
13 Isotope geochemistry related to petrology

13.1 INTRODUCTION

Some of the major petrologic advances in recent years can be attributed to isotope geochemistry. The first contributions were in the field of absolute age determinations. Not only was the long-debated question of the age of the Earth settled, but absolute dating provided a means of unraveling the chronology of that large fraction (90%) of Earth history that had previously been designated "Precambrian" because of its lack of an adequate paleontological record with which to subdivide it. With increased refinements and new techniques, absolute dating now tackles problems ranging from the cosmological, such as determining the age of heavy elements in our solar system, to the very specific, such as the time of last movement on faults at a potential nuclear power plant site.

Perhaps of still greater importance to petrology is the contribution that isotope geochemistry has made to determining the provenance of magmas. Isotopic analyses can distinguish between magmas of mantle and crustal origin. In addition, degrees of contamination of mantle-derived magmas by crustal rocks can be measured through isotopic changes that could not be detected using major element chemistry. Isotopes can also indicate how much meteoric water is circulated through the rock cycle. In addition, isotopic studies reveal important information about the mantle itself, such as how its composition can change with time as a result of removal of partial melts or introduction of metasomatizing fluids.

Isotope geochemistry is such a large subject that only some of its petrologically most important aspects can be dealt with in this chapter. What is an isotope, and how does isotope geochemistry differ from what might be referred to as normal geochemistry? Atoms of an element that have different numbers of neutrons are known as isotopes. They consequently have different atomic masses, but their numbers of protons and electrons are the same (for a particular element), and thus normal chemical processes do not distinguish between most isotopes. Indeed, isotopic analyses cannot be done by normal chemical means but must be done with a mass spectrometer. At first, the inability of chemical processes to fractionate most isotopes suggests that isotopic analyses of rocks might serve little use. This, however, is not the case. The lack of fractionation of most isotopes by chemical processes means that once a rock has developed a particular isotopic ratio, this ratio will remain unchanged except in special cases, regardless of the chemical or physical

processes that take place; thus the isotopic ratio serves as an indelible fingerprint with which to identify the rock. Elements themselves cannot possibly be used in this way, because every process induces some chemical change, which can be explained only if the process is fully understood (this is usually not the case).

Isotopic ratios can change through radioactive decay and mass fractionation. Some isotopes are radioactive and decay, at known rates, into isotopes of other elements. For example, ^{87}Rb , which substitutes for K in minerals, decays to ^{87}Sr , which in turn substitutes for Ca in minerals. Rubidium and strontium are chemically so different that they will be fractionated if exposed to processes such as partial melting. If left undisturbed, however, this pair provides the basis of one of the most useful absolute age determination methods. Isotopes with an atomic mass of less than about 20 can be fractionated to a measurable extent by some physical and chemical processes in which the mass of the isotopes makes a difference. For example, light isotopes can escape more easily than heavy ones during evaporation; consequently, ratios of the isotopes of H, He, and O in the surface layer of the oceans are depleted in the light isotopes relative to their ratios in the deep ocean. A list of all isotopes and their properties, including decay products and rates of decay if they are radioactive, can be found at <http://atom.kaeri.re.kr/ton/index.html> or <http://t2.lanl.gov/data/map.html>.

In general, most isotopic studies of petrologic interest fall into one of three main categories: (1) absolute dating using radioactive isotopes, (2) evolution of isotopic reservoirs in the mantle and crust, and (3) stable isotopes as indicators of ancient environments. These may overlap considerably, but the divisions provide a convenient basis for a brief survey of the subject, which is all that can be done in this chapter. For more extensive coverage, the books by Jager and Hunziker (1979), Faure (1986), Dickin (1995), Valley (2001), Faure and Mensing (2004) and Sharp (2006), and the articles by Hart and Allègre (1980), O'Nions et al. (1980), DePaolo (1981a), and O'Nions (1984) are recommended.

13.2 RADIOACTIVE DECAY SCHEMES

Some isotopes are inherently unstable and will, with time, change or "decay" to stable isotopes. The rate of decay is determined only by the instability of the radioactive nucleus and cannot be changed by external forces. This immutability

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}Rb and ^{87}Rb ; the first is stable, but ^{87}Rb decays to ^{87}Sr , which is just one of four stable isotopes of strontium, the others being ^{88}Sr , ^{86}Sr , and ^{84}Sr . Uranium has several isotopes, two of which, ^{238}U and ^{235}U , decay to ^{206}Pb and ^{207}Pb , respectively. Potassium has three isotopes, ^{39}K , ^{40}K , and ^{41}K , but only ^{40}K is unstable. It, however, can decay in two ways, either to ^{40}Ca or to ^{40}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 (α). 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 (β), is formed when a neutron in the nucleus changes into a proton. β 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}Rb for it to change to ^{87}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}Rb and ^{87}Sr are the same, the decay process cannot involve α 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 β 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}U and ^{235}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 α particles must be emitted. Because each α particle has a charge of +2, the loss of 8 α 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 α particles must be accompanied by the emission of 6 β 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 α 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 β particle. The reaction is



Of these three decay processes, only the emission of α particles has any significant effect on the material surrounding the decaying atom. Where this material is pleochroic, the bombardment by α 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 α particles are particles given off by the spontaneous fission of ^{238}U and to a very much smaller extent of ^{235}U and of ^{232}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}U , and on this is based the fission track method of absolute dating.

13.3 RATE OF RADIOACTIVE DECAY

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

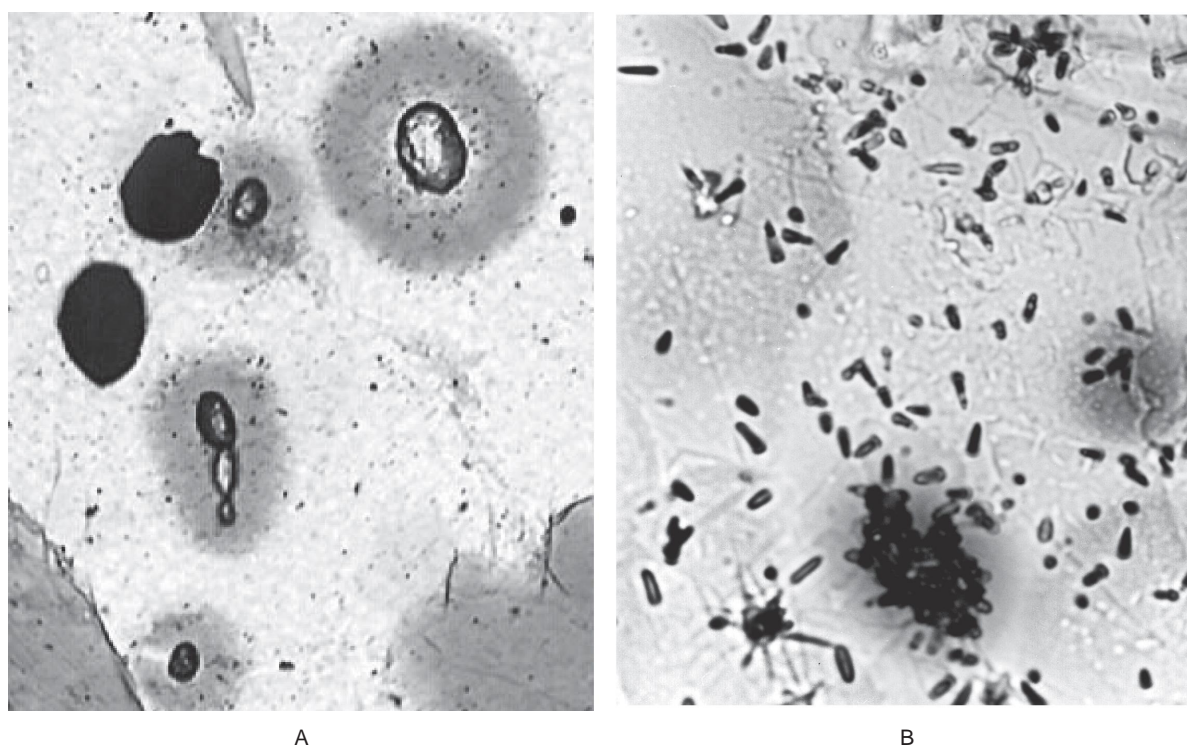


Fig. 13.1 (A) Yellow pleochroic halos surrounding zircon crystals in cordierite. Zircon typically contains small amounts of U and Th, which, on undergoing radioactive decay, affect the structure of the surrounding mineral. Plane light; width of field is 0.3mm. (B) Fission tracks in biotite, revealed 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 0.2mm.

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

$$\text{rate of decay} / N \quad (13:1)$$

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:

$$\frac{dN}{dt} / -N \quad \text{or} \quad \frac{dN}{dt} / -\lambda N \quad (13:2)$$

where the constant of proportionality, λ , is known as the decay constant. Typical values of λ range from 10^{-4} a^{-1} for the rapid decay of ${}^{14}\text{C}$ to ${}^{14}\text{N}$, to 10^{-12} 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:

$$\frac{dN_p}{N_p} = -\lambda dt$$

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}C is 5730 a, and for ^{147}Sm is 1.06×10^{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 4.55×10^9 a. Since the formation of the Earth, approximately half the original ^{238}U has decayed, but very little ^{147}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 $1 + \lambda t + \frac{(\lambda t)^2}{2!} + \frac{(\lambda t)^3}{3!} + \dots + \frac{(\lambda t)^n}{n!}$. Because λ is so small (about 10^{-10} 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

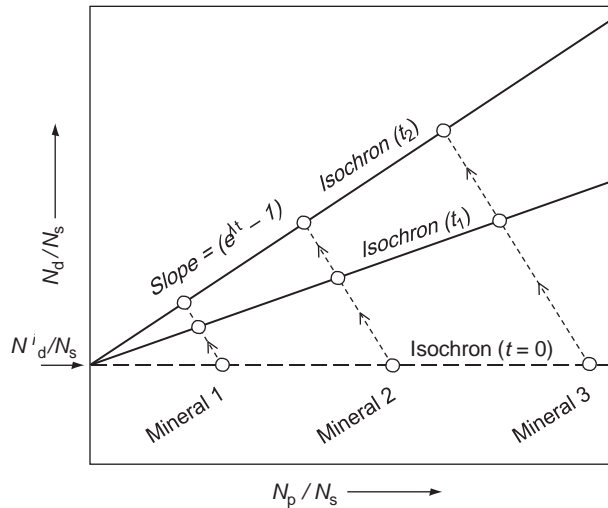


Fig. 13.2 Plot of Eq. (13.8) where N_p is the number of atoms of the parent nuclide, N_d the number of atoms of the daughter element, and N_s the number of atoms of a nonradiogenic isotope of this same element. Three minerals formed in a rock at the same time have different concentrations of the parent nuclide but all have the same initial ratio of N_d^i/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}Sr is formed from the decay of ^{87}Rb , but in any geological environment there is already some ^{87}Sr present, formed from earlier decay of ^{87}Rb or inherited from the formation of the solar system. Isotopic ratios of ^{87}Sr and ^{87}Rb are measured against the amount of the stable isotope ^{86}Sr , and an isochron fitted to the following equation:

$$\frac{^{87}\text{Sr}}{^{86}\text{Sr}} = \frac{^{87}\text{Sr}^i}{^{86}\text{Sr}^i} + \frac{^{87}\text{Rb}}{^{86}\text{Sr}} (e^{\lambda t} - 1) \quad (13:9)$$

where $^{87}\text{Sr}^i/^{86}\text{Sr}^i$ is the initial ratio of these isotopes and λ 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

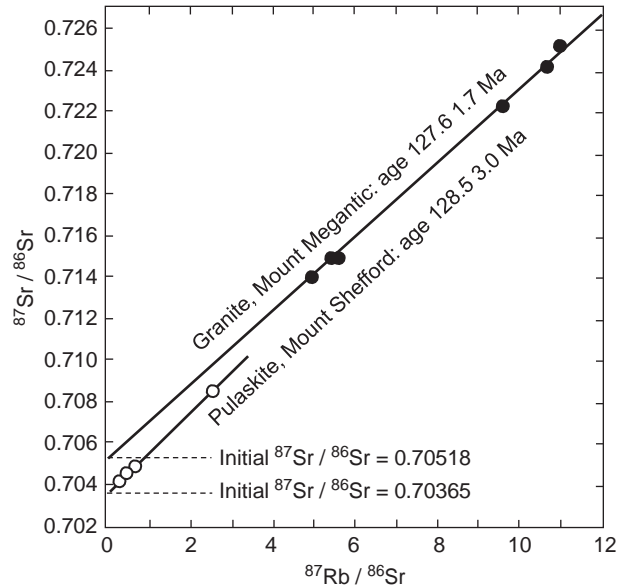


Fig. 13.3 Rb–Sr isochrons plotted through data for rocks from two Monteregian intrusions, Quebec. The slopes of the two lines are similar; consequently, the intrusions have similar ages. Granitic rocks of Mount Megantic, however, have a higher initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio than do nepheline 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}Rb substituting for K. These minerals, then, will have their radioactive clocks reset by recrystallization. The expelled ^{87}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}U to ^{206}Pb and ^{235}U to ^{207}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.

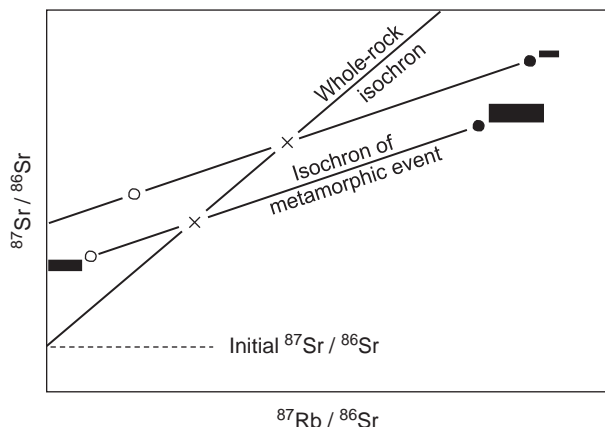


Fig. 13.4 Large-sample, whole-rock analyses (crosses) for Rb and Sr isotopes can give reliable isochrons, despite metamorphic overprinting, if Rb and Sr have not moved out of the volume sampled. Local redistribution of Rb and Sr within this volume between minerals of high Rb (solid circles) and low Rb (open circles) allows isochrons to be constructed that give the age of the metamorphism.

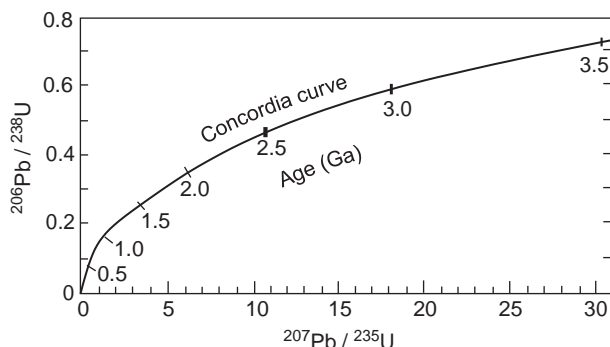


Fig. 13.5 Plot of Eq. (13.12) showing the variation in the $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ratios in a system that has remained closed to U and Pb. Ages in Ga are marked on the concordia curve.

Using Eq. (13.5), we can write for the two decay schemes

$$^{206}\text{Pb} \frac{1}{4} \text{ } ^{238}\text{U} (e^{\lambda_{238}t} - 1) \tag{13:10}$$

and

$$^{207}\text{Pb} \frac{1}{4} \text{ } ^{235}\text{U} (e^{\lambda_{235}t} - 1) \tag{13:11}$$

where $\lambda_{238} = 1.55125 \times 10^{-10} \text{ a}^{-1}$ and $\lambda_{235} = 9.8485 \times 10^{-10} \text{ a}^{-1}$. The slower decay rate of ^{238}U relative to that of ^{235}U means that the ratio of $^{206}\text{Pb}/^{238}\text{U}$ grows more slowly than that of $^{207}\text{Pb}/^{235}\text{U}$ during the early stages of decay. The relative changes in these isotopic ratios can be found simply by equating Eqs. (13.10) and (13.11) through a common time. This gives

$$\frac{^{206}\text{Pb}}{^{238}\text{U}} \frac{1}{4} \exp \frac{r}{\lambda_{238}} \ln (1 + \frac{^{207}\text{Pb}}{^{235}\text{U}} - 1) \tag{13:12}$$

Equation (13.12), which is plotted in Figure 13.5, shows how the isotopic ratios of $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ change

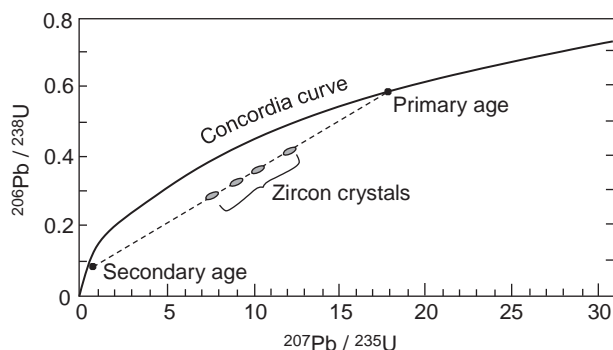


Fig. 13.6 Many rocks and minerals, such as the zircon crystals shown in this diagram, do not plot on the concordia curve; that is, the ratios of $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ are not concordant and indicate that the system has been disturbed. One interpretation of the linear array exhibited by the zircons in this diagram is that they formed 3.0Ga ago but were later disturbed by an event 0.6Ga ago.

with time in a completely closed system. This line is known as the concordia curve, because ages determined by either Eq. (13.10) or (13.11) on a closed system give the same (concordant) results and thus plot on the same line. The plot in Figure 13.5 is known as a concordia diagram, and is the most commonly used graph for displaying U–Pb age data.

Many geological systems have not remained closed since their formation, and because of the two different decay rates, any disturbance of the system results in different ages being determined from the two decay schemes. Because the ages do not match, they are said to be discordant. In the concordia diagram, these discordant samples do not lie on the concordia curve, but instead typically plot to the right of it (Fig. 13.6). Discordant samples that are genetically related commonly form a linear array in the concordia diagram (Fig. 13.6). Such a plot can contain considerable information about the history of a rock, but the interpretation is not always unambiguous and must be supported with sound geological field evidence.

The simplest and most common explanation for a linear array of discordant ages is that some initial age, given by the older intercept of the linear array with the concordia line, was disturbed by an event that occurred at the time given by the younger intercept of the linear array with the concordia line. For example, in Figure 13.6, the discordant ages shown are typical of what is obtained from a population of zircon crystals separated from a single large sample. Zircon is a particularly good mineral for absolute dating because it takes uranium into its structure but excludes lead. In addition, it has low diffusion rates and commonly preserves complex zoning, which can be analyzed using modern microanalytical tools, such as the ion-beam probe. The intercept of the array of zircon crystals in Figure 13.6 with the concordia line at 3.0Ga could be the time of crystallization of these zircon crystals from a magma, whereas the secondary age of 0.6Ga could be a metamorphic event which partially but not completely reset the U–Pb clocks. Numerous other, more complicated interpretations can be advanced, if supported with

appropriate geological evidence. The ability of the U–Pb method to record the timing of successive events has made it a particularly powerful tool in unraveling complicated geologic histories.

The potassium–argon method of dating differs from other common methods by involving a decay product that is an inert gas. Even at moderately low temperatures (see discussion below), this gas is a fugitive component and is typically not incorporated in minerals. Thus a newly formed mineral contains no argon to begin with, but with time, ^{40}K decays slowly to ^{40}Ar ; this argon remains in place as long as the system is not disturbed. The method, in principle, then, is not affected by initial isotopic ratios, as is the Rb–Sr method.

The K–Ar method is complicated slightly by the fact that ^{40}K decays both to ^{40}Ar and ^{40}Ca . The decay constant for ^{40}K (λ_{K}) of $5.543 \times 10^{-10} \text{ a}^{-1}$ is actually the sum of the two decay constants, one from the production of ^{40}Ar ($\lambda_{\text{Ar}} = 0.581 \times 10^{-10} \text{ a}^{-1}$) and the other from the production of ^{40}Ca ($\lambda_{\text{Ca}} = 4.962 \times 10^{-10} \text{ a}^{-1}$). According to Eq. (13.5), the amount of decay product produced from ^{40}K is $^{40}\text{K} e^{\lambda_{\text{K}}t} - 1$. The decay products consist of both argon and calcium, which are present in amounts that are proportional to their respective decay rates. Thus the fraction of the total decay products consisting of ^{40}Ar at time t is

$$^{40}\text{Ar} \frac{1}{4} \frac{\lambda_{\text{Ar}}}{\lambda_{\text{K}}} \left(e^{\lambda_{\text{K}}t} - 1 \right) \quad (13:13)$$

which on rearranging gives

$$t \frac{1}{\lambda_{\text{K}}} \ln \left(\frac{\lambda_{\text{K}}}{\lambda_{\text{Ar}}} \frac{^{40}\text{Ar}}{^{40}\text{K}} + 1 \right) \quad (13:14)$$

This equation expresses the age of a sample in terms of an easily measured isotopic ratio, $^{40}\text{Ar}/^{40}\text{K}$.

Absolute dates by the K–Ar method can be obtained on both minerals and whole rocks. These may indicate the time since the formation of a sample, but because most igneous and metamorphic rocks form at moderate to high temperatures, most dates indicate the length of time since the material dropped below some critical temperature at which diffusion of argon out of the sample became negligible. This temperature is known as the blocking temperature, and varies with the minerals involved, but is approximately 350 °C. For large intrusive bodies or deeply buried metamorphic rocks slow cooling may produce a considerable discrepancy between the true age of a rock and its cooling age obtained from the K–Ar method. Such discrepancies can be found between Rb–Sr and K–Ar ages on the same samples. Blocking temperatures for Rb–Sr are a couple of hundred degrees higher than those for K–Ar.

For an age determination by the K–Ar method to be accurate, the assumption that no radiogenic argon was present to begin with must be valid; also, no radiogenic argon that is produced in the mineral or rock can have escaped, nor can any radiogenic argon from an external source have been absorbed. Each of these can, in particular situations, be a source of serious error. Some environments definitely have

an ambient fugacity of ^{40}Ar , which can give a newly formed rock a significant initial content of radiogenic argon. For example, Mesozoic diabase dikes in Liberia, West Africa, which are associated with the early opening of the Atlantic Ocean, give K–Ar ages that are Mesozoic where the dikes cut Paleozoic rocks, but the ages are very much older where they cut Precambrian rocks, which, because of their age, contain high contents of ^{40}Ar (Dalrymple et al., 1975). Some minerals leak ^{40}Ar more easily than others do by diffusion through their structure or along prominent cleavages, and thus they give erroneously young ages. The common K-bearing rock-forming minerals can be arranged according to retentiveness of ^{40}Ar , starting with the least retentive, microcline, and passing up through biotite, sanidine, pyroxene, muscovite, and ending with amphibole, the most retentive. Coarse-grained rocks tend to be less retentive than fine-grained ones. Some minerals, such as beryl, biotite, chlorite, clinopyroxene, and partly kaolinized feldspar, absorb ^{40}Ar and thus give erroneously old ages.

Typically, the outer parts of mineral grains are affected by gain or loss of argon. In the standard K–Ar dating method, there is no way of knowing precisely from where in the grains the analyzed potassium and argon come – the analysis is simply of a bulk sample. In a modified technique that involves measuring the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio, loosely bound argon on grain boundaries can be distinguished from that within the core of grains, and some of the problems of excess or lost argon can be eliminated. In the $^{40}\text{Ar}/^{39}\text{Ar}$ method, ^{40}K is not measured directly. Instead, it is first converted to ^{39}Ar by placing the sample in a flux of high-energy neutrons in a nuclear reactor. Measurement of ^{39}Ar , then, gives a measure of the ^{40}K content prior to bombardment. The sample is heated in a stepwise manner, and the $^{40}\text{Ar}/^{39}\text{Ar}$ released at each stage is determined. The daughter nuclide, ^{40}Ar , and the parent nuclide, ^{40}K , which is now in the form of ^{39}Ar , are released together as argon gas. The first argon released is the most weakly bound, probably coming from grain boundaries. At higher temperatures, more tightly bound argon from the core of grains is emitted. An age can be calculated from the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio obtained at each step. If argon has been gained or lost, or the amount of potassium near grain boundaries has changed, variable $^{40}\text{Ar}/^{39}\text{Ar}$ ratios and ages would be obtained for the first few steps. With continued heating, however, the $^{40}\text{Ar}/^{39}\text{Ar}$ ratio and age should stabilize to produce a plateau on a graph of $^{40}\text{Ar}/^{39}\text{Ar}$ (or age) versus heating step (Fig. 13.7). Only when a significant plateau is obtained can any certainty be placed on the age determination.

Dating by the samarium–neodymium method has been made possible in recent years by increased precision in mass-spectrometric techniques. ^{147}Sm decays to ^{143}Nd so slowly ($t_{1/2} = 1.06 \times 10^{11} \text{ a}$) that age determinations depend on measurements of very small changes in the amount of ^{143}Nd . The method, which is only suitable for ancient rocks, is similar to that for Rb–Sr. Isotopic ratios of $^{147}\text{Sm}/^{144}\text{Nd}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ are determined in a number of samples, which are used to construct an isochron having the form

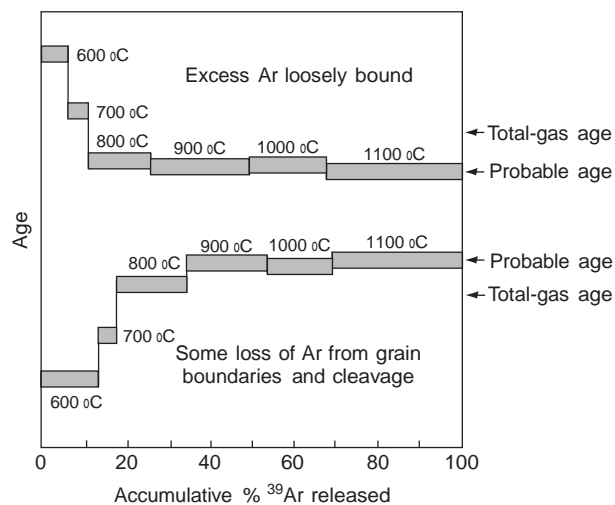


Fig. 13.7 ⁴⁰Ar/³⁹Ar incremental-heating-release spectra for two samples, one containing excess Ar and the other a deficiency of Ar. An age is calculated from the ⁴⁰Ar/³⁹Ar ratio in the gas released at each heating step. Only when the age given at each successive step remains constant (plateau) is the age likely to be reliable. Excess Ar, which might be absorbed on grain boundaries, is usually driven off at low temperature, giving erroneously old ages for the first steps. The age calculated from the total gas released (equivalent to the standard K–Ar method) is older than the plateau age if excess Ar is present. Loss of Ar from the sample gives erroneously young ages at the first heating steps, and the total-gas age is younger than the plateau age.

$$\frac{^{143}\text{Nd}}{^{144}\text{Nd}} = \frac{^{143}\text{Nd}^i}{^{144}\text{Nd}} + \frac{^{147}\text{Sm}}{^{144}\text{Nd}} (e^{\lambda t} - 1) \quad (13:15)$$

where ¹⁴³Nd/¹⁴⁴Nd is the initial ratio of these isotopes. ¹⁴⁴Nd, the isotope against which the others are compared, is radioactive, but with a decay constant of 2.89 × 10⁻¹⁶ a⁻¹ it is effectively a stable isotope. In ancient samples (>3.0 Ga), where the method has been used successfully, the initial ¹⁴³Nd/¹⁴⁴Nd ratio is very close to that for chondritic meteorites, which are considered to be the most representative samples we have of the primordial solar nebular material from which the planet Earth was formed. These ancient rocks, then, formed from a source that had changed little since the beginning of the Earth (O’Nions et al., 1980). One distinct advantage of the Sm–Nd method is that both Sm and Nd, like the rest of the rare earth elements, are relatively immobile and remain in situ during weathering and even metamorphism. Rubidium and strontium, by contrast, are moved easily by solutions. Some of Earth’s oldest rocks from Isua, Greenland, which are 3.8 Ga old, are metamorphosed and yet yield an excellent Sm–Nd isochron.

Dating of ancient rocks can also be done by the rhenium–osmium method (Shirey and Walker, 1998). Rhenium has two isotopes, ¹⁸⁵Re and ¹⁸⁷Re, the latter decaying by β emission to ¹⁸⁷Os with a half-life of 41.6 Ga. Recent improvements in analytical techniques have allowed the low concentrations of these isotopes to be detected with sufficient accuracy to be usable for dating purposes. The concentrations of ¹⁸⁷Re and ¹⁸⁷Os are measured relative to the concentration of the stable

isotope ¹⁸⁸Os and the age is determined from an isochron fitted to the following equation:

$$\frac{^{187}\text{Os}}{^{188}\text{Os}} = \frac{^{187}\text{Os}^i}{^{188}\text{Os}} + \frac{^{187}\text{Re}}{^{188}\text{Os}} (e^{\lambda t} - 1) \quad (13:16)$$

where ¹⁸⁷Osⁱ/¹⁸⁸Os is the initial ratio of these isotopes. The concentration of rhenium and osmium in most rocks is so low and with the low decay rate (λ = 1.66 × 10⁻¹¹ a⁻¹) accurate ages are difficult to obtain on any but the oldest rocks. Both rhenium and osmium are extremely siderophilic elements; that is, they strongly prefer to be in a metal or sulfide phase. The Re–Os method is consequently one of the few ways of determining the age of platinum deposits. The siderophilic nature of these elements means that early in Earth’s history they would have preferentially entered the core. As we will see below, the Re–Os dating method allows limits to be set on when Earth’s core formed.

The hafnium–tungsten method of dating is also relevant to determining the time of core formation (Jacobsen, 2005). ¹⁸²Hf decays by β emission to ¹⁸²W with a half-life of only 9 Ma. With such a high decay rate (λ = 7.7 × 10⁻⁸ a⁻¹) no ¹⁸²Hf remains; that is, the decay process has run its course and is now extinct. However, during early Earth history, the process was still active. We can write a standard decay equation for ¹⁸²Hf to ¹⁸²W with respect to the abundance of the stable isotope ¹⁸³W as follows:

$$\frac{^{182}\text{W}}{^{183}\text{W}} = \frac{^{182}\text{W}^i}{^{183}\text{W}} + \frac{^{182}\text{Hf}}{^{183}\text{W}} (e^{\lambda t} - 1) \quad (13:17)$$

However, because of the high decay rate, ¹⁸²Hf/¹⁸³W is essentially zero, and e^{λt} is approaching ∞. A more useful form of this equation can be written by making use of Eq. (13.3) from which we have

$$\frac{^{182}\text{Hf}}{^{180}\text{Hf}} = \frac{^{182}\text{Hf}_i}{^{180}\text{Hf}_i} e^{-\lambda t}$$

where ¹⁸²Hf is the abundance after decaying for a time t from an initial abundance of ¹⁸²Hf_i. If we divide both sides of this equation by the abundance of the stable isotope ¹⁸⁰Hf, we obtain

$$\frac{^{182}\text{Hf}}{^{180}\text{Hf}} = \frac{^{182}\text{Hf}_i}{^{180}\text{Hf}_i} e^{-\lambda t} \quad \text{or} \quad \frac{^{182}\text{Hf}}{^{180}\text{Hf}} = \frac{^{182}\text{Hf}_i}{^{180}\text{Hf}_i} e^{-\lambda t}$$

This value of ¹⁸²Hf can be substituted into Eq. (13.17) to give

$$\frac{^{182}\text{W}}{^{183}\text{W}} = \frac{^{182}\text{W}^i}{^{183}\text{W}} + \frac{^{180}\text{Hf}}{^{183}\text{W}} \frac{^{182}\text{Hf}_i}{^{180}\text{Hf}_i} (e^{\lambda t} - 1)$$

which simplifies to

$$\frac{^{182}\text{W}}{^{183}\text{W}} = \frac{^{182}\text{W}^i}{^{183}\text{W}} + \frac{^{180}\text{Hf}}{^{183}\text{W}} \frac{^{182}\text{Hf}_i}{^{180}\text{Hf}_i} (1 - e^{-\lambda t}) \quad (13:18)$$

Because the system is now extinct, e^{-λt} ≈ 0 and Eq. (13.18) becomes

$$\frac{^{182}\text{W}}{^{183}\text{W}} = \frac{^{182}\text{W}^i}{^{183}\text{W}} + \frac{^{180}\text{Hf}}{^{183}\text{W}} \frac{^{182}\text{Hf}_i}{^{180}\text{Hf}_i} \quad (13:19)$$

In a plot of $^{182}\text{W}/^{183}\text{W}$ versus $^{180}\text{Hf}/^{183}\text{W}$, samples with a range of compositions can define a fossil isochron, where the slope is the initial ratio of $^{182}\text{Hf}_i/^{180}\text{Hf}_i$. Note that ^{180}Hf is a stable isotope and has not changed. We will have more to say about the hafnium–tungsten system in the next section.

Lutetium–hafnium provide still another pair of isotopes for dating old rocks (Hawkesworth and Kemp, 2006). ^{176}Lu decays by β emission to ^{176}Hf with a half-life of 36.77 Ga. Lutetium is commonly found in significant amounts in zircon crystals, which have long been recognized as ideal phases in which to preserve geological history because of the low diffusion rates of both parent and daughter isotopes. Recent advances in microanalytical techniques, using ion beam probes, laser ablation, and even microdrilling, have allowed detailed isotopic analyses to be done of zoned zircon crystals using the Lu–Hf and U–Pb methods to unravel complex histories preserved within single grains (Davidson et al., 2007).

Dating of zoned crystals of monazite ((Ce,La,Th)PO₄) has been obtained without isotopic analysis by using electron probe microanalysis (EPMA). Although EPMA cannot distinguish between isotopes, the electron beam is capable of rendering much higher resolution images than the other microanalytical techniques. Obtaining an age through EPMA involves a number of assumptions (Williams et al., 2007). First, the monazite is assumed to have contained no significant amount of lead initially. All lead that it now contains came from the radioactive decay of either ^{232}Th , ^{238}U , or ^{235}U . For example, the radioactive decay of ^{232}Th will generate ^{208}Pb . According to Eq. (13.5), the contribution of the ^{208}Pb to the total lead in the EPMA, which is typically expressed in parts per million by weight, is given by

$$\frac{^{208}\text{Pb}}{208} \frac{^{232}\text{Th}}{232} \left(e^{\lambda^{232}t} - 1 \right)$$

where λ^{232} is the decay constant for ^{232}Th (see Table 13.1). The ^{208}Pb and ^{232}Th are both divided by their respective atomic weights to give number of atoms. The EPMA gives only the total amount of uranium and not the amounts of ^{238}U and ^{235}U . The total uranium is consequently partitioned between these two isotopes in the proportion in which they occur in nature; that is, $^{238}\text{U} = 99.28\%$ and $^{235}\text{U} = 0.72\%$. The total lead in the sample will be the sum of the contributions from the ^{232}Th , ^{238}U , and ^{235}U , which can be written as

$$\begin{aligned} \text{Total Pb} \frac{1}{208} &= \frac{r_{^{232}\text{Th}}}{232} \left(e^{\lambda^{232}t} - 1 \right) \quad \text{208} \\ &+ p \frac{r_{\text{Total U}}}{238} \left(0.9928 e^{\lambda^{238}t} - 1 \right) \quad \text{206} \\ &+ p \frac{r_{\text{Total U}}}{235} \left(0.0072 e^{\lambda^{235}t} - 1 \right) \quad \text{207} \end{aligned} \quad (13:20)$$

This equation allows the age (t) of the sample to be calculated from the analyses of the Pb, Th, and U.

Monazite crystals exhibit complex zoning patterns, which can be related to growth at different times and in different environments, or to compositional differences developed at

the same time in different sectors. The preservation of zoning that commonly exhibits steep concentration gradients testifies to the low diffusion rates in monazite, even at moderately elevated temperatures. The closure temperature (temperature below which no significant diffusion occurs) is thought to be $\sim 800^\circ\text{C}$. Monazite, like zircon, is therefore an ideal phase in which to preserve age data.

Absolute dating by the fission track method differs from the previous ones in that it does not involve mass-spectrometric or conventional chemical analysis. Its principle is simple (Fleischer and Price, 1964; Fleischer et al., 1975; Gallagher et al., 1998). ^{238}U undergoes spontaneous fission at a rate of about 10^{-16} a^{-1} . The massive charged fission products damage the structure of the host mineral along a short track (5 to 20 μm). These tracks can be made visible by etching with appropriate chemicals and their number counted under an ordinary optical microscope. For a given content of ^{238}U , the age is proportional to the number of tracks per unit area. ^{235}U and ^{232}Th also undergo fission, but this happens so rarely that they do not contribute significantly to the development of fission tracks. Even the fission rate of ^{238}U is very slow, but fission tracks record every fission event, and thus their measurement is not limited by analytical precision as in mass-spectrometric analyses or EPMA.

The procedure for determining an age by the fission track method first involves finding a mineral with an appropriate ^{238}U content to provide a statistically significant number of tracks. An appropriate uranium content depends on the age of the mineral. Young samples require high contents, but this same amount in older samples could produce too high a track density. The uranium should also preferably be distributed evenly through the sample. Many of the common rock-forming and accessory minerals have been used successfully. Mica, apatite, hornblende, sphene, zircon, and natural glasses are particularly good.

Once the number of fission tracks has been counted, the mineral’s uranium content must be determined. This is done by first heating the sample to anneal out all of the fission tracks. Then the sample is placed, along with a piece of standard glass containing a known amount of uranium, in a nuclear reactor where both receive a dose of neutrons. These neutrons induce fission of ^{235}U , which produces new tracks that can be counted after appropriate etching.

The age of the mineral can be calculated from the three measured fission track densities: that produced by spontaneous fission in the original sample, ρ_s ; that induced in the sample by the neutron flux in the reactor, ρ_i ; and that produced in the dosimeter standard glass, ρ_D . The age is given by

$$\text{fission track age} \frac{1}{4} \frac{C \rho_s \rho_D}{\rho_i} \quad (13:21)$$

The constant, C, includes terms for the fraction of atoms that are ^{238}U , the total number of atoms in sampled volume, length of fission tracks, fraction of tracks that are efficiently etched, and the fission decay constant.

Reliable ages up to 1 Ga have been obtained by this method. Fission tracks, however, can disappear with time, especially if the sample is heated. The age determined by the method is therefore the time since the sample was last heated above a temperature at which annealing takes place. Different minerals anneal at different temperatures. For example, annealing removes fission tracks from apatite at ~ 120 °C, whereas this occurs in zircon at ~ 350 °C. Fission track dates on several minerals from the same rock can reveal the cooling history and erosional uplift rate of the sample. Fission track dating has been particularly useful when used in this way in conjunction with some other method of absolute dating that has a higher blocking temperature and can thus more closely record the true age of the rock.

13.4 EVOLUTION OF ISOTOPIC RESERVOIRS IN THE EARTH

The Earth has been affected throughout geologic time by processes that have differentiated its chemical constituents into the major units of the Earth, the core, mantle, and crust. As discussed in Section 6.1, Earth is believed to have formed with a chondritic bulk composition. Early in its history, however, sinking of metallic iron and other siderophile elements to form the core left a mantle composed predominantly of the silicate fraction of the primordial chondrites. The mantle's composition has subsequently been modified by extraction of small amounts of partial melt to form Earth's crust. The crust's present composition must be largely determined in some complex way by the time-integrated effect of this partial melting process. Phase diagrams and solid–liquid partition coefficients indicate that partial melts can have very different compositions from the solid being melted. Partial melting can therefore be an extremely efficient means of effecting chemical differentiation. Isotopes, at high temperature, however, are not fractionated during partial melting. But most radioactive isotopes have very different solid–liquid partition coefficients from their stable daughter isotopes. Consequently, partial melting does fractionate radioactive nuclides from their decay products. In this way, the isotopic nature of various parts of the Earth has changed throughout geologic time. For example, magmas extracted from the mantle today have different isotopic signatures from those extracted in the past. If we understand the evolution of the isotopic reservoirs, it may be possible to identify magmas derived from that source at any given time by their isotopic character.

Formation of the Earth's core must have occurred very early. Earth's oldest rocks show that a strong magnetic field was already present ~ 4 Ga ago, and this would have required a molten iron core. Can we determine when core formation occurred?

It will be recalled from Eq. (13.17) that ^{182}Hf decays rather rapidly to ^{182}W , with a half-life of only 9 Ma. Although these two isotopes have the same mass, their chemical behavior is quite different. Hafnium is a lithophile element; that is, it prefers to be in silicates. In contrast, tungsten is moderately siderophile and will preferentially enter

metallic iron. Therefore, if the core formed after the ^{182}Hf had decayed to ^{182}W , this tungsten would have sunk along with the iron to form the core, leaving a mantle that would contain less ^{182}W than it would have had it maintained its chondritic composition. On the other hand, if the core formed before the ^{182}Hf had decayed to ^{182}W , this tungsten could not have been removed by the core-forming process. Consequently, the mantle would have a tungsten isotopic composition similar to that of chondrites. This in fact is what is found. Modeling of the core formation using the ^{182}Hf to ^{182}W decay scheme requires that Earth accreted rapidly in ~ 10 Ma and that core formation must have been complete by ~ 30 Ma (Jacobsen, 2005).

Rhenium and osmium are both strongly siderophilic, so they would have accompanied the iron into Earth's core when it formed. Iron meteorites, which represent the cores of planetary bodies from the asteroid belt, confirm that rhenium and osmium did enter the cores of these bodies, and their ages, based on rhenium–osmium dating (Eq. 13.16), indicate formation within the first 15 Ma of solar system history at 4.558 to 4.526 Ga (Shirey and Walker, 1998). Earth's core probably formed in this same interval.

Core formation early in Earth history would have sequestered most of the rhenium and osmium into the core. The mantle would then have been strongly depleted in these elements relative to the initial chondritic composition. Iron meteorites indicate that as molten iron solidifies rhenium and osmium both partition into the solid and consequently their concentration in the remaining liquid decreases. This effect is more pronounced for osmium, and consequently, the rhenium/osmium ratio increases in the liquid as crystallization progresses. Through the radioactive decay of ^{187}Re , the $^{187}\text{Os}/^{188}\text{Os}$ value would be much higher in the outer liquid core than in chondritic compositions. If there were equilibrium between the outer core and mantle, the $^{187}\text{Os}/^{188}\text{Os}$ values in the mantle might be expected to show elevated values relative to chondritic values. However, rocks derived from the mantle indicate values close to chondritic, which has led to the conclusion that this isotopic value was imposed on the mantle by a veneer of chondritic material that was accreted after core formation. Some rocks derived from mantle plumes do show enriched $^{187}\text{Os}/^{188}\text{Os}$, which may reflect some input from the liquid outer core.

The Moon is generally accepted to have formed by a catastrophic impact of a Mars-sized object with Earth (Canup and Asphaug, 2001). Because the Moon has no substantial core, the impact is thought to have occurred after core formation on both Earth and the impactor. The Moon is consequently composed of mantle material from the Earth or the impactor. Jacobsen (2005) argues that the $^{182}\text{W}/^{183}\text{W}$ data best fit the impact occurring at ~ 32 Ma after formation of the Earth.

The decay of ^{146}Sm to ^{142}Nd by alpha emission is another short-lived decay system ($t_{1/2} = 103$ Ma) that can provide precise age constraints on the early history of the Earth (Caro et al., 2003). In this method, the radiogenic ^{142}Nd is measured with respect to the stable ^{144}Nd isotope. The early

Earth would be expected to have a chondritic value of $^{142}\text{Nd}/^{144}\text{Nd}$. Analyses of 3.75-Ga-old metasediments from Isua, Greenland, indicate a slightly elevated $^{142}\text{Nd}/^{144}\text{Nd}$. As discussed in more detail below, the extraction of partial melts from the mantle increases the mantle's Sm/Nd ratio. This, in turn, leads to higher $^{142}\text{Nd}/^{144}\text{Nd}$ through the decay of ^{146}Sm . The Isua analyses therefore indicate that the mantle had already begun to differentiate by 3.75 Ga.

Although the Isua rocks have slightly elevated $^{142}\text{Nd}/^{144}\text{Nd}$, their initial ratio of $^{143}\text{Nd}/^{144}\text{Nd}$ (^{143}Nd is formed by the very slow decay of ^{147}Sm , Eq. (13.15)) is indistinguishable from that of chondritic meteorites. Other slightly younger Archean rocks from South Africa and Western Australia also have initial ratios that, for their particular ages, match the ratio found in chondritic meteorites. The Earth and chondritic meteorites must therefore have had not only the same initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratio but also the same Sm/Nd ratio. Had the Earth had a higher Sm/Nd ratio, for example, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio would have grown at a faster rate than that in the meteorites. Chondritic meteorites and the Earth are therefore believed to have formed from similar primordial solar nebular material, which 4.55 Ga ago had a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.50682 and a Sm/Nd weight ratio of 0.309 (present Sm/Nd=0.308).

Given the Earth's initial $^{143}\text{Nd}/^{144}\text{Nd}$ and Sm/Nd ratios, the evolution of the bulk Earth's $^{143}\text{Nd}/^{144}\text{Nd}$ ratio through geologic time can be calculated from Eq. (13.8) (see Problem 13.5). Figure 13.8 shows how the value of this ratio has evolved from 0.50682 at the time of the Earth's accretion to 0.51265 at the present. It is important to stress that this growth line is for the bulk Earth; actual Earth material will deviate from this depending on the fractionation of the

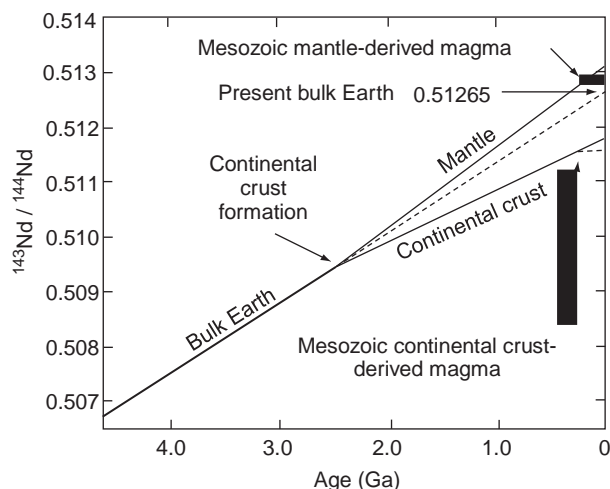


Fig. 13.8 Evolution of the Earth's $^{143}\text{Nd}/^{144}\text{Nd}$ ratio throughout geologic time based on an initial value of 0.50682 and an initial Sm/Nd ratio of 0.309. Formation of a continental crust 2.5 Ga ago would have fractionated Nd into the crust slightly more than it would have Sm. Following crust formation, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio would therefore have grown more rapidly in the mantle than in the crust. Magmas extracted from the mantle since the time of crust formation have higher $^{143}\text{Nd}/^{144}\text{Nd}$ ratios than crustal rocks (short dashed line). See text for discussion.

isotopes during the Earth's differentiation. The sinking of iron and nickel to form the core early in the Earth's history would not have affected the Nd and Sm isotopic ratios because these rare earth elements are strongly lithophile and would simply have been excluded from the core and concentrated in overlying mantle. Differentiation of the remaining material into the crust and mantle would, however, have fractionated these elements, because some of the silicate phases involved in the fractionation incorporate different amounts of the various rare earth elements into their structures.

All of the rare earth elements (REE) have large ionic radii and preferentially enter the rather open structures of the silicates that form the crust of the Earth, rather than entering the denser structures of the minerals in the mantle. Such elements are referred to as large ion lithophile elements (LILE) or elements that are incompatible in the mantle (see Section 14.12). REE that exist in the mantle preferentially enter the more open structure of a melt, if present. Partial fusion and ascent of magma is one way, then, in which the REE can be fractionated into the crust. The REE, however, are not all fractionated to the same degree. With increasing atomic number, the ionic radii of the REE decrease – the so-called lanthanide contraction. Consequently, Nd has a slightly larger ionic radius than Sm has, which makes Nd slightly more incompatible in the mantle than is Sm. Thus, although both elements are strongly fractionated into the crust, Nd is fractionated more than Sm. At present, Nd is estimated to be about 25 times more abundant in the continental crust than in the mantle, whereas Sm is only about 16 times more abundant.

Although Sm and Nd are both fractionated into the crust, the stronger fractionation of Nd means that the Sm/Nd ratio is higher in the mantle than in the crust. Because ^{143}Nd is formed from the decay of ^{147}Sm , the higher Sm/Nd ratio in the mantle causes the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio to grow more rapidly in the mantle than in the crust. Thus, once the Earth became differentiated into a mantle and crust, the growth line of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio split into two, one for the mantle at a level higher than that of the bulk Earth, and one for the continental crust at a level lower than that of the bulk Earth (Fig. 13.8).

Our next problem in understanding the evolution of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio in the Earth is to determine how and when the continental crust came into existence. Did it, for example, develop gradually throughout geologic time, or were there a number of distinct crust-building episodes, or possibly only one?

The discovery of a detrital zircon grain with an age of 4.4 Ga in a metaconglomerate in the Jack Hills of Western Australia has been used as evidence that the continental crust may have already started forming in the Hadean (Wilde et al., 2001). These data were obtained using the U–Pb method with an ion microprobe, which allowed dates to be obtained on different parts of the crystal. In addition, oxygen isotopic data (to be discussed in Section 13.5) were obtained from this crystal, which suggest that Earth's surface was already cool and probably had oceans at this time. The origin of these crystals and the interpretation of their isotopic composition

are hotly debated. The recent discovery of small inclusions of diamonds in the Jack Hills zircons, which have a range of ages from 3.058 to 4.252 Ga, adds to the problem of interpreting these crystals (Menneken et al., 2007). Diamond requires extremely high pressure to form, which can result from deep burial (>200 km) or meteorite impact. The fact that zircons containing these diamond inclusions have such a wide range of ages points to some process that was repeated over an extended period during early Earth history.

Although these zircon crystals may indicate that continental crust was already forming by 4.4 Ga ago, the amount of crust formed must have been small. Had there been any significant amount of continental crust formed prior to the development of the rocks at Isua, Greenland (3.75 Ga), the initial $^{143}\text{Nd}/^{144}\text{Nd}$ for these rocks would not match the primordial values found in meteorites. Indeed, the fact that all rocks older than ~3.0 Ga have initial $^{143}\text{Nd}/^{144}\text{Nd}$ ratios close to those of chondritic meteorites indicates that large amounts of continental crust could not have formed prior to that time. By the end of the Archean (2.5 Ga), however, large areas of continental crust had formed. Since then, more continental crust has undoubtedly formed, but much of it may be reworked Archean crust. For the purpose of our discussion, we will assume, as a first approximation, that the continental crust formed in a single episode 2.5 Ga ago. The fact that it may have had a more prolonged development does not greatly affect our conclusions on the isotopic evolution of the crust and mantle.

Until the formation of the continental crust, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio evolved along the line for the bulk Earth, reaching a value of 0.5094 just prior to the first major period of crust formation (Fig. 13.8). With formation of the crust about 2.5 Ga ago, the REE were fractionated into the crust, the lighter ones more so than the heavy ones. From then on, the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio in the mantle evolved at a faster rate than that in the crust because of the higher Sm/Nd ratio in the mantle. Just prior to crust formation, the bulk Earth $^{147}\text{Sm}/^{144}\text{Nd}$ ratio had evolved to a value of 0.1900. Following crust formation, the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio in that part of the mantle affected by differentiation probably became about 0.2245 and that of the crust became about 0.1435. With these ratios, $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in the upper mantle and crust evolved along the separate lines shown in Figure 13.8 (see Problem 13.6).

It would be interesting to know what fraction of the mantle must have been involved in forming the continental crust, and whether any pristine mantle still exists. Today the largest volumes of mantle-derived magma are erupted as basalts along the mid-ocean ridges, the so-called MORBs. These come from a source that is strongly depleted in incompatible elements, and they have high Sm/Nd and consequently high $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. Because of the enormous volumes of MORB erupted, this depleted source must constitute a significant volume of the mantle. Because it is the most strongly depleted source recognized, we can take it as possibly representing the mantle formed by the extraction of the crust. Knowing the volume of the continental crust and its isotopic composition, we can calculate the volume of mantle having a MORB-like isotopic composition that would be necessary to

provide the bulk Earth composition. Such calculations indicate that the maximum mass of depleted mantle is ~40% of the total mass of the mantle. This indicates that as little as about 600 km of the upper mantle need have been involved in the formation of the continental crust. If the upper mantle is not everywhere as strongly depleted as the source of MORB, a proportionately greater depth of mantle would be involved, possibly as much as 90% (Allègre et al., 1983). Considering the thickness of the mantle, it appears likely that an upper part has been depleted in incompatible elements by the process of crust formation and a separate (decoupled) lower part has maintained its primordial composition to a large extent. Indeed, most isotopic models for the whole Earth require, in addition to the continental crust and a MORB-depleted mantle, a large primitive or enriched reservoir (presumably the lower mantle) to store many of the lithophile elements (Tolstikhin et al., 2006). This conclusion is supported by other geochemical arguments and geophysical evidence (see Section 23.2).

Arguments similar to those used for $^{143}\text{Nd}/^{144}\text{Nd}$ can be used to trace the evolution of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which is tied to the Rb/Sr ratio through the decay of ^{87}Rb to ^{87}Sr . Unfortunately, initial values in ancient rocks do not provide as accurate a measure of primordial values as do those of Nd, because of the mobility of Sr and to a lesser extent Rb during metamorphism. Values obtained from meteorites can be taken as representative of primordial material similar to that which formed the Earth. It is possible to deduce the bulk Earth value for $^{87}\text{Sr}/^{86}\text{Sr}$ from the Nd data, as will be explained below.

Both Rb and Sr are LIL elements, and thus they enter melts in the mantle and are transported into the crust. Rb, however, is far more incompatible in mantle solid phases than is Sr, and therefore Rb is more strongly fractionated into the continental crust. But ^{87}Rb is the isotope that decays to ^{87}Sr . Thus the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, in contrast to that of $^{143}\text{Nd}/^{144}\text{Nd}$, is more radiogenic in the crust than in the mantle. In Figure 13.9, a continental crust, developed 2.5 Ga ago, can be seen to have the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio evolve to much higher values than that of the bulk Earth or the remaining mantle, which is depleted by the formation of the crust (see Problem 13.8).

Figures 13.8 or 13.9 can be used to show how a mantle-derived rock differs isotopically from one formed from crustal material. Consider, for example, a melt derived from a depleted mantle at the beginning of the Mesozoic era (0.245 Ga). Its $^{143}\text{Nd}/^{144}\text{Nd}$ ratio would evolve from an initial value of 0.5127 to a present value of about 0.5129, the precise value depending on the Sm/Nd ratio developed in the melt during partial fusion (Fig. 13.8). Rocks derived from crustal material, by contrast, would be expected to have values less than 0.5120. In terms of the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio (Fig. 13.9), this mantle-derived melt would evolve from an initial value of 0.7026 to a present value of possibly 0.7036, again a very different value from that of a melt derived from an ancient continental crust, which would be expected to have a value near 0.7190. If instead of being derived from a depleted mantle, a melt was formed from mantle that was brought from greater depth (possibly by a mantle plume) and thus

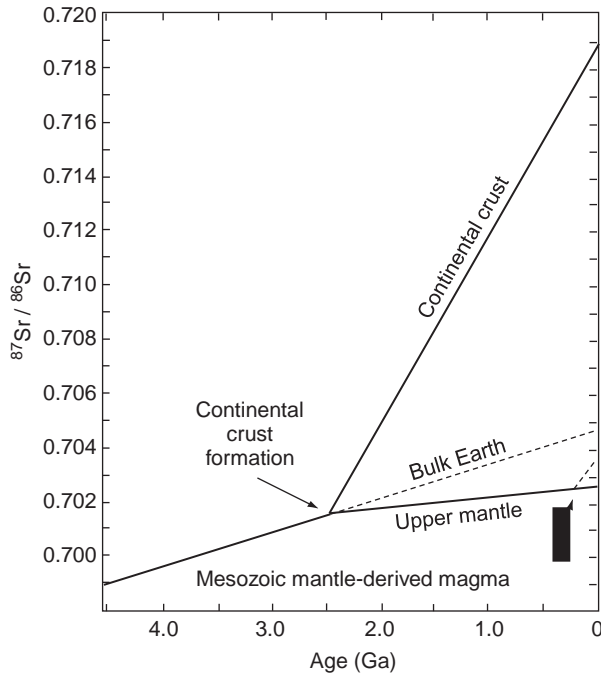


Fig. 13.9 Evolution of the Earth's $^{87}\text{Sr}/^{86}\text{Sr}$ ratio throughout geologic time. The stronger fractionation of Rb relative to Sr into magmas rising from the mantle to form the crust results in the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio growing more rapidly in continental crust than in the bulk Earth or mantle. The continental crust is shown here as forming mainly at one time 2.5 Ga ago. Magmas derived from the mantle after crust formation evolve to lower $^{87}\text{Sr}/^{86}\text{Sr}$ ratios than do continental crustal rocks.

possibly isotopically closer to the composition of the bulk Earth, its isotopic signature would still be quite distinct from that of crustal-derived rocks. For magmas derived from the mantle at much earlier times, the task of distinguishing them from crustal ones obviously becomes more difficult and, in fact, impossible as their age approaches 2.5 Ga. This is why it is difficult to say precisely when a significant amount of continental crust was first formed.

Contamination of a mantle-derived magma by ancient continental crust is also clearly indicated by changes in the Nd and Sr isotopic ratios. Contamination is the simplest explanation for the difference between the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in the two Monteregian intrusive bodies plotted in Figure 13.3. Both intrusions have the same Cretaceous age; that is, their isochrons have identical slopes (about 128 Ma). The pulaskite (syenite with minor nepheline) from Mount Shefford has an initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.70365, which indicates a mantle source (see Fig. 13.9). The granite from Mount Megantic, on the other hand, has an initial value of 0.70518, which is well above the bulk Earth ratio for that age. The Megantic granite must therefore have incorporated some older crust. This intrusion was emplaced through a Grenville-age Precambrian (~1 Ga) basement and a thick sequence of folded lower Paleozoic rocks, any of which could have provided the isotopic contaminant. The Shefford intrusion has risen through a similar crust, but its mode of formation and emplacement must have been different from that of the Megantic granite for it to have preserved a mantle isotopic signature (and its modal nepheline).

The isotopic data for Nd and Sr can be conveniently combined into a single diagram as illustrated in Figure 13.10. The

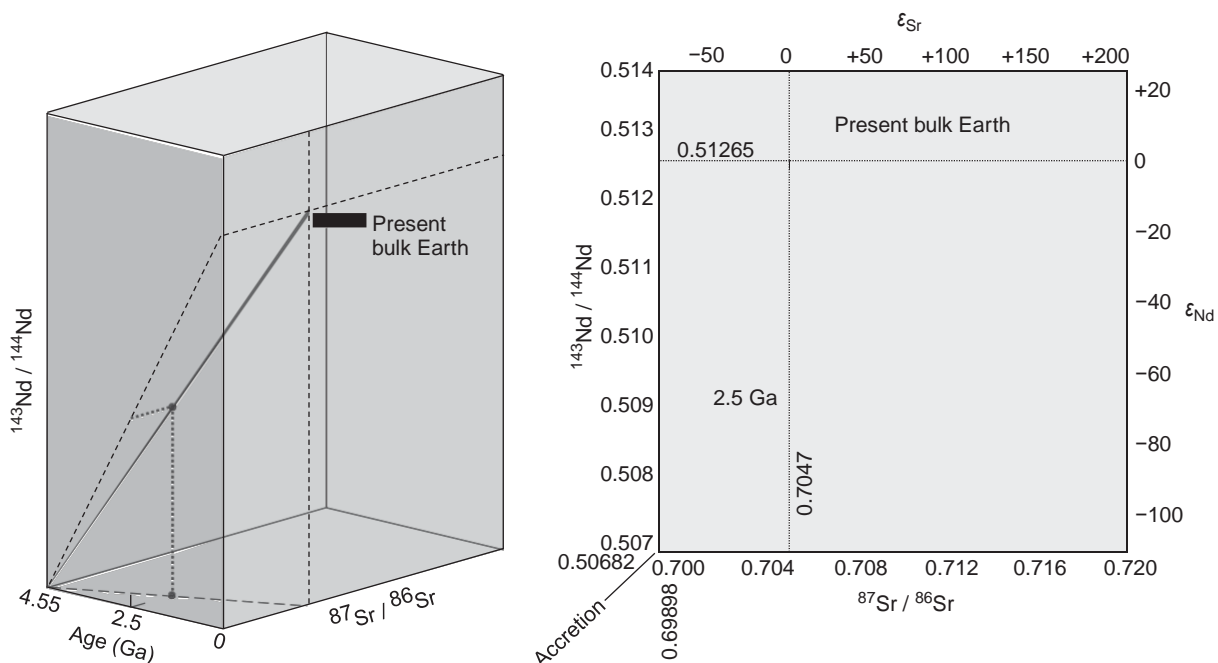


Fig. 13.10 Schematic representation of the evolution of the $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in the bulk Earth (solid heavy line) throughout geologic time. This line is projected onto a plane of constant time (the present) in which $^{143}\text{Nd}/^{144}\text{Nd}$ is plotted against $^{87}\text{Sr}/^{86}\text{Sr}$. See text for definition of ϵ values.

front left face and base of the block diagram are, respectively, Figures 13.8 and 13.9. For simplicity, only the line for the evolution of the bulk Earth has been included in this diagram along with a single point for 2.5 Ga. The evolution of the isotopic composition of the bulk Earth can be traced through the block diagram from its value at the time of accretion (4.55 Ga) to its value at the present day. The data can then be projected onto the front right face of the block diagram in terms of the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. This face, which is shown separately to the right of the block diagram, is constructed for the present time, but other planes representing earlier times can be constructed. On this plane, the bulk Earth is represented by a point (+), but the evolutionary line leading to that point can be projected into this diagram, as shown by the dashed line. The isotopic ratio of the bulk Earth at any time in the past can also be read off this line, as indicated for the one age of 2.5 Ga.

Finally, some geochemists also display this diagram in terms of parameters known as the ϵ_{Nd} and ϵ_{Sr} , which are the fractional deviations ($\times 10^4$) of the $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, respectively, from the values in the bulk Earth at the same time; that is,

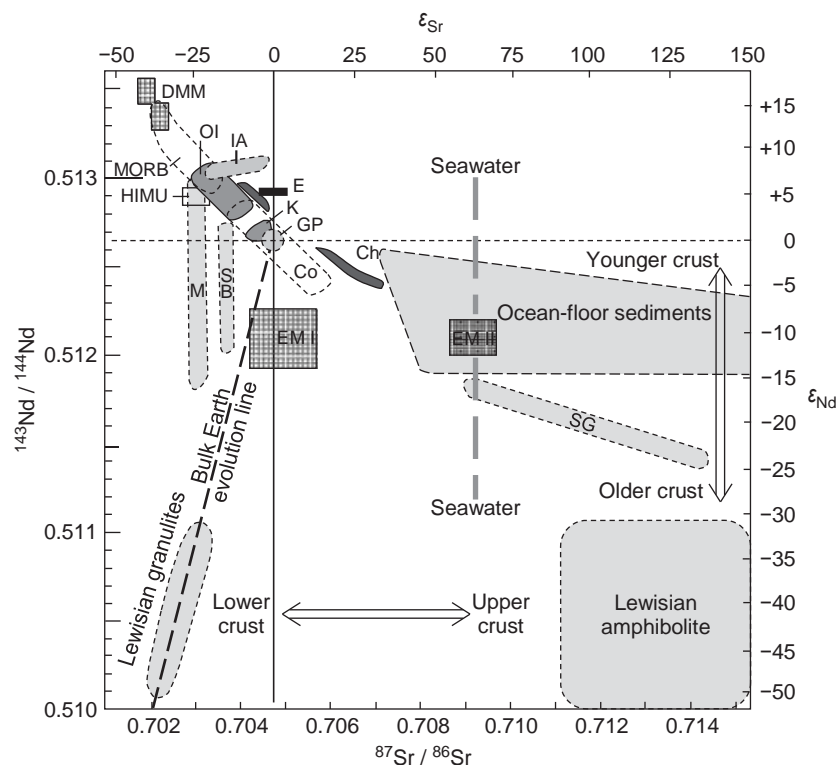
$$\epsilon_{\text{Nd}} \frac{1}{4} = \frac{\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{sample}} - \left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{bulk Earth}}}{\left(\frac{^{143}\text{Nd}}{^{144}\text{Nd}} \right)_{\text{bulk Earth}}} \times 10^4 \quad (13:22)$$

The ϵ_{Sr} is defined in the same way but using the $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. These values are also shown in Figure 13.10. Note that the ϵ values can be calculated for any desired age by adjusting the isotopic ratios for the decay of ^{147}Sm and ^{87}Rb .

A number of important rock types have been plotted in terms of their present $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ ratios in Figure 13.11. This diagram contains much information that needs to be worked through slowly if it is to be appreciated. To help orientate yourself, first locate the present composition of the bulk Earth (+) and the evolutionary line for the bulk Earth; these are identical to those in Figure 13.10. The lines marking the present bulk Earth ratios of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$ divide the diagram into four quadrants. Most mantle-derived rocks plot in the upper left quadrant ($+\epsilon_{\text{Nd}}$, $-\epsilon_{\text{Sr}}$), and most continental crustal rocks plot in the lower right quadrant ($-\epsilon_{\text{Nd}}$, $+\epsilon_{\text{Sr}}$). The quadrants are respectively depleted and enriched in LIL elements.

Passing through the bulk Earth composition is a remarkably linear array of isotopic ratios in rock types ranging from mid-ocean ridge basalt (MORB), oceanic island intraplate basalt (OI), kimberlite (K), garnet peridotite xenoliths (GP), and continental flood basalts (Co). All of these rocks, without doubt, have formed from magma originating in the mantle. Thus, they provide a sampling of mantle isotopic ratios, at least from those parts tapped by the magmas. For this reason, this range of isotopic values is commonly referred to as the mantle array. It indicates a strong negative correlation between Sr and Nd isotopes. Indeed, in light of the previous discussion of the relative degrees of fractionation of Sm–Nd and Rb–Sr, this variation is to be expected; that is, the continental crust was formed of material that had a lower Sm/Nd ratio and a higher Rb/Sr ratio than the bulk Earth. Upon decay of ^{147}Sm to ^{143}Nd and ^{87}Rb to ^{87}Sr , high values of

Fig. 13.11 Plot of important rock types in terms of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. Mid-ocean ridge basalt (MORB) and oceanic islands (OI) (O'Nions et al., 1977; Norry and Fitton, 1983); island-arc rocks (IA) (DePaolo and Johnson, 1979); kimberlite (K), garnet peridotite mantle nodules (GP), and continental flood basalts (Co) (Hawkesworth et al., 1983); central volcanic complexes of Mull (M), Skye basalts (SB), Skye granites (SG), and Lewisian granulites and amphibolites (Carter et al., 1978); andesites of Ecuador (E) and Chile (Ch) (Hawkesworth et al., 1979); and ocean floor sediments (White et al., 1985). Possible mantle source components for oceanic magmas shown as stippled rectangles are from Zindler and Hart (1986): depleted MORB mantle (DMM), high μ (HIMU), enriched mantle I (EM I), and enriched mantle II (EM II). See text for discussion.



$^{143}\text{Nd}/^{144}\text{Nd}$ correlate with low values of $^{87}\text{Sr}/^{86}\text{Sr}$; that is, radiogenic Nd correlates with unradiogenic Sr, and vice versa.

The rock types that constitute the mantle array have formed from sources showing variable degrees of depletion in the LIL elements. This variation may occur laterally or vertically within the mantle. MORBs have formed from the most strongly depleted source, and their restricted compositional range indicates that a rather homogeneous, depleted mantle exists beneath all ocean ridges. Basalts with similar isotopic composition do rarely occur in continental extensional regions, such as the Basin and Range province of the western United States. Oceanic islands that occur within plates (i.e. those not associated with divergent plate boundaries) are composed of rocks with a much wider range of isotopic composition along the mantle array than MORB. Most lie within the region marked OI in Figure 13.11, but they can extend to compositions that are slightly enriched over that of the bulk Earth. Their source is not nearly as depleted as that of MORBs. Their range of composition may result from mixing of material derived from undepleted and depleted sources. Because oceanic islands are believed to develop over mantle plumes, their magmas probably tap a deeper part of the mantle than do MORBs, and thus they have more pristine compositions. Recall that some of these plume-related rocks also have elevated $^{187}\text{Os}/^{188}\text{Os}$, which may indicate a contribution from as deep as the outer core. Alkaline basalts within continental plates have isotopic signatures identical to those of oceanic islands. Both must therefore have developed their signature at depths greater than the base of the thick continental lithosphere, which is so different from the oceanic lithosphere.

Continental flood basalts cover a range of composition along the mantle array, but most have compositions near that of the bulk Earth. This has had various interpretations. Their source could be in a part of the mantle that still preserves bulk Earth isotopic compositions. On the other hand, their source could be in a depleted mantle, but the magma assimilates enough continental crustal material to give a bulk Earth ratio. They could also have formed in a depleted mantle that becomes enriched by metasomatism prior to magmatism. There is, as yet, no resolution to this problem; perhaps all factors play a role in varying degrees in different regions. Kimberlites and their enclosed garnet peridotite xenoliths do have isotopic compositions that are very close to that of the bulk Earth. This implies that mantle with a bulk Earth isotopic composition does exist at depths of about 200 km beneath the continental crust in those regions where kimberlites originate.

The negative correlation between Nd and Sr isotopes in the mantle array and the mantle depletion in LIL elements, which it implies, must be the result of a long-lived phenomenon. For instance, had the depletion in ^{87}Rb occurred only recently, the decay product, ^{87}Sr , would still be present in the source region. But it is not, and the amount of ^{87}Sr that is found is consistent with there having been a deficiency of ^{87}Rb in the source for a considerable period of time. All indications are that this depletion occurred during the

formation of the crust, which the Nd and Sr data indicate has a mean age of between 2.46 and 2.14 Ga (Allègre et al., 1983). Note that this is a mean age; it does not rule out the possibility that the crust-forming process started much earlier (Wilde et al., 2001).

It was previously mentioned that the bulk Earth composition for $^{87}\text{Sr}/^{86}\text{Sr}$ cannot be determined as accurately as that for $^{143}\text{Nd}/^{144}\text{Nd}$ because of the greater susceptibility of Rb and Sr to change during metamorphism. The strong negative correlation between these two isotopic ratios in the mantle array, however, allows the accurately known $^{143}\text{Nd}/^{144}\text{Nd}$ ratio to be used to determine the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, which at present is 0.7047.

Continental crustal rocks range more widely in isotopic composition than do mantle-derived ones, in part because of the strong elemental fractionation involved in crust-forming processes (partial melting, weathering, sedimentation), but also because of the relative volumes of the continental crust and mantle. Most crustal rocks plot in the lower right quadrant of Figure 13.11. In general, the greater the age of a segment of crust the farther to the lower right of the diagram it plots; this will be evident from inspection of the growth curves in Figures 13.8 and 13.9. Within the crust itself, there appears to be fractionation of some isotopes. In Chapter 1 it was shown, from heat flow calculations for the continental crust, that U, Th, and K must be concentrated toward the Earth's surface. Rubidium, which behaves geochemically much like K, also appears to be concentrated upward in the crust. Consequently, the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio generally increases upward in the crust. No such crustal differentiation, however, affects Sm and Nd and thus the $^{143}\text{Nd}/^{144}\text{Nd}$ ratio is unaffected. The result in the plot of Figure 13.11 is a shift from right to left with increasing depth in the crust. This is illustrated by the ancient Lewisian rocks (2.95 Ga) of Scotland. The deepest exposed Lewisian rocks, which are in the granulite facies, have very low $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.702 to 0.703). Shallower amphibolite facies rocks, on the other hand, have high $^{87}\text{Sr}/^{86}\text{Sr}$ values (0.711 to 0.720).

Because mantle-derived magmas and continental crustal rocks plot in very different positions in Figure 13.11, the effects of assimilation or magma mixing between these two should be readily evident. The isotopic variation exhibited by the mantle array is expected to result from partial melting or fractional crystallization. Isotopic variations in other directions imply mixing of different isotopic compositions. If the materials to be mixed have the same Sr/Nd ratios, mixing in Figure 13.11 results in a simple linear array between the two end-member compositions. If the Sr/Nd ratios are different in the two materials, intermediate compositions lie along curved lines (DePaolo and Wasserburg, 1979). In general, continental crustal materials have lower Sr/Nd ratios than do mantle-derived rocks, and as a result mixtures of mantle and crustal rocks lie along gently curved lines that are concave toward the upper right in Figure 13.11.

The basalts of the Islands of Mull and Skye on the north-west coast of Scotland formed during the early opening of the North Atlantic. Unlike lavas that have since erupted along the

Mid-Atlantic Ridge, these early basalts ascended through continental crust, which consists of Lewisian metamorphic rocks. The almost vertical trends of the Mull and Skye basalts in Figure 13.11 are not consistent with fractional crystallization. They do, instead, form a simple linear trend from a depleted magma toward a lower crustal Lewisian granulite composition. This is a clear case of lower crustal contamination of a mantle-derived magma.

On both Mull and Skye, there are large central igneous complexes containing granites, which some geologists have interpreted as having formed from melted crustal rocks or contamination of mantle-derived magmas. Only the granites of Skye (SG) are included in Figure 13.11, and these plot along a curved line between the mantle array and the most radiogenic Lewisian amphibolites. These granites, then, can be interpreted as a mixture of a mantle magma and crustal material. In contrast to the basalts, however, the granites assimilated higher-level crustal rocks.

Contamination of large bodies of mafic magma that have crystallized in the crust can also be demonstrated by their isotopic composition. The mid-Proterozoic (1.1 Ga) Kalka intrusion in central Australia, for example, was emplaced in quartzo-feldspathic granulite facies gneisses. Although some of the rocks of this intrusion have Nd and Sm isotopic compositions that plot very near the bulk Earth composition on the mantle array, most fall along a linear trend extending toward high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios but maintaining approximately the bulk Earth $^{143}\text{Nd}/^{144}\text{Nd}$ ratio. This trend is not included in Figure 13.11, but it approximately follows the $\epsilon_{\text{Sr}}=0$ line to the right of the bulk Earth composition. This trend is directly toward the isotopic composition of the gneisses surrounding the intrusion, and is undoubtedly the product of crustal contamination of a mafic magma (Gray et al., 1981). This assimilation is believed to have been responsible for the copious precipitation of orthopyroxene in this intrusion. Other large mafic intrusions that have crystallized within the crust and that also contain abundant orthopyroxene, such as the Duluth Gabbro, the Bushveld Complex, and the Palisades Sill, have isotopic trends similar to that of the Kalka rocks, plotting to the right of the mantle array. Crustal assimilation seems likely in these intrusions as well.

The amount of crustal contamination of mantle-derived magmas indicated by the isotopic ratios of Nd and Sr is commonly much greater than is permissible based on the major element chemistry. The silica content of basaltic magmas, which is typically about 50 wt %, is changed significantly when continental crustal material, which typically contains >70 wt% SiO_2 , is assimilated. Many basaltic magmas whose isotopic composition indicates there has been considerable assimilation of continental crustal material (high $^{87}\text{Sr}/^{86}\text{Sr}$ values) still contain almost pristine silica contents. The most likely explanation for this paradox is that contamination involves only a small fraction of the crustal rocks, but that fraction is particularly enriched in the isotopes concerned, especially Sr. This fraction might be derived, for example, by partial fusion of the crustal rocks or by extraction of hydrous fluids.

The igneous rocks developed above a subduction zone – the calcalkaline series – form one important group of rocks for which large-scale crustal contamination is commonly invoked to explain their composition. Five possible components may play roles in the formation of calcalkaline magmas: the mantle wedge overlying the subduction zone, subducted rocks of the oceanic crust (principally MORB), subducted sedimentary rocks, seawater, and crustal contaminants picked up during magma ascent. Each of these components is potentially identifiable from its isotopic signature. Thus, isotopic analysis of calcalkaline rocks may shed light on the origin of these rocks. We will examine the isotopic composition of calcalkaline rocks in two very different environments: first, where an island arc develops entirely between oceanic plates at a sufficient distance from continental areas that there can be no possible contribution from continental material, and second where a continental plate overrides an oceanic plate.

The New Britain island arc, which has been studied isotopically by DePaolo and Johnson (1979), is sufficiently far removed from continental masses to eliminate any possible continental contribution to these rocks. They nonetheless include rocks ranging from basalt to rhyolite. Their Nd and Sr isotopic compositions fall in a very small area in Figure 13.11(IA). They form a linear trend with a very slight positive slope extending from compositions on the mantle array at the depleted end of the oceanic island field to ϵ_{Sr} values of almost zero. Other island arcs have similar isotopic compositions. The trend is not one that can be explained by fractional crystallization or varying degrees of partial melting. It must involve mixing of various components. The primary source appears to be mantle that is not as depleted as that from which most MORBs are derived, but it is similar to material on anomalous ridge segments that are not as depleted as normal MORB or to some intraplate oceanic islands. The source is not simply melted average MORB, which is too depleted. The most likely major source for these rocks, then, is in the mantle wedge above the subducted plate.

The most striking feature of the isotopic composition of the island-arc rocks is their trend toward increasing $^{87}\text{Sr}/^{86}\text{Sr}$ ratios with almost constant $^{143}\text{Nd}/^{144}\text{Nd}$ ratios. Mixing of a mantle source with ocean floor sediments would not produce such a trend. Most ocean floor sediments are ultimately derived from continental areas and thus their isotopic composition places them in the lower right quadrant of Figure 13.11. Mixing of this material with mantle material would produce rocks that plot along a smooth curve with a negative slope. The most likely explanation for the isotopic trend is the incorporation of seawater in the magmas. At present, seawater has an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7092, but its content of Nd is so small ($<3 \times 10^{-5}$ ppm) that addition of seawater to any rock on the mantle array results in the isotopic composition simply being shifted to the right. Seawater can be incorporated directly as pore water trapped in the subducted plate, but it can also be stored in the ocean floor rocks in the form of hydrous alteration minerals. Its transport into the overlying mantle wedge upon subduction can be either as rising

solutions or as partly melted MORB. The Nd and Sr isotopes imply that most of the magma generated in oceanic island arcs must come from the mantle wedge above the subduction zone, fluxed by seawater that is released from the downgoing oceanic plate. The slight positive slope to the island arc trend in Figure 13.11 could be produced from a small contribution of MORB that has been shifted to the right as a result of seawater alteration. A small amount of melting of ocean floor basalt may therefore occur in the subducted plate, especially if that ocean floor is young and still hot, as would occur if a mantle ridge were subducted. Plank and Langmuir (1993) have shown that trace element characteristics of some island arcs can be correlated with the composition of sediments being subducted. Some elements may be transferred from sediments into the mantle wedge by fluids released during subduction. The contribution of material from ocean-floor sediments, however, must be small, otherwise their strong isotopic signature would be detected.

Calcalkaline rocks developed on continental crust have a very different isotopic pattern from those developed in oceanic island arcs. As an example, data for the Andes have been included in Figure 13.11 (Hawkesworth et al., 1979). In Ecuador (E in Fig. 13.11), andesites have Nd and Sr isotopic compositions that plot slightly to the right of the mantle array, and they are more depleted than the bulk Earth composition. Andesites in Chile (Ch in Fig. 13.11) also plot to the right of the mantle array, but they are enriched relative to the bulk Earth composition. In contrast to the oceanic island arc rocks, these continental andesites form trends that roughly parallel the mantle array. Their trends can be interpreted as resulting from the mixing of three major components – a depleted mantle source, seawater, and a component that is enriched relative to the bulk Earth composition – but the interpretation is far from unequivocal.

Melting of subducted MORB does not appear to have played an important role in generating andesites. The trace element enrichment in andesites relative to that in MORB would require less than 5% partial melting of MORB for their generation. Yet 30% melting would be required to provide the major element chemistry. The trace element and isotopic compositions of the andesites are therefore best provided by a mantle source similar to that of the island arc rocks.

The simplest explanation for the andesites plotting to the right of the mantle array is the involvement of seawater. Further explanation of their trend, however, is complicated by numerous factors. First, trends paralleling the mantle array could be due to fractional crystallization, varying degrees of partial melting, or mixing of appropriate compositions. Clearly, compositions that are enriched relative to the bulk Earth composition are involved, but this could be subducted oceanic sediments, continental crustal material, or even mantle that was enriched in incompatible elements. There are, unfortunately, too many possible components for the Nd and Sr isotopes to define the sources uniquely. There is no question, however, that andesites consist predominantly of a mantle-derived component.

Finally, the Sm–Nd and Rb–Sr data can also be used to show that episodes of magmatic activity may be preceded by periods of mantle metasomatism. This has been well documented for intraplate alkaline magmatism (Norry and Fitton, 1983). In Figure 13.11, oceanic island rocks plot on the mantle array in the depleted quadrant; that is, they have relatively high $^{143}\text{Nd}/^{144}\text{Nd}$ and low $^{87}\text{Sr}/^{86}\text{Sr}$ ratios, which imply that the source regions must have had, for some considerable time, low relative concentrations of ^{144}Nd to ^{147}Sm and ^{87}Rb to ^{86}Sr . Many oceanic island and continental alkaline complexes, however, have relatively high ^{144}Nd and ^{87}Rb contents. Indeed, many of these have Sm/Nd (low) and Rb/Sr (high) ratios that, if present in their source regions for any length of time, would have generated low $^{143}\text{Nd}/^{144}\text{Nd}$ and high $^{87}\text{Sr}/^{86}\text{Sr}$ ratios. The fact that they have not can only mean that the more incompatible elements were recently introduced; that is, magmatism was preceded by a period of metasomatism in which the more incompatible elements, Nd and Rb, were introduced into a depleted mantle.

Another long-lived isotopic system that is commonly used to investigate the age and provenance of rocks involves the decay of ^{176}Lu to ^{176}Hf with a half-life of 35.7 Ga. Lutetium is the heaviest of the rare earth elements, whereas Hf is an element similar to zirconium, and commonly substitutes in the mineral zircon. Both the parent and daughter isotopes are measured with respect to the stable ^{177}Hf isotope. The $^{176}\text{Hf}/^{177}\text{Hf}$ ratio steadily grows with decay of the ^{176}Lu . However, when partial melts are extracted from the mantle, the Lu/Hf ratio in the mantle is increased several times over that found in the complementary crust, with the result that the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio in the mantle grows more rapidly than in the crust. Its growth is similar to that of $^{143}\text{Nd}/^{144}\text{Nd}$, but because of the stronger partitioning of Lu/Hf between mantle and crust, the contrast in the $^{176}\text{Hf}/^{177}\text{Hf}$ is greater. When zircon crystallizes, hafnium is strongly partitioned into the crystal, but lutetium is not. Consequently, zircon crystals tend to preserve the $^{176}\text{Hf}/^{177}\text{Hf}$ ratio at the time of crystallization, which remains essentially unchanged due to the low Lu/Hf ratio. In contrast, garnet crystals take in large amounts of lutetium, while rejecting hafnium. Consequently, the Lu–Hf system provides an excellent way of dating garnets, which have the benefit of a relatively high closure temperature of ~600 °C. Lutetium and hafnium have also been used in the same way as samarium and neodymium to determine the source of magmas above subduction zones. Handley et al. (2007) use both Lu–Hf and Sm–Nd analyses to show that subduction-related magmas in Indonesia were derived primarily from a fertile mantle wedge to which a small amount of fluid was added from subducted altered ocean floor rocks and <1% pelagic sediment.

Although the remarkably uniform major element composition of ocean-floor basalts suggests that the mantle beneath oceans is homogeneous, isotopic studies of these basalts and oceanic islands show, unequivocally, that the mantle is heterogeneous. These basalts can have components derived from possibly as many as five different sources, each with its own characteristic isotopic signature (Zindler and Hart, 1986; Hofmann, 1997;

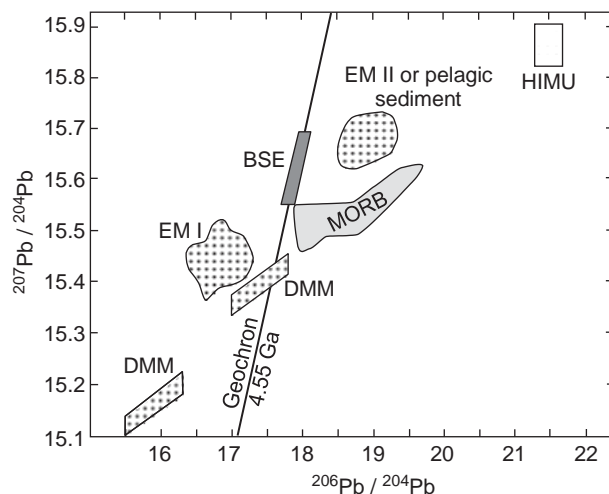


Fig. 13.12 Plot of possible mantle source components for oceanic magmas in terms of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$. Two possible depleted MORB mantle sources (DMM), high μ (HIMU), enriched mantle I (EM I), and enriched mantle II (EM II) are shown by stippled areas. Also shown is the typical range for MORBs. The composition of the bulk silicate Earth (BSE) is shown on a geochron for 4.55 Ga.

Shirey and Walker, 1998). We have already seen in Figure 13.11 that volcanic rocks have a wide range of compositions in terms of $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{87}\text{Sr}/^{86}\text{Sr}$. Although some of these sources have been plotted in Figure 13.11, other isotopic systems must be involved to distinguish between some of them. By adding to this array the isotopic data from ^{238}U – ^{206}Pb , ^{235}U – ^{207}Pb , ^{232}Th – ^{208}Pb , ^{176}Lu – ^{176}Hf , and ^{187}Re – ^{188}Os systems, the five mantle sources can be characterized.

The most abundant volcanic rock of the ocean's floor is the normal mid-ocean ridge basalt (N-type MORB). This is derived from a source that has undergone repeated melt removal, which has depleted it in incompatible elements; that is, elements that prefer to enter a melt rather than remain in the crystals of the mantle (olivine, pyroxene, spinel, garnet). This depleted MORB mantle (DMM), which is the most depleted of all the sources, is characterized by high $^{143}\text{Nd}/^{144}\text{Nd}$, and low $^{87}\text{Sr}/^{86}\text{Sr}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ relative to the bulk silicate Earth (BSE), which is based on a chondritic parent from which the metallic core has separated. The DMM can be further divided into two possible sources, one with slightly higher $^{206}\text{Pb}/^{204}\text{Pb}$ than the other (Fig. 13.12). The other sources all show some enrichment in incompatible elements relative to the BSE (Figs. 13.11 and 13.12). One source has a very high U/Pb (= μ) and is therefore referred to as high μ (HIMU). Decay of the ^{238}U causes this source to have a high $^{206}\text{Pb}/^{204}\text{Pb}$ but otherwise it is similar to DMM in having high $^{143}\text{Nd}/^{144}\text{Nd}$ and relatively low $^{87}\text{Sr}/^{86}\text{Sr}$. HIMU is thought to be mantle that contains recycled oceanic crust. Enriched mantle I (EM I) has high $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{208}\text{Pb}/^{204}\text{Pb}$ for a given $^{206}\text{Pb}/^{204}\text{Pb}$, low $^{143}\text{Nd}/^{144}\text{Nd}$, but low $^{87}\text{Sr}/^{86}\text{Sr}$. The enrichment in this source may have been caused by metasomatism or the recycling of lower continental crust. Enriched mantle II (EM II) is similar to EM I except that $^{87}\text{Sr}/^{86}\text{Sr}$ is high. This mantle may contain recycled upper continental crust.

The fifth source was referred to by Hart et al. (1992) as the focus zone (FOZO) and it is characterized by high $^3\text{He}/^4\text{He}$. This isotopic signature is found at hot spots, such as Hawaii and Iceland. The primitive ^3He is thought to come from a deep mantle source entrained in the mantle plume.

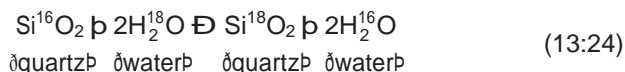
13.5 STABLE ISOTOPES

For most elements, the difference in mass between their isotopes is so small that isotopic fractionation is not likely to occur, especially at elevated temperatures within the Earth. Relative mass differences between isotopes of the light elements, however, are large, and consequently these isotopes can be fractionated by both chemical and physical processes. With the present resolution of mass-spectrometric techniques, isotopic fractionation can be detected in elements with atomic numbers up to 20 (Ca), but work has focused mainly on the stable isotopes of H, He, O, and S.

As with other isotopic analyses, measurements of the light stable isotopes are more conveniently and accurately made using isotopic ratios rather than absolute amounts. Analyses are expressed in terms of the delta value, δ , which is the per million (‰) fractional difference between the isotopic ratio in the sample and a standard. The heavier isotope is made the numerator. Thus for the $^{18}\text{O}/^{16}\text{O}$ ratio, the delta value is expressed as

$$\delta^{18}\text{O} \text{ ‰} = \frac{^{18}\text{O}/^{16}\text{O}_{\text{sample}} - ^{18}\text{O}/^{16}\text{O}_{\text{standard}}}{^{18}\text{O}/^{16}\text{O}_{\text{standard}}} \times 10^3 \quad (13:23)$$

Isotopic fractionation can result from chemical or physical processes, and it can reflect equilibrium or kinetic conditions. Take, for example, the simple exchange reaction of oxygen isotopes between quartz and water:



This reaction does not go all the way to the right or to the left. Instead, some equilibrium distribution exists that is determined by the free-energy change of the reaction (see Chapter 9). Because the free-energy change is a function of temperature, the distribution of the isotopes between the two phases can serve as a geothermometer. This, then, is an example of equilibrium fractionation. In contrast, the more rapid evaporation of H_2^{16}O relative to H_2^{18}O from water is a kinetic fractionation. An important difference between the equilibrium and kinetic fractionation process is that kinetic fractionation is transient, and if carried to completion results in no fractionation. In the previous example, evaporation of water may at first favor the molecules with the lighter oxygen, but if all of the water is evaporated, the isotopic composition of the vapor will be the same as that of the initial water. At any temperature, however, there would be some equilibrium distribution of oxygen isotopes between the liquid and vapor phases that would be independent of time.

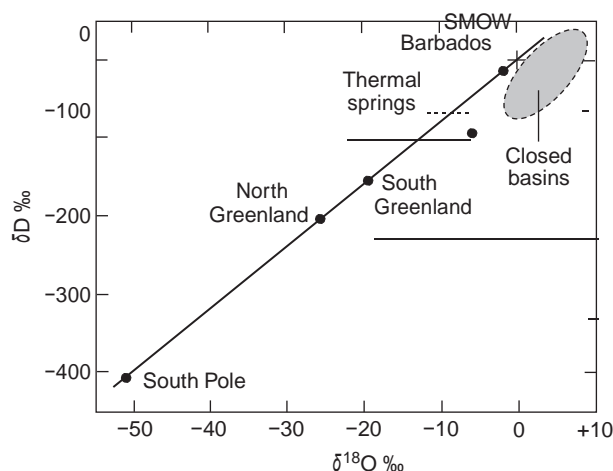


Fig. 13.13 Variation in the deuterium (^2H) to hydrogen (^1H) ratio (δD , see Eq. (13.23)) versus the $\delta^{18}\text{O}$ value for surface waters.

Fractionation has produced such varied isotopic compositions in different environments that in many cases the isotopes can be used to identify the source of material or the environment in which a rock formed. The following is a brief introduction to those stable isotopes that are commonly encountered in the petrologic literature. For a detailed discussion see Sharp (2006) or Valley (2001).

13.5.1 Oxygen and hydrogen isotopes

Isotopic ratios of $^{18}\text{O}/^{16}\text{O}$ and $^2\text{H}/^1\text{H}$ (D/H) are both measured with respect to the standard known as standard mean ocean water (SMOW). $\delta^{18}\text{O}$ values range from about -50 to $+30$ and δD values range from -400 to 0 . A very strong correlation exists between the $\delta^{18}\text{O}$ and δD in natural waters and the latitude (Fig. 13.13); toward the poles, oxygen and hydrogen become progressively enriched in lighter isotopes. This is a consequence of the preferential precipitation of heavy isotopes from clouds. As clouds move away from the equatorial region toward the poles, they become progressively depleted in the heavier isotopes, which are removed by the rain. The same trend can be seen as a function of the distance clouds travel into a continent from an ocean. The line relating the δD and $\delta^{18}\text{O}$ in Figure 13.13 has a slope of 8, which is the value that would be predicted from the equilibrium fractionation of these isotopes between liquid and vapor. Two sources of natural surface water that fall off the main trend are closed basins and hot springs. Evaporation of light ^{16}O from water in closed basins increases the $\delta^{18}\text{O}$ value. Hot springs are enriched in ^{18}O relative to normal groundwater because of interaction with surrounding rocks, which invariably have higher $\delta^{18}\text{O}$ values.

One of the most spectacular successes in the use of oxygen isotopes was in showing that the Pleistocene glaciations could be correlated with the orbital mechanics of the Earth around the Sun, the so-called Milankovitch cycles. This correlation, which is documented in all introductory geology textbooks, is based

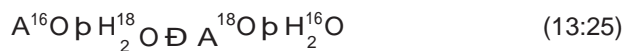
on the oxygen isotopic composition of ocean floor sediments. During periods of major glacial advance, precipitation, which is always richer in ^{16}O than seawater, becomes trapped on continents in the form of ice, and consequently seawater becomes slightly enriched in ^{18}O . Ocean-floor sediment

formed from pelagic organisms reflect this elevated $\delta^{18}\text{O}$, with the degree of enrichment reflecting the amount of ice on the continent and hence the severity of the glaciation. Profiles of $\delta^{18}\text{O}$ through the ocean-floor sediment are almost identical to Earth's calculated temporal change in heat flux from the Sun, which has cycles of 23 000, 41 000, and 100 000 years (Milankovitch cycles), due respectively to the precession and change in tilt of Earth's axis and the change in the eccentricity of its orbit about the Sun.

Typical $\delta^{18}\text{O}$ values for mantle-derived rocks (peridotites, gabbros, basalts, andesites, and syenites) and chondritic meteorites are from $+5\text{‰}$ to $+7\text{‰}$, whereas continental-derived rocks are higher and more variable. For example, Peck et al. (2000) found that the oxygen isotopes in zircon crystals in Archean rocks of the Canadian Shield had a remarkably restricted range of $\delta^{18}\text{O}$ of $5.77\text{‰} \pm 0.6\text{‰}$, which suggests that they crystallized from magmas that had equilibrated with primitive mantle. In contrast, zircon crystals in Proterozoic rocks had higher and more variable $\delta^{18}\text{O}$ of $8.2\text{‰} \pm 1.7\text{‰}$, which indicates that by that time material from a continental crust must have been transported to depth and incorporated into magmas. Surface processes, such as weathering, that are involved in forming sediments produce elevated $\delta^{18}\text{O}$, and as a result continental rocks typically have higher $\delta^{18}\text{O}$. Because most granites are formed from partially melted continental crust they have $\delta^{18}\text{O}$ ranging from $+7\text{‰}$ to $+13\text{‰}$. Rhyolites in oceanic island arcs, on the other hand, have $\delta^{18}\text{O}$ values similar to those in the associated basaltic rocks, which indicates that they differentiated from a common mantle source. $\delta^{18}\text{O}$ values for sedimentary rocks are positive, and for limestones can be as high as $+30\text{‰}$. Pristine igneous rocks do not have the negative values of $\delta^{18}\text{O}$ that characterize natural surface water. Interaction of igneous rocks with meteoric water can therefore be detected easily from the oxygen isotopes. For example, Tertiary basalts around the central complex of the Isle of Mull on the west coast of Scotland have had their $\delta^{18}\text{O}$ values lowered to -6.5‰ by convecting groundwater systems set up during the cooling of the central complex. Similarly, during the cooling of the Skaergaard intrusion, East Greenland, a convecting groundwater cell was set up by the cooling intrusion and meteoric water that was able to percolate easily through the surrounding fractured basalts exchanged oxygen with the Skaergaard rocks and lowered their $\delta^{18}\text{O}$ values to -5‰ (Norton and Taylor, 1979). Where the intrusion is in contact with the less fractured gneissic country rocks (see Fig. 15.15) the $\delta^{18}\text{O}$ values of the igneous rocks still retain their primary character ($\delta^{18}\text{O} > 5.7\text{‰}$).

Oxygen isotopes provide one of the most reliable geothermometers, and, considering the abundance of oxygen in minerals, one of the most widely applicable, especially for rocks formed at low to moderate temperatures. Equation

(13.24) expresses the exchange reaction of ^{18}O and ^{16}O between quartz and water. Similar reactions can be written for all oxygen-bearing minerals. We can generalize such a reaction as



where AO is some oxygen-bearing mineral. The equilibrium constant, K, for this reaction can be expressed as

$$K^{1/4} = \frac{(^{18}\text{O}_\text{A})(^{16}\text{O}_\text{H}_2\text{O})}{\delta^{18}\text{O}_\text{A} \text{p} \delta^{18}\text{O}_\text{H}_2\text{O}} \frac{^{18}\text{O}_\text{A}}{^{16}\text{O}_\text{A}} \frac{^{16}\text{O}_\text{H}_2\text{O}}{^{18}\text{O}_\text{H}_2\text{O}} \quad (13:26)$$

where $^{18}\text{O}_\text{A}$ is the concentration of ^{18}O in phase A. But, from Eq. (13.23) it follows that

$$\frac{^{18}\text{O}_\text{A}}{^{16}\text{O}_\text{A}} \text{p} \frac{^{18}\text{O}_\text{SMOW}}{^{16}\text{O}_\text{SMOW}} = \frac{^{18}\text{O}_\text{A}}{1000} \text{p} 1$$

Therefore,

$$K^{1/4} = \frac{\delta^{18}\text{O}_\text{A} \text{p} 1000}{\delta^{18}\text{O}_\text{H}_2\text{O} \text{p} 1000} \quad (13:27)$$

For most of the common rock-forming minerals, $K > 1$; that is, ^{18}O is concentrated in the mineral rather than in the water, with quartz effecting the largest fractionation. The one prominent exception is magnetite, which preferentially takes in the lighter isotope. The value of K varies with temperature ($K = e^{-\Delta G/RT}$), approaching a value of 1 at high temperatures for all mineral–water pairs.

If minerals and the fluids from which they crystallized could be analyzed for their oxygen isotopes, Eq. (13.27) would form the basis for a geothermometer. Unfortunately, the fluid phase is normally no longer available for analysis. We may still use Eq. (13.27), however, if two minerals crystallize together, preferably minerals that have very different equilibrium constants. Quartz and magnetite best satisfy this condition, but other mineral pairs can be used. For the quartz–magnetite pair, Eq. (13.27) can be rearranged as follows:

$$\left(\delta^{18}\text{O}_\text{H}_2\text{O} \text{p} 1000 \right)^{1/4} = \frac{\delta^{18}\text{O}_\text{Qz} \text{p} 1000}{K_\text{Qz}} \quad (13:28)$$

and

$$\left(\delta^{18}\text{O}_\text{H}_2\text{O} \text{p} 1000 \right)^{1/4} = \frac{\delta^{18}\text{O}_\text{Mt} \text{p} 1000}{K_\text{Mt}} \quad (13:29)$$

Combining these two equations, the delta value of the fluid is eliminated, leaving

$$\frac{\delta^{18}\text{O}_\text{Qz}}{K_\text{Qz}} \text{p} \frac{\delta^{18}\text{O}_\text{Mt}}{K_\text{Mt}} \quad (13:30)$$

Because the values of K, which are functions of temperature, are known from experiments and the delta values of quartz and magnetite can be measured mass spectrometrically,

the equation can be solved for temperature. The general thermometer expression valid for metamorphic and igneous temperatures is (e.g. Valley, 2001; Sharp, 2006)

$$1000 \ln \alpha_{\text{A-B}} \text{p} \frac{a_1 \times 10^6}{T^2} \quad (13:31)$$

where a_0 is a constant, a_1 is the temperature coefficient of fractionation, T is in kelvin, and $\alpha_{\text{A-B}}$ is defined as

$$\alpha_{\text{A-B}}^{1/4} = \frac{K_\text{A}^{1/4}}{K_\text{B}} \frac{1000 \text{p} \delta^{18}\text{O}_\text{A}}{1000 \text{p} \delta^{18}\text{O}_\text{B}}$$

for the two coexisting phases A and B. The a_0 term is usually taken as zero for fractionations between anhydrous minerals, and nonzero if hydrous minerals or water are involved. Thermometers are calibrated using experiments, empirical field data, or theoretical calculations. More complex thermometer expressions exist, but Eq. (13.31) has proven to be very useful for a wide range of geological applications.

Temperatures determined in this way record the temperature when the isotopes last equilibrated, which may be different from the temperature at which the minerals first formed. Isotopic ratios may later be disturbed by exchange with circulating groundwater. Normally, unless concordant temperatures are obtained from several different mineral pairs in the same rock, little reliance can be placed on a single measurement.

Geothermometry using oxygen isotopes has proved reliable over the entire range of normal crustal temperatures; that is, from magmatic to surface temperatures. It has been used successfully on igneous, metamorphic, sedimentary, and hydrothermal rocks, and has even been used to determine paleoclimatic temperatures.

13.5.2 Sulfur isotopes

The four isotopes of sulfur have masses of 32, 33, 34, and 36. Only the ratio of the two most abundant isotopes ($^{34}\text{S}/^{32}\text{S}$) is normally measured. The $\delta^{34}\text{S}$ is measured with respect to the sulfur in troilite (FeS) from the Canon Diablo meteorite. The delta values defined in this way cover a wide range of values in sulfides and sulfates from different environments. These values are of particular importance to the study of sulfide ore bodies, especially with regard to the light they may shed on the origin of these deposits.

Most $\delta^{34}\text{S}$ values of terrestrial sulfur average around the values found in meteorites, which probably closely approaches a primordial solar value. It is not surprising, therefore, that magmatic sulfides in rocks derived from the mantle have delta values near zero. Sulfates in evaporites formed from seawater, on the other hand, have delta values of about +20, which is similar to that of seawater. Even sulfates deposited in veins have much higher delta values (about +20) than coexisting sulfides. Some magmatic sulfide deposits in mafic igneous rocks have delta values as high as +10. The sulfide deposit at Noril'sk, Russia, provides a good example. Here diabase intruded and assimilated sedimentary gypsum. This increased

the delta value of the primary sulfur, and produced a magmatic sulfide deposit with anomalously heavy sulfur. Sulfides deposited in sediments by the action of bacteria can have delta values that range widely, from -30 to $+30$.

Fractionation of sulfur isotopes between coexisting sulfides (and sulfates) is significant and can be used as the basis of a geothermometer in the same way that oxygen isotopes are used. Sphalerite and galena, pyrite and chalcopyrite, pyrite and sphalerite, and sulfide and sulfate all provide sensitive geothermometers. Considerable care must be taken, however, to ensure that the mineral pairs analyzed did indeed crystallize together. Pyrite, for example, can crystallize over a very wide temperature range.

13.5.3 Helium isotopes

Helium, which has two isotopes with atomic masses 3 and 4, is an inert gas and is therefore not chemically bound in the Earth. Moreover, its mass is low enough that it is able to escape from the Earth into space. Helium in the atmosphere, consequently, must be replenished by outgassing from the Earth's interior. Within the Earth, helium has two principal sources: primordial helium trapped at the time of Earth accretion, and radiogenically produced helium, which because of the concentration of radioactive elements toward the Earth's surface, is produced largely at shallow depths. Both of these sources have characteristic isotopic signatures, which can serve as a means of identifying sources.

The isotopic composition of helium produced by radioactive decay is very different from that of primordial helium. The isotopic ratio of $^3\text{He}/^4\text{He}$ (referred to as R) in the primordial solar system, which was the result initially of nuclear fusion, can be estimated from its value in meteorites, which is about 3×10^{-4} . Radioactive decay, on the other hand, produces mainly ^4He through α decay. Some ^3He is produced by fission of ^{238}U and some by the interaction of α particles with nuclei of light elements. This interaction produces a neutron flux that can combine with lithium, for example, to produce ^3He . The reaction is as follows: ^6Li combines with a neutron to produce an α particle plus ^3H ; through β emission the ^3H decays to ^3He . The combined effect of these various radioactive processes is to produce an R value of 2×10^{-8} , which is very much lower than the primordial ratio. Cosmic rays are also capable of generating helium, but this is not a significant source on Earth.

Rocks that have risen directly from deep in the mantle have R values of about 10^{-5} . In contrast, ancient granitic crustal rocks have R values of about 10^{-8} , which simply reflects their high content of radiogenic helium. The ratio in the atmosphere is 1.4×10^{-6} , which must result from a mixture of primordial and radiogenic helium. In general, the higher the R value, the larger must be the contribution from a deep source. MORB typically has R values from seven to nine times that of the atmosphere, whereas oceanic island

values can be as much as 30 times larger. Hot springs in areas of recent volcanism also have high R values. At Yellowstone, for example, R values are relatively constant at seven times the atmospheric value within the caldera but drop off sharply outside it. Some values within the caldera are as high as 16 times atmospheric. Similar values are obtained in Icelandic hot springs. In recent volcanic areas, helium isotopes are therefore capable of indicating a mantle component. In older rocks, however, the primordial helium component is soon diluted and swamped by the radiogenic helium derived from surrounding crustal rocks; then the mantle signature is no longer detectable.

13.6 PROBLEMS

13.1 For the following radioactive decay reactions determine the type of decay process involved.



13.2 ^{147}Sm decays to ^{143}Nd with a decay constant of $6.54 \times 10^{-12} \text{ a}^{-1}$. ^{144}Nd is a stable isotope whose abundance in the bulk Earth has remained constant throughout time. If the present $^{147}\text{Sm}/^{144}\text{Nd}$ ratio in the bulk Earth is 0.1870, what would it have been at the time of Earth accretion (4.55 Ga)?

13.3 From the data presented in Figure 13.3, show that the isochron for the Megantic granite does correspond to an age of 127.6 Ma. The most Rb-rich analysis in this plot has an $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 11.04 and an $^{87}\text{Sr}/^{86}\text{Sr}$ ratio of 0.7252.

13.4 Using Eq. (13.12), construct a concordia curve in the $^{206}\text{Pb}/^{238}\text{U}$ versus $^{207}\text{Pb}/^{235}\text{U}$ diagram. Where in this diagram might zircon crystals plot that were initially formed in a 2.6-Ga-old granite that was metamorphosed at 1.0 Ga?

13.5 At the time of accretion (4.55 Ga), the Earth is believed to have had a $^{143}\text{Nd}/^{144}\text{Nd}$ ratio of 0.50682 and a $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of 0.1926. Plot a graph of the value of the $^{143}\text{Nd}/^{144}\text{Nd}$ for the bulk Earth throughout geologic time and record the value of this ratio at an age of 2.5 Ga before present.

13.6 Using the information from Problem 13.5, calculate the evolution of the $^{143}\text{Nd}/^{144}\text{Nd}$ ratios in the crust and mantle if the crust is taken as having formed 2.5 Ga before present. The $^{147}\text{Sm}/^{144}\text{Nd}$ ratios in the crust and mantle at time of formation can be taken as 0.1435 and 0.2245, respectively.

13.7 Repeat Problem 13.5 but for $^{87}\text{Sr}/^{86}\text{Sr}$. The initial $^{87}\text{Sr}/^{86}\text{Sr}$ for the Earth was 0.69898 and the $^{87}\text{Rb}/^{86}\text{Sr}$ was 0.0857.

13.8 Repeat Problem 13.6 but for $^{87}\text{Sr}/^{86}\text{Sr}$. The $^{87}\text{Rb}/^{86}\text{Sr}$ ratios in the crust and mantle at time of formation were 0.48423 and 0.0332, respectively.