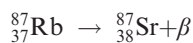


is the basis of isotopic age determinations involving such element pairs as Rb–Sr, U–Pb, and K–Ar. The first element of each of these pairs has an isotope (or isotopes) that decays to an isotope of the second. Rubidium has two isotopes  $^{85}\text{Rb}$  and  $^{87}\text{Rb}$ ; the first is stable, but  $^{87}\text{Rb}$  decays to  $^{87}\text{Sr}$ , which is just one of four stable isotopes of strontium, the others being  $^{88}\text{Sr}$ ,  $^{86}\text{Sr}$ , and  $^{84}\text{Sr}$ . Uranium has several isotopes, two of which,  $^{238}\text{U}$  and  $^{235}\text{U}$ , decay to  $^{206}\text{Pb}$  and  $^{207}\text{Pb}$ , respectively. Potassium has three isotopes,  $^{39}\text{K}$ ,  $^{40}\text{K}$ , and  $^{41}\text{K}$ , but only  $^{40}\text{K}$  is unstable. It, however, can decay in two ways, either to  $^{40}\text{Ca}$  or to  $^{40}\text{Ar}$ . Each of these reactions involves a change in the nucleus of the parent isotope, but in each case, the way in which this takes place is different.

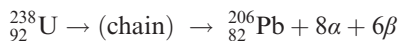
A nucleus can change by radioactive decay in four different ways. One is by emitting a particle consisting of two neutrons and two protons from the nucleus. This group of four nuclear particles is equivalent to a helium nucleus and is known as an *alpha particle* ( $\alpha$ ). It is the source of much of the helium in the Earth. The alpha particle has an atomic mass of 4 and a charge of +2. Another mode of decay involves the emission of an electron from the nucleus. This electron, which is known as a *beta particle* ( $\beta$ ), is formed when a neutron in the nucleus changes into a proton.  $\beta$  particles have negligible mass. A third type of decay involves the capture of an electron by the nucleus where it combines with a proton to form a neutron. This decay process is known as *electron capture* (ec). The fourth mode affects only uranium and thorium, and involves the *spontaneous fission* of the nucleus into two nuclei of approximately equal mass.

Let us consider what changes must take place in the nucleus of  $^{87}_{37}\text{Rb}$  for it to change to  $^{87}_{38}\text{Sr}$ . The superscripts here refer to the atomic mass of the *isotope*, and the subscripts refer to the atomic number of the *element*. The atomic number is the number of protons in the nucleus, which defines that element. Because the atomic masses of  $^{87}\text{Rb}$  and  $^{87}\text{Sr}$  are the same, the decay process cannot involve  $\alpha$  particles. The change, instead, involves an increase by one in the number of protons. This can be achieved only by a neutron changing into a proton, which requires that a  $\beta$  particle be emitted from the nucleus. The reaction can be written as

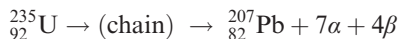


The decay of uranium isotopes to those of lead is more complicated than that of rubidium to strontium. Both  $^{238}\text{U}$  and  $^{235}\text{U}$  decay in a long chain of reactions involving intermediate radioactive isotopes of the elements Po, Th, Ra, Pa, Bi, At, Ac, Rn, Fr, and Tl. Some of these isotopes require thousands of years to decay, whereas others last only fractions of a second. Despite the complexity of the chain reactions, the overall nuclear reactions can be written easily. The decay of  $^{238}_{92}\text{U}$  to  $^{206}_{82}\text{Pb}$  involves a mass loss of 32, which indicates that 8  $\alpha$  particles must be emitted. Because each  $\alpha$  particle has a charge of +2, the loss of 8  $\alpha$  particles would cause the charge on the nucleus to drop to 76, but it only decreases to 82, the atomic number of lead. Consequently, the

loss of 8  $\alpha$  particles must be accompanied by the emission of 6  $\beta$  particles. The overall reaction can then be written as

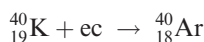


In a similar way the decay of  $^{235}_{92}\text{U}$  can be written as

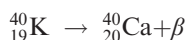


Although the overall decay scheme from U to Pb is used for dating rocks, the abundance and decay of some of the intermediate members of the series, such as thorium and radium, are used to study relatively short-lived processes in magma chambers. This topic is discussed in Section 15.3.

The decay of  $^{40}_{19}\text{K}$  to  $^{40}_{18}\text{Ar}$  and  $^{40}_{20}\text{Ca}$  involves no change in mass and so cannot involve  $\alpha$  particles. The charge on the nucleus decreases by one when  $^{40}_{19}\text{K}$  changes to  $^{40}_{18}\text{Ar}$  so an electron must be captured by the nucleus, where it combines with a proton to form a neutron. The reaction can be written as



The decay of  $^{40}_{19}\text{K}$  to  $^{40}_{20}\text{Ca}$ , on the other hand, involves an increase in the nuclear charge and must therefore involve emission of a  $\beta$  particle. The reaction is



Of these three decay processes, only the emission of  $\alpha$  particles has any significant effect on the material surrounding the decaying atom. Where this material is pleochroic, the bombardment by  $\alpha$  particles affects the way in which light is absorbed. The result is a darkened region around the radioactive source that is known as a *pleochroic halo* (Fig. 13.1 (A)). With time, pleochroic haloes grow more intense. Unfortunately, there are too many variables to make halo intensity a reliable means of determining absolute ages.

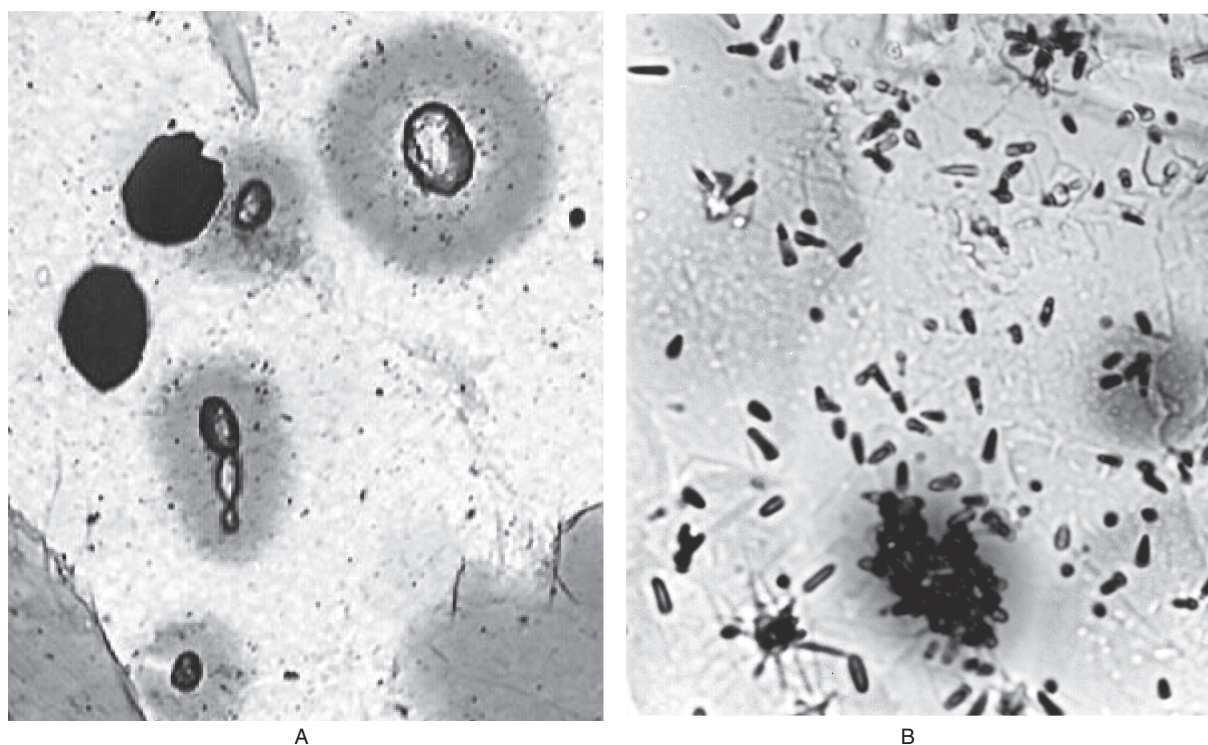
Having far greater effect on the surroundings than  $\alpha$  particles are particles given off by the spontaneous fission of  $^{238}\text{U}$  and to a very much smaller extent of  $^{235}\text{U}$  and of  $^{232}\text{Th}$ . These heavy nuclei split into two nuclei of approximately equal mass and liberate ~200 MeV of energy. Following fission, the two nuclei recoil in opposite directions from each other, and as they pass through the surrounding mineral, they damage its structure, leaving a *fission track* (Fig. 13.1(B)). Although these damaged zones are so small that they are visible only in the electron microscope, etching of polished surfaces can highlight and enlarge them to the point that they are readily visible in a normal optical microscope. The older a mineral is, the more fission tracks it will contain for a given content of  $^{238}\text{U}$ , and on this is based the fission track method of absolute dating.

### 13.3 RATE OF RADIOACTIVE DECAY

All radioactive decay, whether involving  $\alpha$  particles,  $\beta$  particles, electron capture, or fission is a statistical process; the more atoms present of the radioactive nuclide, the more

Table 13.1 Radioactive decay schemes and constants

Radioactive isotope	Daughter isotope	Type of decay	Decay constant ( $\text{a}^{-1}$ )	Half-life $t_{1/2}$ (a)
$^{14}_6\text{C}$	$^{14}_7\text{N}$	$\beta$	$1.21 \times 10^{-4}$	5730
$^{40}_{19}\text{K}$	$^{40}_{20}\text{Ca}, ^{40}_{18}\text{Ar}$	$\beta, \text{ec}$	$5.543 \times 10^{-10}$	$1.25 \times 10^9$
$^{87}_{37}\text{Rb}$	$^{87}_{38}\text{Sr}$	$\beta$	$1.42 \times 10^{-11}$	$48.8 \times 10^9$
$^{147}_{62}\text{Sm}$	$^{143}_{60}\text{Nd}$	$\alpha$	$6.54 \times 10^{-12}$	$106.0 \times 10^9$
$^{176}_{71}\text{Lu}$	$^{176}_{72}\text{Hf}$	$\beta$	$1.94 \times 10^{-11}$	$35.7 \times 10^9$
$^{182}_{72}\text{Hf}$	$^{182}_{74}\text{W}$	$2\beta$	$7.7 \times 10^{-8}$	$9 \times 10^6$
$^{187}_{75}\text{Re}$	$^{187}_{76}\text{Os}$	$\beta$	$1.666 \times 10^{-11}$	$41.6 \times 10^9$
$^{232}_{90}\text{Th}$	$^{208}_{82}\text{Pb}$	$6\alpha, 4\beta$	$4.9475 \times 10^{-11}$	$13.9 \times 10^9$
$^{235}_{92}\text{U}$	$^{207}_{82}\text{Pb}$	$7\alpha, 4\beta$	$9.8485 \times 10^{-10}$	$0.704 \times 10^9$
$^{238}_{92}\text{U}$	$^{206}_{82}\text{Pb}$	$8\alpha, 6\beta$	$1.55125 \times 10^{-10}$	$4.47 \times 10^9$



**Fig. 13.1** (A) Yellow pleochroic halos surrounding zircon crystals in cordierite. Zircon typically contains small amounts of U and Th, which, on undergoing radioactive decay, affect the structure of the surrounding mineral. Plane light; width of field is 0.3 mm. (B) Fission tracks in biotite, revealed by etching for 20s with concentrated hydrofluoric acid. Individual tracks are formed by single uranium atoms that have spontaneously split into two atoms of approximately equal mass. Clusters of tracks near the bottom of the photograph are associated with a pleochroic halo, at the center of which is a small crystal of zircon. The pleochroic halo near the right of the photograph is beneath the surface, so tracks within it have not been etched. Plane light; width of field is 0.2 mm.

chance a decay has of occurring. This can be expressed mathematically as

$$\text{rate of decay} \propto N \quad (13.1)$$

where  $N$  is the number of atoms present of the radioactive nuclide. According to the nomenclature of chemical reaction rates, such a process is referred to as a *first-order* reaction because the power to which  $N$  is raised in the rate expression is 1. We can write the rate of this process as the change in the number of atoms with time, inserting a minus sign to indicate that the change is negative, that is, decay:

$$\frac{dN}{dt} \propto -N \quad \text{or} \quad \frac{dN}{dt} = -\lambda N \quad (13.2)$$

where the constant of proportionality,  $\lambda$ , is known as the *decay constant*. Typical values of  $\lambda$  range from  $10^{-4} \text{ a}^{-1}$  for the rapid decay of  $^{14}\text{C}$  to  $^{14}\text{N}$ , to  $10^{-12} \text{ a}^{-1}$  for the very slow decay of  $^{147}\text{Sm}$  to  $^{143}\text{Nd}$  (Table 13.1).

Equation (13.2) gives the instantaneous change in the number of atoms with time. If we wish to know the total change in  $N$  over some interval of time, the equation must be integrated:

$$\int_{N=N_0}^{N=N_p} \frac{dN}{N} = -\lambda \int_0^t dt$$

Here  $N_p$  and  $N_0$  are, respectively, the present and original numbers of atoms of the parent nuclide. Integrating yields

$$\ln \frac{N_p}{N_0} = -\lambda t$$

or

$$N_p = N_0 e^{-\lambda t} \quad (13.3)$$

This equation describes how the number of atoms of the parent nuclide decays with time.

For purposes of comparison and illustration, the concept of *half-life* is introduced; that is, the length of time necessary for the number of atoms of a nuclide to decay to one-half the initial number. In this case,  $\frac{1}{2}N_0$  is substituted for  $N_p$  in Eq. (13.3), and then the half-life,  $t_{1/2}$ , is given by

$$t_{1/2} = \frac{0.693}{\lambda} \quad (13.4)$$

Thus the half-life for the decay of  $^{14}\text{C}$  is 5730 a, and for  $^{147}\text{Sm}$  is  $1.06 \times 10^{11}$  a. It is instructive to compare the half-lives given in Table 13.1, keeping in mind that the age of the Earth is  $4.55 \times 10^9$  a. Since the formation of the Earth, approximately half the original  $^{238}\text{U}$  has decayed, but very little  $^{147}\text{Sm}$  has decayed. Isotopes that have a half-life considerably greater than the age of the Earth do not make accurate radiometric clocks, except for very old rocks, because of the analytical uncertainty associated with measuring extremely small amounts of daughter isotope. Conversely, isotopes with very short half-lives can be used for dating only young rocks, because of difficulties in accurately measuring extremely small amounts of parent isotope in old rocks.

Equation (13.3) is of no practical use because we cannot measure  $N_0$ , but we do know that each time a parent nuclide decays, it produces a daughter nuclide. Therefore,  $N_0 = N_p + N_d$ , where  $N_d$  is the present number of atoms of daughter nuclide. Substituting this into Eq. (13.3) and eliminating  $N_0$ , we obtain

$$\frac{N_p}{N_p + N_d} = e^{-\lambda t}$$

which, on rearranging, gives

$$N_d = N_p(e^{+\lambda t} - 1) \quad (13.5)$$

For an approximate solution to this equation, the term  $e^{\lambda t}$  can be expanded in a power series as  $1 + \lambda t + (\lambda t)^2/2! + (\lambda t)^3/3! + \dots + (\lambda t)^n/n!$ . Because  $\lambda$  is so small (about  $10^{-10} \text{ a}^{-1}$ ), only the first two terms of the expansion are significant. Substituting these into Eq. (13.5) gives the approximate relation

$$N_d \approx N_p \lambda t \quad (13.6)$$

Before using Eq. (13.5) to determine the absolute age of a rock, we must consider the possibility that although

radioactive decay has produced daughter nuclides from the parent, some daughter nuclide may have been present in the environment prior to the beginning of the decay of the system under consideration. In such a case, the present number of atoms of the daughter nuclide would be the sum of the initial number present,  $N_d^i$ , and those produced by decay from the parent in the system. We can rewrite Eq. (13.5) as

$$N_d = N_d^i + N_p(e^{\lambda t} - 1) \quad (13.7)$$

This equation, then, allows us to determine the age of a rock if the numbers of atoms of parent and daughter nuclides can be determined. Although this can be done, in practice it is more convenient and more accurate, with a mass spectrometer, to measure isotopic ratios. For example, this can be done if the daughter element has another isotope that is stable and not affected by radioactive decay. We can then divide both sides of Eq. (13.7) by the number of atoms of the stable isotope,  $N_s$ , and obtain

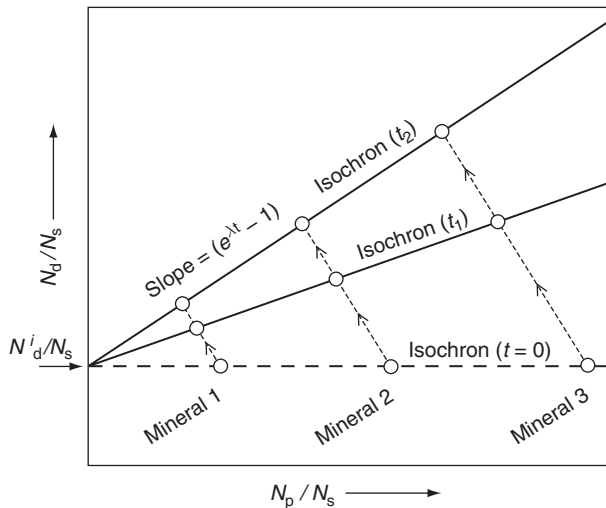
$$\frac{N_d}{N_s} = \frac{N_d^i}{N_s} + \frac{N_p}{N_s}(e^{\lambda t} - 1) \quad (13.8)$$

This, then, is the working equation for determining absolute ages from measured isotopic ratios involving parent, daughter, and stable nuclides.

Equation (13.8) contains two unknowns, the initial ratio,  $N_d^i/N_s$ , and the age,  $t$ . To solve for either of these unknowns requires two equations. These could be obtained by analyzing two different minerals that are known to have crystallized at the same time or analyzing two different rocks that had a common source and time of origin. There are special cases where the initial ratio is known, in which case an age can be obtained from a single analysis. We will examine examples of both of these cases.

Equation (13.8) is also the equation of a straight line (Fig. 13.2). It has an intercept on the ordinate of  $N_d^i/N_s$ , the initial ratio, and a slope of  $(e^{\lambda t} - 1)$ , which is proportional to the age. If a number of different minerals crystallize together, in a magma for example, each contains the same initial isotopic ratio, that of the magma, because there can be no fractionation of isotopes between phases at high temperature, especially of the heavy isotopes. Each mineral starts life, then, with the same isotopic ratio of  $N_d^i/N_s$ ; that is, they lie on the horizontal dashed line in Figure 13.2. Each mineral, however, contains different quantities of the radioactive parent (points along the dashed line). With time, various amounts of daughter product are generated, depending on the amount of parent, so the initial ratio is added to by an amount  $(N_p/N_s)(e^{\lambda t} - 1)$ . At any instant in time, the isotopic ratio in each of the minerals lies on a sloping straight line such as that shown in Figure 13.2. With increasing time, the slope of the line becomes steeper, but its intercept on the vertical axis remains the same.

In practice, the initial isotopic ratio is unknown. If, however, geological evidence indicates that a group of minerals was formed together at the same time, their isotopic ratios, when plotted in a diagram such as that of Figure 13.2, would



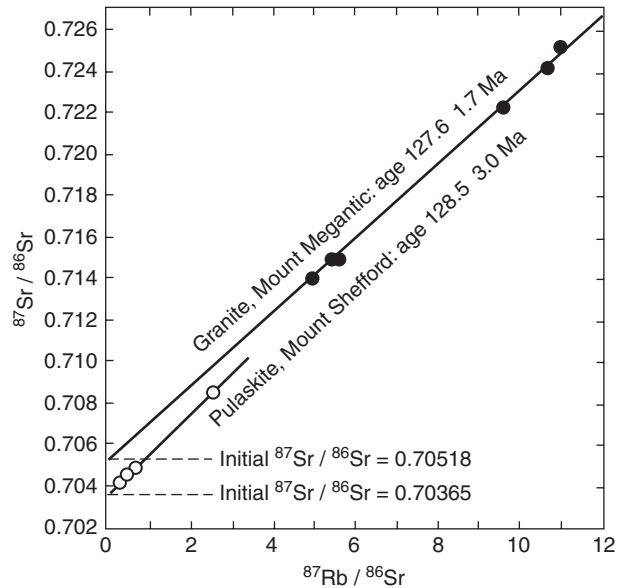
**Fig. 13.2** Plot of Eq. (13.8) where  $N_p$  is the number of atoms of the parent nuclide,  $N_d$  the number of atoms of the daughter element, and  $N_s$  the number of atoms of a nonradiogenic isotope of this same element. Three minerals formed in a rock at the same time have different concentrations of the parent nuclide but all have the same initial ratio of  $N_d/N_s$ . With time, the parent nuclide decays, and the amount of daughter product formed is proportional to the amount of parent present. At any time ( $t$ ), the minerals plot on a straight line known as an isochron; the age can be determined from the slope of this line.

be expected to lie on a straight line, from which could be determined both the initial isotopic ratio and the absolute age. Such a line is known as an *isochron*, because all points on it have the same age. Isochrons can also be constructed using whole-rock isotopic analyses of rocks that have a range of compositions and that field evidence indicates were formed from a common source at approximately the same time – as, for example, a suite of differentiated rocks within a layered intrusion.

The *rubidium–strontium method* of absolute dating is the most common technique making use of this type of analysis of the data.  $^{87}\text{Sr}$  is formed from the decay of  $^{87}\text{Rb}$ , but in any geological environment there is already some  $^{87}\text{Sr}$  present, formed from earlier decay of  $^{87}\text{Rb}$  or inherited from the formation of the solar system. Isotopic ratios of  $^{87}\text{Sr}$  and  $^{87}\text{Rb}$  are measured against the amount of the stable isotope  $^{86}\text{Sr}$ , and an isochron fitted to the following equation:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \frac{^{87}\text{Sr}^i}{^{86}\text{Sr}} + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda t} - 1) \quad (13.9)$$

where  $^{87}\text{Sr}^i/^{86}\text{Sr}$  is the initial ratio of these isotopes and  $\lambda$  is  $1.42 \times 10^{-11} \text{ a}^{-1}$ . Figure 13.3 shows two typical isochrons fitted to data from two Monteregian intrusions in southern Quebec (Eby, 1984). The slopes of the two isochrons are similar, and therefore the two intrusions have approximately the same age. The difference between the two isochrons is in their initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, that for the granite from Mount Megantic having a value of 0.70518 and that for the pulaskite from Mount Shefford having a value of 0.70365. As will be



**Fig. 13.3** Rb–Sr isochrons plotted through data for rocks from two Monteregian intrusions, Quebec. The slopes of the two lines are similar; consequently, the intrusions have similar ages. Granitic rocks of Mount Megantic, however, have a higher initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio than do nepheline syenites (pulaskite) of Mount Shefford, indicating that Megantic rocks assimilated larger amounts of crustal rocks, which normally have a high  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio. (After Eby, 1984.)

shown in the next section, these differences in initial isotopic ratio can be used to distinguish mantle and crustal sources of magma, and, in the case of mantle-derived magmas, the amount of crustal contamination.

In addition to providing information on the initial  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios, the Rb–Sr method of dating is particularly useful because Rb and Sr enter common rock-forming minerals, such as micas, feldspars, and amphiboles, substituting for K and Ca, respectively. Recrystallization of a rock is likely to cause radiogenic strontium to be expelled from these minerals because this strontium would have originally been present as  $^{87}\text{Rb}$  substituting for K. These minerals, then, will have their radioactive clocks reset by recrystallization. The expelled  $^{87}\text{Sr}$ , however, will enter nearby calcium-bearing minerals, such as apatite and plagioclase, so that the whole-rock Rb–Sr data will be unchanged. In this way, Rb–Sr dating, especially of large whole-rock samples, is able to see through metamorphic events (Fig. 13.4). Care must be taken, however, because whole-rock data can be affected by fluxes of fluids. In addition, dating of young material is unreliable unless samples contain high concentrations of Rb, because of the long half-life ( $t_{1/2} = 4.89 \times 10^{10} \text{ a}$ ) of the rubidium decay.

The *uranium–lead method* of absolute dating is useful because the two decay schemes,  $^{238}\text{U}$  to  $^{206}\text{Pb}$  and  $^{235}\text{U}$  to  $^{207}\text{Pb}$ , which have different decay constants, provide independent measures of the age of a sample. Thus, if uranium or lead has been removed from or added to a sample, the ages determined from the two methods will not agree; that is, the ages will be *discordant*. If, on the other hand, the sample has remained closed, the two ages will be *concordant*.