

We have seen that radioactivity is not dependent on the chemical bonding of atoms, or on temperature, or on pressure. Radioactivity can be described as an event whose probability of occurrence is independent of time and depends only on the duration of measurement. The probability that a radioactive nuclide will decay per unit of time is denoted λ . This probability, better known as the decay constant, is specific to the radioactive nuclide under consideration. Radioactive decay, like incoming calls at a telephone exchange, is a prime example of a Poisson process, in which the number of events is proportional to the time over which the observation is made. In the absence of any other loss or gain, the proportion of parent atoms (or radioactive nuclides) disappearing per unit of time t is constant:

$$\frac{dP}{P dt} = -\lambda \quad (4.1)$$

For a number of parent atoms $P = P_0$ at time $t = 0$, this equation integrates as:

$$P = P(t) = P_0 e^{-\lambda t} \quad (4.2)$$

In this form, Eq. 4.2 is not generally useful for measuring ages. The half-life $T_{1/2}$, which is the time it takes for half of the parent nuclides to decay, is $\ln 2/\lambda \approx 0.69/\lambda$. After five half-lives, 97% of the radioactive isotopes have decayed away, and 99.6% have decayed after eight half-lives. The product λP measures the number of decay events per unit time. It is commonly referred to as the activity of the radioactive nuclide P and denoted $[P]$. The becquerel (Bq) is a unit equal to one decay event (count) per second. A liter of seawater has an activity of 12 Bq, mostly because of the potassium-40 and uranium naturally dissolved in it. The human body contains enough potassium-40 and carbon-14 to register an activity

of 5000–10,000 Bq as perfectly natural in origin. A granite cobblestone normally produces a radioactivity of several thousand Bq.

In order to determine the age of a system using (4.2) from the measurement of the number of parent atoms at the present time, we must also know P_0 . If we do, then we have a chronometer based on the *decay of a radiogenic nuclide* and the age will be given by:

$$t = \frac{1}{\lambda} \ln \frac{P_0}{P} \quad (4.3)$$

Dating using the ^{14}C decay gives a good example:

$$t = \frac{1}{\lambda_{^{14}\text{C}}} \ln \frac{^{14}\text{C}_0}{^{14}\text{C}} \quad (4.4)$$

If we don't, a different solution is in order. For each parent atom, a daughter atom (or radiogenic nuclide) is created, usually of a single element, whose number can be denoted D . In a closed system and for a stable daughter nuclide D , the number of parent and daughter atoms is constant. Therefore:

$$D = D_0 + P_0 - P = D_0 + P(e^{\lambda t} - 1) \quad (4.5)$$

The term $P(e^{\lambda t} - 1)$ is a measure of the accumulation of the radiogenic nuclide during time t . Even if D and P are measured, this equation is no more a timing device than the previous one unless we know the number of daughter atoms D_0 at time $t = 0$. A simple case where this condition applies is when the initial number of daughter nuclides is small enough so as to be negligible. We will refer to such chronometers as *systems with high parent/daughter ratios*. This approximation is fairly generally valid for the potassium–argon dating method and for uranium–lead dating of zircons described later, and the time t will be given by:

$$t = \frac{1}{\lambda} \ln \left(1 + \frac{D}{P} \right) \quad (4.6)$$

For example, for the ^{238}U – ^{206}Pb chronometer:

$$t = \frac{1}{\lambda_{^{238}\text{U}}} \ln \left(1 + \frac{^{206}\text{Pb}}{^{238}\text{U}} \right) \quad (4.7)$$

When the previous methods fail (typically D_0 cannot be neglected with respect to D), a different assumption can often be used, which is the basis of the isochron method. This method dates an event of isotopic homogenization, typically the precipitation of minerals from the same melt or solution, and removes the ambiguity arising from our ignorance of the initial state of the system. Isotopic homogenization results from the fact that the chemical properties of different isotopes from the same element are very similar, though as seen in Chapter 3 not identical. To help our understanding, this principle is illustrated in Fig. 4.1 by a playful comparison. A fenced yard with a tree in the center represents two crystalline sites with different energy levels. In the first case, we release a few dozen cats and dogs into the yard–tree system and we can well imagine that after some brisk movement among our elements, they will arrange themselves in appropriate sites, cats in

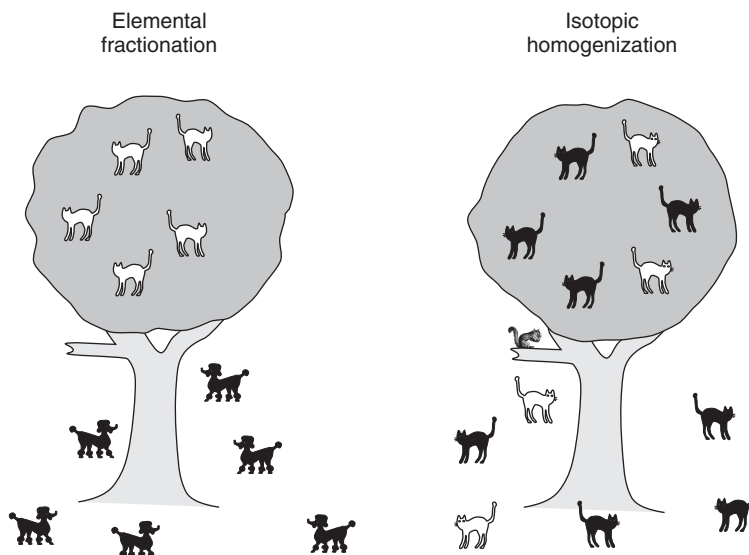


Figure 4.1

Left: Cats and dogs interact vigorously affecting site occupation (tree or yard). Just like two elements with different chemical properties, they arrange themselves so as to achieve the most stable configuration. Right: White cats and black cats have very similar properties and like isotopes of the same element are arranged randomly among the available sites. The most likely arrangement is an identical proportion of isotopes in each site.

the tree and dogs on the ground in the yard, under the tree. Cats and dogs are two different elements in competition for the same sites: they arrange themselves spontaneously so as to move to the most stable configuration! Any alternative configuration is either intrinsically unstable (dogs in the tree, cats on the ground) or out of equilibrium (cats and dogs on the ground). Now, we clear these animals out and then release into the yard a few dozen cats that only differ by the color of their fur, either black or white. The probability that a cat will take to the tree or the ground is independent of the color of its coat, the energy of interaction is low, and the most likely arrangement is one of maximum entropy where the proportion of white and black cats is the same at each site. Our black and white cats are isotopes with very similar properties that share the sites evenly regardless of their energy level.

If elements and their isotopes are allowed to move easily between sites in crystals, liquids, and gases, either because the liquid states enable effective mixing or because thermal diffusion allows atoms to move rapidly, the elements with variable properties will arrange themselves in accessible sites so as to minimize the total energy of the system. On the other hand, isotopic exchanges of a single element between phases contribute little to the energy balance of the system and such isotopes will be evenly distributed so as to maximize the entropy of the system. For the needs of geochronology, both natural mass fractionation and instrumental mass bias are purely and simply eliminated by internal normalization against some arbitrary reference ratio (see box). As carbonates precipitate out from seawater, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is exactly the same in calcite and in the seawater from which it precipitates;

as the mantle melts, $^{143}\text{Nd}/^{144}\text{Nd}$ is the same in the molten liquid as in the residue. There are, admittedly, processes where melting occurs in disequilibrium, but even if thermodynamic fractionation persisted at such high temperatures it would be corrected out by the internal standardization procedure (see box). In the rest of the discussion, we will therefore ignore mass-dependent fractionation.

Why radiogenic tracers are insensitive to phase changes and normalization values

The question often arises of how “are we so sure that these tracers are not upset by magmatic, metamorphic, or sedimentary processes just as oxygen and carbon isotopes are?” A common answer, albeit quite incorrect, is that the atomic weights of these tracers are heavy enough to make such fractionation negligible. Fractionation of the stable isotopes of strontium ($A \approx 88$) and mercury (≈ 200) are well established, both in nature and during mass-spectrometric analysis. The correct answer is that stable isotope fractionation is carefully separated from the fractionation induced by radiogenic decay by internal normalization to a reference isotope ratio. To measure isotopic ratios of interest for radiogenic isotopes, e.g. the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, both isotopic instrument bias and natural thermodynamic and kinetic fractionation are eliminated by standardization to an arbitrary stable isotope ratio (Fig. 4.2) using the theory developed for stable isotopes. For strontium, the universal choice is $^{88}\text{Sr}/^{86}\text{Sr} = 8.3752$. From a linear approximation similar to (3.27), the magnitude f of the mass bias can be inferred from the measurement of this ratio:

$$\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{meas}} = 8.3752 (1 + 2f) \quad (4.8)$$

and the resulting value of f introduced into the similar expression for the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{normalized}} = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{meas}} (1 + f) \quad (4.9)$$

$$= \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{meas}} \times \left[1 + \frac{1}{2} \frac{\left(\frac{^{88}\text{Sr}}{^{86}\text{Sr}}\right)_{\text{meas}} - 8.3752}{8.3752} \right] \quad (4.10)$$

This completes the internal isotopic normalization which removes any isotope fractionation that is not due to radioactive decay. Note the values +2 and +1 for the mass differences between the masses at the numerator and denominator of the isotopic ratios.

For technical and historical reasons, the standardization of isotopic ratios of certain elements such as neodymium may refer to different isotopic values: the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios taken from the literature must therefore be compared with utmost care. We saw in the previous chapter that with the delta notation, the problem of bias calibration among different laboratories or using different reference ratios disappears as soon as the isotope compositions are taken with respect to a common reference sample. For neodymium and hafnium, it is common practice to compare the sample isotopic compositions to that of the mean of

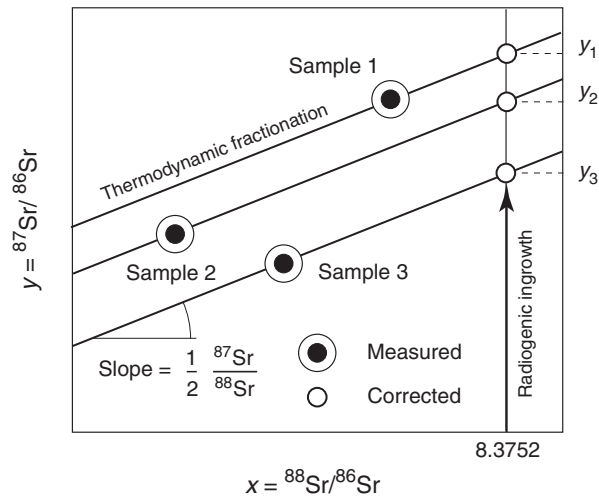


Figure 4.2

Principle of standardization of radiogenic isotope abundances (here $y = {}^{87}\text{Sr}/{}^{86}\text{Sr}$) relative to a reference ratio (here $x = {}^{88}\text{Sr}/{}^{86}\text{Sr}$). The various straight lines represent both natural and analytic thermodynamic isotopic fractionation depending on mass. The different ordinates between the straight lines represent the effect of radioactive accumulation of ${}^{87}\text{Sr}$, which varies from one sample to another. Standardization to $x = 8.3752$ eliminates thermodynamic fractionation leaving only radiogenic variability y_1 , y_2 , and y_3 . Note the slope equal to $(87-86)/(88-86) \times {}^{87}\text{Sr}/{}^{88}\text{Sr}$.

chondritic meteorites, and to use a relative deviation notation, analogous to the δ notation in use for oxygen isotopes: $\varepsilon_{\text{Nd}}(T)$ is defined as:

$$\varepsilon_{\text{Nd}}(T) = \left[\frac{({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{sample}}(T)}{({}^{143}\text{Nd}/{}^{144}\text{Nd})_{\text{chondr}}(T)} - 1 \right] \times 10\,000 \quad (4.11)$$

which is the deviation in parts per 10 000 of the ${}^{143}\text{Nd}/{}^{144}\text{Nd}$ ratio in the sample relative to that of chondrites of the same age T . In a similar way, $\varepsilon_{\text{Hf}}(T)$ can be defined for the ${}^{176}\text{Hf}/{}^{177}\text{Hf}$ ratio.

Lead is an exception because it has only a single stable isotope, which rules out internal standardization and explains the intrinsically lower precision of measurement of some data (a few parts per 10 000) compared with that of Sr, Nd, or Hf ($10\text{--}30 \times 10^{-6}$).

In (4.2), let us divide P by the number P' of atoms of a stable isotope of the same element as the radioactive nuclide. As the system is closed, the number of stable nuclides P' remains constant, which we denote $P' = P'_0$. This gives:

$$\left(\frac{P}{P'} \right)_t = \left(\frac{P}{P'} \right)_0 e^{-\lambda t} \quad (4.12)$$

The additional condition required to make the decay equation a chronometer is no longer to assume P_0 but rather to determine the isotope ratio $(P/P')_0$ when the system formed,

which is already a far less restrictive condition. This method is employed for many short-lived nuclides (^{14}C , ^{10}Be , ^{210}Pb) created by solar or galactic radiation interacting with the atmosphere or rocks (cosmogenic nuclides). In the case of the carbon-14 clock, P refers to the radioactive ^{14}C isotope, while P' is the most abundant isotope ^{12}C of carbon, and a hypothesis is made about the isotopic abundance of ^{14}C in the upper atmosphere. The principle of standardization to a stable isotope is also utilized for radioactive nuclides derived from the decay of uranium isotopes (^{234}U , ^{230}Th , ^{231}Pa), but the equations are then a little more complex.

Equation (4.5) may also be divided by the number D' of atoms of a stable isotope of the same element as the radiogenic nuclide. As the system is closed, the number of stable nuclides remains constant and $D' = D'_0$. This yields:

$$\left(\frac{D}{D'}\right)_t = \left(\frac{D}{D'}\right)_0 + \left(\frac{P}{D'}\right)_t (e^{\lambda t} - 1) \quad (4.13)$$

Equation (4.13) is known as the isochron equation: in a plot of $x = P/D'$ and $y = D/D'$, a set of sub-systems of the same age T and the same initial isotope ratio $(D/D')_0$ will lie on a straight line of slope $e^{\lambda t} - 1$. The P/D' ratio is usually referred to, somewhat improperly, as the parent/daughter ratio. Writing this equation for two samples 1 and 2 that formed at the same time with the same isotope composition $(D/D')_0$ and subtracting them from one another, we obtain an expression for the time:

$$t = \frac{1}{\lambda} \ln \frac{(D/D')_2 - (D/D')_1}{(P/D')_2 - (P/D')_1} \quad (4.14)$$

Thus, for the system ^{87}Rb – ^{87}Sr , P stands for ^{87}Rb , D for ^{87}Sr , and D' for ^{86}Sr , and we can write:

$$\left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_t = \left(\frac{^{87}\text{Sr}}{^{86}\text{Sr}}\right)_0 + \left(\frac{^{87}\text{Rb}}{^{86}\text{Sr}}\right)_t (e^{\lambda_{87\text{Rb}} t} - 1) \quad (4.15)$$

This expression defines Nicolaysen's (1961) isochron. It has the familiar form of the equation of a straight line $y = y_0 + mx$, where $x = (^{87}\text{Rb}/^{86}\text{Sr})_t$, $y = (^{87}\text{Sr}/^{86}\text{Sr})_t$, with intercept $y_0 = (^{87}\text{Sr}/^{86}\text{Sr})_0$ and slope $m = e^{\lambda_{87\text{Rb}} t} - 1$. Time t is derived from the expression:

$$t = \frac{1}{\lambda_{87\text{Rb}}} \ln \frac{(^{87}\text{Sr}/^{86}\text{Sr})_2 - (^{87}\text{Sr}/^{86}\text{Sr})_1}{(^{87}\text{Rb}/^{86}\text{Sr})_2 - (^{87}\text{Rb}/^{86}\text{Sr})_1} \quad (4.16)$$

(all the ratios measured today).

For an isolated sample with a high parent/daughter ratio, i.e. $(P/D')_1 \ll (P/D')_2$ and for which the $(D/D')_1$ can be assumed, the age derived in this way is a *model age*.

Figure 4.3 shows two examples of isochron diagrams. A simple way of understanding isochrons is to appreciate that the existence of an alignment in the isochron diagram, in which relations between the quantities plotted change with time, cannot be fortuitous and depend on us to observe it today: if the samples form an alignment at the present time, an alignment must also have existed at each time since their formation. Since the D/D' ratio

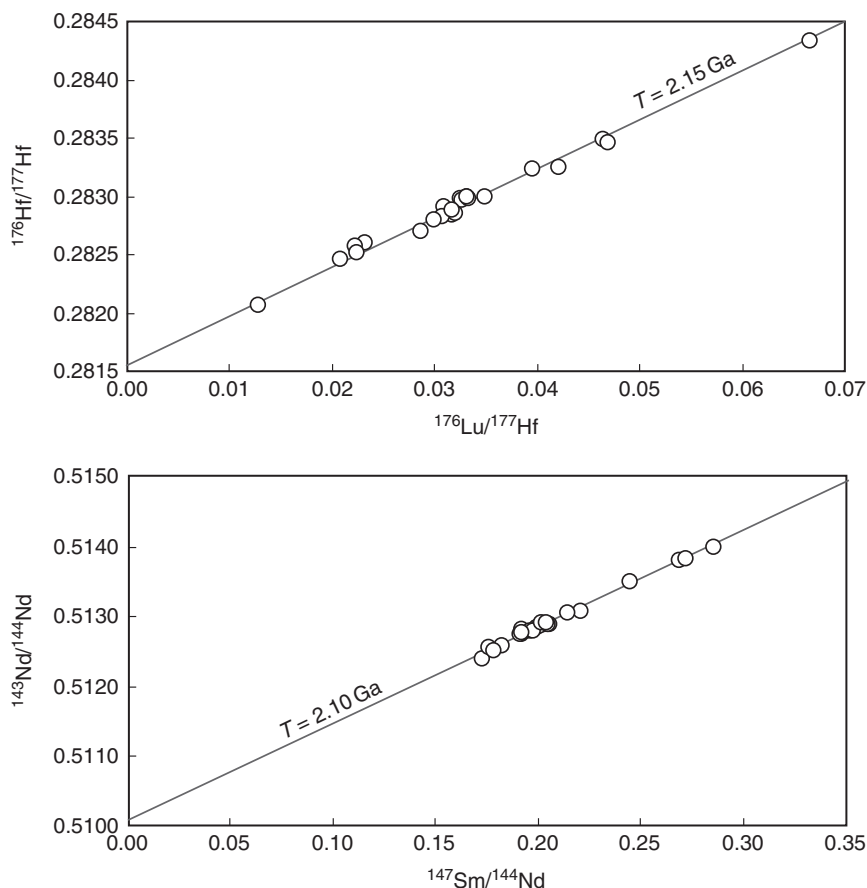


Figure 4.3

Two examples of isochrons for the $^{176}\text{Lu} \rightarrow ^{176}\text{Hf}$ (top, $\lambda^{-1} = 1.865 \times 10^{-11} \text{ a}^{-1}$) and the $^{147}\text{Sm} \rightarrow ^{143}\text{Nd}$ (bottom, $\lambda^{-1} = 0.654 \times 10^{-11} \text{ a}^{-1}$) systems on the same samples of Proterozoic basalts from West Africa (Abouchami *et al.*, 1990; Blichert-Toft *et al.*, 1999). Samples of the same age, and for which the range of isotopic compositions of the daughter element at the time of emplacement can be considered negligible with respect to the range caused by radiogenic ingrowth, will lie on a straight line. The slope of the isochron gives the age t of the lava flows and the intercept the mean isotopic ratio of the daughter element at that particular moment.

of any sample devoid of parent nuclide is unchanged, alignments simply rotate with time around the intercept.

Isochrons can alternatively be viewed as mixing lines between two end-members. The first end-member ($x = 0, y = (D/D')_0$) is the initial inventory of the daughter element, whereas the second end-member ($x = \infty, y = \infty, y/x = e^{\lambda t} - 1$) represents pure radiogenic ingrowth.

Let us now take a quick guided tour of dating methods, beginning with those based on the measurement of radioactive nuclides; then the systems with high parent/daughter ratios, in which the initial quantities of radiogenic nuclides can be neglected; and, finally, systems with low parent/daughter ratios, where the isochron method is applicable. In general, a clock can be applied to samples whose age does not exceed five times the radioactive

Table 4.1 Decay constants of the major radioactive systems: the daughter nuclide is shown when it is used for dating

System	λ (y^{-1})	System	λ (y^{-1})	System	λ (y^{-1})
^{138}La – ^{138}Ce	2.24×10^{-12}	^{40}K – ^{40}Ca	4.96×10^{-10}	^{26}Al	9.80×10^{-7}
^{147}Sm – ^{143}Nd	6.54×10^{-12}	^{235}U – ^{207}Pb	9.85×10^{-10}	^{36}Cl	2.30×10^{-6}
^{87}Rb – ^{87}Sr	1.42×10^{-11}	^{146}Sm – ^{142}Nd	6.73×10^{-9}	^{230}Th	9.20×10^{-6}
^{187}Re – ^{187}Os	1.64×10^{-11}	^{244}Pu	8.66×10^{-9}	^{234}U	2.83×10^{-6}
^{176}Lu – ^{176}Hf	1.865×10^{-11}	^{182}Hf – ^{182}W	7.7×10^{-8}	^{231}Pa	2.11×10^{-5}
^{232}Th – ^{208}Pb	4.95×10^{-11}	^{129}I – ^{129}Xe	4.30×10^{-8}	^{14}C	1.21×10^{-4}
^{40}K – ^{40}Ar	5.81×10^{-11}	^{53}Mn – ^{53}Cr	1.87×10^{-8}	^{226}Ra	4.33×10^{-4}
^{238}U – ^{206}Pb	1.55×10^{-10}	^{10}Be	4.62×10^{-7}	^{210}Pb	3.11×10^{-2}

period. Table 4.1 shows that the clocks spread over a wide range but certain age ranges are not well covered, especially that at around one million years.

Note that physical time elapsing in the real world is normally given in seconds (s), which is not a very helpful unit in the Earth sciences, while geological ages, through which we go back through time, are noted in anni (a), from the Latin *annus*. Derived units ky and ka (thousand years), My and Ma (million years), Gy and Ga (billion years) apply to physical time and time interval (or age), respectively. Appendix D shows the division of geological time into absolute ages. The geological time scale is the product of the work of literally thousands of scientists throughout the last century and cannot be credited to one particular work. An overview of the techniques commonly used for the determination of elemental concentrations and isotopic ratios is given in Appendix E.

4.1 Dating by radioactive nuclides

This group of methods relates essentially to nuclides produced by cosmic radiation, but we will see that the approach can be generalized to the descendants of uranium and thorium with methods based on the surpluses of these nuclides. Here we make an assumption about the initial isotopic composition of the element to which the radioactive nuclide belongs.

4.1.1 Carbon-14

This method of dating, which is certainly the most familiar to the general public, is not the oldest historically. However, it has revolutionized archeology and earned its inventor, Libby (see Arnold and Libby, 1949), the Nobel Prize for Chemistry in 1960. The Earth is subjected to bombardment from high-energy galactic cosmic rays, mostly protons and α particles, which react with the Earth's atmosphere. The interaction of these particles with nitrogen and oxygen produces secondary particles, mostly neutrons. In spite of a

limited lifetime, neutrons do not have to overcome the Coulomb barrier of the nucleus and react more easily than charged particles of the same energy, such as protons. An important source of ^{14}C is the reaction between neutrons and nitrogen, which produces radioactive carbon-14 and a proton:



The ^{14}C atom decays to ^{14}N by β^- emission with a decay constant $\lambda_{^{14}\text{C}}$ of $1.2 \times 10^{-4} \text{ y}^{-1}$. Before disappearing, it mixes very quickly with the stable isotopes of carbon, the most important of which is ^{12}C . Equation 4.8 can now be written:

$$\left(\frac{^{14}\text{C}}{^{12}\text{C}}\right)_t = \left(\frac{^{14}\text{C}}{^{12}\text{C}}\right)_0 e^{-\lambda_{^{14}\text{C}}t} \quad (4.18)$$

Plants exchange their carbon with the atmosphere, with which they are in isotopic equilibrium until they die. It can be seen that if the ratio $(^{14}\text{C}/^{12}\text{C})_0$ in the atmosphere is constant and known, measurement of the $^{14}\text{C}/^{12}\text{C}$ ratio in wood or a fossil carbonate will date the death of the organism.

This approach is complicated by several effects. First, ever since the nineteenth century, the burning of coal and oil has released a large quantity of “dead” carbon devoid of ^{14}C into the atmosphere, thus complicating estimates of the $(^{14}\text{C}/^{12}\text{C})_0$ ratio. To make things worse, above-ground nuclear explosions until the mid 1970s have contaminated the atmosphere with artificial ^{14}C , some of which has invaded the surface of the oceans. Finally, the variation in solar activity modulates galactic cosmic radiation received by the Earth and therefore changes the rate of production of ^{14}C in the atmosphere over very long periods. To overcome these difficulties, the ^{14}C scale has been calibrated for more recent ages by dendrochronology – a method based on counting the growth rings of very old trees – Californian bristle-cone pines or German oaks. For older ages, calibration is achieved by comparison with the thorium-230 method on corals.

There are various applications for the ^{14}C method; it can provide dates as old as 40 000 years ago. Measurement methods using a linear accelerator have pushed this limit a little further back, but above all they have reduced the quantities of material required for analysis to be conducted. The ^{14}C method has been used very successfully in archeology and Quaternary geology. It also has applications in dating groundwater sources and, as we will see later, deep water of the oceans.

4.1.2 Beryllium-10

The radioactive nuclide ^{10}Be is one of the pieces produced by spallation, the breaking of atmospheric ^{14}N and ^{16}O nuclei by cosmic rays. Metallic Be is rapidly oxidized to BeO , scavenged by atmospheric particles, and finally incorporated into soil and sediments by rain water and run off. The ^{10}Be decay constant is $4.62 \times 10^{-7} \text{ y}^{-1}$ and it is customary to normalize its abundance to that of the stable isotope ^9Be . Beryllium is an element similar to aluminum and is found in clay and soils. Beryllium-10 dating is much used in oceanography for measuring sedimentation rates or manganese-nodule growth rates. For samples

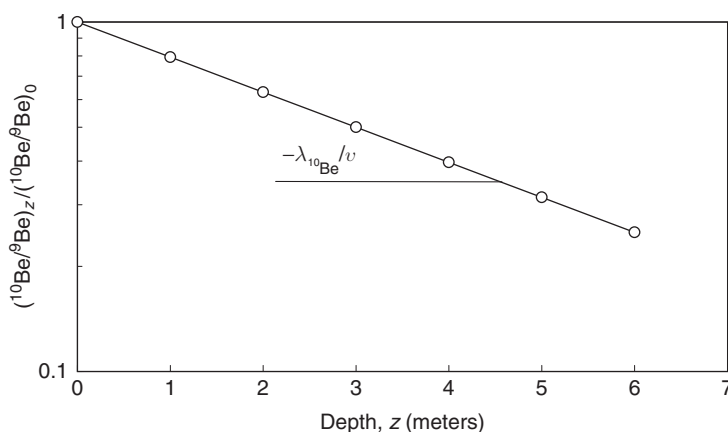


Figure 4.4

Measurement of sedimentation rate v by variation in relative abundance of the cosmogenic isotope ^{10}Be with depth. The isotopic ratio is standardized to its surface value (0). The scale is semi-logarithmic.

taken at depth z in a sediment core in which the sedimentation rate can be assumed to have remained constant, the equivalent to (4.18) can be written as:

$$\left(\frac{^{10}\text{Be}}{^9\text{Be}}\right)_t = \left(\frac{^{10}\text{Be}}{^9\text{Be}}\right)_0 \exp\left(-\lambda_{^{10}\text{Be}} \frac{z}{v}\right) \quad (4.19)$$

where v is the sedimentation rate. On the condition that the $^{10}\text{Be}/^9\text{Be}$ ratio at the time of deposition does not vary locally over the time interval sampled by the core, the $^{10}\text{Be}/^9\text{Be}$ ratios measured in different samples should decrease exponentially with age. The logarithm of the $^{10}\text{Be}/^9\text{Be}$ ratio should therefore vary linearly with depth z (Fig. 4.4) in the core. The slope $-\lambda_{^{10}\text{Be}}/v$ is hence a measure of sedimentation rate.

This method can also be employed for measuring erosion rates. Neutrons produced by interaction of cosmic radiation with the atmosphere are stopped by the ground, where they cause spallation reactions, i.e. fragmentation of the atoms of the material. The production of ^{10}Be from silicon atoms in quartz is of particular interest. The number of ^{10}Be atoms produced in the ground per unit volume varies with depth z beneath the surface as $R_0 e^{-z/l}$, where R_0 is the surface production and l is the attenuation distance or mean penetration distance of cosmic particles into the rock. Over time t , thickness $dz = v dt$ of the rock has been eroded, where v is the erosion rate. The number dN of ^{10}Be atoms transiting between depth z and depth $z + dz$ is $-(vN(z + dz) - vN(z))$ per unit time, since the erosion rate is directed toward negative depths. Let us assume that the erosion rate is constant and that the ^{10}Be production rate remains constant over the time interval of interest. At equilibrium we can write that removal by erosion and radioactivity balances production by cosmic radiation:

$$- [vN(z + dz) - vN(z)] + R_0 e^{-z/l} dz - \lambda N(z) dz = 0 \quad (4.20)$$

and a little mathematics give the expression:

$$N(z) = \frac{R_0}{\lambda + v/l} e^{-z/l} \quad (4.21)$$

It can be seen, then, that if we know the rate of production R_0 and the attenuation distance l , the abundance $N(z = 0)$ of ^{10}Be at the surface provides a direct estimate of the rate v of erosion.

4.1.3 The thorium-230 excess method

This is a somewhat different case, as this nuclide, with a radioactive half-life of 75 000 years, is not created by radiation but by another parent nuclide whose half-life is long enough for its rate of production to be considered constant on time scales of less than one million years. It is one of the examples of clocks based on a chain of radioactive decay (Fig. 4.5) in which nuclides decay from one to another by α or β^- radioactive processes. The vast majority of intermediate nuclides have half-lives too short to act as useful clocks. There are only four radioactive chains. These chains, which have a long-lived, heavy nuclide as their parent, are those of ^{232}Th , ^{235}U , ^{238}U , and ^{237}Np . The first three end with three isotopes of lead, ^{208}Pb , ^{207}Pb , ^{206}Pb , and we will see that their relative abundances in modern lead are utilized as clocks. The fourth chain is that of neptunium-237, an extinct radiogenic nuclide ending with the single isotope bismuth-209. It is not detectable in natural products.

Uranium-238 decays to ^{234}Th , then to ^{234}U and, finally, to ^{230}Th , which is itself radioactive. The two intermediate nuclides, ^{234}Th and ^{234}U , are so short-lived that we can ignore them here. The change in the number $N_{230\text{Th}}$ of ^{230}Th nuclides can therefore be written as the difference between production by the parent ^{238}U and radioactive decay:

$$\frac{dN_{230\text{Th}}}{dt} = -\lambda_{230\text{Th}} N_{230\text{Th}} + \lambda_{238\text{U}} N_{238\text{U}} \quad (4.22)$$

The complete set of equations and their solutions were found by Bateman (1910). After a few hundreds of thousand years, the number of ^{230}Th nuclides reaches steady state and the two terms of the right-hand side cancel out. This state, where all activity levels are equal for all the nuclides in the chain, is known as secular equilibrium. The activity $[^{238}\text{U}]$ remains essentially constant during the time it takes to establish secular equilibrium (roughly $1/\lambda_{230\text{Th}}$, or several 100, 000 years) and variation $d[^{238}\text{U}]/dt$ with time is therefore zero. Allowing for this property and multiplying (4.22) by $\lambda_{230\text{Th}}$, we obtain:

$$\frac{d\{[^{230}\text{Th}] - [^{238}\text{U}]\}}{dt} = -\lambda_{230\text{Th}} \{[^{230}\text{Th}] - [^{238}\text{U}]\} \quad (4.23)$$

in which the square brackets represent activity. The difference $[^{230}\text{Th}] - [^{238}\text{U}]$ is known as ^{230}Th excess (the term excess is taken by reference to the amount present at secular equilibrium), and is written $[^{230}\text{Th}]_{\text{ex}}$. Equation (4.23) integrates as:

$$[^{230}\text{Th}]_{\text{ex}} = [^{230}\text{Th}]_{\text{ex},0} e^{-\lambda_{230\text{Th}} t} \quad (4.24)$$

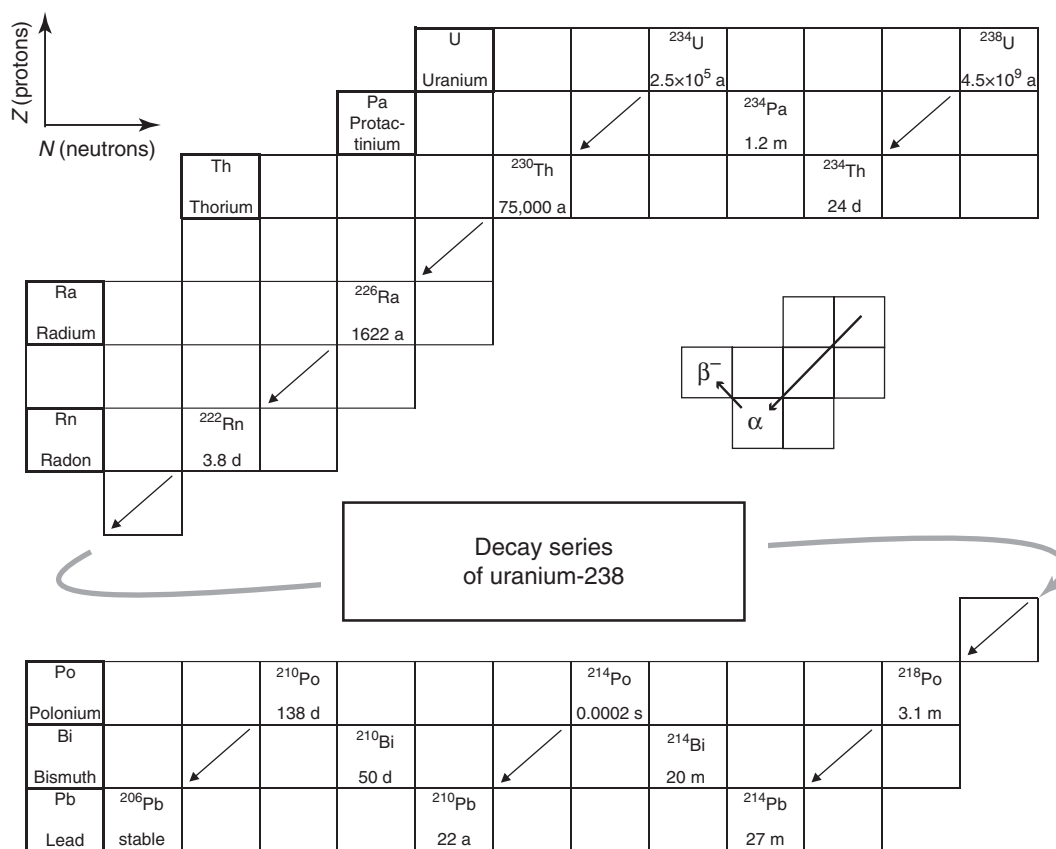


Figure 4.5 Decay series of ^{238}U . The decay period of unstable nuclides is shown. The number of neutrons is given on the x-axis and the atomic number on the y-axis. Jumps induced by α and β^- decay are shown in the inset box. Units: year (a), day (d), minute (m), second (s).

where the subscript 0 denotes the initial time. If, as with ^{10}Be , we wish to measure a sedimentation rate, time t is replaced by the ratio between depth z and rate of sedimentation v , and the logarithm of $[^{230}\text{Th}]_{\text{ex}}$ is plotted as a function of z for several samples collected at different depths from a single core: the slope of the alignment indicates the $-\lambda_{230\text{Th}}/v$ ratio, and so v can be determined from it.

These concepts apply to excesses of several nuclides descending from ^{238}U , such as ^{234}Th , ^{234}U , ^{210}Pb , and from ^{235}U , such as ^{231}Pa . These methods are often said to be based on “uranium disequilibrium series,” to indicate that the chronometric information lies with the deviation of a given parent/daughter pair from secular equilibrium. There are many fields of application, from oceanography to dating of Quaternary lacustrine or marine sediments. Lead-210 (^{210}Pb), with a half-life $T^{1/2} = 23.3$ years, notably forms in the atmosphere and in rain water by decay of radon-222 (the offspring of ^{238}U , see Fig. 4.5), a gaseous nuclide given off constantly by the ocean, mantle, and crust. It is used for determining the rates of accumulation of ice or of sedimentation during the last century. It is also very helpful for studying pollution processes.

4.2 Systems with high parent/daughter ratios

There are many important clocks for which the quantities of daughter isotopes at time $t = 0$ can be ignored. The potassium–argon method and uranium–lead method on zircon are the best known, but the old uranium–helium method has recently been resurrected to address the chronology of erosion processes. Also worth mentioning in this category are the many clocks based on the descendants of uranium, such as ^{238}U – ^{230}Th , which have been amazingly successful at dating corals and cave deposits.

4.2.1 The potassium–argon method

This is the workhorse of geochronology. The method relies on the potassium-40 nucleus capturing a K-shell electron so that $^{40}\text{K} + e^- \rightarrow ^{40}\text{Ar}$. The radioactive constant or probability of decay per unit time for this process is $\lambda_\epsilon = 5.81 \times 10^{-11} \text{ y}^{-1}$. Potassium-40 also decays by an ordinary β^- process into ^{40}Ca (dual decay), for which the radioactive constant is $\lambda_\beta = 4.96 \times 10^{-10} \text{ y}^{-1}$. The proportion of ^{40}K atoms taking the ^{40}Ar pathway is equal to the relative probability $\lambda_\epsilon / (\lambda_\epsilon + \lambda_\beta)$ or 10.5%. Using N for the number of nuclides, equation (4.5) then becomes:

$$N_{40\text{Ar}}(t) = N_{40\text{Ar}}(0) + \frac{\lambda_\epsilon}{\lambda_\epsilon + \lambda_\beta} N_{40\text{K}}(t) \left[e^{(\lambda_\epsilon + \lambda_\beta)t} - 1 \right] \quad (4.25)$$

with the sum of probabilities of decay, by one or other pathway, in the exponential, and the proportion of daughter nuclides that are atoms of ^{40}Ar in the factor term. The principle behind the method is that the $^{40}\text{Ar}_0$ term can be neglected relative to the second term. Although argon is present in notable quantities in the atmosphere (1%) and in the interstitial gases of rocks, this inert gas is not very soluble at ambient pressure in melts and minerals since it forms only weak van der Waals'-type bonds with mineral ions. At higher pressure, however, substantial amounts of argon may remain trapped in submarine glasses or metamorphic minerals (excess argon).

For analysis, argon is extracted from rocks by heating and melting in ultra-vacuum lines and analyzed with a mass spectrometer. The ultra-vacuum is necessary to prevent atmospheric contamination. Such contamination inevitably occurs anyway as minerals adsorb small quantities of atmospheric gases onto their surfaces or in grain fractures. To obviate this, we use the fact that atmospheric argon has several isotopes and that the atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio is 296. We simply subtract 296 times the quantity of ^{36}Ar measured, from the ^{40}Ar measured in the sample, to obtain the radiogenic argon (Fig. 4.6). This can only be done with precision when radiogenic ^{40}Ar is not dominated by that originating in the atmosphere: measuring young ages for rocks with a low potassium content is therefore a technical feat of skill. It is thanks to the potassium–argon method that the scale of magnetic reversals can be calibrated, as it is the only method for dating the lava on which the paleomagnetic measurements are made. It will be seen when studying the thermal history

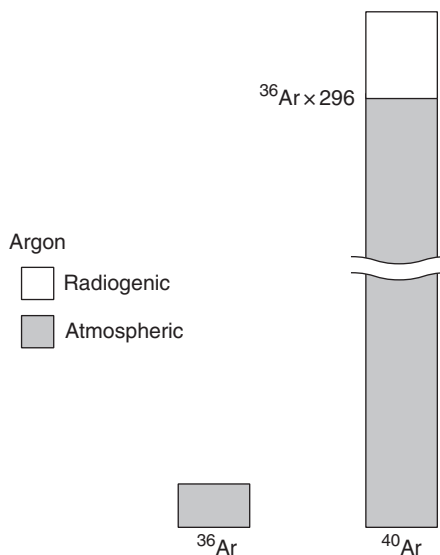


Figure 4.6

Correction of the atmospheric argon contribution to mass 40. The $^{40}\text{Ar}/^{36}\text{Ar}$ ratio in the atmosphere being invariably constant and equal to 296, radiogenic ^{40}Ar is inferred by the difference between total ^{40}Ar and $296 \times ^{36}\text{Ar}$.

of rocks in the chapter on diffusion, that this chronometer also provides a measure of post-orogenic cooling rates and rates of exhumation of mountain ranges. Applications in other fields find it difficult to compete with other methods, notably U–Pb on zircons.

An important and widely used variant of the standard ^{40}K – ^{40}Ar method involves irradiating the sample in a nuclear reactor with fast neutrons (energy > 1 MeV) to produce the reaction $^{39}\text{K} + n \Rightarrow ^{39}\text{Ar} + p$. It is here not ^{40}K , but the ^{39}Ar produced in the reaction that is measured. Accordingly, this is termed the ^{39}Ar – ^{40}Ar method, which replaces the separate measurement of two isotopes of two different elements, ^{40}K and ^{40}Ar , with a precise measurement of the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio of two isotopes of argon. A control sample of known age (monitor), irradiated at the same time, provides a measure of the yield of the reaction and thus allows the age of the samples to be determined by cross-calibration with the standard. This method, combined with progressive extraction of argon from the irradiated sample, has several advantages, described in more specialized texts (e.g. McDougall and Harrison, 1999), including the identification of possible argon losses after the formation of minerals.

4.2.2 Dating zircons by the uranium–lead method

This method is the Ferrari of geochronology for long geological time scales; it is precise and resistant against disturbances occurring after closure of the system, but difficult to implement. In recent years, its development has considerably benefited

from the improved cleanliness of chemical extractions and *in situ* methods of analysis (secondary ion mass spectrometry and laser-ablation inductively coupled plasma mass spectrometry, ICP-MS). The advantage of the method lies in the radioactive (^{238}U and ^{235}U) and radiogenic nuclides (^{206}Pb and ^{207}Pb) being isotopes of the same elements: uranium for one and lead for the other. In the absence of any initial radiogenic lead, (4.13) applied to the systems ^{238}U – ^{206}Pb ($\lambda_{238\text{U}} = 0.155\ 125 \times 10^{-9} \text{ y}^{-1}$) and ^{235}U – ^{207}Pb ($\lambda_{235\text{U}} = 0.984\ 85 \times 10^{-9} \text{ y}^{-1}$) gives:

$$\begin{aligned} \left(\frac{^{206}\text{Pb}}{^{238}\text{U}}\right)_t &= e^{\lambda_{238\text{U}}t} - 1 \\ \left(\frac{^{207}\text{Pb}}{^{235}\text{U}}\right)_t &= e^{\lambda_{235\text{U}}t} - 1 \end{aligned} \quad (4.26)$$

This double clock is routinely applied to the radiogenic lead and uranium of an accessory, but common, zirconium silicate of granite and metamorphic rocks, zircon (ZrSiO_4). Uranium U^{4+} substitutes in large quantities for Zr^{4+} ; but Pb^{2+} , which is of very different ionic radius (0.133 nm) and charge from Zr^{4+} (0.084 nm), is essentially excluded at equilibrium. As with atmospheric argon, there may nonetheless be contamination by lead at mineral surfaces or in grain fractures. Because of the presence in the atmosphere of tetraethyl lead, used until the 1990s as an anti-knocking agent in fuel, man-made pollution may also be significant. A very similar technique to that described for argon is employed, involving subtraction from the total lead content of the contaminated lead, whose isotopic composition is relatively well known by using a stable isotope ^{204}Pb . *In situ* isotopic analysis using modern ion probes also allows the zones for analysis to be selected so that contamination is almost completely eliminated.

The pair of equations in (4.26) defines the locus of points for which the ages indicated by both methods concur, the locus being traditionally called concordia proposed by Wetherill in 1956. This concordia flattens out toward older ages (Fig. 4.7), as ^{235}U decays much more rapidly than ^{238}U : natural uranium today contains only 0.7% ^{235}U compared with 8% ^{235}U three billion years ago. Although methods were developed to attempt to correct the effect of disagreement related to losses of lead after closure of the system, they are now of little value because of the improvement in techniques. The ratio of the x -axis to the y -axis is proportional to the isotope ratio $^{206}\text{Pb}/^{207}\text{Pb}$:

$$\frac{(^{206}\text{Pb}/^{238}\text{U})_t}{(^{207}\text{Pb}/^{235}\text{U})_t} = \frac{1}{(^{207}\text{Pb}/^{206}\text{Pb})_t} \times \frac{1}{(^{238}\text{U}/^{235}\text{U})_t} \quad (4.27)$$

The second term on the right-hand side is constant and equal to 1/137.88. The denominators of the ratios plotted on the x - and y -axes are therefore proportional and their ratio $^{238}\text{U}/^{235}\text{U}$ is constant. It follows from the discussion of ratio behavior during mixing, presented earlier (Fig. 2.4), that mixtures of zircons or overgrowth will be reflected by alignments in the concordia plot: the intercepts of these alignments with the concordia will therefore a priori yield interesting ages.

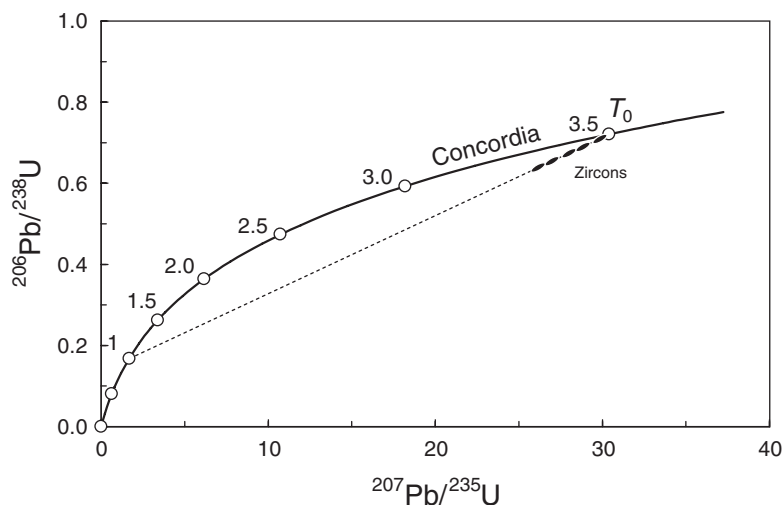


Figure 4.7

The concordia curve is the locus of points for which the x - and y -axes yield identical ages for both the ^{235}U – ^{207}Pb and ^{238}U – ^{206}Pb methods. The numbers 1, 2.0, 2.5, etc., on the curve correspond to geological ages of 1, 2.0, 2.5, etc., billions of years. Zircons extracted from a single sample, and shown here by the black ellipses, indicate an age T_0 of crystallization of 3.5 Ga, with 1.0 Ga old overgrowth. The dashed lined is a mixing line between the two zircon generations.

4.3 The isochron method

When minerals and rocks form, they already contain some of the radiogenic isotopes used for dating. The daughter nuclide may be present in large, yet unknown, concentrations. The isochron method was devised to provide an age, even when the amount of radiogenic isotope initially present in the system is not negligible with respect to that produced by radioactive decay after its formation. The key assumption is that the initial isotopic composition of the element to which the radiogenic nuclide belongs is unknown, but constant, in all the samples analyzed. Isotopic homogenization is assumed to be complete at $t = 0$, which may be the case where minerals crystallize from a magma or from seawater within a time interval that can be considered as very short compared to the age of the rocks. A large number of geochronological systems are used in this way: ^{87}Rb – ^{87}Sr , ^{147}Sm – ^{143}Nd , ^{176}Lu – ^{176}Hf , and ^{187}Re – ^{187}Os are examples (note that chronological systems are denoted by hyphenating the parent and daughter isotopes in the order P – D). In addition to the chronological aspect, the variations in the isotopic abundances of radiogenic isotopes are useful in studying many geological processes. Let us take as an example the ^{147}Sm – ^{143}Nd system, for which the stable reference isotope is usually ^{144}Nd , and in (4.13) replace P with ^{147}Sm , D with ^{143}Nd , and D' with ^{144}Nd . For a closed system, the isochron equation becomes:

$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_t = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_0 + \left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}}\right)_t \left(e^{\lambda_{147}\text{Sm}t} - 1\right) \quad (4.28)$$

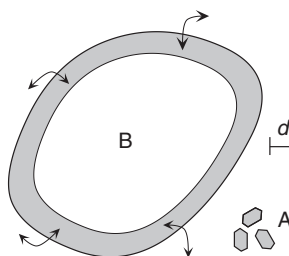


Figure 4.8

Closed system and open system. If we imagine that during a metamorphic perturbation an element has moved an average distance d , small systems (minerals A) will be “opened” much more intensely than large ones (large sample B), where only the outer skin will have exchanged with the ambient medium. The shaded area represents the material involved in exchange outside the system.

Samples, for example basalts extracted from a single source in the mantle, that formed at t with the same $(^{143}\text{Nd}/^{144}\text{Nd})_0$ ratio but with different $^{147}\text{Sm}/^{144}\text{Nd}$ ratios, presumably by different degrees of melting, will form an alignment known as the isochron (Fig. 4.3), whose slope gives the age of formation. It is commonly held that, for the isochron to be valid, the rocks must be “co-genetic” and the initial isotopic homogeneity must be perfect. However, as a result of improved analytical techniques and instrumentation, there is always an achievable level of precision for which the assumption of initial isotopic homogeneity breaks down. A less conservative, but more realistic, statement is that the initial isotopic variability must remain negligible compared with that related to the accumulation of radiogenic nuclides: this explains why isochrons of old age, such as those obtained from meteorites or lunar rocks, “look” better than those from recent granites, or why isochrons of reasonable age can be obtained from samples that are not necessarily taken from a homogeneous medium, such as sedimentary sample suites.

Let us look at the problem of how the isochron withstands subsequent perturbations of the closed-system regime. Let us imagine, for example, a series of basalts formed from a single mantle source in Archean time, some 2.7 billion years ago, and subjected to intense thermal perturbation when, caught up in the formation of a mountain belt some 600 million years ago, they were transported to great depth and raised to temperatures of the order of 600–800 °C. Such metamorphism will create new minerals in basaltic rocks, probably an assemblage of pyroxene and garnet known as eclogite. Suppose that a mean distance d can be defined over which the elements Sm and Nd migrate in the course of metamorphic recrystallization, ranging probably from a few millimeters to a few centimeters (Fig. 4.8). If our sample is very much smaller than d , we can presume that the exchanges of Sm and Nd are complete and that the minerals, normally of very small size, will all have adopted the ambient Nd isotopic composition, i.e. that of the rock at this location. If the sample size is much greater than d , only the outer part over a depth d will have engaged in exchange with the exterior. The interior will have been disturbed, but the exchanges will have remained confined within the sample. If this open fringe represents only a small volume compared with the bulk of the sample, it will be considered that the sample has not been affected by the disturbance.

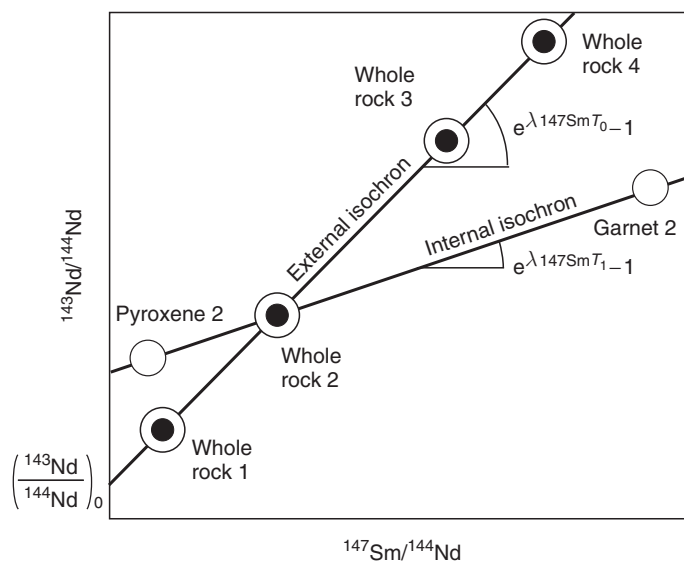


Figure 4.9

During a metamorphic event, large samples (whole rock) will remain virtually closed (see Fig. 4.8) and the “external” isochron will record the age T_0 of rock formation. However, the minerals of rock 2 (pyroxene, garnet) will have exchanged their isotopes and their $^{143}\text{Nd}/^{144}\text{Nd}$ isotope ratios will be in equilibrium with that of the mean ambient value, i.e. that of the rock. The “internal” isochron therefore gives the age T_1 of the disturbance.

This pattern of exchange suggests the sampling strategy (Fig. 4.9). To determine the age of any metamorphic perturbation, the minerals of a rock are separated, here garnet and pyroxene, whose small size ensures that they will have been returned to isotopic equilibrium during metamorphism. The age indicated by what is termed the internal (or mineral) isochron will be that of the metamorphic event. Conversely, to obtain the age of formation of the rock, the largest possible samples must be taken so as to minimize the effect of exchanges with the exterior. The whole rock isochron will be obtained from small fractions of large samples that have been thoroughly ground and mixed.

There are many methods of dating using isochrons. Historically, ^{87}Rb – ^{87}Sr chronology has yielded many ages for the emplacement of granites, whereas the dating of white mica (muscovite) or black mica (biotite), whose high $^{87}\text{Rb}/^{86}\text{Sr}$ ratio ensures good age precision, have dominated metamorphic geochronology alongside ^{40}K – ^{40}Ar ages. The mobility of rubidium, an alkali element, and of strontium, an alkaline-earth element, in metamorphic and hydrothermal fluids unfortunately often disturbs this chronometer. ^{147}Sm – ^{143}Nd chronology is valuable for dating old basaltic rocks. Samarium and neodymium, two of the rare-earths, are much less mobile, but the method has also been known to go awry. Dating high-temperature and high-pressure metamorphism, especially with pyroxene–garnet internal isochrons, has yielded good results by this method, as has, more recently, the ^{176}Lu – ^{176}Hf system. Dating of basaltic rocks and peridotites, but also of sulfide ore deposits and petroleum by the ^{187}Re – ^{187}Os method, two highly siderophile elements, has also proved to be very successful.

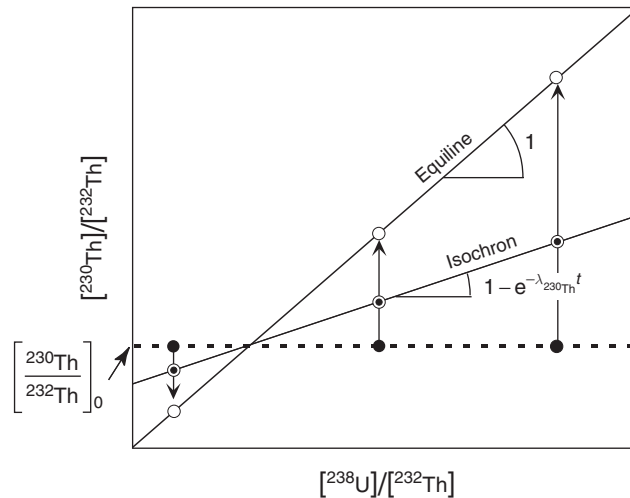


Figure 4.10 The U-Th isochron. Samples derived from the same sedimentary or magmatic reservoir initially have the same $[^{230}\text{Th}/^{232}\text{Th}]$ isotope ratio but different U/Th ratios. They line up first on a horizontal line and then migrate progressively toward the equiline, which is the stable state of secular equilibrium. Square brackets indicate activity.

A first special application of the isochron method is that of the ^{230}Th dating method, which is especially useful for recent volcanic rocks. If we re-write (4.24) by allowing for the definition of excess ^{230}Th and if we then divide both sides by the activity of the thorium-232 isotope (which decays slowly enough for this activity to be considered constant), we obtain:

$$\left(\frac{[^{230}\text{Th}]}{[^{232}\text{Th}]}\right)_t = \left(\frac{[^{230}\text{Th}]}{[^{232}\text{Th}]}\right)_0 e^{-\lambda_{230\text{Th}}t} + \left(\frac{[^{238}\text{U}]}{[^{232}\text{Th}]}\right)_t (1 - e^{-\lambda_{230\text{Th}}t}) \quad (4.29)$$

The right-hand side is the sum of two terms, which we will meet many times: the first term expresses the demise of the initial condition, while the second term describes how fast the system is moving towards steady state. It can be seen from an isochron plot $x = [^{238}\text{U}]/[^{232}\text{Th}]$, $y = [^{230}\text{Th}]/[^{232}\text{Th}]$ (Fig. 4.10) that samples formed at $t = 0$ with the same $[^{230}\text{Th}]/[^{232}\text{Th}]_0$ ratio will lie on a horizontal line. With time the alignment pivots around the point of intersection with the line $y = x$, known as the equiline, until its slope becomes unity: at this point, the system is in secular equilibrium ($[^{230}\text{Th}] = [^{238}\text{U}]$, see above). The slope of the alignment gives an age, at least as long as we are far from equilibrium. This method is often applied to minerals extracted from lavas to date their crystallization. It can only be applied for ages of less than 350,000 years.

A second special application is that of the lead-lead method. By utilizing the stable lead isotope of mass 204, the two equations of the isochron can be written:

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_t - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_0 = \left(\frac{^{238}\text{U}}{^{204}\text{Pb}}\right)_t (e^{\lambda_{238\text{U}}t} - 1) \quad (4.30)$$

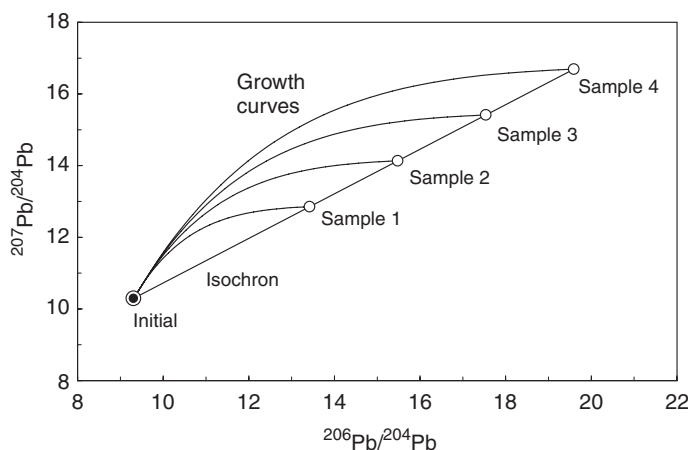


Figure 4.11 $^{206}\text{Pb}/^{204}\text{Pb}$ and $^{207}\text{Pb}/^{204}\text{Pb}$ ratios of samples formed with the same initial isotopic composition of lead but different U/Pb ratios evolve along growth curves so that the isotopic ratios remain on an isochron with a slope indicative of the age of formation.

$$\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_t - \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_0 = \left(\frac{^{235}\text{U}}{^{204}\text{Pb}}\right)_t (e^{\lambda_{235}\text{U}t} - 1) \quad (4.31)$$

By dividing (4.31) by (4.30), we obtain:

$$\frac{(\frac{^{207}\text{Pb}}{^{204}\text{Pb}})_t - (\frac{^{207}\text{Pb}}{^{204}\text{Pb}})_0}{(\frac{^{206}\text{Pb}}{^{204}\text{Pb}})_t - (\frac{^{206}\text{Pb}}{^{204}\text{Pb}})_0} = \left(\frac{^{235}\text{U}}{^{238}\text{U}}\right)_t \frac{e^{\lambda_{235}\text{U}t} - 1}{e^{\lambda_{238}\text{U}t} - 1} \quad (4.32)$$

Because the present ratio $^{235}\text{U}/^{238}\text{U}$ is a constant equal to 1/137.88, (4.32) can be recast as $(y - y_0)/(x - x_0) = m$. In a plot $x = (^{206}\text{Pb}/^{204}\text{Pb})_t$, $y = (^{207}\text{Pb}/^{204}\text{Pb})_t$ (Fig. 4.11), (4.32) describes an isochron straight line going through the point of coordinates (x_0, y_0) and with slope m . The advantage of this method is that it requires only the isotope ratios of lead to be determined and not the concentrations, in particular that of uranium which is commonly strongly affected by water circulation in the water table and by weathering. For this reason, this method was commonly used for dating all sorts of sedimentary and magmatic rocks until superseded by zircon geochronology. It will be seen that this was the first method ever to yield the age of the Solar System and it is still widely used to date meteorites and planetary samples.

4.4 Radiogenic tracers

The property that phase separation, such as melting and crystallization, fractionates parent/daughter ratios has received enormous attention and created the fertile concept of radiogenic tracers. We have previously discussed the point that phase change does not fractionate the normalized isotopic ratios themselves, a common source of confusion.

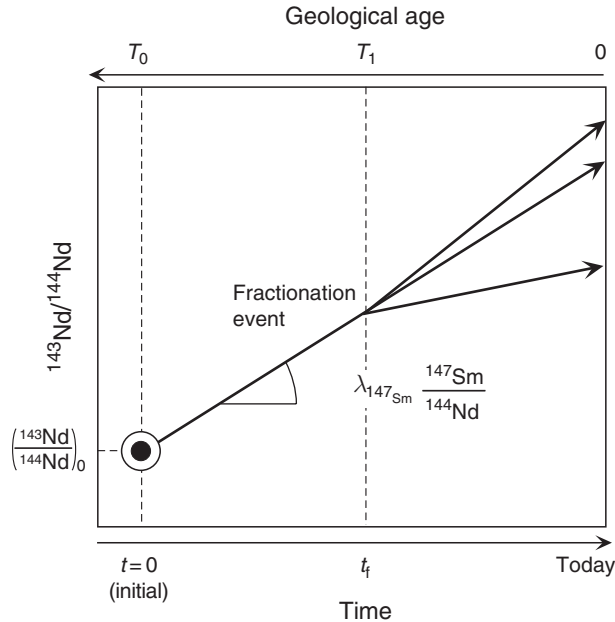


Figure 4.12 Evolution of the $^{143}\text{Nd}/^{144}\text{Nd}$ isotopic ratio by radiogenic decay of ^{147}Sm . This ratio changes almost linearly with time t and the slope of the evolution curve indicates the $^{147}\text{Sm}/^{144}\text{Nd}$, and therefore the Sm/Nd ratio, of the system. Magmatic, sedimentary, or metamorphic events, here represented as occurring at T_1 , may fractionate the Sm/Nd ratio of various sub-systems.

The initial isotopic ratios $(D/D')_0$ obtained as intercepts of isochrons were once a by-product of geochronology. These ratios, which describe the values of $^{87}\text{Sr}/^{86}\text{Sr}$, $^{143}\text{Nd}/^{144}\text{Nd}$, $^{176}\text{Hf}/^{177}\text{Hf}$, etc., at the time the rocks formed, have become, together with the isotopic ratios measured in modern samples, a prime source of geochemical information about parent/daughter ratios in various geological systems. If (4.28) is considered not as an isochron equation but as expressing a change in the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio versus time (Fig. 4.12), we have a means of evaluating the mean Sm/Nd ratio of the system. Let us recast this equation as:

$$\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_t = \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_0 + \left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}}\right)_0 (1 - e^{-\lambda_{147\text{Sm}}t}) \quad (4.33)$$

The slope of the evolution curve (the so-called growth curve) in Fig. 4.12 is simply obtained by taking the derivative of $1 - e^{-\lambda_{147\text{Sm}}t}$ with respect to t . Because of the very slow decay of ^{147}Sm , the approximation $e^{-\lambda_{147\text{Sm}}t} \approx 1 - \lambda_{147\text{Sm}}t$ holds. This slope is very nearly equal to $\lambda_{147\text{Sm}}(^{147}\text{Sm}/^{144}\text{Nd})_0$. Upon division by the appropriate isotopic abundance factors (here 0.15/0.24) and multiplication by the ratio of atomic masses of the two elements (150.4/144.2), the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio can be converted into a Sm/Nd weight ratio.

Let us first use the chronometric equation to infer the mean “time-integrated” parent/daughter ratio that apparently prevailed during the entire history of a particular sample, from the Earth formed to the sample as part of the modern world. The initial $^{143}\text{Nd}/^{144}\text{Nd}$

ratio of the Solar System is known, typically from meteorite work. The mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio prevailing as the system evolved can be deduced from (4.33):

$$\left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}}\right)_0 \approx \frac{1}{\lambda_{^{147}\text{Sm}} t} \left[\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_{\text{today}} - \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}}\right)_{\text{initial}} \right] \quad (4.34)$$

Let us first deduce the time-integrated $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the source of different samples from their $^{143}\text{Nd}/^{144}\text{Nd}$ values. Let us pick up a basalt from the East Pacific Rise (0.5131) and a clay mud collected from the mouth of the Amazon (0.5108). The basalt source is the upper mantle, whereas the clay is derived from erosion of South American continental crust. Equation (4.34) can therefore be used to calculate the mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the upper mantle and that of the continental crust from the beginning of the Earth's history. Of course, these are virtual ratios, as the crust and mantle have complex histories that cannot be fully captured by a single parameter, but they give us useful information about the nature of the fractionation processes that have affected these geological units. Meteorite studies tell us that at the time the Solar System formed 4.56 billion years ago, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio was 0.5067. The mean $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the mantle in which the neodymium evolved before passing into the basalt was therefore:

$$\left(\frac{^{147}\text{Sm}}{^{144}\text{Nd}}\right)_{\text{mantle}} = \frac{0.5131 - 0.5067}{(6.54 \times 10^{-12}) \times (4.56 \times 10^9)} = 0.215$$

For the continent that was the source of the clay, this calculation gives a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.138.

Similar calculations can be made for the ^{87}Rb – ^{87}Sr and U–Pb systems. Let us assume that the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio is 0.7023 for the basalt and 0.7140 for the clay, i.e. that this increases when $^{143}\text{Nd}/^{144}\text{Nd}$ decreases. Using equations similar to those we just derived for Nd and a chondritic initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.6992, the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio turns out to be 0.046 for the upper-mantle and 0.22 for the continental-crust source of the clay. For lead, the linear approximation would have to be abandoned, which raises no serious problem.

The Sm/Nd, Rb/Sr, and U/Pb ratios therefore differ between the continental crust and the upper mantle, so that the more incompatible element of each pair (Nd, Rb, and U) is more concentrated in the crust than the corresponding more compatible element (Sm, Sr, and Pb). A process capable of fractionating these ratios as the continental crust forms must therefore be imagined, for example, melting followed by selective extraction of magmas.

By plotting on an isochron diagram the present-day $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ ratios of any rock sample of continental crust and those of the average upper mantle (the mid-ocean ridge basalt source, see Chapter 12), a theoretical age T_{Nd} can be defined at which this particular piece of continental crust could have separated from the upper mantle. This age, usually referred to as the Nd model age of this particular crustal sample, is obtained by writing (4.34) once for the rock and once for the upper mantle, and by eliminating the $^{143}\text{Nd}/^{144}\text{Nd}_0$ ratio between the two expressions:

Table 4.2 Solid/melt fractionation of the parent and daughter nuclides of common systems and its effect on the long-term evolution of the isotope composition of the daughter element

Parent–Daughter	Parent/daughter ratio*		Daughter element*	
	In melt	In residue	In melt	In residue
^{87}Rb – ^{87}Sr	Higher	Lower	More radiogenic	Less radiogenic
^{147}Sm – ^{143}Nd	Lower	Higher	Less radiogenic	More radiogenic
^{176}Lu – ^{176}Hf	Lower	Higher	Less radiogenic	More radiogenic
^{187}Re – ^{187}Os	Higher	Lower	More radiogenic	Less radiogenic
^{232}Th – ^{208}Pb	Higher	Lower	More radiogenic	Less radiogenic
^{238}U – ^{206}Pb	Higher	Lower	More radiogenic	Less radiogenic

*With respect to source material

$$T_{\text{Nd}} = \frac{1}{\lambda_{^{147}\text{Sm}}} \times \frac{(^{143}\text{Nd}/^{144}\text{Nd})_{\text{rock}} - (^{143}\text{Nd}/^{144}\text{Nd})_{\text{mantle}}}{(^{147}\text{Sm}/^{144}\text{Nd})_{\text{rock}} - (^{147}\text{Sm}/^{144}\text{Nd})_{\text{mantle}}} \quad (4.35)$$

If our Amazon mud has a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.120, a value that is quite representative of the continental crust in general, the model age for local separation of the crust and the upper mantle is therefore:

$$T_{\text{Nd}} = \frac{1}{0.654 \times 10^{-12}} \times \frac{0.5108 - 0.5131}{0.120 - 0.215} = 3.7 \times 10^9 \text{ years}$$

Radiogenic isotopes are most commonly utilized, then, for tracing sources, which we will examine in detail later. The principle is that when rock melts, the parent/daughter ratios are affected in a way that depends on the residual mineral assemblage, while the isotopic ratios remain unaffected. Thus, for mantle melting, Sm/Nd and Lu/Hf ratios are higher in the melt residue than in the liquid, while the contrary is true of Rb/Sr, Re/Os, and U–Th/Pb (Table 4.2).

4.5 Helium isotopes

Radiogenic helium ^4He is produced by the decay of the two natural isotopes of uranium (^{238}U and ^{235}U) and of the only long-lived isotope of thorium (^{232}Th). We have seen earlier that these decay processes are in fact the start of a chain of events. For example, in order to pass from ^{238}U to its distant descendant ^{206}Pb , the initial nuclide must lose $(238-206)/4 = 8 \alpha$ particles, which, by capture of the rock matrix electrons torn off during particle

expulsion, become that number of ^4He atoms. The only stable reference isotope is ^3He . The growth equation of the $^4\text{He}/^3\text{He}$ isotope ratio is therefore:

$$\begin{aligned} \left(\frac{^4\text{He}}{^3\text{He}}\right)_t &= \left(\frac{^4\text{He}}{^3\text{He}}\right)_0 + 8 \left(\frac{^{238}\text{U}}{^3\text{He}}\right)_0 \left(1 - e^{-\lambda_{238\text{U}}t}\right) \\ &\quad + 7 \left(\frac{^{235}\text{U}}{^3\text{He}}\right)_0 \left(1 - e^{-\lambda_{235\text{U}}t}\right) + 6 \left(\frac{^{232}\text{Th}}{^3\text{He}}\right)_0 \left(1 - e^{-\lambda_{232\text{Th}}t}\right) \end{aligned} \quad (4.36)$$

which can be rearranged as:

$$\begin{aligned} \left(\frac{^4\text{He}}{^3\text{He}}\right)_t &= \left(\frac{^4\text{He}}{^3\text{He}}\right)_0 + \left(\frac{^{238}\text{U}}{^3\text{He}}\right)_0 \left(1 - e^{-\lambda_{238\text{U}}t}\right) \\ &\quad \times \left[8 + 7 \left(\frac{^{235}\text{U}}{^{238}\text{U}}\right)_0 \frac{1 - e^{-\lambda_{235\text{U}}t}}{1 - e^{-\lambda_{238\text{U}}t}} + 6 \left(\frac{^{232}\text{Th}}{^{238}\text{U}}\right)_0 \frac{1 - e^{-\lambda_{232\text{Th}}t}}{1 - e^{-\lambda_{238\text{U}}t}} \right] \end{aligned} \quad (4.37)$$

At a given point in time $(^{235}\text{U}/^{238}\text{U})_0$ is a constant, while $(^{232}\text{Th}/^{238}\text{U})_0$ is indistinguishable from the nearly invariant Th/U ratio. The last expression therefore shows that $^4\text{He}/^3\text{He}$ essentially reflects the evolution of the ratio of the incompatible refractory isotope ^{238}U to the volatile stable isotope ^3He in the system. The isotope geochemistry of helium is an incomparable tool for investigating the outgassing of the mantle and also to model water circulation in aquifers. Note that, by force of habit, many geochemists continue to use the inverse $^3\text{He}/^4\text{He}$ ratios standardized to the value for atmospheric helium (1.4×10^{-6}) instead of the $^4\text{He}/^3\text{He}$ ratios.

Exercises

1. What is the proportion of radiogenic $^{40}\text{Ar}^*$ in the total ^{40}Ar of a sample with a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of (1) 50 000 (2) 2000 (3) 300? If the total ^{40}Ar content is known to within 1%, what do you expect for the precision on the concentration of radiogenic $^{40}\text{Ar}^*$ in each case? Assume that atmospheric argon has a $^{40}\text{Ar}/^{36}\text{Ar}$ ratio of ≈ 296 .
2. Calculate the age of a basalt containing 1.7 wt% K_2O and $6.0 \times 10^{-11} \text{ mol g}^{-1} \text{ } ^{40}\text{Ar}$. Assume that the atomic proportion of ^{40}K in natural potassium is 0.0117 %.
3. Two samples are irradiated with fast neutrons in the same vial. The K–Ar age of one of them (the monitor) is known. It is observed that some of the ^{39}K of the samples is transformed into ^{39}Ar . Using the monitor to assess the yield of the nuclear reaction, devise a method to infer the K–Ar age of the unknown sample from the age of the monitor and the $^{40}\text{Ar}^*/^{39}\text{Ar}$ ratios of the sample and the monitor (* labels radiogenic argon).
4. A famous Rb–Sr isochron work: the Baltimore gneiss (Wetherill *et al.*, 1968). Draw the whole-rock (WR) $^{87}\text{Sr}/^{86}\text{Sr}$ vs. $^{87}\text{Rb}/^{86}\text{Sr}$ and the biotite–whole-rock isochrons for

Table 4.3 Rb–Sr isotopic data for the Baltimore gneiss, Maryland (Wetherill *et al.*, 1968)

Sample		$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
B105	WR	2.244	0.738
B20C	WR	3.642	0.7612
B20	WR	3.628	0.7573
	biotite	116.4	1.2146
B41	WR	6.59	0.7992
	biotite	289.7	1.969
B4	WR	0.2313	0.7074

Table 4.4 Sm–Nd isotopic data for Apollo 17 basalt 75075 (Lugmair *et al.*, 1975)

	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Sm}/^{144}\text{Nd}$
Plagioclase	0.1942	0.51300
Ilmenite	0.2416	0.51417
Whole-rock	0.2566	0.51454
Pyroxene	0.2930	0.51542

the following samples (Table 4.3). Infer the emplacement age and the perturbation age of these rocks.

- The Sm–Nd dating of Apollo 17 basalt 75075 (Lugmair *et al.*, 1975). Plot the results of Table 4.4 in a $^{143}\text{Sm}/^{144}\text{Nd}$ vs. $^{147}\text{Sm}/^{144}\text{Nd}$ isochron diagram, draw the internal (mineral) isochron and determine the eruption age of this basalt ($\lambda_{^{147}\text{Sm}} = 0.654 \times 10^{-11} \text{ a}^{-1}$).
- ^{176}Lu – ^{176}Hf dating of Birimian basalts from Burkina Faso (Blichert-Toft *et al.*, 1999). Plot the results of Table 4.5 in a $^{176}\text{Hf}/^{177}\text{Hf}$ vs. $^{176}\text{Lu}/^{177}\text{Hf}$ isochron diagram, draw the external (whole-rock) isochron and determine the emplacement age of these basalts ($\lambda_{^{176}\text{Lu}} = 1.865 \times 10^{-11} \text{ a}^{-1}$). Do you think these basalts were erupted with the same $^{176}\text{Hf}/^{177}\text{Hf}$ initial value? If not, why do you think the isochron looks so good?
- Write the master equation for the ^{187}Re – ^{187}Os isochron using ^{188}Os as the stable reference isotope.
- Introducing ^{40}K – ^{40}Ca dating: the Pikes Peak granite (Wyoming). What are the respective probabilities that ^{40}K decays into ^{40}Ca and ^{40}Ar ? What is the isochron equation of the ^{40}K – ^{40}Ca system if one uses the stable isotope ^{42}Ca as the reference? Draw the internal (mineral) isochron for the PP 76-2 sample (Table 4.6). What is the age of the last homogenization of Ca in the Pikes Peak granite?
- Minerals extracted from a basaltic andesite at the Soufrière St. Vincent in the Antilles give the activity ratios listed in Table 4.7. Plot the Th–U isochron diagram and calculate the age of the last Th isotopic homogenization of these minerals.

Table 4.5 Lu–Hf isotopic data for basalts from Burkina Faso

Sample	$^{176}\text{Lu}/^{177}\text{Hf}$	$^{176}\text{Hf}/^{177}\text{Hf}$
B44	0.0325	0.282976
B47B	0.0331	0.282992
B46	0.0209	0.282461
BN75	0.0224	0.282515
BN11A	0.0352	0.283011
BN208A	0.0667	0.284325
BN209A	0.0848	0.285037
BN263A	0.0469	0.283458
BN280B	0.0652	0.284246

Table 4.6 K–Ca isotopic data for Pikes Peak sample PP 76-2 (Marshall and DePaolo, 1982)

	$^{40}\text{K}/^{42}\text{Ca}$	$^{40}\text{Ca}/^{42}\text{Ca}$
Whole-rock	0.1224	151.109
Plagioclase	0.0123	151.040
K-feldspar	0.800	151.577
Biotite	1.294	151.941

Table 4.7 U–Th activity ratios of minerals in a basaltic andesite from the Soufrière St. Vincent in the Antilles (Heath *et al.*, 1998)

	$[\text{}^{238}\text{U}]/[\text{}^{232}\text{Th}]$	$[\text{}^{230}\text{Th}]/[\text{}^{232}\text{Th}]$
Whole-rock	1.253	1.496
Olivine	1.089	1.183
Clinopyroxene	1.145	1.259
Plagioclase	1.136	1.244
Groundmass	1.244	1.450
Magnetic	1.230	1.458

- Determination of the growth rate of a ferromanganese nodule from the excess of ^{230}Th in different layers below the nodule surface. Plot the excesses listed in Table 4.8 in a semi-log diagram. Find the growth rate from the slope of the alignment.
- Dating the oldest terrestrial zircons (Wilde *et al.*, 2001). Table 4.9 lists the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios of four zircons from the Jack Hills conglomerate (Australia).

Table 4.8 $^{230}\text{Th}_{\text{ex}}$ (excess) at different depths in a ferromanganese nodule

Depth z (mm)	$^{230}\text{Th}_{\text{ex}}$
0.0	1242
0.2	788
0.4	488
0.6	285
0.8	180
1.0	119

Table 4.9 U–Pb isotopic data for four old zircons from Jack Hills (Australia)

	$^{206}\text{Pb}/^{238}\text{U}$	$^{207}\text{Pb}/^{235}\text{U}$
1	0.928	69.5
2	0.919	68.2
3	0.965	71.9
4	0.968	74.6

Table 4.10 U–Pb isotopic data for basaltic samples from Mauna Kea, Hawaii

Sample	Pb (ppm)	U (ppm)	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$	$^{208}\text{Pb}/^{204}\text{Pb}$
SR0137-5.98	1.0	0.285	18.43	15.48	37.97
SR0157-6.25	0.593	0.192	18.44	15.48	38.00
SR0346-5.60	1.525	0.211	18.52	15.48	38.10
SR0664-5.10	0.765	0.415	18.55	15.49	38.14
SR0930-15.85	0.521	0.212	18.51	15.49	38.13
SR0967-2.75	0.695	0.319	18.49	15.48	38.11
Canyon Diablo			9.3066	10.293	29.475

Plot the concordia between 4.2 and 4.5 Ga and plot the Jack Hills data on the same diagram. What is the probable age of these zircons?

12. A rather difficult one! In the mid 1960s, it was proposed that an independent age of the Earth could be derived from the Pb isotope compositions of modern basalts, but this idea later proved to be incorrect. Plot $x = ^{207}\text{Pb}^*/^{235}\text{U}$ and $y = ^{206}\text{Pb}^*/^{238}\text{U}$ of basaltic samples from Mauna Kea, Hawaii, in the concordia diagram. The Pb isotope compositions and the U and Pb concentrations of the samples are provided in Table 4.10. In this context, the * superscript denotes the radiogenic isotopes accumulated since the Earth formed. Suppose that at that time, the Pb isotope composition of the Earth was that

Table 4.11 Pb isotopic data for five meteorites (Patterson, 1956)

Meteorite sample	$^{206}\text{Pb}/^{204}\text{Pb}$	$^{207}\text{Pb}/^{204}\text{Pb}$
Nuevo Laredo	50.28	34.86
Forest City	19.27	15.95
Modoc	19.48	15.76
Henbury	9.55	10.38
Canyon Diablo	9.46	10.34

Table 4.12 Sr isotopic data for six samples of modern shales

Sample	$^{87}\text{Rb}/^{86}\text{Sr}$	$^{87}\text{Sr}/^{86}\text{Sr}$
a	6.2	0.7121
b	2.7	0.7102
c	0.5	0.7083
d	52.5	0.7111
e	13.1	0.7081
f	21.4	0.7096

of the iron sulfide of the Canyon Diablo meteorite. We can safely assume a constant molar weight for Pb (207.2) and U (238.0) and the modern $^{238}\text{U}/^{235}\text{U}$ ratio is 137.8. What is the range of $^{207}\text{Pb}^*/^{206}\text{Pb}^*$ ratios of the mantle source of modern basalts (see Section 11.2)? Why is the age of the upper intercept of the concordia close to the age of the Solar System? Discuss where the pitfall is. (Hint: from the Pb concentrations, calculate the moles of initial ^{204}Pb per mass unit present in each sample and use the Canyon Diablo values to derive the same parameter for the other isotopes).

- Pat's legacy: the age of the Solar System (Patterson, 1956). Lead isotopes were analyzed in the five meteorites listed in Table 4.11. Plot the $^{207}\text{Pb}/^{204}\text{Pb}$ vs. $^{206}\text{Pb}/^{204}\text{Pb}$ ratios. By trial and error, find Clair Patterson's estimate for the age of the last Pb isotopic homogenization of the Solar System as a whole.
- Isochrons improve with age. Table 4.12 lists the Sr isotopic data for six samples of modern shales. Using your favorite spreadsheet or any convenient software, calculate the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios of each sample 100 My, 2700 My, and 4560 My into the future. Plot the isochrons for today and for each of these future dates. Use your software to calculate the slope and the correlation coefficients and discuss the results.
- Isochron or mixing line? A series of modern lavas are speculated to have formed by mixing (hybridization) of mingling basaltic and rhyolitic magmas. Table 4.13 lists the Nd isotopic data of two end-member magmas. Calculate the $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios of hybrid rocks formed by 20–80, 40–60, 60–40, and 80–20 % of

Table 4.13 Nd isotopic data of the basaltic and granitic end-members

	[Nd] (ppm)	$^{147}\text{Sm}/^{144}\text{Nd}$	$^{143}\text{Nd}/^{144}\text{Nd}$
Rhyolite	40	0.11	0.5115
Basalt	15	0.17	0.5128

basalt–rhyolite mixtures. Plot the mixing line with its end-members in the isochron diagram and “age” the samples by 1 Gy and 2 Gy. Calculate the apparent ages of the alignment for 0, 2, and 3 Gy into the future. Devise a strategy to decide whether an alignment in the isochron diagram is a mixing line or a true isochron.

16. Sketch out the evolution of the Bulk Silicate Earth ($^{147}\text{Sm}/^{144}\text{Nd} = 0.1967$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.512638$ today) in a $^{143}\text{Nd}/^{144}\text{Nd}$ vs. t evolution diagram between 2 Ga and the present and the evolution of a crustal rock formed at 2 Ga from the primitive mantle with a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.11. What is the modern ϵ_{Nd} of this rock?
17. Compare the evolution diagram $^{143}\text{Nd}/^{144}\text{Nd}$ vs. t and the isochron diagram $^{143}\text{Nd}/^{144}\text{Nd}$ vs. $^{147}\text{Sm}/^{144}\text{Nd}$. Plot the points representing the modern depleted mantle ($^{147}\text{Sm}/^{144}\text{Nd} = 0.222$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.51312$) and a crustal sample with $^{147}\text{Sm}/^{144}\text{Nd} = 0.12$ and $^{143}\text{Nd}/^{144}\text{Nd} = 0.5111$. First, find graphically in each diagram the model age at which the protolith of this crustal sample was extracted from the depleted mantle. Second, derive a common expression that will let you calculate this model age with precision.

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