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Abstract

Shell effects on nuclear stability have created an island of relative stability for nuclides near $A = 230\text{--}240$ and $Z = 90\text{--}92$. Three nuclides, ^{232}Th , ^{238}U , and ^{235}U , have half-lives long enough for significant amounts to have survived since the heavy elements in the Earth's crust were created. When one of these nuclides decays, it starts a journey that ends with an isotope of lead ($Z = 82$, $A \approx 208$). The predominant steps in this journey are α and β decays, so that each of the long-lived parents heads a distinct chain. Each chain, as well as a fourth one that is extinct, is described.

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13. Natural Radioactive Decay Chains

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Abstract

Shell effects on nuclear stability have created an island of relative stability for nuclides near $A = 230\text{--}240$ and $Z = 90\text{--}92$. Three nuclides, ^{232}Th , ^{238}U , and ^{235}U , have half-lives long enough for significant amounts to have survived since the heavy elements in the Earth's crust were created. When one of these nuclides decays, it starts a journey that ends with an isotope of lead ($Z = 82$, $A \approx 208$). The predominant steps in

this journey are α and β decays, so that each of the long-lived parents heads a distinct chain. Each chain, as well as a fourth one that is extinct, is described.

13.1 Introduction

Radioactivity was discovered (1896) from observations of radioactivity occurring in natural radioactive chains. There are other instances of natural radioactivity, such as ^{14}C , ^{40}K , and ^{187}Re , but none of these nuclides leads to a radioactive product and therefore starts a chain. Note that many radionuclides occur in chains, e.g., $^{100}\text{Sn} \rightarrow 6 \text{ EC}/\beta^+ \rightarrow ^{100}\text{Ru}$, but early members of the chains have short half-lives and disappear before the chain is completed. The distinguishing characteristic of the natural chains is that they begin with a radionuclide with a long enough half-life that some of it has survived since the Earth was formed and leads to intermediate components with short – sometimes very short – half lives.

Details of the natural radioactive decay series are particularly important for several radioactive dating methods (Chap. 17 of this Volume). These methods depend on differences in chemical properties of chain components in a geological environment and on growth-and-decay among the components. See Chap. 7 in Vol. 1.

There is considerable variety in the modes of decay of heavy elements; if spontaneous fission is considered a mode of radioactive decay, then there are many chains that meet this criterion of long-to-short. However, this chapter does not include fission except as a mechanism of terminating a chain. The natural radioactive chains are represented in Figs. 13.1 – 13.4. The relative intensities of various decay modes given in those figures do not show the full precision of current information. See the appendix “Table of Nuclides” by R. B. Firestone for current values.

					^{238}U 2.3×10^7 years	
					100 4494 4445	
		RdTh	^{228}Th 1.91 years		^{232}Th 1.4×10^{10} years	
		MsTh ₂	100 5423 5340	^{228}Ac 6.1 h	100 4013 3950	
		ThX	^{224}Ra 3.64 days		^{228}Ra 5.76 years	MsTh ₁
			100 5686 5449			
		Tn	^{220}Rn 56 s			
			100 6288			
ThC'	^{212}Po 0.3 μs		^{216}Po 0.15 s	ThA		
ThC	100 8784	^{212}Bi 61min	100 6779			β
	^{208}Pb	35.9 6051	^{212}Pb 10.6 h	ThB		α
ThC''		^{208}Tl 3.1 min				

Fig. 13.1

The $4n$ (^{232}Th) chain. The “rules of the game” are shown by the arrows in the lower right corner. See text for more details

					^{234}U 0.24 My		^{238}U 4470 My
					100 4776 4715	1.17 min 0.16% IT $^{234\text{m}}\text{Pa}^*$ 6.7 h	100 4196 4147
					^{230}Th 7.5×10^4 years		^{234}Th 24.1 days
					100 4688 4621		
					^{226}Ra 1599 years		
					100 4784 4602		
			^{218}Rn 35 ms		^{222}Rn 3.8 days		
			100 7133	^{218}At 1.5 s	100 5490		
	^{210}Po 138 days		^{214}Po 164 μs	99.9 6694	^{218}Po 3.1 min		
	100 5304	^{214}Bi 5.0 days	100 7687	^{214}Bi 20 min	99.98 5490		
	^{206}Pb	1.3×10^{-4} 4648	^{210}Pb 22 years	100 5450 5513	^{214}Pb 26 min		
		^{206}Tl 4.2 min	1.9×10^{-6} 3720	^{210}Tl 1.3 min			
			^{206}Hg 8.15 min				

Fig. 13.2

The $4n + 2$ (^{238}U) chain. *Note that the decay of ^{234}Th leads to 1.17 min $^{234\text{m}}\text{Pa}$, most of which decays directly to ^{234}U . In 0.16% of the cases, 6.7 h ^{234}Pa is formed by IT

						²³⁷ Np 2.14 My	
					²³³ U 0.159 My	100 4788 4771	²³⁷ U 6.75 days
					100 4824 4783	²³³ Pa 27.0 days	
					²²⁹ Th 7340 years		²³³ Th 22.3 min
				²²⁵ Ac 10.0 days	100 4845 4901		
				100 5829 5793	²²⁵ Ra 14.9 days		
				²²¹ Fr 4.8 min			
				100 6341 6127			
				²¹⁷ At 32 ms			
			²¹³ Po 4 μs	100 7067			
		²⁰⁹ Bi 2×10^{19}	100 8375	²¹³ Bi 45.6 min			
			²⁰⁹ Pb 3.25 h	2.09 5870 5550			
		²⁰⁵ Tl		²⁰⁹ Tl 2.2 min			

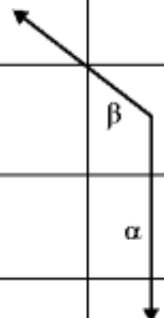


Fig. 13.4

The $4n + 1$ (²³⁷Np) chain

The dominant steps in the chains are α and β decays, which either decrease the mass number by 4 (α decay) or leave it unchanged (β decay). Therefore, there are four chains (including one which is extinct on Earth) corresponding to mass numbers $A = 4n$ (²³²Th and descendants) through $A = 4n + 3$ (²³⁵U and descendants), where n is an integer. In the figures, rows correspond to elements, with atomic number increasing from the bottom to the top. Columns have constant $N - Z$; they contain nuclides that are related by α decay. For a given chain only half of the cells in such a row-and-column array are members of the given chain. (The other half corresponds to a chain differing by 2 mass numbers.) The components are in shaded boxes, and the chains progress two steps down (α decay) or one step up and to the left (β decay). The long-lived parent and the stable end-product have a deeper shade. For α decay of a particular nuclide, the percentage of decays that use that mode is given below it, followed (in italics) by the energies (in keV) of the most intense α groups. If there is no competing β decay, the α percentage is 100. If both α and β decay occur, the fraction of β decay is the complement of the α fraction. For example, in Fig. 13.1 ²¹²Bi α decays 35.9% of the time, so 64.1% of the time β decays.

Many individual components in the series are referred to by names derived from their positions in the series and other details that are no longer of much interest except to reveal the history of discovery of

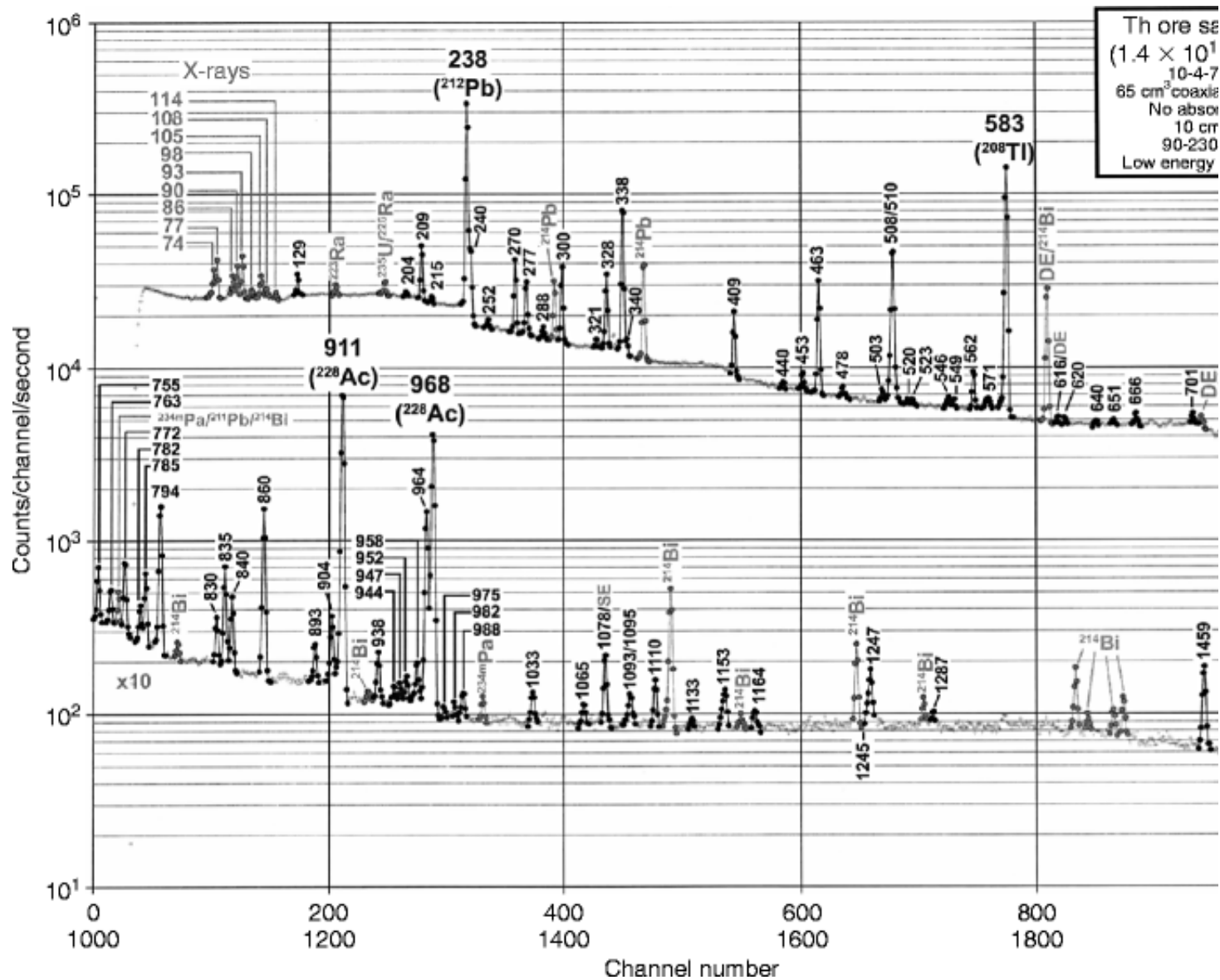
structure of each series. The most common names of this type for the ^{232}Th series are given in Fig. 13.1 . Since ^{228}Ra and ^{228}Ac are sandwiched between two isotopes of thorium, they were called mesothorium 1 and 2 (meso: intermediate or in the middle), with symbols MsTh_1 and MsTh_2 . ^{228}Th has higher specific activity (activity per unit mass) than ^{232}Th and was called radiothorium (RdTh). Tn (^{220}Rn) is short for thoron, the gaseous component similar to radon from radium. Relatively simple chemical procedures could show that there were three species following Tn , and these were named ThA (^{216}Po), ThB (^{212}Pb), and ThC (^{212}Bi). Later it was determined that ^{212}Po (ThC') and ^{208}Tl (ThC'') are also involved. Each of the chains could be extended (with many branches) to shorter-lived precursors. Although these precursors are not properly considered members of the natural chains, several of them are included in the diagrams to show likely production paths of the chains in the nuclear fuel cycle. For example, neutron capture in ^{232}Th produces short-lived ^{233}Th , which decays to ^{233}Pa and then to ^{233}U (see Fig. 13.4), which can be used as reactor fuel.

13.1.1 4n Chain

The chain is defined in Fig. 13.1 . Because α decay changes mass number by 4, the overall loss of 24 mass numbers between ^{232}Th and ^{208}Pb requires six α 's. But six α 's would change atomic number by 12, and the overall change is only 8; there must be a net of four β decays (β decays less electron captures), each increasing atomic number by 1 without changing mass number. In fact there are no electron capture decays in any of the chains – for reasons related to general trends in nuclear stability – and there are exactly four β decays in this chain.

The parent of the 4n series, 1.405×10^{10} year ^{232}Th , is the longest-lived nuclide in the Th–U region. It is comparable to the age of the universe, so more than half of all of the ^{232}Th ever produced (and not consumed by nuclear reactions) is still present. Because of the long half-life, ^{232}Th has unusually low specific activity (rate of decay per unit mass). Little easily absorbed radiation, such as α particles and low-energy electrons and photons, escapes the necessarily thick samples of moderate activity.

The last steps in the chain are unusual; ^{212}Po has a remarkably short half-life (and high decay energy), and ^{208}Tl emits a high energy γ ray (2,615 keV). This γ ray is a distinctive feature of background spectra of most γ ray spectrometers (See Fig. 13.7).



13.2 Island of Stability

The general trend in stability of various combinations of protons and neutrons can be understood in terms of the Weizsäcker formula, which is given as Eq. (2.3) in “Basic Properties of the Atomic Nucleus” (Chap. 2 of Vol. 1). The first two terms of this semiempirical formula are related to the volume and surface of a nucleus; together they prefer large nuclei. The third term is proportional to the Coulomb energy of a charged sphere; it prefers a neutral nucleus. The fourth term has no classical interpretation, but it can be understood as arising from quantum mechanical exclusion; it prefers equal numbers of protons and neutrons. When these terms are combined, the lowest energy (most stable) combination of A nucleons is given by

$$Z_A(A) = \frac{A \left(2 - \frac{m_n - m_H}{a_a} \right)}{4 + \frac{a_c}{a_a} A^{2/3}}$$

(13.1)

where a_a is the asymmetry coefficient and a_c is the Coulomb coefficient. Note that Z_A is the minimum on the parabolic mass curve for mass number A . For small A the minimum corresponds to nearly equal numbers of protons and neutrons; the symmetry term dominates. For large A , Z is considerably less than N , e.g., ^{208}Pb with $N = 126$ and $Z = 82$. These general trends are displayed in N vs. Z plot, such as Fig. 2.7 in Chap. 2 of Vol. 1 on “Basic Properties of the Atomic Nucleus.” The main relevant feature of the figure is the distribution of stable nuclides in the vicinity of $A \approx 200$.

Figure 21.11 of Chap. 21, “Superheavy Elements,” gives a clearer picture of the nuclides beyond $A \approx 200$. There is an abrupt absence of nuclides with moderate much less long half-lives between ^{208}Pb and ^{232}Th . This is due to shell effects that are not included in the semiempirical equation. Of course shell effects are crucial for stabilizing the several “islands” of stability among heavy elements, which include the parents of the natural decay series as well as surprisingly stable isotopes of elements well beyond uranium.

Table 13.1 shows the α -decay energies of the $4n$ series and the energies predicted by the semiempirical equation without shell effects. The equation agrees with the facts near the middle – at ^{220}Rn . The predicted half-lives are too short in the Th–U region, and too long for Po (just above the shell). The Hg–Pb isotopes are predicted to have rather short half-lives for α decay. To be sure some of them are energetically unstable, but not enough that barrier penetration proceeds at an appreciable rate.

Table 13.1

Shell effects on α -decay energies (in MeV) and half-lives in the $4n$ chain. Note that for very rare α decays it is difficult to obtain experimental Q_α values. (In the case of ^{228}Ra nuclides, e.g., 19 ppb are only expected to undergo α decay, while the rest disintegrates by β decay according to Fig. 13.1)

Nuclide	Q_α	Q from eqn.	α half-life	Half-life from mass eqn.
^{236}U	4.572	7.62	2.3×10^7 years	0.9 s
^{232}Th	4.083	6.92	1.4×10^{10} years	20 s
^{228}Ra	~ 4.1	6.21	(3×10^8) years	5×10^3 s
^{228}Th	5.520	7.63	1.911 years	0.02 s
^{224}Ra	5.789	6.95	3.66 days	5 s
^{220}Rn	6.405	6.25	56 s	150 s
^{216}Po	6.907	5.53	0.146 s	1 day
^{212}Pb	~ 3.1	4.80	(Not known)	3 years
^{212}Bi	6.207	5.56	2.8 h	5 h
^{212}Po	8.954	6.29	0.3 μs	10 s

13.3 Time Dependence

The equations for growth and decay of genetically related radioactive materials were developed (Bateman 1910) in order to understand the complicated relations among the components of the natural decay chains. Time dependence remains important. First, it is of interest to anticipate how radioactivity will develop in freshly prepared samples. Second, processes such as weathering of waste deposits disturb the growth and decay relations, and analysis of the relative activities of the several components can indicate the rates and times of the disturbances. Third, the processes have been valuable in dating very old geological samples. See Chap. 7 of Vol. 1 for information on the rates of genetically related radioactive materials and, in particular, the Bateman equations describing members of arbitrarily long chains. Note that each set of equations describes the components of a chain defined for particular branches. Different branches require different set of equations. These points are illustrated in the following sections.

The time dependence of a genetically related pair can be described as equilibrium (if the half-life of parent is longer than that of the descendant) or no equilibrium (half-life of parent shorter than that of the descendant). Cases involving equilibrium are further classified as secular (half-life of the parent is long compared to the descendant and to the time duration of interest) or transient (decay of parent must be considered); the distinction depends on one's criterion for change. In most cases it is difficult to measure rates with uncertainties less than 0.1%, so one might require that less than 0.1% of the parent decay and that the rate of decay of descendant be more than 99.9% of the initial activity of the parent. For these conditions to obtain, the half-life of the parent must be at least 7,000 times the half-life of the descendant.

13.3.1 Approach to Equilibrium

If one excludes the extinct $4n + 1$ series, the parents of all three natural series have decayed less than 0.1% during human history, and the smallest parent/descendant ratio of half-lives (18,000 for $4n + 2$) is greater than 7,000 (see above). Therefore they can be in secular equilibrium with their descendants. For geological time scales, the entire series will follow the decay curve of the parent within 0.1%.

Parts of chains, such as the important genetic pair ^{226}Ra – ^{222}Rn , may also demonstrate secular equilibrium. The growth and decay relations of radon isotopes are perhaps of greatest general interest. About half of the radiation exposure of the general population is due to ^{222}Rn and its descendants. Its immediate parent, ^{226}Ra , has a long half-life ($160,000 \times$ that of ^{222}Rn) and is often displaced from its Th and U ancestors. For example, Ra in groundwater might be absorbed on a deionizer column, while any associated Rn would pass through unless embedded in the support material by recoil. If there is no flow for a period of time, the Rn will build up and eventually (perhaps within a month) reach secular equilibrium. For any given shorter time, the radon activity A_{Rn} will follow the simple growth curve given by $(1 - e^{-\lambda t}) A_{\text{Ra}}$, where λ is the decay constant for radon and t is the time since radium was freed from radon. The case is represented in Fig. 7.9 of Chap. 7 in Vol. 1.

The decay of ^{227}Ac to ^{227}Th is an example of transient equilibrium. (See Fig. 13.3 for half-lives and branching ratios.) An initially pure sample of ^{227}Ac will have increasing amounts of ^{227}Th until the rate of decay of ^{227}Th is nearly the same as the rate of decay of ^{227}Ac to it. If the ^{227}Th were fed at a constant rate, it would reach 99.9% of that rate in 9.966×18.7 days ≈ 186.6 days. However, during that time the ^{227}Ac would decay by 1.61%. Therefore the proper Bateman equation must be used to include both growth of ^{227}Th and decay of ^{227}Ac . The maximum in the decay rate of ^{227}Th occurs when it is equal to the production rate, namely, 0.9858 of the initial rate of decay of ^{227}Ac to ^{227}Th at 3,930 h (164 days).

					²³⁹ Pu 24.1 ky		
					100 5156 5143	²³⁹ Np 2.4 days	
					²³⁵ U 7×10^8 years		²³⁹ U 23 min
				²³¹ Pa 3.3×10^4 years	100 4400 4365		
			²²⁷ Th 18.7 days	100 5013 4950	²³¹ Th 25.6 h		
			100 6038 5978	²²⁷ Ac 21.8 years			
			²²³ Ra 11.4 days	1.38 4953 4941			
			100 5716 5607	²²³ Fr 22 min			
			²¹⁹ Rn 4.0 s	6×10^{-3} 5340			
			100 6819 6553	²¹⁹ At 0.9 min			
	²¹¹ Po 0.52 s		²¹⁵ Po 1.8 ms	97 6280			
	100 7450	²¹¹ Bi 2.2 min	100 7386	²¹⁵ Bi 7.4 min			
	²⁰⁷ Pb 6623 6278	99.72 36 min	²¹¹ Pb				
		²⁰⁷ Tl 4.8 min					

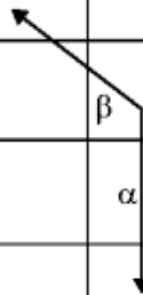


Fig. 13.3

The $4n + 3$ (²³⁵U) chain

Note that the weak 1.38% branch from ²²⁷Ac to ²²³Fr has been ignored and only a genetically related pair has been considered. When these factors are included, the correct equations are essential.

13.3.2 Branching Decay

When one takes into consideration that only 98.62% of the decay of ²²⁷Ac goes to ²²⁷Th and that 1.38% goes to ²²³Fr, one finds that the maximum fractional activities for ²²⁷Th and ²²³Fr are 0.975 and 0.0138, respectively. Note that the ²²³Fr reaches maximum sooner (when the production rate is nearly equal to the initial production rate); it meets the criterion for secular equilibrium. A subtle point is that one must distinguish between total and partial decay constants. The total describes the rate of disappearance of a species, while the partial decay constants describe the rate of production of the product of a particular branch. These points are developed in more detail in the next section.

13.3.3 Multiple Step Series

Consider one more step in the series originating from ²²⁷Ac, passing through the branches described

above, and rejoining at ^{223}Ra . Separate equations are required for the separate branches. One can consider the terms in the Bateman equations to have three parts: a product of λ 's in the numerator, a product of differences in λ 's in the denominator, and an exponential factor. For branched decay of component i , the λ_i in the numerator is the partial decay constant, and the λ_i 's in the denominator and the exponential for i are the total decay constants. Another way to view the use of partial decay constants in the numerator is to multiply the entire equation by the fraction for that particular branch. This is not a simplification, because chains with different branches have different numerators and some different exponential factors.

These calculations for $^{227}\text{Ac} \rightarrow ^{223}\text{Ra}$ for several times are given in Table 13.2 and Fig. 13.5. Note that the weak branch through 21.8 min ^{223}Fr produces ^{223}Ra more quickly, but eventually the main branch dominates. The total amount of ^{223}Ra at any time is the sum of the amounts coming through separate branches. If the calculations had been made for longer times, it would be clear that ^{223}Ra is in transient equilibrium with ^{227}Ac .

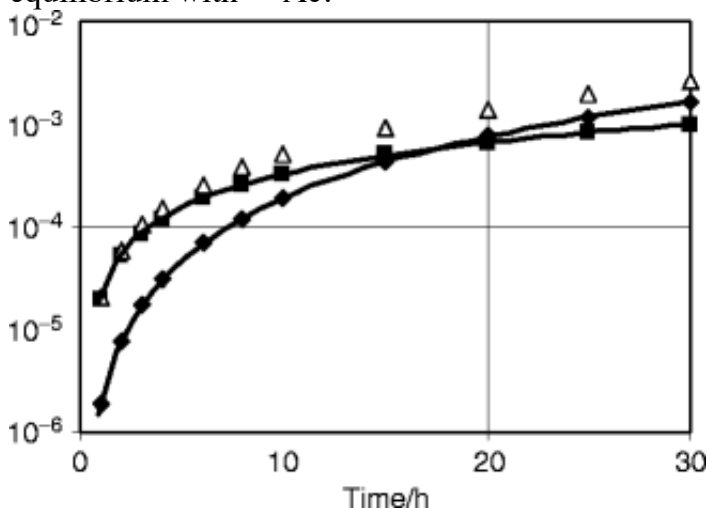


Fig. 13.5

Growth of ^{223}Ra in initially pure ^{227}Ac as a fraction of the initial ^{227}Ac activity. The squares show the Ra produced through Fr, the diamonds through Th. The triangles show the sum, the actual amount of Ra produced by all available paths

Table 13.2

Calculations for the relative activities of ^{227}Ac , ^{227}Th , ^{223}Fr , and ^{223}Ra in aged samples of initially pure ^{227}Ac . The convention used for representing numbers is $aE \pm b \equiv a \times 10^{\pm b}$. The Ac activity is not given; the final rate is 0.99982 times the initial rate. The fractions of each nuclide's production rate are given in the body of the table. The actual activities, relative to the activity of Ac, are obtained by multiplying Th and the Ra growing from it by 0.986. For Fr and the Ra obtained from it, the factor is 0.0138

Time (h)	Th-227	Ra-223	Fr-223	Ra-223
0	0.00E+00	0.00E+00	0.00E+00	0.00E+00
1	1.54E-03	1.95E-06	8.52E-01	1.40E-03
2	3.08E-03	7.80E-06	9.78E-01	3.76E-03
3	4.62E-03	1.75E-05	9.97E-01	6.26E-03
4	6.16E-03	3.11E-05	1.00E+00	8.77E-03
6	9.22E-03	6.99E-05	1.00E+00	1.38E-02
8	1.23E-02	1.24E-04	1.00E+00	1.88E-02
10	1.53E-02	1.93E-04	1.00E+00	2.37E-02
15	2.29E-02	4.31E-04	1.00E+00	3.60E-02
20	3.04E-02	7.62E-04	1.00E+00	4.81E-02
25	3.79E-02	1.18E-03	1.00E+00	6.01E-02
30	4.53E-02	1.69E-03	1.00E+00	7.20E-02
35	5.26E-02	2.29E-03	1.00E+00	8.36E-02
40	5.99E-02	2.97E-03	1.00E+00	9.52E-02
45	6.71E-02	3.73E-03	1.00E+00	1.07E-01
50	7.43E-02	4.57E-03	1.00E+00	1.18E-01

13.3.4 Multiple Separations

As a final example of time dependence, consider the effect of several chemical purifications on the relative amounts of Th and Ra components of the 4n (^{232}Th) series. Assume that these components initially are in secular equilibrium. This would not be the case if the sample consisted of thorium that had been isolated from an ore in modern times.

If the object is to obtain pure ^{228}Ra , isolation from the equilibrium chain does not suffice; an equal amount of ^{224}Ra will be obtained. Of course, aging the sample will improve purity, because the ^{224}Ra will decay more quickly than the ^{228}Ra . These trends are shown in Fig. 13.6. The amount of ^{228}Ra will decrease slowly, but that effect is ignored in this example. After about 22 days, the amount of ^{224}Ra growing from ^{228}Ra will be equal to the residual amount from the initial purification. If nothing is done, the sample will become progressively less pure. If the ^{228}Th is removed, growth is interrupted and decay in the fraction of ^{224}Ra resumes. However, for this purer ^{228}Ra sample, growth and decay effects become equal sooner, in this case about 10 days. Seven days later the $^{224}\text{Ra}/^{228}\text{Ra}$ ratio will be about 0.006; if higher purity were needed, more (and more frequent) purifications would be required.

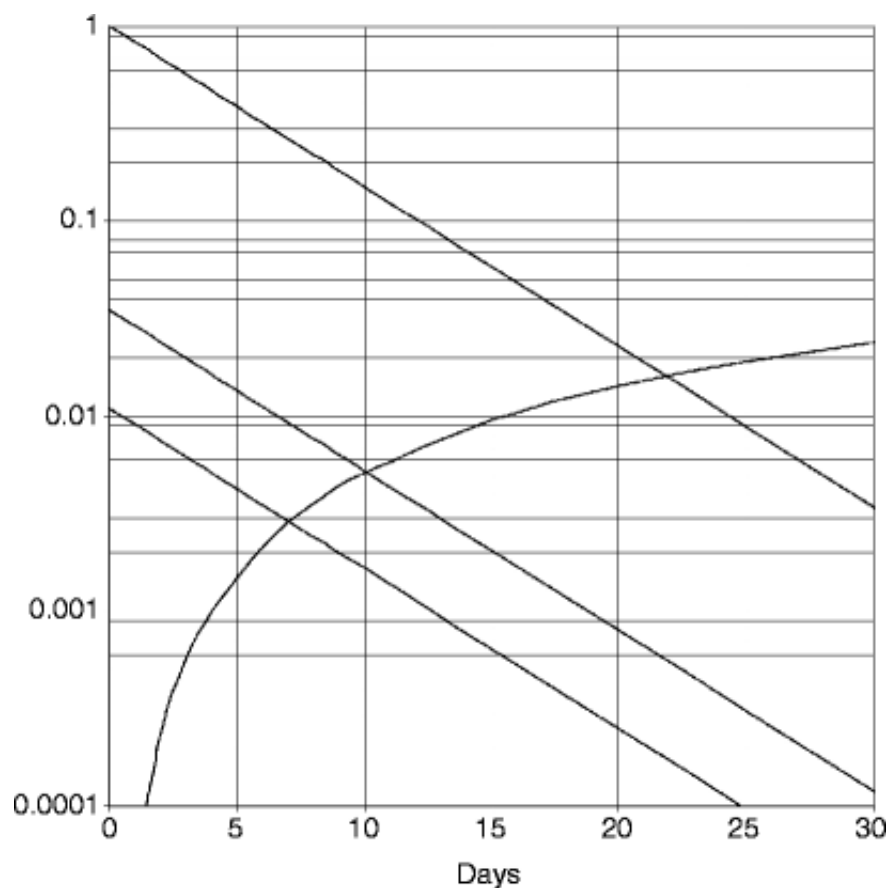


Fig. 13.6

Growth and decay of ^{224}Ra after isolation of radium from $4n$ series at secular equilibrium. The top curve gives the decay of ^{224}Ra after the first isolation relative to the secular rate. The growth curve shows the time dependence of ^{224}Ra that comes from ^{228}Ra (via ^{228}Ac and ^{228}Th). The middle decay curve shows ^{224}Ra that decays (with the clock restarted) after thorium is removed when growth and decay are equal (about 22 days from $t = 0$). The bottom decay curve shows decay following a third purification (about 10 days after the second)

The thorium after the initial purification would have equal activities of ^{228}Th and ^{232}Th . If pure ^{232}Th were needed, a similar series of purifications would eventually (about 20 years for 99.9% ^{232}Th) suffice. Even without subsequent processing, it would take many decades for the ^{228}Th to return to equilibrium with ^{232}Th . Getting pure ^{228}Th would be easier; the thorium growing into the purified radium would be pure ^{228}Th .

13.4 Physical Properties

The most sensitive detection of natural radioactive materials is by α spectroscopy. However, to realize good resolution it is necessary to have thin sources, which requires radiochemical purification in most cases. Therefore, γ rays are most convenient for measuring the components in complex mixtures, but γ rays emphasize the β -decay steps.

In addition to β decay and γ -ray emission, the elements near and beyond Pb in the chart of nuclides are unstable with respect to breakup, such as emission of α particles or heavier nuclei. The α , β , and γ emissions preserve the $4n + x$ chains, but emission of heavy ions might not, and fission certainly will not preserve the chains.

13.4.1 Alpha Rays

The energies of the most intense α groups are given in Figs. 13.1 – 13.4. The lower members of the chains emit the highest energy α particles, and the energies of different nuclides are generally quite different. A semiconductor detector can give ~ 20 keV resolution (full width at half maximum – FWHM) for α spectroscopy if thin sources are used. In the ^{232}Th chain, all of the intense α groups differ by more than 50 keV except the main group of ^{228}Th (5,423 keV, 71%) and the secondary group of ^{224}Ra (5,449 keV, 5%). Note that it would be difficult to obtain a thin source of a mixture of components without using chemical procedures, and chemistry would emphasize a few elements.

Similarly, the various isotopes of a given element isolated from a mixture of natural chains are likely to be resolvable. Radium occurs in all four chains, but ^{225}Ra in the $4n + 1$ chain is a nearly pure β emitter (Table 13.3).

Table 13.3

Energies of α groups from Ra isotopes

Chain	Isotope	α energy/keV	Abundance/%
4n	^{224}Ra	5,685	94
		5,449	6
4n + 1	^{225}Ra	4,006	Very weak
4n + 2	^{226}Ra	4,784	94
		4,602	6
4n + 3	^{223}Ra	5,747	9
		5,716	53
		5,607	26
		5,540	9

13.4.2 Gamma Rays

Most of the γ rays emitted in the decay chains are emitted following β decay. Most of the Q values for α decay are considerably larger than those for β decay, but β decay is much more likely to populate states that are just barely accessible energetically. Therefore, the use of γ -ray spectroscopy to measure the amounts of various components in a mixture emphasizes the β decays. Figure 13.7 shows the γ -ray spectrum (Helmer et al. 1999) of a sample of thorium ore, i.e., a sample that has been undisturbed for long enough time that the chain is in secular equilibrium. Table 13.4 lists the energies and intensities of the most intense γ rays emitted by components of the chain.

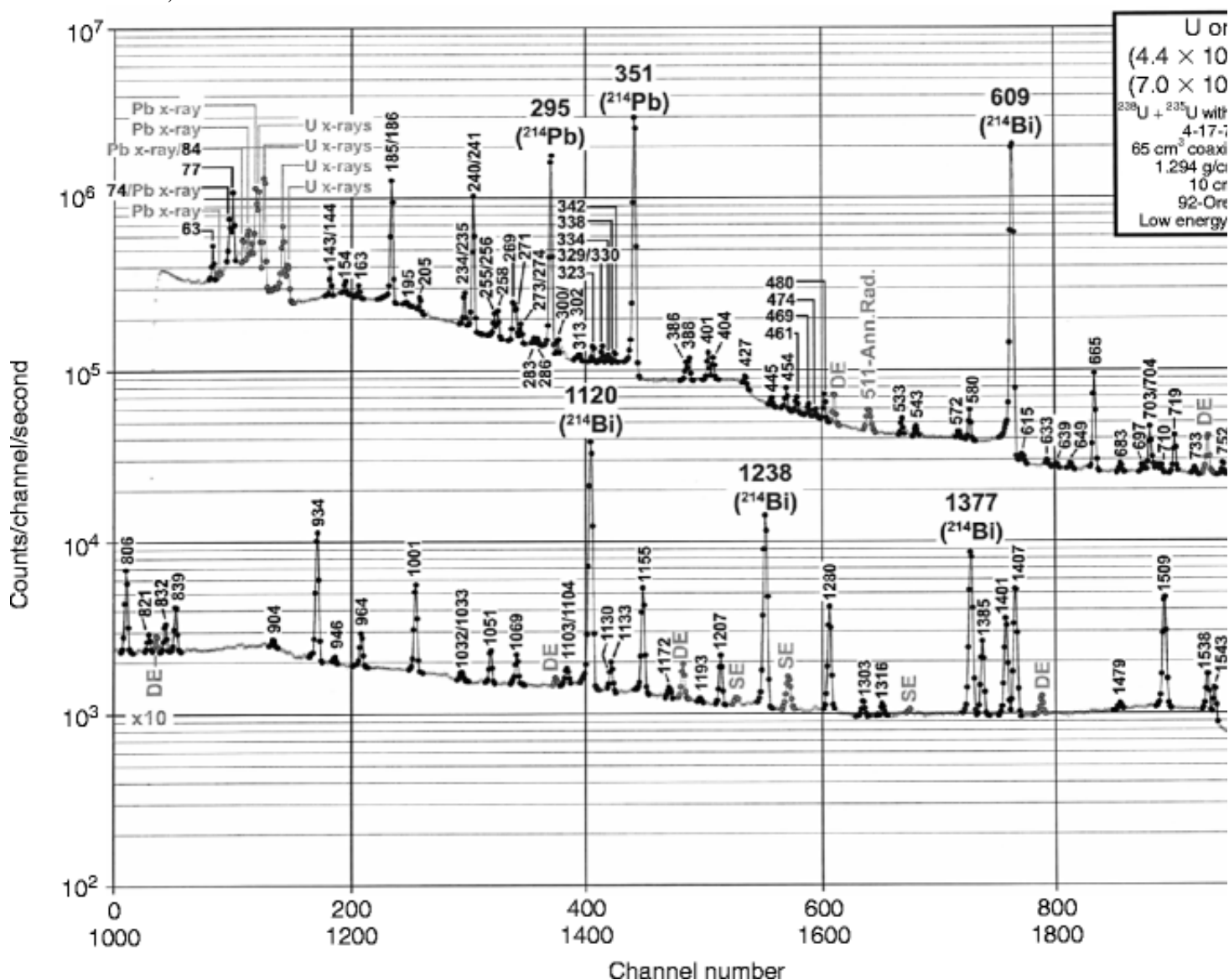
Table 13.4

Energies and intensities of γ rays in the 4n chain

Nuclide	γ -ray energy/keV	γ -ray intensity/%	Nuclide	γ -ray energy/keV	γ -ray intensity/%
^{232}Th	63.8	0.27	^{220}Rn	549.7	0.07
	410.88	0.018	^{216}Po	804.9	0.0018
^{228}Ra	13.5	14	^{212}Pb	238.6	43.6
^{228}Ac	911.2	29	^{212}Bi	727.3	6.7
	969.0	17.4	^{212}Po	None	
^{228}Th	84.9	1.21	^{208}Tl	583.0	86
	215.8	0.28		2614.4	100
^{224}Ra	240.8	3.9			

It is difficult under any circumstances to observe the γ rays emitted by ^{232}Th itself. The Q value for α decay is small and transition rates are very sensitive to small changes in the energy available for α decay. Because of the high atomic number of the daughter Ra, the transition from the excited state to the ground state mostly occurs via internal conversion rather than γ emission. Because of the long half-life and corresponding low specific activity, attenuation in the source material is serious. Finally, the detector

Figure 13.8 shows the γ -ray spectrum of uranium ore (Helmer et al. 1999). The spectrum of recently purified uranium is considerably different; most of the high-energy γ rays emitted by the ore arise from decays of the chain members near the end (primarily ^{214}Bi). Their growth is slowed by long-lived intermediates, such as ^{230}Th and ^{231}Pa .



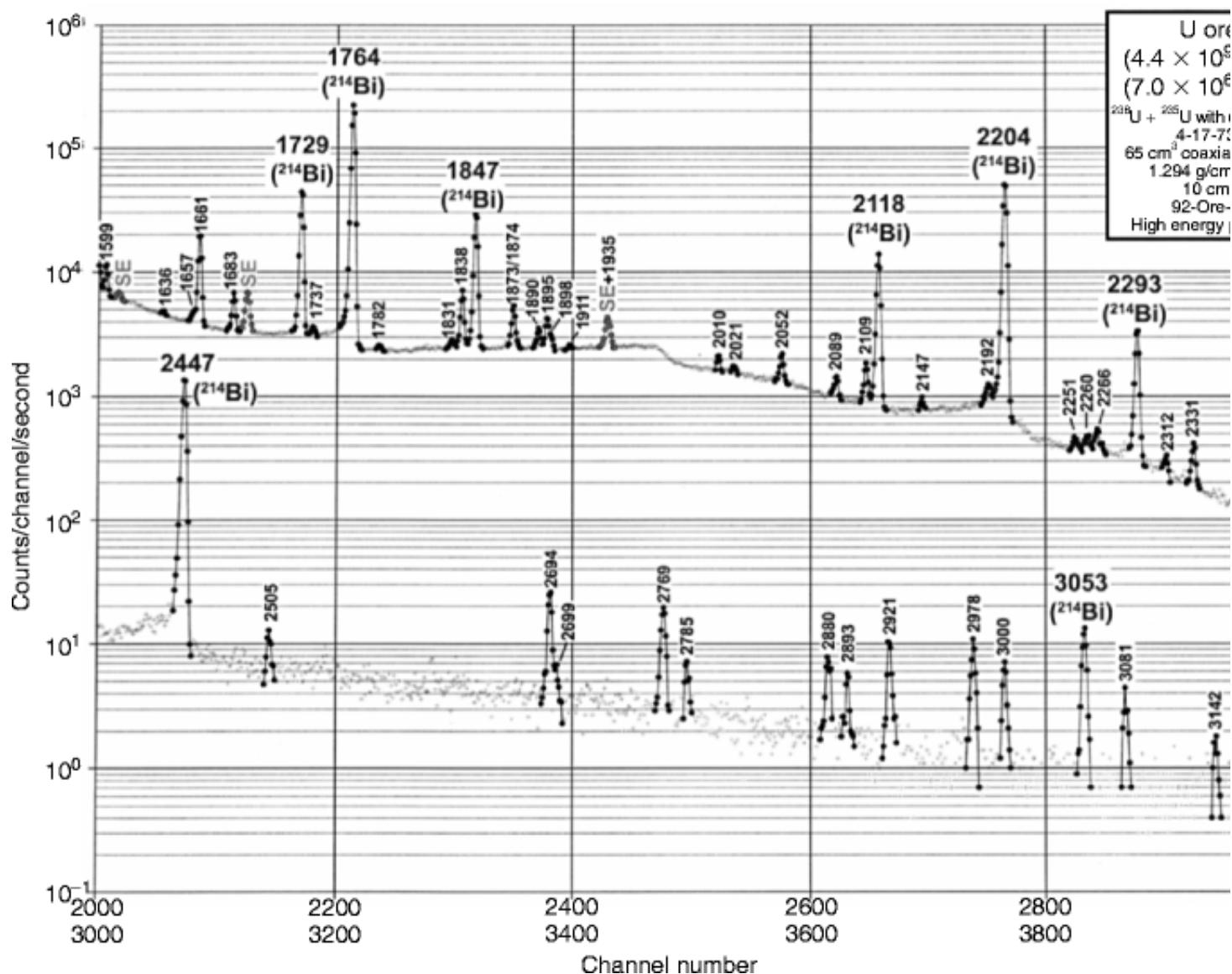


Fig. 13.8
 Gamma-ray spectrum of U series (Helmer et al. 1999)

13.4.3 Recoil

The substantial energy imparted to the residual nucleus in α decay is important because, in the chains, the residual nucleus may itself be radioactive and its fate is observable. For example, in α decay of ^{228}Th to the ground state of ^{224}Ra , the α particle has 5,423 keV of energy. The ^{224}Ra “recoils” with an initial energy of 97 keV, which is large compared with the energy required to vaporize one atom of Ra. If the thorium is in a thin deposit in a vacuum, the recoil will move in a direct line (opposite the direction of the emission of the α particle) until it strikes an object.

The recoil can be used to prepare thin sources. The recoils can embed in a catcher, such as a metal disk, placed close to a thin deposit. Of course, the process can repeat; subsequent α decays can produce other recoils, but each such cycle eliminates one member of the chain in the catcher.

If the source is covered with a thin layer such as evaporated gold or a VYNS film, the recoils will be retained. It is important to do so in order to prevent contamination of an α detector, particularly a semiconductor spectrometer operated with a vacuum between the source and the detector.

If a radon atom decays in a gas, although the recoils will stop in the gas, they often will be charged and can be collected by electrostatic attraction to a charged plate.

Recoils can interfere with ordinary chemical processing. If a parent nuclide is adsorbed on a surface, such as a bead of ion-exchange resin or the surface of a container, the recoil can embed deep in the support material and not be in equilibrium with the external chemical environment.

13.4.4 Heavy Ion Emission

All of the members of the natural decay chains are unstable with respect to spontaneous fission, but the probabilities are small. The decay chains follow the side of the valley of stability where the fissionability parameter Z^2/A is relatively small. However, fission is such an extraordinary event that even a few events can be detected, as long as they can be distinguished from events such as muon-induced fission. For the natural chains ^{238}U has the highest fraction of decays by spontaneous fission, 5.4×10^{-7} .

Although this leads to a multitude of natural decay chains consisting of fission followed by decays through fission product chains, the process will not be considered in this chapter.

Because fusion reactions such as $3\ ^4\text{He} \rightarrow\ ^{12}\text{C} + \text{Q}$ and $4\ ^4\text{He} \rightarrow\ ^{16}\text{O} + \text{Q}'$ are exothermic ($Q = 7.275\text{ MeV}$ and $Q' = 11.16\text{ MeV}$), when several α decays occur in sequence, the corresponding “crossover” decays can occur. For example, in the $4n$ chain the primary flow from ^{228}Th is a sequence of four α decays to ^{212}Pb . The crossover process would be $^{228}\text{Th} \rightarrow\ ^{16}\text{O} +\ ^{212}\text{Pb} + 39.06\text{ MeV}$. In fact, the process $^{228}\text{Th} \rightarrow\ ^{20}\text{O} +\ ^{208}\text{Pb} + 44.72\text{ MeV}$ is even more energetically favorable and is found to occur in $1.13 \times 10^{-11}\%$ of the decays of ^{228}Th . The low probability corresponds to the improbability of such a large particle as ^{20}O to tunnel through the Coulomb barrier. In this case the crossover does not lead to a product outside the chain. In some cases the mass number of the emitted heavy ion is not a multiple of 4 (e.g., ^{14}C), and the process crosses to another chain. Several known cases of heavy ion emission are listed in Table 13.5. (A more complete list is given in Chap. 18 in this Volume.) None is sufficiently probable as there are significant violations of the $4n + x$ rule for chains.

Table 13.5

Instances of heavy ion emission by members of the natural decay chains

Chain	Emitter	Heavy ion	Probability	Product	Q value	Partial $T_{1/2}$
4n	^{228}Th	^{20}O	1.13×10^{-13}	^{208}Pb	44.7 MeV	1.7×10^{13} years
	^{224}Ra	^{14}C	4.3×10^{-11}	^{210}Pb		2.3×10^8 years
4n + 1	^{225}Ac	^{14}C	6.4×10^{-12}	^{211}Bi		
	^{221}Ra	^{14}C	1.2×10^{-12}	^{207}Pb		
	^{221}Fr	^{14}C	8.8×10^{-13}	^{207}Tl		
4n + 2	^{234}U	Ne	9×10^{-12}	Pb		
	^{234}U	Mg	1.4×10^{-11}	Hg		
	^{230}Th	^{24}Ne	5.6×10^{-13}	^{206}Hg		
	^{226}Ra	^{14}C	3.2×10^{-11}	^{212}Pb	28.2 MeV	5×10^{13} y
	^{222}Ra	^{14}C	3.5×10^{-8}	^{208}Pb	33.0 MeV	34 years
4n + 3	^{235}U	^{20}Ne	8×10^{-12}	^{215}Pb		
	^{223}Ra	^{14}C	6×10^{-10}	^{209}Pb		

In some cases, heavy ion emission has been characterized in considerable detail. The structure in the ^{14}C emissions from ^{223}Ra has been observed. The energies are 29.8, 29.1, and 28.6 MeV, which populate ^{209}Pb levels at 0 (9/2+), 779 (11/2+), and 1,423 keV (spins and parities, in parenthesis) with relative intensities 15, 84, and 4, respectively.

The nuclides in the natural radioactive decay chains are not the most favorable candidates for heavy ion emission; they have unfavorable N/Z ratios. As shown in the example of emission of oxygen isotopes by ^{228}Th , emission of a $Z = N$ fragment leads to a product that is far from the center of β stability. Of course, emitting a fragment with $Nb\ Z$ (e.g., ^{20}O) displaces the emitted particle from β stability. If the emitter is on the proton excess side of stability, its decay benefits from extra “push” and can reach more stable products. The partial half-lives for heavy particle emission are very sensitive functions of the Q values. Although 38 s ^{222}Ra is not a member of a natural chain, it is included in the table to illustrate this point. Even though ^{222}Ra has a much shorter physical half-life than ^{226}Ra , the fraction of decays that involve ^{14}C emission is much higher – 3.5×10^{-8} versus 3.2×10^{-11} . The ratio of partial half-lives (see the last column of the table) is even more striking.

Heavy ion emission would be grouped with spontaneous fission and not considered in this chapter were it not for the convenience the chains afford as a source of radioactive materials with which to study the process. Products such as ^{222}Ra can be produced in charged-particle bombardments, but that implies the presence of energetic ions, which can complicate the detection of a few heavy ions from decay. The ranges of the heavy ions emitted by processes analogous to α decay are a few milligrams per square centimeter. Thin sources are needed, and the carrier-free materials that can be isolated from the chains serve this purpose well. It is likely that heavy particle emission will be found to be a decay mode for most heavy elements.

13.5 Chemical Properties

The most significant chemical property of most members of the chains is that each element is carrier-free – there are no inactive atoms to compete with the radioactive ones for chemical sites, such as ion-exchange sites on the inner surface of a container. In extreme cases, such as polonium in the ^{232}Th chain, there will be few if any atoms at a given time. The specific activity of ^{232}Th is 4,070 Bq/g. If 1 g of thorium is in equilibrium with its chain, the activities of 0.15 s ^{216}Po and 0.3 μs ^{212}Po will be 4,070 Bq and 2,609 Bq (64.1%), respectively. On average there will be 881 atoms of ^{216}Po present at any given time. Only 0.1% of the time is even one atom of ^{212}Po present. Francium is even more rare. It occurs only in the ^{235}U chain (and the extinct $4n + 1$), and then only in a 1.4% branch. There are only a few grams of Fr in the entire crust of the Earth.

The chemical properties span a range similar to the representative elements in the first few rows of the periodic table. Francium and radium are certainly characteristic of alkali and alkaline earth elements. Both Fr and Ra have only one oxidation state in chemical combinations and have little tendency to form complexes. Thallium in the 1+ oxidation state has alkali-like properties, but it does form complexes and has extensive chemistry in its 3+ state. Similarly, lead can have alkaline earth characteristics, but differs from Ra in forming complexes and having a second, 4+, oxidation state. Bismuth and actinium form 3+ ions in solution and are similar to the lanthanides and heavy ($Z > 94$) actinides. Thorium also has a relatively simple chemistry, with similarities to zirconium and hafnium. Protactinium is famous for difficult solution chemistry; it tends to hydrolyze and deposit on surfaces unless stabilized (e.g., by >6 M sulfuric acid). The chemistry of uranium as the uranyl ion UO_2^{2+} is fairly simple, but several other oxidation states are possible.

These properties and references for monographs giving detailed radiochemical characteristics (published by the U.S. National Academy of Sciences beginning in 1960 in a series NAS-NS 30xx, e.g., NAS-NS 3040 for lead) are given in Table 13.6 (see also LANL 2004).

Table 13.6

Chemistry of the chain elements. *Astatine and francium were discovered as the products of nuclear reactions. They are present in only one of the natural chains (^{235}U), and even then not in the main branch (see Fig. 13.3). The masses given in the last three columns refer to undisturbed (secular) equilibrium along the whole chain. See text for more details

Element	Oxidation state(s)	Monograph NAS-NS 30xx	Year of discovery	Mass/g of ^{232}Th	Mass/g of ^{238}U	Mass from $^{235}\text{U/g}$ of U
Thallium	1 3		1861	136 ag	0.1	82 ag
Lead	2 4	3040	Ancient	Various	Various	Various
Bismuth	3 5	3061	1753	7.6 fg	7.7 pg	38 ag
Polonium	2 4	3037	1898	0.3 ag	75 pg	~3 atoms
Astatine	-1 1 3 5 7	3012	1940*	—	—	<1atom
Radon	0	3025	1900	120 ag	2.2 pg	1.2 ag
Francium	1	3003	1939*	—	—	5.6 ag
Radium	2	3057	1898	0.4 ng	340 ng	303 fg
Actinium	3	3020	1899	49 fg	—	215 pg
Thorium	4	3004	1828	1 g	44 ng	1.2 pg
Protactinium	4 5	3016	1913		757 ag	332 ng
Uranium	3 4 5 6	3050	1789		1 g	7.2 mg

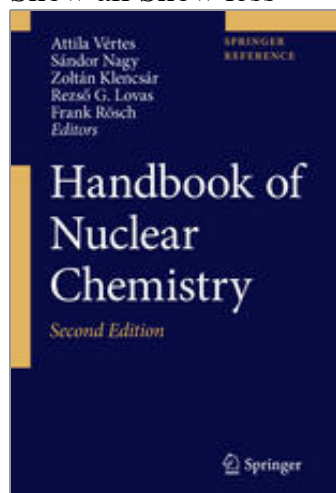
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