Mn25Manganese</div>	<div>Fe26Iron</div>	<div>Co27Cobalt</div>	<div>Ni28Nickel</div>	<div>Cu29Copper</div>	<div>Zn30Zinc</div>	<div>Ga31Gallium</div>	<div>Ge32Germanium</div>	<div>As33Arsenic</div>	<div>Se34Selenium</div>	<div>Br35Bromine</div>	<div>Kr36Krypton</div>						
<div>Rb37Rubidium</div>	<div>Sr38Strontium</div>	<div>Y39Yttrium</div>	<div>Zr40Zirconium</div>	<div>Nb41Niobium</div>	<div>Mo42Molybdenum</div>	<div>Tc43Technetium</div>	<div>Ru44Ruthenium</div>	<div>Rh45Rhodium</div>	<div>Pd46Palladium</div>	<div>Ag47Silver</div>	<div>Cd48Cadmium</div>	<div>In49Indium</div>	<div>Sn50Tin</div>	<div>Sb51Antimony</div>	<div>Te52Tellurium</div>	<div>I53Iodine</div>	<div>Xe54Xenon</div>						
<div>Cs55Cesium</div>	<div>Ba56Barium</div>	<div>La57Lanthanum</div>	<div>Hf72Hafnium</div>	<div>Ta73Tantalum</div>	<div>W74Tungsten</div>	<div>Re75Rhenium</div>	<div>Os76Osmium</div>	<div>Ir77Iridium</div>	<div>Pt78Platinum</div>	<div>Au79Gold</div>	<div>Hg80Mercury</div>	<div>Tl81Thallium</div>	<div>Pb82Lead</div>	<div>Bi83Bismuth</div>	<div>Po84Polonium</div>	<div>At85Astatine</div>	<div>Rn86Radon</div>						
<div>Fr87Francium</div>	<div>Ra88Radium</div>	<div>Ac89Actinium</div>																HALOGENS		NOBLE GASES			
ALKALI METALS		ALKALI EARTH METALS																					
LANTHANIDES				<div>La57Lanthanum</div>	<div>Ce58Cerium</div>	<div>Pr59Praseodymium</div>	<div>Nd60Neodymium</div>	<div>Pm61Promethium</div>	<div>Sm62Samarium</div>	<div>Eu63Europium</div>	<div>Gd64Gadolinium</div>	<div>Tb65Terbium</div>	<div>Dy66Dysprosium</div>	<div>Ho67Holmium</div>	<div>Er68Erbium</div>	<div>Tm69Thulium</div>	<div>Yb70Ytterbium</div>	<div>Lu71Lutetium</div>					
ACTINIDES				<div>Ac89Actinium</div>	<div>Th90Thorium</div>	<div>Pa91Protactinium</div>	<div>U92Uranium</div>	<div>Np93Neptunium</div>	<div>Pu94Plutonium</div>	<div>Am95Americium</div>	<div>Cm96Curium</div>												

**Fig. 2.2** The elements that have stable isotope variations useful for environmental studies. The shaded elements do not have more than one isotope that is stable and not radiogenic. While

all others potentially can display stable isotope variations, significant isotopic variations in the environment have been documented for the circled elements

per gram (ppm) and so are amenable to analysis. Further considerations of the abundances that can be measured are discussed below.

The following sections provide a general guide to the range of isotopes available, and the most widespread uses in the terrestrial environment. It is not meant to be exhaustive, as there are many innovative uses of isotopes, but rather indicative of the sorts of problems can be approached, and what isotopic tools are available for particular question. More details about the most commonly used methods, as well as the most innovative new applications, are reported elsewhere in this volume. Section 2.3 provides a brief survey of the analytical methods available.

## 2.2 Applications of Isotopes in the Environment

In the following sections, applications of isotopes to environmental problems are presented according to the different sources of radioactive isotopes and causes of variations in stable isotopes.

### 2.2.1 Atmospheric Short-Lived Nuclides

A range of isotopes is produced from reactions involving cosmic rays, largely protons, which bombard the

Earth from space. The interactions between these cosmic rays and atmospheric gases produce a suite of radionuclides with half-lives ranging from less than a second to more than a million years (see list in Lal and Baskaran 2011). There are a number of nuclides that have sufficiently long half-lives to then enter into environmental cycles in various ways (see Table 2.1). The best-known nuclide is  $^{14}\text{C}$ , which forms  $\text{CO}_2$  after its production and then is incorporated into organic matter or dissolves into the oceans. With a half-life of 5730a, it can be used to date material that incorporates this  $^{14}\text{CO}_2$ , from plant material, calcium carbonate (including corals), to circulating ocean waters. Information can also be obtained regarding rates of exchange between reservoirs with different  $^{14}\text{C}/^{12}\text{C}$  ratios, and biogeochemical cycling of C and associated elements. Other nuclides are removed from the atmosphere by scavenging onto aerosols and removed by precipitation, and can provide information on the rates of atmospheric removal. By entering into surface waters and sediments, these nuclides also serve as environmental tracers. For example, there are two isotopes produced of the particle-reactive element Be,  $^7\text{Be}$  ( $t_{1/2} = 53.3$  days) and  $^{10}\text{Be}$  (1.4Ma). The distribution of  $^7\text{Be}/^{10}\text{Be}$  ratios, combined with data on the spatial variations in the flux of Be isotopes to the Earth's surface, can be used to quantify processes such as stratospheric-tropospheric exchange of air masses, atmospheric circulation, and the removal rate

**Table 2.1** Atmospheric radionuclides

Isotope	Half-life	Common applications
$^3\text{H}$	12.32a	Dating of groundwater, mixing of water masses, diffusion rates
$^7\text{Be}$	53.3 day	Atmospheric scavenging, atmospheric circulation, vertical mixing of water, soil erosion studies
$^{10}\text{Be}$	$1.4 \times 10^6\text{a}$	Dating of sediments, growth rates of Mn nodules, soil erosion study, stratosphere-troposphere exchange, residence time of aerosols
$^{14}\text{C}$	5730a	Atmospheric circulation, dating of sediments, tracing of C cycling in reservoirs, dating groundwater
$^{32}\text{Si}$	140a	Atmospheric circulation, Si cycling in the ocean
$^{32}\text{P}$	25.3 day	Atmospheric circulation, tracing oceanic P pool
$^{33}\text{P}$	14.3 day	
$^{35}\text{S}$	87 day	Cycling of S in the atmosphere
$^{39}\text{Ar}$	268a	Atmospheric circulation and air-sea exchange
$^{81}\text{Kr}$	$2.3 \times 10^5\text{a}$	Dating of groundwater
$^{129}\text{I}$	$1.6 \times 10^7\text{a}$	Dating of groundwater
$^{210}\text{Pb}$	22.3a	Dating, deposition velocity of aerosols, sources of air masses, soil erosion, sediment focusing

Selected isotopes generated within the atmosphere that have been used for environmental studies, along with some common applications. All isotopes are produced by nuclear reactions in the atmosphere induced by cosmic radiation, with the exception of  $^{210}\text{Pb}$ , which is produced by decay of  $^{222}\text{Rn}$  released from the surface

of aerosols (see Lal and Baskaran 2011). The record of Be in ice cores and sediments on the continents can be used to determine past Be fluxes as well as to quantify sources of sediments, rates of sediment accumulation and mixing (see Du et al. 2011; Kaste and Baskaran 2011). Other isotopes, with different half-lives or different scavenging characteristics, provide complementary constraints on atmospheric and sedimentary processes (Table 2.1).

A number of isotopes are produced in the atmosphere from the decay of  $^{222}\text{Rn}$ , which is produced within rocks and soils from decay of  $^{226}\text{Ra}$ , and then released into the atmosphere. The daughter products of  $^{222}\text{Rn}$  (mainly  $^{210}\text{Pb}$  (22.3a) and  $^{210}\text{Po}$  (138 days)) that are produced in the atmosphere have been used as tracers to identify the sources of aerosols and their residence times in the atmosphere (Kim et al. 2011; Baskaran 2011). Furthermore,  $^{210}\text{Pb}$  adheres to particles that are delivered to the Earth's surface at a relatively constant rate and are deposited in sediments,

and its subsequent decay provides a widely used method for determining the age of sediments and so the rates of sedimentation.

A number of isotopes are incorporated into the hydrologic cycle and so provide means for dating groundwaters. This includes the noble gases  $^{39}\text{Ar}$  ( $t_{1/2} = 268\text{a}$ ),  $^{81}\text{Kr}$  (230ka) and  $^3\text{H}$  (Kulongoski and Hilton 2011) which dissolve into waters and then provide ideal tracers that do not interact with aquifer rocks and so travel conservatively with groundwater, but are present in such low concentrations that their measurement has proven to be difficult. The isotope  $^{129}\text{I}$  (16Ma) readily dissolves and also behaves conservatively: with such a long half-life, however, it is only useful for very old groundwater systems. The readily analyzed  $^{14}\text{C}$  also has been used for dating groundwater, but the  $^{14}\text{C}/^{12}\text{C}$  ratio changes not only because of decay of  $^{14}\text{C}$ , but also through a number of other processes such as interaction with C-bearing minerals such as calcium carbonate; therefore, more detailed modelling is required to obtain a reliable age.

General reviews on the use of isotopes produced in the atmosphere for determining soil erosion and sedimentation rates, and for providing constraints in hydrological studies, are provided by Lal (1991, 1999) and Phillips and Castro (2003).

## 2.2.2 Cosmogenic Nuclides in Solids

Cosmogenic nuclides are formed not just within the atmosphere, but also in solids at the Earth's surface, and so can be used to date materials based only upon exposure history, rather than reflecting the time of formation or of specific chemical interactions. The cosmic particles that have escaped interaction within the atmosphere penetrate into rocks for up to a few meters, and interact with a range of target elements to generate nuclear reactions through neutron capture, muon capture, and spallation (emission of various fragments). From the present concentration and the production rate, an age for the exposure of that surface to cosmic rays can be readily calculated (Lal 1991). A wide range of nuclides is produced, although only a few are produced in detectable amounts, are sufficiently long-lived, and are not naturally present in concentrations that overwhelm additions from cosmic ray interactions. An additional complexity in

obtaining ages from this method is that production rates must be well known, and considerable research has been devoted to their determination. These are dependent upon target characteristics, including the concentration of target isotopes, the depth of burial, and the angle of exposure, as well as factors affecting the intensity of the incident cosmic radiation, including altitude and geomagnetic latitude. Also, development

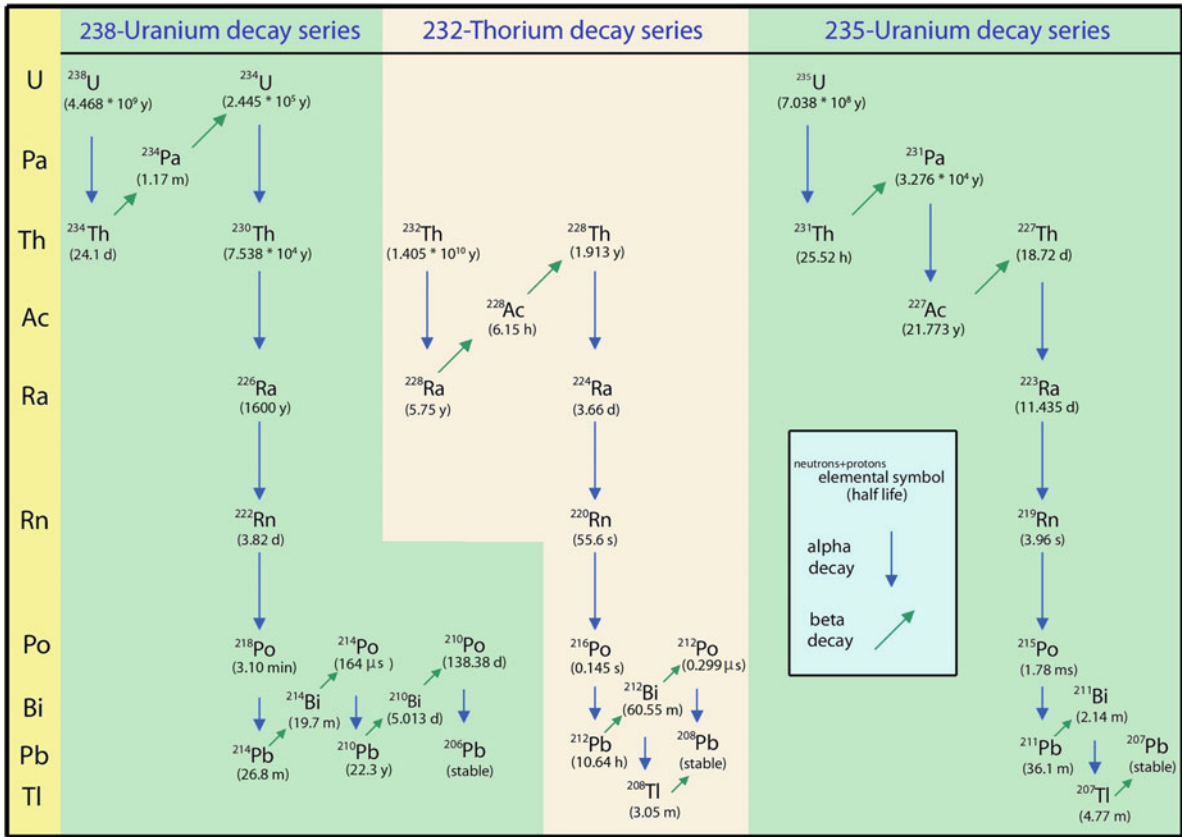
of these methods has been coupled to advances in analytical capabilities that have made it possible to measure the small number of atoms involved. It is the high resolution available from accelerator mass spectrometry (see Sect. 2.3.2) that has made it possible to do this in the presence of other isotopes of the same element that are present in quantities that are many orders of magnitude greater.

The most commonly used cosmogenic nuclides are listed in Table 2.2 (see also Fig. 2.3). These include several stable isotopes,  $^3\text{He}$  and  $^{21}\text{Ne}$ , which accumulate continuously within materials. In contrast, the radioactive isotopes  $^{10}\text{Be}$ ,  $^{14}\text{C}$ ,  $^{26}\text{Al}$ , and  $^{36}\text{Cl}$  will continue to increase until a steady state concentration is reached in which the constant production rate is matched by the decay rate (which is proportional to the concentration). While this state is approached asymptotically, in practice within  $\sim 5$  half-lives concentration changes are no longer resolvable. At this

**Table 2.2** Widely used cosmogenic nuclides in solids

Isotope	Primary targets	Half-life	Commonly dated materials
$^{10}\text{Be}$	O, Mg, Fe	1.4Ma	Quartz, olivine, magnetite
$^{26}\text{Al}$	Si, Al, Fe	705ka	Quartz, olivine
$^{36}\text{Cl}$	Ca, K, Cl	301ka	Quartz
$^3\text{He}$	O, Mg, Si, Ca, Fe, Al	Stable	Olivine, pyroxene
$^{21}\text{Ne}$	Mg, Na, Al, Fe, Si	Stable	Quartz, olivine, pyroxene

The most commonly used isotopes that are produced by interaction of cosmic rays the primary target elements listed



**Fig. 2.3** The  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$  decay series. The presence of the series of short-lived nuclides throughout the environment is due to their continuous production by long-lived parents

point, no further time information is gained; such samples can then be assigned only a minimum age.

There have been a considerable number of applications of these methods, which have proven invaluable to the understanding of recent surface events. There are a number of reviews available, including those by Niedermann (2002), which focuses on  $^3\text{He}$  and  $^{21}\text{Ne}$ , and Gosse and Phillips (2001). A full description of the methods and applications is given by Dunai (2010). Some of the obvious targets for obtaining simple exposure ages are lava flows, material exposed by landslides, and archaeological surfaces. Meteorite impacts have been dated by obtaining exposure ages of excavated material, and the timing of glacial retreats has been constrained by dating boulders in glacial moraines and glacial erratics. The ages of the oldest surfaces in dry environments where little erosion occurs have also been obtained. Movement on faults has been studied by measuring samples along fault scarps to obtain the rate at which the fault face was exposed.

Cosmogenic nuclides have also been used for understanding landscape evolution (see review by Cockburn and Summerfield 2004) and erosion rates (Lal 1991). In this case, the production rate with depth must be known and coupled with an erosion history, usually assumed to occur at a constant rate. The concentrations of samples at the surface (or any depth) are then the result of the production rate over the time that the sample has approached the surface due to erosion and was subjected to progressively increasing production. The calculations are somewhat involved, since production rates due to neutron capture, muon reactions, and spallation have different depth dependencies, and the use of several different cosmogenic nuclides can provide better constraints (Lal 2011). Overall, plausible rates have been obtained for erosion, which had hitherto been very difficult to constrain. The same principle has been applied to studies of regional rates of erosion by measuring  $^{10}\text{Be}$  in surface material that has been gathered in rivers (Schaller et al. 2001), and this has provided key data for regional landscape evolution studies (Willenbring and von Blanckenburg 2010).

### 2.2.3 Decay Series Nuclides

The very long-lived nuclides  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$  decay to sequences of short-lived nuclides that

eventually lead to stable Pb isotopes (see Fig. 2.3 and Table 2.3). The decay of these parents thus supports a continuous definable supply of short-lived nuclides in the environment that can be exploited for environmental studies, especially for determining ages and rates over a range of timescales from days to hundreds of thousands of years. The abundance of each isotope is controlled by that of its parent, and since this dependence continues up the chain, the connections between the isotopes can lead to considerable complexity in calculating the evolution of some daughters. However, since the isotopes represent a wide range of elements with very different geochemical behaviours, such connections also present a wealth of opportunities for short-term geochronology and

**Table 2.3** Decay series nuclides used in environmental studies

Isotope	Half-life	Common applications
$^{238}\text{U}$	$4.468 \times 10^9 \text{a}$	Dating, tracing sources of U
$^{234}\text{U}$	$2.445 \times 10^4 \text{a}$	Dating of carbonates, tracing sources of water
$^{232}\text{Th}$	$1.405 \times 10^{10} \text{a}$	Quantifying lithogenic component in aqueous system, atmosphere
$^{230}\text{Th}$	$7.538 \times 10^4 \text{a}$	Dating, scavenging, ventilation of water mass
$^{234}\text{Th}$	24.1 day	Particle cycling, POC export, rates of sediment mixing
$^{228}\text{Th}$	1.913a	Particle scavenging and tracer for other particulate pollutants
$^{227}\text{Th}$	18.72 day	Particle tracer
$^{231}\text{Pa}$	$3.276 \times 10^4 \text{a}$	Dating, sedimentation rates, scavenging
$^{228}\text{Ra}$	5.75a	Tracing water masses, vertical and horizontal mixing rates
$^{226}\text{Ra}$	1600a	Dating, water mass tracing, rates of mixing
$^{224}\text{Ra}$	3.66 day	Residence time of coastal waters, mixing of shallow waters
$^{223}\text{Ra}$	11.435 day	Residence time of coastal waters, mixing of shallow waters
$^{227}\text{Ac}$	21.773a	Dating, scavenging
$^{222}\text{Rn}$	3.82 day	Gas exchange, vertical and horizontal diffusion
$^{210}\text{Pb}$	22.3a	Dating (e.g. carbonates, sediments, ice cores, aerosols, artwork); sediment mixing, focusing and erosion; scavenging; resuspension
$^{210}\text{Po}$	138 day	Carbon export, remineralization, particle cycling in marine environment

Radioactive isotopes within the  $^{238}\text{U}$ ,  $^{235}\text{U}$ , and  $^{232}\text{Th}$  decay series that have been directly applied to environmental studies. The remaining isotopes within the decay series are generally too short-lived to provide useful environmental information and are simply present in activities equal to those of their parents



environmental rate studies (see several papers in Ivanovich and Harmon 1992; Baskaran 2011).

The abundance of a short-lived nuclide is conveniently reported as an activity ( $= N\lambda$ , i.e. the abundance times the decay constant), which is equal to the decay rate ( $dN/dt$ ). In any sample that has been undisturbed for a long period ( $>\sim 1.5$  Ma), the activities of all of the isotopes in each decay chain are equal to that of the long-lived parent element, in what is referred to as secular equilibrium. In this case, the ratios of the abundances of all the daughter isotopes are clearly defined, and the distribution of all the isotopes in a decay chain is controlled by the distribution of the long-lived parent. Unweathered bedrock provides an example where secular equilibrium could be expected to occur. However, the different isotopes can be separated by a number of processes. The different chemical properties of the elements can lead to different mobilities under different environmental conditions. Uranium is relatively soluble under oxidizing conditions, and so is readily transported in groundwaters and surface waters. Thorium, Pa and Pb are insoluble and highly reactive with surfaces of soil grains and aquifer rocks, and adsorb onto particles in the water column. Radium is also readily adsorbed in freshwaters, but not in highly saline waters where it is displaced by competing ions. Radon is a noble gas, and so is not surface-reactive and is the most mobile.

Isotopes in the decay series can also be separated from one another by the physical process of recoil. During alpha decay, a sufficient amount of energy is released to propel alpha particles a considerable distance, while the daughter isotope is recoiled in the opposite direction several hundred Angstroms (depending upon the decay energy and the matrix). When this recoil sends an atom across a material's surface, it leads to the release of the atom. This is the dominant process releasing short-lived nuclides into groundwater, as well as releasing Rn from source rocks. This mechanism therefore can separate short-lived daughter nuclides from the long-lived parent of the decay series. It can also separate the products of alpha decay from those of beta decay, which is not sufficiently energetic to result in substantial recoil. For example, waters typically have ( $^{234}\text{U}/^{238}\text{U}$ ) activity ratios that are greater than the secular equilibrium ratio of that found in crustal rocks, due to the preferential release of  $^{234}\text{U}$  by recoil.

A more detailed discussion of the equations describing the production and decay of the intermedi-

ate daughters of the decay series is included in Appendix 2. In general, where an intermediate isotope is isolated from its parent, it decays according to (2.2). Where the activity ratio of daughter to parent is shifted from the secular equilibrium value of 1, the ratio will evolve back to the same activity as its parent through either decay of the excess daughter, or grow-in of the daughter back to secular equilibrium (Baskaran 2011). These features form the basis for dating recently produced materials. In addition, U- and Th- series systematics can be used to understand dynamic processes, where the isotopes are continuously supplied and removed by physical or chemical processes as well as by decay (e.g. Vigier and Bourdon 2011).

The U-Th series radionuclides have a wide range of applications throughout the environmental sciences. Recent reviews cover those related to nuclides in the atmosphere (Church and Sarin 2008; Baskaran 2010; Hirose 2011), in weathering profiles and surface waters (Chabaux et al. 2003; Cochran and Masque 2003; Swarzenski et al. 2003), and in groundwater (Porcelli and Swarzenski 2003; Porcelli 2008). Recent materials that incorporate nuclides in ratios that do not reflect secular equilibrium (due either to discrimination during uptake or availability of the nuclides) can be dated, including biogenic and inorganic carbonates from marine and terrestrial environments that readily take up U and Ra but not Th or Pb, and sediments from marine and lacustrine systems that accumulate sinking sediments enriched in particle-reactive elements like Th and Pb (Baskaran 2011). The migration rates of U-Th-series radionuclides can be constrained where continuing fractionation between parent and daughter isotopes occurs. These rates can then be related to broader processes, such as physical and chemical erosion rates as well as water-rock interaction in groundwater systems, where soluble from insoluble nuclides are separated (Vigier and Bourdon 2011). Also, the effects of particles in the atmosphere and water column can be assessed from the removal rates of particle-reactive nuclides (Kim et al. 2011).

## 2.2.4 Anthropogenic Isotopes

Anthropogenic isotopes are generated through nuclear reactions created under the unusual circumstances of high energies and high atomic particle fluxes, either within nuclear reactors or during nuclear weapons

explosions. These are certainly of concern as contaminants in the environment, but also provide tools for environmental studies, often representing clear signals from defined sources. These include radionuclides not otherwise present in the environment that can therefore be clearly traced at low concentrations (e.g.  $^{137}\text{Cs}$ ,  $^{239,240}\text{Pu}$ ; Hong et al. 2011; Ketterer et al. 2011), as well as distinct pulses of otherwise naturally-occurring species (e.g.  $^{14}\text{C}$ ). There is a very wide range of isotopes that have been produced by such sources, but many of these are too short-lived or do not provide a sufficiently large signal over natural background concentrations to be of widespread use in environmental studies. Those that have found broader application are listed in Table 2.4.

The release of radioactive nuclides into the environment from reactors, as well as from nuclear waste reprocessing and storage facilities, can occur in a number of ways. Discharges through airborne effluents can widely disperse the isotopes over a large area and enter soils and the hydrological cycle through fallout, as observed for the Chernobyl release in 1986. Discharges of water effluents, including cooling and process waters, can be followed from these point sources in circulating waters, such as from the Sellafield nuclear processing and power plant, which released radionuclides (e.g.  $^{137}\text{Cs}$ ,  $^{134}\text{Cs}$ ,  $^{129}\text{I}$ ) from the western coast of England into the Irish Sea and

which can be traced high into the Arctic Ocean (discussed in Hong et al. 2011). Leaks into the ground from storage and processing facilities can also release radionuclides that are transported in groundwater, at locations such as the Hanford nuclear production facility in Washington State. At the Nevada Test Site, Pu was found to have migrated  $>1$  km, facilitated by transport on colloids. Releases by all of these mechanisms at lower levels have been documented around many reactor facilities. Even where levels are too low to pose a health concern, the isotopes can be readily measured and their sources identified. Transuranics are also utilized as tracers for investigating soil erosion, transport and deposition in the environment (Ketterer et al. 2011; Matisoff and Whiting 2011).

As discussed above, cosmic rays entering the atmosphere cause nuclear reactions that produce a number of radioisotopes. Atmospheric bomb testing, which peaked in the late 1950s and diminished dramatically after 1963, produced a spike in the production of some of these radionuclides (e.g.  $^{14}\text{C}$ ), and high atmospheric concentrations have persisted due to long atmospheric residence times or continuing fluxes from nuclear activities. These higher concentrations can then be used as markers to identify younger materials. The most widely used isotopes in this category are  $^3\text{H}$  and  $^{14}\text{C}$ . There are a number of others, including  $^{85}\text{Kr}$  (10.72a),  $^{129}\text{I}$  (15.7Ma), and  $^{36}\text{Cl}$  ( $3.0 \times 10^5\text{a}$ )

**Table 2.4** Anthropogenic isotopes most commonly used in environmental studies

Isotope	Half-life	Main sources	Examples of major uses	Notes
$^3\text{H}$	12.32a	Bomb testing	Tracing rainwater from time of bomb peak in ground waters and seawater	Background cosmogenic $^3\text{H}$
		Reactors	Ages determined using $^3\text{H}$ - $^3\text{He}$	
$^{14}\text{C}$	5730a	Bomb testing	Identifying organic and inorganic carbonate materials produced in last 60 years	Background cosmogenic $^{14}\text{C}$
$^{54}\text{Mn}$	312 day	Bomb testing	Trophic transfer in organisms	No background
$^{137}\text{Cs}$ , $^{134}\text{Cs}$	30.14a	bomb testing, reactors, reprocessing plants	Tracing seawater, soil erosion, sediment dating and mixing, sources of aerosols	No background
$^{90}\text{Sr}$	28.6a	Reactors, bomb testing	Tracing seawater, sources of dust	No background
$^{239}\text{Pu}$ , $^{240}\text{Pu}$	24100a 6560a	Reactors, bomb testing	Tracing seawater, identifying sources of Pu, sediment dating, soil erosion, tracing	No naturally-occurring Pu
$^{241}\text{Pu}$	14.4a		atmospheric dust	
$^{131}\text{I}$	8.02 day			
$^{129}\text{I}$	$1.57 \times 10^7\text{a}$	Bomb testing, reactors	Dating groundwater, water mass movements	Background cosmogenic $^{129}\text{I}$
$^{85}\text{Kr}$	10.72a	Bomb testing	Dating groundwater	
$^{36}\text{Cl}$	$3.0 \times 10^5\text{a}$	Bomb testing	Dating groundwater	Background cosmogenic $^{36}\text{Cl}$
$^{241}\text{Am}$	432.2a	Reactors	Tracing sources of Am	No naturally-occurring Am

The anthropogenic isotopes that can be used as point source tracers, or provide global markers of the time of formation of environmental materials



that have not been as widely applied, partly because they require difficult analyses. For a discussion of a number of applications, see Phillips and Castro (2003).

For the anthropogenic radionuclides that have half-lives that are long compared to the times since their release, time information can be derived from knowing the time of nuclide production, e.g. the present distribution of an isotope provides information on the rate of transport since production or discharge. An exception to this is  $^3\text{H}$ , which has a half-life of only 12.3 years and decays to the rare stable isotope  $^3\text{He}$ . By measuring both of these isotopes, time information can be obtained, e.g.  $^3\text{H}$ - $^3\text{He}$  ages for groundwaters, which measure the time since rainwater incorporating atmospheric  $^3\text{H}$  has entered the aquifer (Kulongoski and Hilton 2011).

### 2.2.5 Radiogenic Isotopes

There are a number of radioactive isotopes with half-lives that are useful for understanding geological time-scales, but do not change significantly over periods of interest in environmental studies. However, these isotopes have produced substantial variations in the isotopes of the elements that have daughter isotopes. The resulting isotopic signatures in rocks, sediments, and ores have been exploited in environmental studies. An example is the Rb-Sr system, which is the most commonly used. The long-term decay of  $^{87}\text{Rb}$  produces  $^{87}\text{Sr}$ , and so the abundance of this isotope, relative to a stable isotope of Sr such as  $^{86}\text{Sr}$ , varies according to the equation:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \left( \frac{^{87}\text{Sr}}{^{86}\text{Sr}} \right)_0 + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda_{87}t} - 1), \quad (2.4)$$

where the  $(^{87}\text{Sr}/^{86}\text{Sr})_0$  ratio is the initial isotope ratio and  $\lambda_{87}$  is the decay constant of  $^{87}\text{Rb}$ . Clearly, the present  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio is greater for samples that have greater ages,  $t$ , and samples with larger Rb/Sr ratios. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio therefore varies between different rock types and formations. Since Rb is an alkali metal and Sr is an alkaline earth, these elements behave differently in geological processes, creating large variations in Rb/Sr, and so large variations in  $^{87}\text{Sr}/^{86}\text{Sr}$ . The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio has been shown to vary widely in surface rocks, and so any Sr released into soils, rivers, and groundwaters has an isotopic signature that reflects

its source. Changes in local sources can also be identified; for example, Keller et al. (2010) identified thawing of permafrost from the changes in stream water  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio as tills with greater amounts of carbonate deeper in soil profiles were weathered. Strontium isotopes have been used as tracers for identifying populations of migratory birds and fish in streams and rivers (Kennedy et al. 1997; Chamberlain et al. 1997) as well as in archaeology (Slovak and Paytan 2011). Sr isotopes have also been used to trace agricultural products, which have incorporated Sr, along with Ca, from soils incorporating Sr isotope ratios of the underlying rocks. The sources and transport of dust across the globe have been traced using the isotopic compositions of Sr, Nd, and Pb (Grousset and Biscaye 2005). Variations in the Pb isotopic ratios between environmental samples (soil, aerosols, household paint, household dust, and water samples in house) and children's blood have been utilized to identify and quantify the sources of blood Pb in children (Gulson 2011).

Other isotope systems that can be used for similar purposes are listed in Table 2.5. In each case, chemical differences between the chemical behaviour of the parent and daughter isotopes have led to variations in their ratio over geological timescales, and so identifiable variations in the environment can be exploited for tracing. The most obvious differences are often regional, as reflected in the isotopic compositions in rivers, especially for Sr and Nd. More local studies can identify different rocks, or even separate minerals, involved in weathering or contributing to waters (Tripathy et al. 2011). Using this information, groundwater flow paths and the sources of inorganic constituents can be deduced.

### 2.2.6 Stable Isotopes

In addition to variations in isotope ratios produced by the production or decay of nuclides due to nuclear processes, there are variations in the distribution of other isotopes between different phases or chemical species. These are subtle, as isotopes of an element still behave in fundamentally the same way, but the slight variations in atomic mass result in differences in bonding and kinetics. This is due to differences in vibrational energies reflecting differences in the masses of atoms, since the vibrational frequency of a

**Table 2.5** Radiogenic isotopes commonly used in environmental studies

Decay scheme	Half-life	Isotope ratio	Comments
$^{87}\text{Rb} \rightarrow ^{87}\text{Sr}$	$4.88 \times 10^{10}\text{a}$	$^{87}\text{Sr}/^{86}\text{Sr}$	Bioarchaeology, erosion rates
$^{147}\text{Sm} \rightarrow ^{143}\text{Nd}$	$1.06 \times 10^{11}\text{a}$	$^{143}\text{Nd}/^{144}\text{Nd}$	Regional variations due to age, rates of weathering, source tracking of sediments
$^{238}\text{U} \rightarrow ^{206}\text{Pb}$	$4.468 \times 10^9\text{a}$	$^{206}\text{Pb}/^{204}\text{Pb}$	Distinguish sources of Pb ores and sources of Pb; tracing sources of Pb to human body
$^{235}\text{U} \rightarrow ^{207}\text{Pb}$	$7.038 \times 10^8\text{a}$	$^{207}\text{Pb}/^{204}\text{Pb}$	
$^{232}\text{Th} \rightarrow ^{208}\text{Pb}$	$1.405 \times 10^{10}\text{a}$	$^{208}\text{Pb}/^{204}\text{Pb}$	
$^{176}\text{Lu} \rightarrow ^{176}\text{Hf}$	$3.71 \times 10^{10}\text{a}$	$^{176}\text{Hf}/^{177}\text{Hf}$	Complements Nd/Sm
$^{187}\text{Re} \rightarrow ^{187}\text{Os}$	$4.6 \times 10^{10}\text{a}$	$^{187}\text{Os}/^{188}\text{Os}$	Organic-rich sources have distinctly high Re/Os
$^{238}\text{U}, ^{235}\text{U}, ^{232}\text{Th} \rightarrow ^4\text{He}$	As above	$^3\text{He}/^4\text{He}$	Dating by $^4\text{He}$ accumulation
$^{40}\text{K} \rightarrow ^{40}\text{Ar}$	$1.397 \times 10^9\text{a}$	$^{40}\text{Ar}/^{36}\text{Ar}$	Tracing deep sources of volatiles
			Dating

The isotopes that are produced by long-lived parents and so exhibit variations in geological materials that can be used as tracers in environmental studies

molecule is directly proportional to the forces that hold atoms together, such as electron arrangements, nuclear charges and the positions of the atoms in the molecule, and inversely proportional to the masses of the atoms. The result is stable isotope fractionation, which is generally considered only for isotopes that are neither radioactive nor radiogenic, since variations in these isotopes often cannot be readily separated from decay effects. While studies of such fractionations were originally confined to light elements (e.g. H, O, N, S), isotopic variations have now been found even in the heavy stable elements Tl (Rehkamper and Halliday 1999) and U (Stirling et al. 2007), and so across the entire periodic table.

The difference in the ratio of two isotopes of the same element in species or phases A ( $R_A$ ) and B ( $R_B$ ) can be described by a fractionation factor  $\alpha$

$$\alpha = \frac{R_A}{R_B}. \quad (2.5)$$

Fractionation between isotopes of the same element generally appear to be linear; e.g. the ratio of isotopes two mass units apart will be fractionated twice as much as the ratio of elements one mass unit apart (mass dependent fractionation). Since the changes in isotopic values are generally very small, values are typically given as parts per thousand (permil) deviations from a standard; e.g. for example, for O,

$$\delta^{18}\text{O}_{\text{sample}} = \frac{(^{18}\text{O}/^{16}\text{O})_{\text{sample}} - (^{18}\text{O}/^{16}\text{O})_{\text{standard}}}{(^{18}\text{O}/^{16}\text{O})_{\text{standard}}} \times 10^3. \quad (2.6)$$

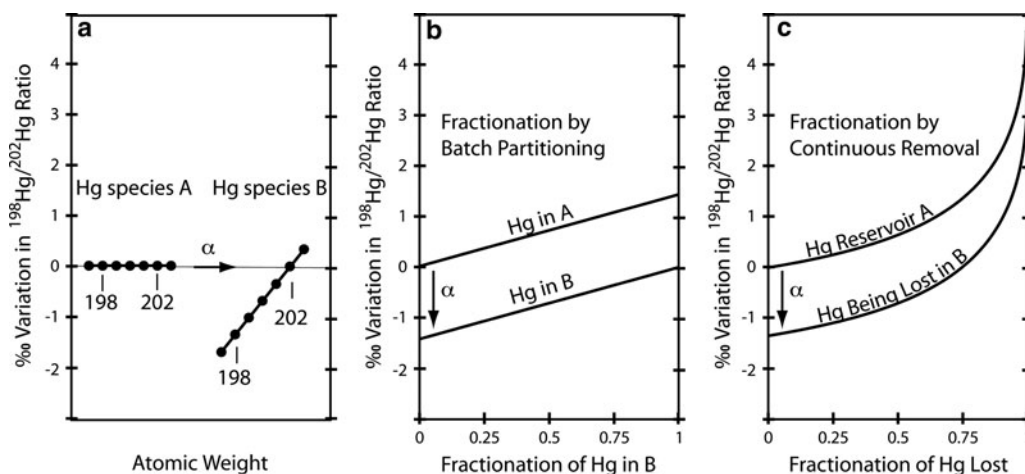
Therefore, results are reported relative to a standard. In some cases, however, several standards are in use, especially when analytical procedures are being developed, making comparisons between datasets difficult. In those cases where smaller variations can be measured precisely, values are given in parts per  $10^4$  (as  $\epsilon$  values). When the isotopic composition of two phases in equilibrium are measured, the difference between them can be related to the fractionation factor by

$$\delta^{18}\text{O}_A - \delta^{18}\text{O}_B \approx (\alpha - 1) \times 10^3. \quad (2.7)$$

Therefore, the fractionation factor between two phases can be obtained by measuring the difference in isotopic composition between phases in equilibrium.

Schauble (2004) provides a summary of the general patterns seen in equilibrium isotope fractionation. Fractionation effects are largest for low mass elements, and scale according to the difference in atomic masses of two isotopes relative to the average mass of the element squared, i.e.  $\Delta m/m^2$ . Heavy isotopes will favour species in which the element has the stiffest bonds. In environmental systems, this includes bonds of metals with the highest oxidation state, those with a bond partner with a high oxidation state, and bonds with anions with low atomic number (including organic ligands).

Fractionation can occur not only by equilibrium partitioning, but also due to kinetic processes. This includes transport phenomena such as diffusion, where lighter isotopes have higher velocities (inversely proportional to the square root of atomic/



**Fig. 2.4** An example of stable isotope fractionation. (a) When Hg is partitioned between two phases, isotopic fractionation can occur; the heavier isotopes are preferentially incorporated into phase B, so that  $\alpha(^{198}\text{Hg}/^{202}\text{Hg})_A = (^{198}\text{Hg}/^{202}\text{Hg})_B$ . Fractionation between all the isotopes is generally linear, i.e. the extent of fractionation between any two isotopes is proportional to the mass difference between them. (b) If there is equilibrium batch partitioning between A and B, then there is a difference of  $\alpha$

between both phases, and the specific composition of each depends upon mass balance; e.g. if there is very little of phases A, then the ratio of phase B is about equal to the bulk value, while phase A has a value that is  $\alpha$  times higher. (c) If there is continuous removal of phase B, so that only each increment being removed is in equilibrium with phase A, then this process of Rayleigh distillation will drive the isotopic composition of A to more extreme compositions than a batch process

molecular weight) that generate fractionation over diffusive gradients. This can also be due to reaction kinetics related to the strength of bonding, where lighter isotopes have bonds that can be broken more readily and so can be enriched in reactants. This can be seen in many biological processes, where uptake of elements can involve pathways involving multiple reactions and so considerable fractionation. It is important to note that it is not always possible to determine if equilibrium or kinetic fractionation is occurring; while laboratory experiments often endeavour to ensure equilibrium is reached, it is not always clear in the natural environment. Also, where kinetic fractionation is produced in a regular fashion, for example due to microbial reduction, it may not be easily distinguished from inorganic equilibrium fractionation processes

When the isotopes of an element are distributed between two separate phases or species in equilibrium, then the difference in isotope ratio is determined by (2.7). However, the absolute ratio of each is determined by mass balance according to the simple mixing equation

$$R_{\text{Total}} = R_A f_A + R_B (1 - f_A). \quad (2.8)$$

For example, as shown in Fig. 2.4, if an element is partitioned between two phases, and the mixture is almost entirely composed of phase A, then that phase will have the ratio close to that of the total mixture, while the ratio of phase B will be offset by the fractionation factor. If the mixture is almost entirely composed of phase B, it is the composition of phase A that will be offset from the bulk. Intermediate values of  $R$  for each phase will reflect the balance between the two phases according to (2.8). Such batch partitioning is more likely to apply where both forms are entirely open to chemical exchange, e.g. two different species in solution.

Often equilibrium is not maintained between a chemical species or phase and the source reservoir. In this case, the isotopic composition of the source evolves according to Rayleigh distillation, in which a small increment of a phase or species is formed in equilibrium with the source, but is immediately removed from further interaction, and so does not remain in equilibrium with the changing source. For example, crystals precipitating from solution are unlikely to continue reacting with the solution. If the source originally had an isotope ratio  $R_0$ , and the isotopes of an element of interest are fractionated with material being removed according to

a fractionation factor  $\alpha$ , then when in total a fraction  $f$  of the element has been removed, the integrated effect will be to generate a ratio  $R_A$  in the source according to the equation:

$$\frac{R_A}{R_0} = f^{(\alpha-1)}. \quad (2.9)$$

This is illustrated in Fig. 2.4; once a significant amount of an element has been removed, the ratio of the source has changed to a greater degree than by batch partitioning, and more extreme ratios can be obtained when  $f$  approaches 1 (most of the element has been removed). As long as the same fractionation factor affects each increment, (2.9) will describe the evolution of the solution, whether the fractionation is due to equilibrium or kinetic fractionation. Such evolution is likely to apply where solid phases are formed from solution, where water-rock interaction occurs, and where biological uptake occurs.

While fractionation between isotopes of an element is generally mass dependent, i.e. proportional to the mass difference between any two isotopes, there are a few circumstances where mass-independent fractionation is observed and a number of theories have been proposed to explain this phenomenon. Examples include O isotopes in stratospheric and tropospheric ozone (due to rotational energies of asymmetric molecules; Gao and Marcus 2001), S in Archean sediments (possibly from S photo-dissociated in the early atmosphere; Farquhar et al. 2000), and Hg isotopes involved in photochemical reactions in the environment (due to nuclear volume and magnetic isotope effects; see Blum 2011). These provide an added dimension for diagnosing the processes affecting these elements.

A wide range of applications has been explored for stable isotope fractionations. Oxygen isotopes vary in precipitation, and have been used as a hydrological tracer, while C, S, and N have been used to trace biogeochemical cycles (see e.g. reviews in Kendall and McDonnell 1998) and tracers of human diet (Chesson et al. 2011; Schwarcz and Schoeninger 2011). Isotopic variations in Li, Mg, and Sr have been related to adsorption and incorporation in clays, and so can be used to understand weathering and trace element migration (Burton and Vigier 2011; Reynolds 2011). Various metals with multiple redox states, including Fe, Cr, U, Mo, Ni, Cu, Zn, Cd, Hg, Se, and Tl, have isotopic variations that have been used to understand redox processes in present and past environments (see the

four papers by Bullen 2011; Johnson 2011; Nielsen and Rehkämper 2011; Rehkämper et al. 2011).

Stable isotopes can also be used in understanding environmental contamination. Chemical processing can generate isotopic differences in industrial products that provide a means for identifying sources. For example, C and Cl isotope differences have been found between different manufacturers of chlorinated solvents (van Warmerdam et al. 1995) and this can be used to trace contaminant migration. It has also been shown that degradation of these compounds can fractionate Cl isotopes, so that the extent of degradation can be determined (Sturchio et al. 1998, 2011). As another example, Cr isotopes are fractionated in groundwaters when Cr is reduced to a less soluble species, and so decreases in concentrations due to dilution can be distinguished from decreases due to precipitation (Ellis et al. 2002).

Other examples of documented isotope variations that have been used to understand environmental processes are listed in Table 2.6. Measurements are all made using mass spectrometry. Samples are corrected for instrumental fractionation using either comparison with standards in gas-source mass spectrometry and ICPMS, or using a double spike and TIMS and ICPMS (see below).

## 2.3 Measurement Techniques

There are two fundamental approaches to measuring the abundance of isotopes. Radioactive isotopes can be measured by quantifying the radiation resulting from decay, and then relating the decay rate to the abundance using (2.1). A number of these counting methods are widely used, especially for short-lived nuclides. Alternatively, atoms of any isotope can be directly measured by mass spectrometry, which separates ions according to mass followed by direct counting. These methods typically involve greater investment in instrumentation, but can often detect more subtle variations. The techniques are discussed further in the following sections.

### 2.3.1 Counting Methods

There are a number of techniques available for the detection of alpha, beta, and gamma radiation that

**Table 2.6** Commonly used stable isotopes

Element	Typical reported ratio	Examples of applications
H	$^2\text{H}/^1\text{H}$ (D/H)	Tracing both production and origin of food, groundwater sources
Li	$^6\text{Li}/^7\text{Li}$	Weathering processes, adsorption of Li in aquifers
B	$^{10}\text{B}/^9\text{B}$	
C	$^{13}\text{C}/^{12}\text{C}$	Tracing both production and origin of food, paleodiet reconstruction, hydrocarbon exploration, environmental forensics
N	$^{15}\text{N}/^{14}\text{N}$	N cycling, tracing both production and origin of food
O	$^{18}\text{O}/^{16}\text{O}$	Tracing both production and origin of food, sulphate and nitrate cycle in the atmosphere and aqueous system, oxidation pathways of compounds, paleoclimate (air temperature, humidity and amounts of precipitation), sources of groundwater
Mg	$^{26}\text{Mg}/^{24}\text{Mg}$	Lithological studies, adsorption of Mg in aquifers
Si	$^{30}\text{Si}/^{28}\text{Si}$	Global Si cycle, weathering rates, biogeochemical cycling of Si
S	$^{34}\text{S}/^{32}\text{S}$	Sulfur cycling in the atmosphere, sources of S in the environment
Cl	$^{37}\text{Cl}/^{35}\text{Cl}$	Forensics, source tracking of organochlorine and inorganic chlorate, fractionation in deep brines
Ca	$^{44}\text{Ca}/^{40}\text{Ca}$	Vertebrate paleodiet tracer, biogeochemical pathways of Ca
Cr	$^{53}\text{Cr}/^{52}\text{Cr}$	Source tracking of Cr contamination, Cr reduction
Fe	$^{56}\text{Fe}/^{54}\text{Fe}$	Fe redox cycling, Fe incorporation in aquifers
Ni	$^{60}\text{Ni}/^{58}\text{Ni}$	Sources and transport of Ni; methanogenesis
Cu	$^{65}\text{Cu}/^{63}\text{Cu}$	Sources and transport of Cu; partitioning of Cu between ligand-bound dissolved and particulate phases
Zn	$^{66}\text{Zn}/^{64}\text{Zn}$	Transport of Zn along cell walls of xylem; micronutrient transport in plants; pathways of anthropogenic Zn
Se	$^{80}\text{Se}/^{76}\text{Se}$	Redox reactions
Sr	$^{88}\text{Sr}/^{86}\text{Sr}$	Sr adsorption in aquifers

(continued)

**Table 2.6** (continued)

Element	Typical reported ratio	Examples of applications
Mo	$^{97}\text{Mo}/^{94}\text{Mo}$	Sources, transport of Mo, paleo-redox changes in aqueous system
Cd	$^{114}\text{Cd}/^{110}\text{Cd}$ , $^{112}\text{Cd}/^{110}\text{Cd}$	Paleo-ocenography, reconstruction of past nutrient levels in seawater
Os	$^{187}\text{Os}/^{188}\text{Os}$	Tracking anthropogenic and weathering sources of Os
Mo	$^{97}\text{Mo}/^{95}\text{Mo}$	Redox reactions
Hg	$^{202}\text{Hg}/^{198}\text{Hg}$ , $^{199}\text{Hg}/^{198}\text{Hg}$ , $^{201}\text{Hg}/^{198}\text{Hg}$	Forensics, sources tracking, reaction pathways of Hg using both mass-dependent and mass-independent fractionation
Tl	$^{205}\text{Tl}/^{203}\text{Tl}$	Paleoinput of Fe and Mn, hydrothermal fluid flux
Pb	$^{206}\text{Pb}/^{204}\text{Pb}$ , $^{207}\text{Pb}/^{204}\text{Pb}$ , $^{208}\text{Pb}/^{204}\text{Pb}$	Source identification of Pb in metals, tracing pathways of Pb to human system, tracing dust
Po	$^{210}\text{Po}$	POC export, remineralization of particles, biogenic particle cycling
U	$^{238}\text{U}/^{235}\text{U}$	Depleted/enriched uranium identification, redox

can be applied depending upon the mode and energy of decay, as well as the emission spectrum that is produced. In some circumstances, an isotope will decay to another short-lived isotope that can be more readily measured and then related to the abundance of the parent (e.g.  $^{210}\text{Pb}$  using  $^{210}\text{Po}$  measured by alpha spectrometry or  $^{226}\text{Ra}$  using  $^{214}\text{Pb}$  or  $^{214}\text{Bi}$  measured by gamma spectrometry).

Following is a brief description of the different analytical methods available. For many isotopes, there are several measurement options, and the best method is determined by the type of sample, the abundance of the isotope of interest, and the precision required. A more extensive review is given by Hou and Roos (2008).

### 2.3.1.1 Alpha Spectrometry

Isotopes that are subject to alpha decay can be measured by detecting and counting the emitted alpha particles. Contributions from the decay of other

isotopes can be distinguished by alpha particle energy, although there is overlap between alpha energies emitted by some of the nuclides. However, practical difficulties arise due to the interaction of alpha particles with atoms of other species that are loaded in the source along with the sample. This can cause a spread in particle energies and so reduce the energy resolution of the alpha spectrum, making the data often unusable. Therefore, good chemical separation and purification from other elements is critical, and the isotope of interest must be then deposited as a thin layer to minimize adsorption by the element of interest itself (self-shielding). This is done by electroplating onto metal discs or by sorbing onto thin  $\text{MnO}_2$  layers. Accurate determination of the concentration of these isotopes requires careful control of chemical yields during processing as well as of counter efficiency. A detailed review of the chemical procedures adopted for measuring alpha-emitting radionuclides in the U-Th-series is given in Lally (1992).

A number of detectors have been utilized for alpha measurements that include ionization chambers, proportional counters, scintillation detectors (plastic and liquid), and semiconductor detectors. Of these, the semiconductors (in particular, surface barrier and ion-implanted silicon detectors) have been the most widely used detectors due to their superior energy resolution and relatively high counting efficiency (typically 30% for a  $450\text{-mm}^2$  surface-barrier detector). More detailed comparison of the various types of detector material is given in Hou and Roos (2008).

The very low background of alpha detectors (0.8–2 counts for a particular isotope per day), relatively high efficiency ( $\sim 30\%$  for  $450\text{ mm}^2$  surface area detectors) and very good energy resolution (about 17–20 keV for 5.1 MeV) lead to detection limits of 0.010–0.025 mBq (where Bq, a Becquerel, is a decay per second); this can be related to an abundance using (2.1), so that, e.g. for a  $1 \times 10^5$  year half-life radionuclide this corresponds to as little as 0.08 femtomoles. While the long preparation times associated with chemical separation, purification, electroplating and counting impose a practical constraint on sample throughput, the relatively low-cost of alpha spectrometers and their maintenance is an advantage.

### 2.3.1.2 Beta Spectrometry

For isotopes that are subject to beta decay, abundances can be measured by detecting and counting the beta particles (electrons) that are emitted. The most common detector is a Geiger-Müller (GM) counter, which employs a gas-filled tube where atoms are ionized by each intercepted beta particle, and this is converted into an electrical pulse. Background signals from cosmic rays are reduced through shielding and anti-coincidence counters, which subtract counts that correspond to detections of high-energy particles entering the counting chamber.

Although adsorption by surrounding atoms is not as efficient as for alpha particles, it is still significant, and so samples are often deposited as thin sources onto a metal disc to increase counting efficiencies. Also, filters that contain particles collected from air and water samples can be measured directly. Dissolved species of particle-reactive elements (e.g. Th) can be concentrated from large water volumes by scavenging onto precipitated Fe or Mn oxides that are then collected onto filters. These filters can be analyzed directly (Rutgers van der Loeff and Moore 1999).

It should be noted that GM counters do not distinguish between beta particles by energy, and so cannot separate contributions from different isotopes through the energy spectrum. While isotopes can often be isolated by chemical separation, some elements have several isotopes and some isotopes have short-lived beta-emitting daughter isotopes that are continuously produced. In these cases, multiple counting can be done to identify and quantify different isotopes based upon their different half-lives. Also, selective absorbers of various thicknesses between the source and counter can be used to suppress interference from isotopes that produce lower energy beta particles.

The counting efficiency of a GM counter varies depending on the thickness of the source and on counter properties. One of the commonly used GM counters, the Risø Counter (Risø National Laboratory, Roskilde, Denmark), has a typical efficiency of  $\sim 40\%$  for most commonly occurring beta-emitting radionuclides. A typical background of this anti-coincidence counter, with 10 cm of lead shielding, is 0.15–0.20 counts per minute, corresponding to  $\sim 0.8$  mBq. This can be compared to the detection limit for an alpha-emitting radionuclide; the background of a new



alpha detector is 0.03–0.09 counts per hour, which corresponds to 0.03–0.08 mBq (at ~30% counting efficiency). Thus, the detection limit in alpha spectrometry is more than an order of magnitude higher than that of beta spectrometry.

The GM counter is not suitable for analyzing isotopes such as  $^3\text{H}$  and  $^{14}\text{C}$  that emit low-energy (~200 keV) electrons, which are adsorbed in the detector window. For these nuclides, a liquid scintillation counter (LSC) is used, in which a sample is dissolved in a solvent solution containing compounds that convert energy received from each beta particle into light, and the resulting pulses are counted. This method has minimal self-adsorption and relatively easy sample preparation, and can be used for all beta-emitters. However, background count rates are substantially higher than in GM counters.

### 2.3.1.3 Gamma Spectrometry

Alpha and beta-emitting radionuclides often decay to atoms in excited energy states, which then reach the ground state by emitting gamma radiation at discrete characteristic energies. Gamma rays can be detected when they ionize target atoms, so that the resulting charge can be measured. Gamma rays can penetrate a considerable distance in solid material, so that isotopes of interest do not need to be separated from sample material before counting, unless preconcentration from large volumes is required. Therefore, the method has the advantage of being non-destructive and easy to use.

A number of detectors have been used for the detection and quantification of gamma rays emitted from radionuclides of interest. Lithium-doped Ge (Ge(Li)) and Si (Si(Li)) semiconductor detectors have been widely used due to their high-energy resolution. For example, using large-volume Ge crystals with relatively high efficiencies, absolute efficiencies of ~70% have been achieved in Ge-well detectors for small samples (1–2 mL volume) at energies of 46.5 keV ( $^{210}\text{Pb}$ ) and 63 keV ( $^{234}\text{Th}$ ). This efficiency decreases to about 24–30% for 10 mL geometries due to the wider solid angle between the counting vial and Ge-crystal (Jweda 2007). However, the counting efficiency of gamma spectrometry with planar or co-axial detectors is generally quite low (<10%), and is dependent upon detector geometry and gamma energy. An advantage of the gamma counting method is that

energy spectra are obtained, so that a number of gamma-emitting radionuclides can be measured simultaneously. The typical energy resolution for the Ge-well detector is high, ~1.3 keV at 46 keV and ~2.2 keV at 1.33 MeV.

The backgrounds in gamma-ray detectors are high compared to alpha and beta detectors, mainly due to cosmic-ray muons and Earth's natural radioactivity. Graded shields (of Cu, Cd, Perspex, etc) have considerably reduced the background mainly arising from environmental radioactivity surrounding the detector, and anti-coincidence techniques have helped to cut down background from muons. Ultra-low background cryostats have also helped to reduce the overall background of the gamma-ray detector. Nonetheless, the detection limit is typically several orders of magnitude higher than for beta and alpha counting.

### 2.3.2 Mass Spectrometry

For measuring stable isotopes, or as an alternative to counting decays of atoms, it is possible to count the atoms directly. This requires a separation of atoms and this can be achieved by utilizing the fact that the path of charged particles travelling through a magnetic field is diverted along a radius of curvature  $r$  that is dependent upon mass and energy:

$$r = \left( \frac{2V}{e H^2} \right)^{1/2} (m/z)^{1/2}, \quad (2.10)$$

where  $V$  is accelerating potential,  $z$  is charge of the ion,  $e$  is the magnitude of electronic charge, and  $H$  is the intensity of the magnetic field. The accelerated ions will traverse a semi-circular path of radius  $r$  while within the magnetic field. When all ions of an element have the same charge and subject to the same magnetic field, they are accelerated to the same velocity, so that the path radii are only a function of mass. Ions will therefore exit the magnetic field sorted in beams according to mass. This property therefore dictates the basic features of a mass spectrometer: a source where the element of interest is ionized to the same degree and the atoms are accelerated with as little spread in energy as possible; a magnet with a field that is homogeneous throughout the ion paths; detectors located where each beam can be collected separately; and a flight tube that

maintains a vacuum along the ion paths, reducing energy-scattering collisions. These methods generally require separation of the element of interest from other constituents that may produce isobaric interferences (either as separate ions or as molecular species) or interfere with the generation of ions. More sophisticated instruments are equipped with further filters, including energy filters that discriminate between ions based on their energy and so separate ions that otherwise interfere due to scattering.

Mass spectrometers can provide high sensitivity measurements of element concentrations as well. While comparisons with standards to calibrate the instrument are needed, these measurements can be limited by variations between sample and standard analysis. In this case, higher precisions can be obtained using isotope dilution, in which a spike that has the relative abundance of at least one isotope artificially enhanced is mixed with the sample once the sample is dissolved. The resulting isotope composition reflects the ratio of spike to sample, and if the amount of spike that is added is known, then the amount of sample can be calculated with high precision directly from measurement of the isotope composition. A further advantage of this approach is that this isotope composition is not affected by losses during chemical separation or analysis. Spikes can also be used to correct for isotope fractionation that occurs within the instrument. In this case, a double spike, which is enriched in two isotopes, is added. The measured ratio of these two isotopes can then be used to calculate the instrument fractionation, and this correction can be applied to the ratios of other measured stable isotopes to obtain corrected sample values.

There are many designs of magnet geometries, as well as electric fields, in order to improve focusing and resolution. However, for isotope geochemistry there are a number of basic, widely used approaches, as discussed below and in the review articles by Goldstein and Stirling (2003) and Albarede and Beard (2004).

### **2.3.2.1 Thermal Ionization Mass Spectrometry (TIMS)**

In this design, samples are manually loaded onto metal filaments installed within the source. Under vacuum, the

metal is resistance-heated, and atoms are evaporated. Some atoms are ionized, and are then accelerated down the flight tube and into the magnetic field. The proportion of atoms that are ionized can be very low depending upon the element, but can be enhanced using various techniques, including the use of different filament metals, loading the sample in a mixture that raises the evaporation temperature, and using a second filament held at much higher temperature to ionize atoms vaporized from the evaporation filament. While TIMS can produce ion beams with a narrow range of energies and generate high precision data, it is time-consuming and the proportion of vaporizing atoms that ionize can be low for elements with high ionization potentials. However, it is the analytical tool of choice for high precision data for some elements. Due to signal variability between samples, concentration data must be obtained using isotope dilution. Also, variable isotope fractionation during analysis is usually corrected for by assuming that the ratio of stable, nonradiogenic isotopes is equal to a standard value and so that there is no natural isotope fractionation. Therefore, detection of natural stable isotope fractionation in the samples requires the use of a double spike.

### **2.3.2.2 Inductively-Coupled Plasma Source Mass Spectrometry (ICP-MS)**

In ICP-MS, samples in solution are introduced into an Ar plasma where ions are efficiently ionized. An ion extraction system then transfers ions from the high-pressure plasma source to the vacuum system of the mass analyzer. However, ions exit the source with a much greater energy spread than in TIMS sources, and precise measurements require additional correction of ion beams. The most recent generation of instruments, with electrostatic fields and additional magnets to focus beams, and techniques such as collision cells to decrease interferences, have achieved high sensitivity and high precision data. These instruments have been found to be versatile and have been used for a wide range of elements. Isotopic fractionation within the instrument can be quite consistent and so corrected for by alternating analyses of samples with those of standards. Corrections can also be made using other elements within the sample with similar masses, which exhibit comparable fractionations. Therefore, it is this

method that has been used to document stable isotope variations in many elements. Also, sample throughput is considerably greater than for the TIMS method. Methods for high spatial resolution analyses are advancing using laser ablation for in situ sampling, which is coupled to an ICPMS for on-line analysis. For further information, see Albarede and Beard (2004).

### 2.3.2.3 Gas Source Mass Spectrometry

Volatile elements, including H, O, S, and the noble gases, are measured using a mass spectrometer that has a gas source, where samples are introduced as a gas phase and are then ionized by bombardment of electrons emitted from a heated metal filament. Fractionation of the sample during introduction, ionization, and analysis is corrected for by monitoring a standard, which is introduced and analyzed under identical conditions and run between samples.

### 2.3.2.4 Accelerator Mass Spectrometry (AMS)

There are a number of isotopes that have such low concentrations that they are difficult to measure precisely by mass spectrometry. C has a  $^{14}\text{C}/^{12}\text{C}$  ratio of  $<1 \times 10^{12}$ , and measurement precision is limited by isobaric interferences. The problem is similar for other cosmogenic nuclides such as  $^{10}\text{Be}$ ,  $^{26}\text{Al}$ ,  $^{36}\text{Cl}$ , and  $^{129}\text{I}$ . The development of accelerator mass spectrometry has made it possible to precisely measure as few as  $10^4$  atoms of  $^{14}\text{C}$ , and so has extended the time scale of high precision  $^{14}\text{C}$  age dating on substantially smaller samples than by counting methods, as well as making it possible to obtain accurate measurements on the longer-lived cosmogenic nuclides. In accelerator mass spectrometry, negative ions are accelerated to extremely high energies using a tandem accelerator and then passed through a stripper of low pressure gas or a foil, where several electrons are stripped off to produce highly charged positive ions and where molecules are dissociated, thereby eliminating molecular interferences. Subsequent mass discrimination involves the use of an analyzing magnet, with further separation of interfering ions made possible using an electrostatic analyzer (which separates ions by kinetic energy per charge) and a velocity filter. Detection is made by counters that allow determination of the rate

of energy loss of the ion, which is dependent upon the element, and so allows further separation of interfering ions. There are a number of AMS facilities worldwide, and each is generally optimally configured for a particular set of isotopes. A more extended review is provided by Muzikar et al. (2003).

### Comparison Between Alpha Spectrometry and Mass Spectrometry

Techniques for decay counting as well as for mass spectrometry have been continuously evolving over more than 60 years, with progressively improving precision and sensitivity. For measuring radioactive isotopes, both approaches can be used, although often to different levels of precision. For measuring the abundance of any radioactive isotope, the precision possible by mass spectrometry can be compared to that achievable by decay counting. Considering only the uncertainty, or relative standard deviation, due to counting (Poisson) statistics, then for a total number of atoms  $N$  of a nuclide with a decay constant of  $\lambda$  that are counted by a mass spectrometer with an ionization efficiency of  $\eta_i$  and where there is a fraction  $F$  of ions counted, the uncertainty is

$$P_{\text{ms}} = (N F \eta_i)^{-1/2}. \quad (2.11)$$

A reasonable value for  $F$  is 20%; the ionization can differ by orders of magnitude between elements. Alternatively, if the decay rate of these atoms is measured in a counting system of counting efficiency  $\eta_c$  and over a time  $t$ , then

$$P_c = (N \lambda t \eta_c)^{-1/2}. \quad (2.12)$$

A reasonable maximum value for  $t$  is 5 days, and a typical counting efficiency for alpha counting is 30%. The precision for counting is better as the decay constant increases, and so as the half-life decreases. For an ionization efficiency during mass spectrometry of  $\eta_c = 1 \times 10^{-3}$ , counting is equally precise for nuclides with  $\lambda = 0.02 \text{ year}^{-1}$  ( $t_{1/2} = 30$  years). Nuclides with longer half-lives would be more precisely measured by mass spectrometry. While the values of the other parameters may vary, and precisions are often somewhat worse due to factors other than counting statistics, in general isotopes with half-lives of less than  $\sim 10^2$  years are more effectively

measured by decay counting methods (Chen et al. 1992; Baskaran et al. 2009).

## 2.4 The Future of Isotope Geochemistry in the Environmental Sciences

Isotope geochemistry has become an essential tool for the environmental sciences, providing clearly defined tracers of sources, quantitative information on mixing, identification of physical and chemical processes, and information on the rates of environmental processes. Clearly, this tool will continue to be important in all aspects of the field, including studies of contamination, resource management, climate change, biogeochemistry, exploration geochemistry, archaeology, and ecology. In addition to further utilization of established methods, new applications will continue to be developed. These will likely include discovering new isotope and trace element characteristics of materials, and defining isotope variations that are diagnostic of different processes. One particular area of great potential is in understanding the role of microbial activity in geochemical cycles and transport.

There will certainly be further development of new isotope systems as isotopic variations in elements other than those now widely studied are discovered. Advances in instrumentation and analytical techniques will continue to improve precision and sensitivity, so that it will be possible to identify and interpret more subtle variations. Methods for greater spatial resolution will also improve with better sample preparation and probe techniques, so that time-dependent variations could be resolved in sequentially-deposited precipitate layers and biological growth bands in corals and plants. New applications will follow the development of new methods for extraction of target elements, greater understanding of controls on particular isotopes, and certainly new ideas for isotope tracers. Isotope variations of new elements, in particular stable isotope variations, will be explored, further widening the scope of isotope geochemistry.

Overall, it is inevitable that there will be increasing integration of isotopic tools in environmental studies.

## Appendix 1: Decay Energies of Decay Series Isotopes

**Table 2.7** Commonly measured isotopes of the  $^{238}\text{U}$  decay series data taken from Firestone and Shirley (1999)

Isotope	Half-life	Decay	Emission energy (MeV) <sup>a</sup>	Yield (%)
$^{238}\text{U}$	$4.468 \times 10^9 \text{ a}$	$\alpha$	4.198 ( $\alpha_0$ ) 4.151 ( $\alpha_1$ ) 4.038 ( $\alpha_2$ )	77 23 0.23
$^{234}\text{Th}$	24.1 day	$\beta^-$ $\beta^-$ $\gamma$	0.199 0.104 0.093	70.3 19 5.58
$^{234}\text{Pa}$	1.17 m	$\gamma$ $\beta^-$ $\beta^-$	0.063 2.290 1.500	4.85 98.2 1.8
$^{234}\text{U}$	$2.445 \times 10^5 \text{ a}$	$\alpha$	4.775 ( $\alpha_0$ ) 4.722 ( $\alpha_1$ ) $\gamma$	72.5 27.5 10.4
$^{230}\text{Th}$	$7.538 \times 10^4 \text{ a}$	$\alpha$	4.687 ( $\alpha_0$ ) 4.621 ( $\alpha_1$ )	76.3 23.4
$^{226}\text{Ra}$	$1.6 \times 10^3 \text{ a}$	$\alpha$	4.784 ( $\alpha_0$ ) 4.601 ( $\alpha_1$ ) $\gamma$	94.55 5.45 3.51
$^{222}\text{Rn}$	3.82 day	$\alpha$	5.489 ( $\alpha_0$ )	~100
$^{218}\text{Po}$	3.10 min	$\alpha$	6.002 ( $\alpha_0$ )	~100
$^{214}\text{Pb}$	26.8 min	$\beta^-$ $\gamma$ $\gamma$ $\gamma$	1.023 ( $\beta_0$ ) 0.3519 0.2952 0.2420	~100 35.9 18.5 7.5
$^{214}\text{Bi}$	19.7 min	$\alpha$ $\beta^-$ $\gamma$ $\gamma$	5.621 ( $\alpha_0$ ) 3.272 ~100 1.120	0.021 ~100 0.609 15.0
$^{214}\text{Po}$	164 $\mu\text{s}$	$\alpha$	7.687 ( $\alpha_0$ )	15.9
$^{210}\text{Pb}$	22.3 year	$\beta^-$ $\gamma$	0.0635 ( $\beta_0$ ) 0.0465	~100 16 4.25
$^{210}\text{Bi}$	5.013 day	$\beta^-$	1.163 ( $\beta_0$ )	100
$^{210}\text{Po}$	138.38 day	$\alpha$	5.304 ( $\alpha_0$ )	100
	Stable	—	—	—
$^{206}\text{Pb}$	138.38 day	$\alpha$	5.304 ( $\alpha_0$ )	100

<sup>a</sup>Energies of beta decay are maxima

**Table 2.8** Commonly measured isotopes of the  $^{235}\text{U}$  decay series data taken from Firestone and Shirley (1999)

Isotope	Half-life	Decay	Emission energy (MeV) <sup>a</sup>	Yield (%)
$^{235}\text{U}$	$7.038 \times 10^8 \text{ a}$	$\alpha$ $\gamma$ $\gamma$	4.215–4.4596 0.1857 0.1438	93.4 57.3 10.96

(continued)

**Table 2.8** (continued)

Isotope	Half-life	Decay	Emission energy (MeV) <sup>a</sup>	Yield (%)
<sup>231</sup> Th	25.52 h	$\beta^-$	0.3895	100
		$\gamma$	0.0256	14.5
		$\gamma$	0.0842	6.6
<sup>231</sup> Pa	$3.276 \times 10^4$ a	$\alpha$	4.934–5.059	86.5
		$\alpha$	4.681–4.853	12.3
		$\gamma$	0.0274	10.3
		$\gamma$	0.300–0.303	4.7
<sup>227</sup> Ac	21.773a	$\alpha$ (1.38%)	4.941–4.953	87.3
		$\beta$ (98.62%)	0.0449	~100
<sup>227</sup> Th	18.72 day	$\alpha$	5.960–6.038	50.6
			5.701–5.757	37.2
		$\gamma$	0.236	12.3
			0.256	7.0
<sup>223</sup> Ra	11.435 day	$\alpha$	5.539–5.747	96.8
		$\gamma$	0.2695	13.7
<sup>219</sup> Rn	3.96 s	$\alpha$	6.819 ( $\alpha_0$ )	79.4
			6.553 ( $\alpha_1$ )	12.9
			6.425 ( $\alpha_2$ )	7.6
<sup>215</sup> Po	1.78 ms	$\alpha$	7.386 ( $\alpha_0$ )	100
<sup>211</sup> Pb	36.1 min	$\beta^-$	1.373	100
<sup>211</sup> Bi	2.14 min	$\alpha$ (99.72%)	6.623	83.8
			6.278	16.2
		$\beta^-$ (0.28%)	0.579	100
		$\gamma$	0.351	13.0
<sup>207</sup> Tl	4.77 min	$\beta^-$	1.423	100
<sup>207</sup> Pb	Stable	–	–	–

<sup>a</sup>Energies of beta decay are maxima**Table 2.9** Commonly measured isotopes of the <sup>232</sup>Th decay series data taken from Firestone and Shirley (1999)

Isotope	Half-life	Decay	Emission energy (MeV) <sup>a</sup>	Yield (%)
<sup>232</sup> Th	$1.405 \times 10^{10}$ a	$\alpha$	4.013	77.9
			3.954	22.1
<sup>228</sup> Ra	5.75a	$\beta^-$	0.046	100
<sup>228</sup> Ac	6.15 h	$\beta^-$	2.127	100
		$\gamma$	0.9112	26.6
			0.9690	16.2
			0.3383	11.3
<sup>228</sup> Th	1.913a	$\alpha$	5.423	71.1
			5.340	28.2
<sup>224</sup> Ra	3.66 day	$\alpha$	5.685 ( $\alpha_0$ )	94.9
			5.449 ( $\alpha_1$ )	5.1
		$\gamma$	0.2410	3.97
<sup>220</sup> Rn	55.6 s	$\alpha$	6.288 ( $\alpha_0$ )	99.89
			5.747 ( $\alpha_1$ )	0.11
<sup>216</sup> Po	0.145 s	$\alpha$	6.778 ( $\alpha_0$ )	~100
<sup>212</sup> Pb	10.64 h	$\beta^-$	0.574	100
		$\gamma$	0.2386	43.3
			0.3001	3.28

(continued)

**Table 2.9** (continued)

Isotope	Half-life	Decay	Emission energy (MeV) <sup>a</sup>	Yield (%)
<sup>212</sup> Bi	60.55	$\alpha$ (35.94%)	6.051	69.9
			6.090	27.1
		$\beta^-$	2.254	100
		$\gamma$		
<sup>212</sup> Po	0.299 $\mu$ s	$\alpha$	8.784 ( $\alpha_0$ )	100
<sup>208</sup> Tl	3.05 min	$\beta^-$	1.372	100
		$\gamma$	0.405	3
			0.832	2.8
<sup>207</sup> Pb	Stable	–	–	–

<sup>a</sup>Energies of beta decay are maxima

## Appendix 2: Decay Series Systematics

Within a decay series, the evolution of the abundance of a daughter radioactive isotope is dependent upon its decay rate as well as production from its radioactive parent. Since the abundance of the parent is in turn dependent upon that of its parent, and so on up the decay chain, the systematics can become complicated, although for most applications simplifying circumstances can be found. The evolution of the abundances of isotopes within a decay series is described by the Bateman equations (see Bourdon et al. 2003 for derivations). For a decay series starting from the long-lived parent  $N_1$  and ending with a stable isotope  $S$ ,

$$N_1 \rightarrow N_2 \rightarrow N_3 \rightarrow N_4 \rightarrow \dots S. \quad (2.13)$$

The long-lived parent evolves according to the basic decay equation:

$$(N_1) = (N_1)_0 e^{-\lambda_1 t}. \quad (2.14)$$

$(N_1)$  is the activity, so that

$$(N_1) = \frac{dN_1}{dt} = -\lambda_1 N_1. \quad (2.15)$$

The next two nuclides in the decay series evolves according to the equations

$$(N_2) = \frac{\lambda_2}{\lambda_2 - \lambda_1} (N_1)_0 (e^{-\lambda_1 t} - e^{-\lambda_2 t}) + (N_2)_0 e^{-\lambda_2 t} \quad (2.16)$$

$$\begin{aligned}
 (N_3) = & \frac{(N_1)_0 \lambda_2 \lambda_3}{\lambda_2 - \lambda_1} \left( \frac{e^{-\lambda_1 t}}{(\lambda_2 - \lambda_1)(\lambda_3 - \lambda_1)} \right. \\
 & + \frac{e^{-\lambda_2 t}}{(\lambda_1 - \lambda_2)(\lambda_3 - \lambda_2)} + \left. \frac{e^{-\lambda_3 t}}{(\lambda_1 - \lambda_3)(\lambda_2 - \lambda_3)} \right) \\
 & + \frac{(N_2)_0 \lambda_3}{(\lambda_3 - \lambda_2)} (e^{-\lambda_2 t} - e^{-\lambda_3 t}) + (N_3)_0 e^{-\lambda_3 t}.
 \end{aligned}
 \quad (2.17)$$

The equations become increasingly complex, but are rarely necessary for environmental applications. Further, these equations can be greatly simplified under most circumstances.

- For all environmental timescales, the abundance of the long-lived parent ( $N_1$ ) of the chain is constant, and  $e^{-\lambda_1 t} \approx 1$ . Further,  $\lambda_2 - \lambda_1 \approx \lambda_2$  and  $\lambda_3 - \lambda_1 \approx \lambda_3$ .
- When a system has been closed for a long time, i.e. when  $e^{-\lambda_2 t} \approx e^{-\lambda_3 t} \approx 0$ , the above equations reduce to  $(N_1 \lambda_1) = (N_2 \lambda_2) = (N_3 \lambda_3)$ , so that all the nuclides have the same activity as their parents, i.e. are in secular equilibrium, and the entire chain has the same activity as that of the long-lived parent. This is the state within very long-lived materials, such as unweathered rocks, and is the state all systems evolve towards when nuclides are redistributed.
- The activity of the daughter evolves towards secular equilibrium with its parent according to its half-life (and *not* that of the half life of its parent). This could be grow-in, where the daughter starts with a lower activity, or decay when the daughter starts with a higher activity; in either case it is the difference in the activities that declines at a rate determined by the half-life of the daughter. Therefore, the half-life of the daughter dictates the time-scale for which it is useful.

The linking of all the isotopes in the chain can lead to considerable complexity, since the parent concentration of each nuclide is changing, and so potentially the concentrations of the entire chain must be considered. However, for most applications, this can be greatly simplified by the following considerations:

- When a nuclide is isolated from its parent, then it becomes the head of the decay chain and simply decays away according to the decay equation (2.1); that is, it becomes the top of the chain. An example

is  $^{210}\text{Pb}$ , which is generated in the atmosphere from  $^{222}\text{Rn}$  and then transferred to sediments in fallout, where its activity simply diminishes according to (2.14) with a 22.3a half-life.

- Where the time scale of interest is short compared to the half-life of an isotope, the abundance of that isotope can be considered to be constant. In this case, this nuclide can be considered the head of the decay chain, and the influence of all nuclides higher in the decay series, can be ignored. For example, over periods of several 1,000 years,  $^{230}\text{Th}$  ( $t_{1/2} = 75\text{ka}$ ) remains essentially constant, while  $^{226}\text{Ra}$  ( $t_{1/2} = 1.6\text{ka}$ ) will grow into secular equilibrium according to (2.16).
- Where the time scale of interest is long compared to the half-life of an isotope, the activity of that isotope can be considered to be equal to that of the parent. For example, in a closed mineral, the  $^{222}\text{Rn}$  activity will be equal to that of parent  $^{226}\text{Ra}$  after several weeks, and so while the activity of  $^{210}\text{Pb}$  will grow-in towards that of its parent  $^{222}\text{Rn}$ , this can be represented by measurements of  $^{226}\text{Ra}$ . Therefore, shorter-lived intermediate isotopes can be ignored.
- The most common circumstance when (2.17) is required is dating materials that have incorporated U from waters. Since the ( $^{234}\text{U}/^{238}\text{U}$ ) ratio of waters is often above that of secular equilibrium, obtaining an age from the grow-in of  $^{230}\text{Th}$  requires considering the chain  $^{238}\text{U} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th} \rightarrow \dots$

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