Isotope Geochemistry

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Chapter 2

Decay Systems & Geochronology

2.1 Basics of Radioactive Isotope Geochemistry

2.1.1 Introduction

We can broadly define two principal applications of radiogenic isotope geochemistry. The first is geochronology. Geochronology makes use of the constancy of the rate of radioactive decay to measure time. Since a radioactive nuclide decays to its daughter at a rate independent of everything, we can determine a time simply by determining how much of the nuclide has decayed. We will discuss the significance of this time at a later point. Geochronology is fundamental to our understanding of nature and its results pervade many fields of science. Through it, we know the age of the Sun, the Earth, and our solar system, which provides a calibration point for stellar evolution and cosmology. Geochronology also allows us to trace the origins of culture, agriculture, and civilization back beyond the 5000 years of recorded history, to date the origin of our species to some 200,000 years, the origins of our genus to nearly 2 million years, and the origin of life to at least 3.5 billion years. Most other methods of determining time, such as so-called molecular clocks, are valid only because they have been calibrated against radiometric ages.

The history of geochronology begins with Yale University chemist Bertram Boltwood. In collaboration of Ernest Rutherford (a New Zealander working at Cambridge University), Boltwood had deduced that lead was the ultimate decay product of uranium. In 1907, he analyzed a series of uranium-rich minerals, determining their U and Pb contents. He found that the Pb/U ratio in these minerals was same when minerals were from the same geologic period (the relative geologic time-scale, more or less as we know it today, had been worked out by the mid-nineteenth century) and increased with apparent geologic age. From laboratory experiments, he had calculated that 1 gram of Pb was produced per year for every 10 billion grams of uranium; based on this he calculated ages for his samples ranging from 410 to 2200 million years. These ages meant that the Earth was far older than Lord Kelvin (William Thomson) had estimated a decade earlier from cooling of the Earth, which was about 20 to 40 million years. Boltwood’s ages turned out to be too old by almost a factor of two. There are a variety of reasons for this. For one thing, he was unaware that there were two isotopes of uranium decaying to two isotopes of lead at different rates. Indeed, isotopes had not yet been discovered: it would be five more years before J.J. Thompson of Cambridge University would demonstrate their existence. The main rea-

### TABLE 2.1: Geologically Useful Long-Lived Radioactive Decay Schemes

<table>
<thead>
<tr>
<th>Parent</th>
<th>Decay Mode</th>
<th>λ (10^-12 y^-1)</th>
<th>Half-life (10^9 years)</th>
<th>Daughter</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>^{40}K</td>
<td>β, e, β+</td>
<td>5.5492 x 10^-10</td>
<td>1.28 x 10^9</td>
<td>^{40}Ar</td>
<td>^{40}Ar / ^{36}Ar</td>
</tr>
<tr>
<td>^{87}Rb</td>
<td>β-</td>
<td>1.42 x 10^-11</td>
<td>48.8 x 10^9</td>
<td>^{87}Sr</td>
<td>^{87}Sr / ^{86}Sr</td>
</tr>
<tr>
<td>^{138}La</td>
<td>β-</td>
<td>2.67 x 10^-11</td>
<td>2.59 x 10^11</td>
<td>^{138}Ce</td>
<td>^{138}Ce / ^{142}Ce</td>
</tr>
<tr>
<td>^{147}Sm</td>
<td>α</td>
<td>6.54 x 10^-12</td>
<td>1.06 x 10^11</td>
<td>^{147}Nd</td>
<td>^{147}Nd / ^{144}Nd</td>
</tr>
<tr>
<td>^{176}Lu</td>
<td>β-</td>
<td>1.867 x 10^-11</td>
<td>3.6 x 10^11</td>
<td>^{176}Hf</td>
<td>^{176}Hf / ^{177}Hf</td>
</tr>
<tr>
<td>^{187}Re</td>
<td>β-</td>
<td>1.64 x 10^-11</td>
<td>4.23 x 10^9</td>
<td>^{187}Os</td>
<td>^{187}Os / ^{188}Os</td>
</tr>
<tr>
<td>^{190}Pt</td>
<td>α</td>
<td>1.54 x 10^-12</td>
<td>4.5 x 10^9</td>
<td>^{186}Os</td>
<td>^{186}Os / ^{188}Os</td>
</tr>
<tr>
<td>^{232}Th</td>
<td>α</td>
<td>4.948 x 10^-11</td>
<td>1.4 x 10^9</td>
<td>^{208}Pb</td>
<td>^{208}Pb / ^{204}Pb</td>
</tr>
<tr>
<td>^{235}U</td>
<td>α</td>
<td>9.8571 x 10^-11</td>
<td>7.07 x 10^9</td>
<td>^{207}Pb</td>
<td>^{207}Pb / ^{204}Pb</td>
</tr>
<tr>
<td>^{238}U</td>
<td>α</td>
<td>1.5512 x 10^-10</td>
<td>4.47 x 10^9</td>
<td>^{206}Pb</td>
<td>^{206}Pb / ^{204}Pb</td>
</tr>
</tbody>
</table>

Note: the branching ratio, i.e. ratios of decays to ^{40}Ar to total decays of ^{40}K is 0.1037 according to Renne et al (2010); the conventional value is 0.117. ^{147}Sm and ^{190}Pt also produce ^{4}He, but a trivial amount compared to U and Th.

*This is the value recently suggested by Renne et al. (2010). The conventional value is 5.543 x 10^-10 y^-1.

*The officially accepted decay constant for ^{87}Rb is that shown here. However, recent determinations of this constant range from 1.421 x 10^-11 y^-1 by Rotenberg (2005) to 1.393 x 10^-11 y^-1 by Nebel et al. (2011).

*This is the value recommended by Söderlund et al. (2004).

*Value suggested by Mattinson (2010). The conventional value is 9.8485 x 10^-10 y^-1.
son was perhaps his failure to account for thorogenic Pb; although he was aware that thorium was radioactive, he did not know that Pb was its ultimate decay product.

Physicists at first resisted this new age, but geologists felt vindicated as they had felt that Kelvin’s age was too young. As it turns out, radioactivity also helps explain why Kelvin’s age was wrong: the radioactive decay of U, Th, and K heat the Earth, providing much of the energy for geological processes. The great age of the Earth also required some new, as yet unknown energy source for the Sun and the stars, which Hans Bethe latter deduced to be nuclear fusion.

The other application of radiogenic isotope geochemistry is tracer studies. These studies make use of the differences in the ratio of the radiogenic daughter isotope to other isotopes of the element. This approach, which when combined with geochronology, provides insights into the formation and evolution of the Earth, its parts, and its sister planets. This will be the subject of Chapters 5 through 8 and again in Chapter 12.

The elements of interest here are all experience chemical isotopic fractionations. That is to say, their isotopic ratios vary because of slight differences in the chemical behavior of those isotopes. We will discuss the underlying physics and chemistry of these isotopic fractionations in Chapter 8. We can ignore these effects in this chapter for several reasons. First, natural chemical fractionations for the elements of interest are generally quite small. For example, Krabbenhöft et al. (2010) documented variations in the $^{86}\text{Sr}/ ^{88}\text{Sr}$ ratio of less than $\frac{1}{2}$ per mil in rivers, carbonate rocks, and the ocean. Second, Sr, Nd, Hf, and Os isotope ratios are routinely corrected for such fractionation by measuring the extent to which the ratio of a pair of non-radiogenic isotopes (for example, $^{86}\text{Sr}$ and $^{88}\text{Sr}$ or $^{146}\text{Nd}$ and $^{144}\text{Nd}$) differs from an accepted value and applying a correction for fractionation, assuming the magnitude of the fractionation depends on the masses of the isotopes of interest. The details of this correction are explained in the appendix. This correction is essential because fractionations occurring in the mass spectrometer can be much larger than natural ones (1% or more in the case of the $^{86}\text{Sr}/ ^{88}\text{Sr}$ ratio). Correction for fractionation in this manner is not possible for Pb isotopes because there is only one non-radiogenic isotope. As a consequence, it has traditionally not been possible to measure Pb isotope ratios with the precision of those of other elements (on the other hand, variations tend to be greater, so less precision is required). In the last decade or so, several techniques have been come in to wide use to correct Pb isotope ratios for fractionation, leading to much greater precision than in the past.

2.1.2 The Basic Equations

Table 2.1 lists the principal decay systems used in geology; these are also illustrated in Figure 2.1. As is suggested by the various footnotes, decay constants continue to be a field of active research (and note that in this text we will be using some recently determined values that have not yet become the official ones). All of these decay systems obey the basic equation of radioactive decay, which is:

$$\frac{dN}{dt} = -\lambda N$$  \hspace{1cm} (2.1)

$\lambda$ is the decay constant, which we define as the probability that a given atom would decay in some time $dt$. It has units of time$^{-1}$. Each radioactive nuclide has a unique decay constant governing its probability of decay. With the minor exception of electron capture that we noted in Chapter 1, decay constants are true constants: their value is the same throughout all space and all time. All other equations that we’ll introduce in this and subsequent chapters are derived from this one equation.

Let’s rearrange equation 2.1 and integrate:

$$\int_{N_0}^{N} \frac{dN}{N} = \int_{0}^{t} -\lambda \, dt$$  \hspace{1cm} (2.2)

where $N_0$ is the number of atoms of the radioactive, or parent, isotope present at time $t=0$. Integrating, we obtain:
This can be expressed as:
\[
\frac{N}{N_0} = e^{-\lambda t}
\]

or
\[
N = N_0 e^{-\lambda t}
\]

Suppose we want to know the amount of time for the number of parent atoms to decrease to half the original number, i.e., \( t \) when \( N/N_0 = 1/2 \). Setting \( N/N_0 = 1/2 \), we can rearrange 2.3 to get:
\[
\ln \frac{1}{2} = -\lambda t
\]

and finally:
\[
t_{1/2} = \frac{\ln 2}{\lambda}
\]

This is the definition of the half-life, \( t_{1/2} \).

Now the decay of the parent produces a daughter, or radiogenic, nuclide. The number of daughter atoms produced, \( D^* \), is simply the difference between the initial number of parents and the number remaining after time \( t \):
\[
D^* = N_0 - N
\]

Rearranging 2.4 to isolate \( N \)

and substituting that into 2.06, we obtain:
\[
D^* = N_0 e^{\lambda t} - N = N_0 (e^{\lambda t} - 1)
\]

This tells us that the number of daughters produced is a function of the number of parents present and time. Since in general there will be some atoms of the daughter nuclide around to begin with, i.e., when \( t = 0 \), a more general expression is:
\[
D = D_0 + N_0 (e^{\lambda t} - 1)
\]

where \( D \) is the total number of daughters and \( D_0 \) is the number of daughters originally present.
Isotope Geochemistry

Chapter 2 Geochronology

As an aside, we’ll note that there is a simple linear approximation of this function for times short compared to the inverse of the decay constant. An exponential function can be expressed as a Taylor Series expansion:

\[ e^{\lambda t} = 1 + \lambda t + \frac{(\lambda t)^2}{2!} + \frac{(\lambda t)^3}{3!} + \ldots \]

Provided \( \lambda t \ll 1 \), the higher order terms become very small and can be ignored; hence for times that are short compared to the decay constant inverse (i.e., for \( t \ll 1/\lambda \)), equation 2.8 can be written as:

\[ D \equiv D_0 + N \lambda t \]

Let’s now write equation 2.08 using a concrete example, such as the decay of \(^{87}\)Rb to \(^{87}\)Sr:

\[ ^{87}\text{Sr} = ^{87}\text{Sr}_0 + ^{87}\text{Rb}(e^{\lambda t} - 1) \]

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Notice the absence of the \( \mu \) term. The equation holds for any present-day ratio of \(^{207}\)Pb/\(^{204}\)Pb and \(^{206}\)Pb/\(^{204}\)Pb we measure and thus for all pairs of ratios. The left-hand side is simply the slope of a series of data points from rocks or minerals formed at the same time (and remaining closed systems since time \( t \)) on a plot of \(^{207}\)Pb/\(^{204}\)Pb vs. \(^{206}\)Pb/\(^{204}\)Pb. This means we can determine the age of a system without knowing the parent-daughter ratio. The bad news is that equation 2.16 cannot be solved for \( t \). However,

† We’ll discuss the small variations that occur in this ratio in the next chapter.
2.2.1 Isochron Dating

Let’s rewrite equation 2.12 in more general terms

\[ R = R_0 + R_{P/D} (e^{\lambda t} - 1) \tag{2.17} \]

where \( R_0 \) is the initial ratio and \( R_{P/D} \) is the parent/daughter ratio at time \( t \). Measurement of geologic time is most often based this equation, or various derivatives of it. We’ll refer to it as the *isochron equation*. First let’s consider the general case. Given a measurement of an isotope ratio, \( R \), and a parent-daughter ratio, \( R_{P/D} \), two unknowns remain in equation 2.17: \( t \) and the initial ratio. In general, we can calculate neither from a single pair of measurements. In the special case where the initial concentration of the daughter is very small, we can neglect \( R_0 \) or, if \( R \gg R_0 \), simple assumptions about \( R_0 \) may suffice. But in the general case, we must measure \( R \) and \( R_{P/D} \) on a second system for which we believe \( t \) and \( R_0 \) are the same. Then we have two equations and two unknowns and subtracting the two equations yields

\[ \Delta R = \Delta R_{P/D} (e^{\lambda t} - 1) \tag{2.18} \]

which eliminates \( R_0 \) from the equation and allows us to solve for \( t \). This can be rearranged as:

\[ \frac{\Delta R}{\Delta R_{P/D}} = e^{\lambda t} - 1 \tag{2.19} \]

In practice, one measures many pairs and solving for \( \Delta R/\Delta R_{P/D} \) by regression (indeed, geochronologists would not generally accept an age based on only two measurements), \( t \) may be then be solved for as:

\[ t = \frac{\ln \left( \frac{\Delta R}{\Delta P_{P/D}} + 1 \right)}{\lambda} \tag{2.20} \]

For a given value of \( t \), equation 2.17 has the form \( y = a + bx \), where \( y \) is \( R \), \( a \) is \( R_0 \), \( b \) is \( e^{\lambda t} - 1 \), and \( x \) is \( R_{P/D} \). This is, of course, an equation for a straight line on a plot of \( R \) vs. \( R_{P/D} \) with slope \( b = e^{\lambda t} - 1 \), and intercept \( a = R_0 \). Thus on such a plot, the slope of the line depends only on \( t \) (since \( \lambda \) is a constant for any given decay system). A line whose slope depends only on \( t \) is known as an isochron. Note that on a plot of \(^{206}\text{Pb} / ^{204}\text{Pb} \) vs. \(^{208}\text{Pb} / ^{204}\text{Pb} \), a line may also be an isochron, since its slope depends only on \( t \).

Regression is simply a statistical method of calculating the slope of a line. Regression treatment yields both a slope and an intercept. The latter is simply the initial ratio since, as may be seen from 2.17, \( R = R_0 \) when \( R_{P/D} = 0 \). The geochronological information is contained in the slope, since it depends on \( t \), but important information can also be obtained from the value of the intercept, the initial ratio, since it gives some information about the history prior to time \( t=0 \) of the system being investigated.

There are two important assumptions, or conditions, built into the use of equation 2.20:

1. The system of interest was at isotopic equilibrium at time \( t = 0 \). Isotopic equilibrium in this case means the system had a homogeneous, uniform value of \( R_0 \).
2. The system as a whole and each analyzed part of it was closed between \( t = 0 \) and time \( t \) (usually the present time). By ‘closed’ we mean there has been no transfer of the parent or the daughter element into or out of the system.

Violation of these conditions is the principal source of error in geochronology. Other errors arise from errors or uncertainties associated with the analysis. If the range in variation in measured \( R \) and \( R_{P/D} \) is...
small, the analytical errors can be the limiting factor in the determination of an age. Note that both $R$ and $R_{nd}$ must be known accurately.

Finally, of course, we must also know $\lambda$ accurately. Decay constants are not fundamental constants that can somehow be deduced from the fundamental laws; instead each must be measured and there are limits to the accuracy with which they have been measured. As technology advances and analytical precision increases, the accuracy of radiometric ages is increasingly limited by how well the decay constants are known. Decay constants can be determined in three ways, which we will refer to as counting, accumulation, and calibration. In counting, a known mass of highly purified parent nuclide is allowed to sit for a fixed amount of time (decades in some cases), after which the daughter nuclide is extracted and its mass determined. In the calibration approach, isotope ratios and parent-daughter ratios of two systems, e.g., Lu-Hf and U-Pb, are determined in rocks or minerals that are known to meet the two conditions above. The age is determined using the system whose decay constant is well known, and then equation 2.19 is solved for $\lambda$ for the second system, using $t$ determined in the first. Decay constants for U, Th, and K are now known within an uncertainty of considerably better than 1% (but even at this level, uncertainty in decay constants can limit the precision of age determinations and revisions to the $^{235}U$ decay constant have recently been suggested). Decay constants for Rb, Lu, and Re are less well known and continue to be active research topics, and there have been a number of recent suggested revisions to these values, as Table 2.1 indicates. These nuclides emit relatively low energy $\beta$’s and no $\gamma$’s, so the counting approach has proved problematic. Indeed, two recent attempts to determine the $^{87}$Rb decay constant by accumulation and calibration disagree by 1.5%. The situation for $^{176}$Lu was even worse in the early part of this century, with values determined over the last 15 years varying by 6%. However, the most recent determinations by counting and calibration agree within 1%.

The requirement of a closed and initially homogeneous system described above suggests a meaning for the nature of the event dated by radiogenic isotope geochemistry, and a meaning for time in the first paragraph of this chapter. In general, the event is the last time the system was open to complete exchange of the parent and daughter elements between the various subsystems we sample and analyze, i.e., the last point in time that the system had a homogeneous, uniform value of $R$. Since the rate at which diffusion and chemical reactions occur increases exponentially with temperature, this event is generally a thermal one: i.e., the last time the system was hot enough for such exchange between subsystems to occur. Exactly what temperature is implied can vary widely, depending on the nature of our samples and the particular decay system we are using. Minerals such as biotite and hornblende will lose Ar at temperatures of a few hundred degrees. On the other hand, minerals such as pyroxene can remain closed to Sm and Nd exchange up to nearly 1000°C. The ‘closure’ temperatures of various isotope systems in various minerals can be used to advantage: in some cases, an analysis of a variety of decay systems on a variety of sample types has recorded entire cooling histories.

The process accomplishing isotopic homogenization of a ‘system’ usually involves diffusion, the rate of which, like other reaction rates, increases exponentially with temperature. Diffusion rates will vary depending on the element and the properties of the material through which the element diffuses. We can nevertheless make the general observation that the greater the length scale, the greater will be the time (or the higher the temperature required) for isotopic homogenization to be achieved. For the same temperature and duration of a thermal event, diffusion will more readily achieve isotopic homogenization on a small scale than on a large one. Thus, if our samples or subsystems are ‘whole rocks’ collected meters or perhaps kilometers apart, the event dated will generally be a higher temperature one than an event dated by analysis of individual minerals from a rock specimen whose scale is only a few centimeters.
2.2.1 Calculating an Isochron

The idea of least squares regression is to minimize the squares of the deviations from the function relating one variable to another (i.e., deviations from a line on a graph of the two variables). In the simplest case, the relationship is assumed to be linear, as it is in the isochron equation. The quantity to be minimized is the sum of the squares of deviations:

\[ \sum_{i=1}^{n} e^2 = \sum_{i=1}^{n} (y - a - bx)^2 \quad 2.21 \]

where \( y \) is the observed value, \( a + bx \) is the predicted value, and \( e \) is the difference between the observed and predicted value, i.e., the deviation.

The use of the squares of the deviations means that large deviations will affect the calculated slope more than small deviations. By differentiating equation 2.21, it can be shown that the minimum value for the left side occurs when the slope is:

\[ b = \frac{\sum (x_i - \bar{x})(y_i - \bar{y})}{\sum (x_i - \bar{x})^2} \quad 2.22 \]

where \( \bar{x} \) and \( \bar{y} \) are the means of \( x \) and \( y \) respectively, and \( x_i \) and \( y_i \) are the \( i \)th pair of observations of \( x \) and \( y \) respectively. We can see from 2.22 that the regression slope is the cross product of the deviations of \( x \) and \( y \) from the means divided by the square of the deviations of \( x \) from the mean of \( x \). A more convenient computational form of 2.22 is:

\[ b = \frac{\sum x_i y_i - \sum y_i \sum x_i}{\sum x_i^2 - n \bar{x}^2} \quad 2.23 \]

The intercept is then given by:

\[ a = \bar{y} - b\bar{x} \quad 2.24 \]

The error on the slope is:

\[ \sigma_b = \sqrt{\frac{\sum y_i^2 - \bar{y}^2 n - \frac{(\sum (x_i y_i) - \bar{x} \bar{y} n)^2}{\sum x_i^2 - \bar{x}^2 n}}{(n-2)(\sum x_i^2 - \bar{x}^2 n)}} \quad 2.25 \]

The error on the intercept is:

\[ \sigma_a = \sqrt{\frac{\sum y_i^2 - \bar{y}^2 n - \frac{(\sum (x_i y_i) - \bar{x} \bar{y} n)^2}{\sum x_i^2 - \bar{x}^2 n}}{\frac{n}{n-2} + \frac{\bar{y}^2}{\sum x_i^2 - \bar{x}^2 n}} \quad 2.26 \]

Statistics books generally give an equation for linear least squares regression assuming one dependent and one independent variable where the independent variable is assumed to be known absolutely. While it is true that in the isochron equation \( R \) is a function of \( R_{PD} \) in a geologic sense and hence may be considered the dependent variable, in practice both \( R \) and \( R_{PD} \) are measured quantities and neither is known absolutely: both have errors of measurement associated with them. These must be taken into account for a proper estimate of the slope and the errors associated with it. In some cases, the errors in measurement of \( x \) and \( y \) can be correlated, and this must also be taken into account. The so-called two-error regression algorithm takes account of these errors. This is, however, considerably less straightforward than the above. The approach is to weight each observation according to the measurement error.
(the weighting factor will be inversely proportional to the estimated analytical error – so that observations with larger errors are less important than those with small ones). A solution was published by York (1969), among others. The regression slope is:

\[
b = \frac{\sum \left( Z_i^2 (y_i - \bar{y}) \right) \left[ x_i - \bar{x} \right]}{\sum \left( Z_i^2 (x_i - \bar{x}) \right) \left[ y_i - \bar{y} \right] + \frac{\sum \left( y_i - \bar{y} \right)}{\omega(y_i)} + \frac{\sum \left( y_i - \bar{y} \right)}{\omega(x_i)} + \frac{\sum \left( y_i - \bar{y} \right)}{\alpha_i}}
\]

where \(\omega(x_i)\) is the weighting factor for \(x_i\) (generally taken as the inverse of the square of the analytical error), \(\omega(y_i)\) is the weighting factor for \(y_i\), \(r_i\) is the correlation between the error of measurement of \(x_i\) and \(y_i\), \(\alpha = \sqrt{\omega(x_i)\omega(y_i)}\), \(\bar{x} = \sum Z_i x_i / \sum Z_i\), \(\bar{y} = \sum Z_i y_i / \sum Z_i\) (weighted means), and \(Z_i\) is:

\[
Z_i = \frac{\omega(y_i) + \omega(x_i) - 2br \alpha_i}{\alpha_i^2}
\]

Note that the expression for \(b\) contains \(b\). This requires an iterative solution: not something you want to do in your head, but reasonably easy with a computer. For example, the first estimate of \(b\) could be made using equation 2.23. The difference between this method and the standard one is not great, so convergence is generally quick. The intercept is calculated as in equation 2.24. Calculating the errors associated with \(a\) and \(b\) is fairly complex, but approximate solutions are given by:

\[
\sigma_b = \sqrt{\frac{1}{\sum Z_i (x_i - \bar{x})^2}}
\]

\[
\sigma_a = \sqrt{\frac{\sigma_b}{\sum Z_i}}
\]

From the error on the slope, the error on the age can be derived by simple algebra. The error so derived, however, does not include uncertainty in the value of the decay constant, which may or may not be significant.

A useful measure of the fit of the data to the regression line (isochron) is the mean squared weighted deviations (MSWD). If, as is usual, the weight factors are taken as the inverse square of the estimated analytical errors and assuming errors are uncorrelated, the MSWD is calculated as (Wendt and Carl, 1991):

\[
MSWD = \frac{\sum_{i=1}^{N} \frac{(y_i - bx_i - a)^2}{(b^2 \sigma_{x_i}^2 + \sigma_y^2)}}{N-2}
\]

where \(\sigma_x\) and \(\sigma_y\) are the errors on \(x_i\) and \(y_i\), respectively. An MSWD value less or equal than 1 indicates the deviations from perfect linear correlation between \(x\) and \(y\) are less than or equal to those attributable to associated analytical errors; an MSWD greater than 1 indicates other (geological) factors have contributed to the deviations from linearity and suggest that conditions (1) and (2) above have been violated.

Today, there are programs available that implement these equations, so there is no need to code them anew. One of the most popular and useful is ISOPLOT, a Visual Basic Add-in for Microsoft’s Excel® written by Ken Ludwig of the Berkeley Geochronology Center (BGC) and obtainable at http://bgc.org/isoplot_etc/isoplot.html. This software is useful for a wide variety of other geochro-
Isotope Geochemistry

Chapter 2

Geochronology I

nological problems that we will explore in this and subsequent chapters, including concordia diagrams and \(^{40}\text{Ar}/^{39}\text{Ar}\) dating. Some of the problems in this book require the use of this or similar software. Since its use is well documented in the user’s manual, we will not delve further into it here.

2.3 The K-Ar-Ca System

We have now discussed many of the basic aspects of radiogenic isotope geochemistry and we can now consider how it is applied to solving questions about the Earth. We will begin by discussing geochronology, because this aspect is basic to other aspects of isotope geochemistry. To understand the more chemical and geological aspects of isotope geochemistry, we must first learn to tell time, so to speak. We will consider the various decay systems separately. Many of these have special aspects, but all share a common foundation based on equation 2.1, the basic equation of radioactive decay.

Two aspects of the K-Ar-Ca system make it special. First, it is a branched decay: a \(^{40}\text{K}\) nucleus (an odd-odd nuclide) may decay to either a \(^{40}\text{Ca}\) by \(\beta^-\) or to a \(^{40}\text{Ar}\) atom by electron capture (or much more rarely by positron emission — which is just as well for us). It is impossible to predict how a given \(^{40}\text{K}\) atom will decay, just as it is impossible to predict when it will decay. We can predict quite accurately what proportion of a large number of \(^{40}\text{K}\) atoms will decay in each way, however. The ratio of electron captures to beta decays is called the branching ratio and is defined as:

\[
R = \frac{\lambda_{cc}}{\lambda_{\beta}}
\]

where the two lambda’s are the decay constants (i.e., the probability of decay) for each mode. According to recent work by Renne et al. (2010), the branching ratio is 0.1037, \(\lambda_{cc} = 0.5755 \times 10^{10} \text{ yr}^{-1}\), \(\lambda_{\beta} = 4.9737 \times 10^{10} \text{ yr}^{-1}\). The total decay constant for \(^{40}\text{K}\) is:

\[
\lambda = \lambda_{\beta} + \lambda_{cc} = 5.5492 \times 10^{10} \text{ yr}^{-1}
\]

We need to take account of this branched decay in our equation, because while a K atom decaying to Ca does not produce radiogenic Ar, it is no longer available for \(^{40}\text{Ar}\) production. Thus our equation for radiogenic daughter production (equation 2.7) becomes:

\[
^{40}\text{Ar}^* = \frac{\lambda_{cc}}{\lambda}^{40}\text{K}(e^{\lambda t} - 1)
\]

where the asterisk indicates radiogenic \(^{40}\text{Ar}\) (designating the radiogenic atoms of an element is a widely used convention and we will follow it in this book). Note we can write a similar equation for \(^{40}\text{Ca}^*\) by substituting \(\lambda_{\beta}\) for \(\lambda_{cc}\).

Most, although not all, of the work on the K-Ca-Ar system has focused on Ar because the \(^{40}\text{K}/^{40}\text{Ca}\) ratio is usually small. \(^{40}\text{K}\) is the least abundant of the K isotopes (0.01167%), whereas \(^{40}\text{Ca}\) is the most abundant \(^{40}\text{Ca}\) isotope (96.92%), and Ca is a more abundant element than K (\(^{40}\text{Ca}\) is even-even, \(^{40}\text{K}\) is odd-odd). As a result, variations in the \(^{40}\text{Ca}/^{40}\text{Ca}\) ratio resulting from radioactive decay are quite small and difficult to measure (indeed, there is usually more variation in this ratio due to other causes, which we will discuss in Chapter 11). Only in very favorable circumstances, such as halide salt deposits, is geochronology practical.

As one might expect, particularly in view of the above discussion, one of the most important criteria for a useful radiometric chronometer is that the variations in the radiogenic isotope be large relative to the precision and accuracy with which they can be measured. In this respect, a short half-life is advantageous, and K has one of the shortest half-lives of the long-lived radioactive nuclides. Because of the volatility of Ar, the Earth either lost much of its Ar during its formation, or never acquired much, giving the Earth a rather high K/Ar ratio. Furthermore, much of the Ar the Earth retained is now in the atmosphere (as we’ll learn in Chapter 12). As a result, \(^{40}\text{K}/^{40}\text{Ar}\) ratios in the solid Earth tend to be quite high. Because of the high \(^{40}\text{K}/^{40}\text{Ar}\) ratios and the relatively short half-life of \(^{40}\text{K}\), the K-Ar system is often the one of choice when the task at hand is to date very young events. Meaningful ages (meaning the uncertainty is small relative to the
age) of less than 30,000 years have been determined in favorable circumstances. Much of what we know of the timing of the evolution of our species is based on \(^{40}\text{K}/^{40}\text{Ar}\) dating (including \(^{40}\text{Ar}/^{39}\text{Ar}\) dating that we will discuss shortly).

Much of what is special about K-Ar derives from Ar being a noble gas and its resulting refusal to be chemically bound in crystal lattices. Ar in rocks and minerals is simply trapped there. It has difficulty escaping because the atoms of the lattice block its escape path, but it is does not form chemical bonds with other atoms in the lattice. Thus when a mineral crystallizes from a lava, it will generally, although not always, do so with very little Ar. Pillow basalts formed on the seafloor are one example of exceptions to this rule. The combination of relatively high pressure and rapid transition from the liquid to the solid state can result in trapping of substantial amounts of Ar. Similarly, minerals crystallizing from plutonic rocks may also retain Ar.

In favorable circumstances, essentially no Ar will be trapped in a mineral crystallizing from lava. The great advantage of this, from a geochronological viewpoint, is we have only one unknown, namely \(t\), and we can use equation 2.33 to solve for it by measuring the \(^{40}\text{K}\) and \(^{40}\text{Ar}\) in one sample. Actually, one need not assume that no ‘initial’ Ar whatsoever is present. Indeed, in detail, this would seem a poor assumption since a mineral crystallizing in contact with the atmosphere can be expected to absorb a small but finite amount of atmospheric Ar. This atmospheric Ar is readily corrected for since the atmosphere has a uniform ratio \(^{40}\text{Ar}/^{36}\text{Ar}\) of 295.5. By measuring the amount of \(^{36}\text{Ar}\) present, we can deduce the amount of atmospheric \(^{40}\text{Ar}\) initially present. Our age equation (equation 2.17) becomes simply:

\[
\frac{^{40}\text{Ar}}{^{36}\text{Ar}} = 295.5 + \frac{\lambda}{\lambda_{^{40}\text{Ar}}} e^{-\lambda_{^{40}\text{Ar}}(t-1)}
\]

If we suspect that the composition of ‘initial’ Ar differs significantly from atmospheric, it is then necessary to employ the isochron approach, measuring K and Ar in a number of cogenetic samples and solving simultaneously for \(t\) and the initial \(^{40}\text{Ar}/^{36}\text{Ar}\) ratio.

### 2.3.1 Diffusion, Cooling Rates, and Closure Temperatures

Because Ar is not chemically bound in lattices, the K-Ar clock will generally be reset more readily than other systems. We concluded earlier that an event that ‘resets’ a radiometric clock is generally a thermal one. In the case of K-Ar, we might guess that the system would be reset whenever temperatures are high enough to allow Ar to diffuse out of the rock or mineral of interest. It is worth considering this on a slightly more quantitative level.

It can be shown both theoretically and experimentally that the rate at which a species will diffuse through a medium is related exponentially to temperature:

\[
D = D_0 e^{-E_A/RT}
\]

where \(D\) is the diffusion coefficient, \(D_0\) is the ‘frequency factor’, \(E_A\) is the activation energy, \(R\) is the gas constant and \(T\) is thermodynamic, or absolute, temperature, (i.e., kelvins). The diffusion ‘flux’ is then related to the concentration gradient by:

![Figure 2.2. Log of the diffusion coefficient for argon in biotite against the inverse of thermodynamic temperature. Circles and squares indicate different size fractions of biotite used in 1 kbar experiments. Triangles are 14 kbar experiments. From Harrison et al. (1985).](image-url)
where $C$ is the concentration and $x$ is distance. Figure 2.2 shows a plot of experimentally determined values of $D$ for Ar in biotite plotted against the inverse of temperature. The point to be made here is that relatively small increases in temperature result in large increases in the diffusion coefficient. For example, increasing the temperature from 600° C to 700°C results in a two order of magnitude increase of the diffusion coefficient, and, for a given concentration gradient, of the Ar diffusion flux. Using the values of $E_A$ and $D_0$ given in the figure, we can calculate the diffusion coefficient for temperatures not shown in the graph. The value of $R$ is 8.314 joules/Kelvin-mole (1.987 cal/Kelvin-mole). For a temperature of 300 K (27° C), $D$ would be $4 \times 10^{-36}$ cm$^2$/sec. For any reasonable concentration gradient, there would be no significant Ar loss from biotite, even over extremely long times. At 600 K (327° C), we obtain $D = 6 \times 10^{-19}$ cm$^2$/sec, which implies a slow, but significant diffusion rate. At 700° C, however, loss of Ar would be quite rapid: about 1/3 of the Ar would be lost from biotites of 97µ radius in 2-3 weeks (you can understand then why the experiments were done at these temperatures and not lower ones).

The following equation (from Crank, 1975) is of use in interpreting diffusion coefficients. The equation gives the fraction of the species lost as a function of time ($t$), diffusion coefficient, and the diffusion radius ($a$).

$$f \approx \frac{4}{\pi^{1/2}} \left( \frac{Dt}{a^2} \right)^{1/2} - \frac{Dt}{a^2} - \frac{1}{3\pi^{1/2}} \left( \frac{Dt}{a^2} \right)^{3/2}$$

The equation assumes radial diffusion in a cylinder of infinite length and radius $a$. We can use this equation to understand how Ar loss will vary with temperature*. We assume a value for $a$ of 150 µ, and

Figure 2.3. Fraction of Ar lost from a 150 µ cylindrical crystal as a function of temperature for various heating times. All Ar is lost in 10 Ma at 340°C, or in 1 Ma at 380° C.

---

* Note that this equation implies that diffusional loss will be inversely related to crystal size: larger crystals will lose less.
isotope geochronology

Chapter 2

Geochronology I

use the $D_o$ and $E_A$ values given in Figure 2.2. Figure 2.3 shows the results of this calculation performed for various times (and at various temperatures: $D$ is a function of temperature, of course).

Let's consider the geological implications of this diagram. Imagine a body of rock, either igneous or metamorphic, cooling from high temperature, a temperature high enough so that all Ar is lost. Let's pick up the story when the body is still 400°C and cooling at a rate of 100°C/Ma. At this temperature, the biotite would be just beginning to retain radiogenic Ar; that is, it is not being lost quite as fast as it is being created. After the first additional million years, it would have cooled to 300°C, and biotite would be retaining most of its radiogenic Ar (loss rate of about 10 percent per Ma). If cooling continues at this rate for another million years (in the real world, it is unlikely cooling rates would be so constant), biotite would be losing Ar at a rate of only a tenth of a percent per Ma, a fairly insignificant rate. If the body then cooled completely, and if we sampled biotite for K-Ar dating some 100 Ma later, assuming the biotite was not reheated, the 'age' we would calculate would refer to that 2 Ma period when the biotite cooled from 400°C to 200°C, and probably closer to the time it passed from 400°C to 300°C. We say the biotite 'closed' at that time, and we can estimate the closure temperature at between 300°C and 400°C.

Suppose cooling was slower, say 10°C/Ma. In this case, 10 Ma would be required to cool from 400°C to 300°C, and 20 Ma to cool to 200°C. A much smaller fraction of the radiogenic Ar produced while the biotite was in the 200-400°C range would have been retained. The 'age' we would calculate using equation 2.33 would be younger than in the example above. It would thus seem that under these circumstances, the 'closure temperature' would depend on the cooling rate. This is indeed the case.

Dodson (1973) derived an equation for 'closure temperature' (also sometimes called blocking temperature) as a function of diffusion parameters, grain size and shape, and cooling rate:

$$T_c = \frac{E_A}{R\ln\left(-\frac{ART^2D_0}{a^2E_A\tau}\right)}$$

2.38

where $\tau$ is the cooling rate, $dT/dt$ (for cooling, this term will be negative), $a$ is the characteristic diffusion dimension (e.g., radius of a spherical grain), and $A$ is a geometric factor (equal to 55 for a sphere, 27 for a cylinder, and 9 for a sheet) and temperatures are in Kelvins. Unfortunately, this is not directly solvable since $T_c$ occurs both in and out of the log, but it can be solved by indirect methods†.

There are several important notions we can come away with. First, a 'closure temperature' is a useful concept, but a mineral will not suddenly stop losing Ar, or any other radiogenic component, at its closure temperature. Closure temperature reflects a trade off between loss and creation of the radiogenic component. Second, there are some ultimate geological limitations on the meaning of an age of a slowly cooled rock, such as a large intrusion or regionally metamorphosed body of rock. We might also expect the age we obtain will depend on the mineral we use for dating (since the diffusion coefficient will vary), and perhaps on its composition (there is in fact some compositional dependence of the Ar diffusion coefficient on the Fe/Mg ratio in biotite; but apparently none in hornblende). Finally, we get the sense that it might be rather easy for K-Ar mineral age to be partially reset. This is certainly the case. We discuss next a technique that can at least identify partially reset minerals, and in favorable cases, provide a reasonable estimate of the original 'age'.

2.3.2 $^{40}$Ar-$^{39}$Ar Dating

If you look at a table of isotopes you’ll see $^{39}$Ar has a half-life of 269 years and does not occur naturally. You might justifiably wonder how it could be used for dating. The so-called 40-39 method is ac-

† The Solver, an add-in tool available for Microsoft Excel™ can be used to solve problems such as this. Programs such as Mathematica™ and MatLab™ also have tools for indirect solution built-in.
Chapter 2  Geochronology I

tually $^{40}$K-$^{41}$Ar dating but employing a somewhat different analytical technique for the potassium first described by Merrihue and Turner (1966). The key is the production of $^{39}$Ar by a nuclear reaction on $^{39}$K, the most abundant of potassium’s three isotopes:

$$^{39}\text{K} (\text{n,p}) ^{39}\text{Ar}$$

The reaction is produced by irradiating a sample with fast neutrons in a reactor. It is important to distinguish this reaction from simple neutron capture, but we can nevertheless define a reaction cross-section. The amount of $^{39}$Ar produced is then a function of the amount of $^{39}$K present, the reaction cross-section, the neutron flux, and the irradiation time. Since the $^{40}$K/$^{39}$K ratio in the Earth is constant (at any given time), the amount of $^{40}$K can be calculated from $^{39}$Ar. In practice, the situation is more complex because the reaction cross-section is a function of neutron energy and there typically is a spectrum of energies present. The production of $^{39}$Ar from $^{29}$K can be expressed as:

$$^{39}\text{Ar} = ^{39}\text{K} \tau \phi \sigma \int e \, de$$  \hspace{1cm} 2.39

where $e$ is the neutron energy, $\phi$ is the flux of neutrons with energy $e$, and $\sigma$ is the capture cross section for that energy, and $\tau$ is irradiation time. The $^{40}$Ar*/$^{39}$Ar is then:

$$\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} = \frac{\lambda e}{\lambda} \frac{^{40}\text{K}(e^{\lambda \tau} - 1)}{^{39}\text{K} \tau \phi \sigma \int e \, de}$$  \hspace{1cm} 2.40

In practice, the analysis is performed by simultaneously irradiating and analyzing a standard of known age. The flux, capture cross-section, and decay constant terms will be the same for the standard as for the unknown sample. We can combine them into a single term, C, as:

$$C = \frac{\lambda e}{\lambda} \frac{1}{\tau \phi \sigma \int e \, de}$$  \hspace{1cm} 2.41

and equation 2.40 becomes:

$$\frac{^{40}\text{Ar}^*}{^{39}\text{Ar}} = C \frac{^{40}\text{K}(e^{\lambda \tau} - 1)}{^{39}\text{K}}$$  \hspace{1cm} 2.42

The value of C can be determined from analysis of the standard, so that 2.42 can be solved for the age.

Another problem is the production of both $^{39}$Ar and $^{40}$Ar by other reactions that include $^{40}$K(n,p)$^{40}$Ar, $^{40}$Ca(n,n$\alpha$)$^{36}$Ar, and $^{42}$Ca(n,$\alpha$)$^{39}$Ar. Corrections for these must be made. Generally, $^{37}$Ar, produced by $^{40}$Ca(n,$\alpha$)$^{37}$Ar, is used to make these corrections.

In conventional K-Ar dating, Ar is released from samples by fusing in vacuum. However, we might guess from our knowledge of diffusion that a sample will begin to lose Ar before it reaches its melting temperature. If the ratio of radiogenic $^{40}$Ar to K (and therefore to $^{39}$Ar) were distributed uniformly throughout the sample, a sample of gas taken before the sample fused would produce the same age as for total fusion. We might guess, however, that some parts of a crystal will preferentially lose Ar through diffusion during the initial cooling of the crystal, or perhaps during some subsequent reheating event. Since the diffusion rate is proportional to the concentration gradient, we can anticipate that diffusion will be faster from the rims of crystals where the concentration gradient is higher than in the interior of crystals. So we might expect crystal rims to experience Ar loss at lower temperatures than

Figure 2.4. $^{40}$Ar/$^{39}$Ar age spectrum produced by step heating of a biotite from a granitic gneiss. After Tetley (1978).
crystal interiors. The rims would then record younger ages. As we heat the sample, we would also expect rims to start to give up their Ar at the lowest temperatures, partly for this reason, and partly because the Ar has less distance to go to get out. The lower $^{40}\text{Ar}/^{39}\text{Ar}$ of the gas in the rim would be seen as a lower age (which may or may not have significance). As we increased the temperature, the more retentive parts of the crystal would release their gas, and we could expect the $^{40}\text{Ar}/^{39}\text{Ar}$ and the apparent age to increase. If some parts of the crystals have lost no gas, their $^{40}\text{Ar}/^{39}\text{Ar}$ ratios would record the ‘correct’ age, even though the crystal as a whole has suffered some loss. Figure 2.4 is an Ar release diagram for a biotite exhibiting this sort of behavior. Conventional K-Ar dating would have produced an age intermediate between the ‘correct’ age and the apparent young age of those parts of crystal that have suffered loss of radiogenic $^{40}\text{Ar}$. Thus the combination of the $^{40}\text{Ar}/^{39}\text{Ar}$ method with step-heating provides a means of retrieving useful geochronological information from samples whose value would have otherwise been compromised because of diffusional loss. In a certain sense, we are relaxing our requirement that the system must have remained closed: with $^{40}\text{Ar}/^{39}\text{Ar}$ dating, we require only that some part of the system have remained closed.

Most Ar release spectra are not so simple as that in Figure 2.4. Figure 2.5 shows Ar release spectra for a series of hornblende samples taken at varying distances from the contact with an intrusive granodiorite. All show significant Ar loss as a result of heating from the intrusion. None retain, even at the highest release temperature, the true age of 367 Ma.

2.3.2.1 Other Complications Affecting $^{40}\text{Ar}$-$^{39}\text{Ar}$ Spectra

In the previous section, we saw two examples of $^{40}\text{Ar}/^{39}\text{Ar}$ release spectra: one where there was only minor loss of Ar from the rims, and another where significant fractions of the total Ar had been lost due to metamorphic heating. Figure 2.4 showed spectra that almost perfectly match theoretical patterns for
diffusional loss. Such examples are uncommon; many spectra are more complex. For example, some samples that have been reheated show false plateaus that correspond to ages intermediate between the crystallization age and the reheating age. An additional problem in interpreting such spectra is that samples that have not been subjected to reheating events but cooled slowly originally can show release spectra that mimic those of reheated samples in Figure 2.5.

Recoil of $^{39}$Ar produced by the $^{39}$K(n,p)$^{39}$Ar reaction during irradiation can also produce problems. The recoil results in loss of $^{29}$Ar from sites near the mineral surface. For large grains, this is largely insignificant, but for small grains, this can lead to significant $^{39}$Ar loss, leading in turn to erroneously old apparent ages.

In most cases, the Ar present in a sample will not be pure radiogenic produced Ar. Non-radiogenic argon is often called excess Ar. $^{40}$Ar/$^{39}$Ar ratios used to calculate ages in release spectra are typically corrected for the presence of atmospheric Ar by measuring the $^{40}$Ar/$^{36}$Ar ratio. Atmospheric argon has a constant $^{40}$Ar/$^{36}$Ar ratio of 296.16$. Only $^{40}$Ar present in excess of this ratio is considered radiogenic and used to calculate the $^{40}$Ar/$^{39}$Ar ratio. Nevertheless, some samples can have “initial” $^{40}$Ar/$^{36}$Ar ratios greater than the atmospheric ratio; this will lead to too old an age if not properly accounted for. It is this “excess” argon that is of greatest concern.

Excess Ar can have two sources. First, it can arise when minerals crystallize under a finite partial pressure of Ar. For example, mantle-derived submarine basalts have been shown in some cases to have initial $^{40}$Ar/$^{36}$Ar ratios of up to 40,000. The high $^{40}$Ar/$^{36}$Ar ratio reflects production of $^{40}$Ar by decay of $^{40}$K within the mantle. Minerals crystallizing in the presence of this gas will trap some of this $^{40}$Ar, which will result in an anomalously old age upon analysis. This is referred to as inherited Ar. Second, during a thermal event, $^{40}$Ar diffusing out of some minerals may be taken up by other minerals. Since this $^{40}$Ar is diffusing into the mineral grain, its concentration will be highest in the exterior of grains and thus will tend to be released at the lowest temperatures. An example is shown in Figure 2.6.

When excess Ar is held in more than one crystallographic site, for example different minerals in the analyzed sample, release spectra can reveal a saddle shape. An example is shown in Figure 2.7. This sample is a calcic plagioclase from Broken Hill in Australia. The true metamorphic age is approximately 1600 Ma. Even the minimum values in the bottom of the saddle are too old. Electron microscopy of the plagioclase revealed that it had exsolved into a Ca-rich and Na-rich plagioclase. The saddle shape results because Ar in one of the phases diffuses readily and is thus released at low temperature, and diffuses more slowly in the other, resulting in release at high temperature.

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† This is the newly determined value (Mark et al., 2011). The older, more widely accepted value is 295.5.
A new technique, developed only in the last 20 years, involves releasing Ar from small areas of a sample through laser ablation. This allows release of Ar from areas with diameters less than a millimeter, and provides the possibility of spatial resolution of Ar diffusional loss.

2.3.2.2 $^{40}$Ar-$^{39}$Ar Isochrons

The data from various temperature release steps are essentially independent observations of Ar isotopic composition. Because of this, they can be treated much the same as in conventional isochron treatment. The isochron equation, written for the K-Ar system is:

$$\frac{^{40}Ar}{^{36}Ar} = \left(\frac{^{40}Ar}{^{36}Ar}\right)_0 + \frac{^{40}K}{^{36}Ar} (e^\lambda t - 1) \ 2.43$$

When $^{40}$Ar/$^{36}$Ar data from a series of samples are plotted against $^{40}$K/$^{36}$Ar, the slope of the resulting line will be proportional to age, and the intercept gives the initial $^{40}$Ar/$^{36}$Ar ratio. Since for all release fractions of a sample the efficiency of production of $^{39}$Ar from $^{39}$K is the same and $^{40}$K/$^{39}$K ratios are constant, we may substitute $^{39}$Ar $\times$ C for $^{40}$K:

$$\frac{^{40}Ar}{^{36}Ar} = \left(\frac{^{40}Ar}{^{36}Ar}\right)_0 + \frac{^{39}Ar}{^{36}Ar} C (e^\lambda t - 1) \ 2.44$$

C is a constant that depends on the efficiency of $^{39}$Ar production during irradiation. Thus when $^{40}$Ar/$^{36}$Ar ratios from a series of release fractions are plotted against $^{39}$Ar/$^{40}$Ar, the slope of the resulting line will be proportional to the age of the sample, as is illustrated in Figure 2.8.

The use of the isochron diagram can help to identify excess Ar and its nature (e.g., atmospheric, inherited, etc.). It also provides a crucial test of whether ages obtained in release spectra are meaningful or not. A drawback of this diagram is that $^{36}$Ar, which is the denominator in both the ordinate and abscissa, is often present in only trace amounts and is difficult to measure precisely. Because it appears in both ordinate and abscissa, errors in its measurements can produce correlations that imitate isochrons.

An alternative is to use a plot of $^{36}$Ar/$^{40}$Ar against $^{39}$Ar/$^{40}$Ar (Figure 2.9), often called an inverse isochron plot. We can think of the Ar in a sample as a mixture of a trapped component and a radiogenic component. As such, the data for various release fractions should plot as a straight line on such a plot. The radiogenic com-

Figure 2.8. Hypothetical $^{40}$Ar-$^{39}$Ar isochron diagram. The slope is proportional to the age and the intercept gives the initial $^{40}$Ar/$^{36}$Ar ratio, which is commonly atmospheric, as is illustrated here.

Figure 2.9. Plot of $^{36}$Ar/$^{40}$Ar vs $^{39}$Ar/$^{40}$Ar, also called an inverse isochron diagram. Age is obtained from the value of $^{39}$Ar/$^{40}$Ar corresponding to $^{36}$Ar/$^{40}$Ar = 0.
ponent has a $^{36}\text{Ar}/^{40}\text{Ar}$ ratio of 0 (because $^{36}\text{Ar}$ is not produced by radioactive decay), whereas the trapped, non-radiogenic component can be found by extrapolating to a $^{39}\text{Ar}/^{40}\text{Ar}$ ratio of 0 (corresponding to a $^{39}\text{K}/^{40}\text{Ar}$ ratio of 0; since $^{39}\text{K}$ is proportional to $^{40}\text{K}$, this also corresponds to a $^{40}\text{K}/^{40}\text{Ar}$ ratio of 0). Thus the age may be computed from the $^{39}\text{Ar}/^{40}\text{Ar}$ ratio obtained by extrapolating the correlation line to $^{36}\text{Ar}/^{40}\text{Ar}$ to 0, and the composition of the trapped component by extrapolating to $^{39}\text{Ar}/^{40}\text{Ar}$ of 0.

Figure 2.10 provides an example of how the inverse isochron plot may be used to identify trapped components. The original release data showed a disturbed pattern and lacked a plateau (not shown). The inverse isochron plot (Figure 2.10a) revealed two correlations suggesting the presence of two distinct trapped components. The lower intercept yielded an age of 149.1 Ma. When the data were corrected for the trapped component and replotted on a release spectrum, they produced a plateau corresponding to the same age as the isochron age. The book by Harrison and McDougall (1999) provides much greater detail on $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology.

2.4 Rb-Sr System

The K-Ar system is exceptional in that we can sometimes ignore or readily correct for initial Ar. In the systems we’ll discuss in the remainder of this chapter, both the initial ratio and the age are always unknown, meaning we must solve for both simultaneously through the isochron method. Consequently, this is an opportune time to briefly review and summarize the conditions that must be met to obtain a meaningful isochron.

1. The ratio of parent to daughter should be large. When this is the case, variations in the isotopic composition of the daughter will be large relative to our ability to measure them. Under the best of circumstances, isotope ratios can be measured with a precision of a few ppm. If the total amount of radioactively produced daughter is small relative to the amount present initially, for example if the proportion of radiogenically produced daughter is only a few 10’s of ppm or less of the total amount of daughter, accuracy of ‘ages’ will be compromised.

2. The parent/daughter should have a large range. A large range in parent/daughter ratio leads to a large range in isotope ratios in the daughter. The error on the regression slope, and ultimately the age, is a function of the range of values used in the computation. So given similar analytical precisions, we
will obtain a more precise date with a decay system where the variations in parent-daughter ratio are large than with one where these variations are small.

3. *Deviations from closed system behavior must be minimal* subsequent to the event we are attempting to date. This should be considered when choosing both the decay system and the samples we plan to analyze. As we shall see, some elements tend to be more mobile than others, and some minerals are less reactive than others. Size also plays some role. A large sample is more likely to meet the closed system requirement than a small one (the elements have further to diffuse). Often, metamorphism will disturb a system on the scale of mineral grains, but not a scale of ‘whole rock’ samples taken hundreds of meters apart (however, whole rocks will generally show less variation in parent/daughter ratios than minerals). One must also bear in mind that an atom created by radioactive decay will generally be a misfit in the lattice site it occupies (since the site was originally occupied by the parent). Furthermore, the decay process may damage the site. Such damage is more likely in the case of alpha decay than beta decay or electron capture because of the high energy of the alpha (typically 4 MeV), and the kinetic recoil energy of the daughter nucleus. These factors all lead to higher mobility of the daughter.

4. *The isotopic composition of the daughter must have been homogeneous* at the time of the event we wish to date. On a small scale, homogenization takes place through diffusion, which, as we have seen, is highly temperature dependent. The higher the temperatures obtained during the ‘event’, the more rapidly and completely the system will be homogenized. On scales larger than 10 meters or so, homogenization can only be achieved through convective-driven advective transport. This effectively means homogenization requires the presence of a liquid. This might be a magma or a hydrous fluid circulating through rocks undergoing metamorphism. In any case, both convection and diffusion will be more efficient at higher temperatures, so homogenization is more likely to be achieved at high temperatures than at low ones. Finally, the larger the range in parent/daughter ratios, and hence isotopic composition at the time we measure them, the less important will be any initial variations in isotopic composition.

We will now continue with our consideration of the various decay systems. Rb-Sr geochronology does not differ in principle from Sm-Nd geochronology or Re-Os geochronology, however. Thus our discussion will focus mainly on the geochemistry of these elements and the behavior of these systems with reference to the four points above.

### 2.4.1 Rb-Sr Chemistry and Geochronology

Both Rb and Sr are trace elements in the Earth: their concentrations are generally measured in ppm. Rb is an alkali element (Group 1) with a valence of +1. Like other alkalis, it is generally quite soluble in water and hydrous fluids. As a result, it is among the more mobile elements. Rb has an ionic radius of 148 pm. This large ionic radius means it is excluded from many minerals: it is simply too large to fit in the sites available. Hence it is among the most incompatible elements. However, its radius is sufficiently similar to that of potassium (133 pm) that it substitutes readily for K in K-bearing minerals such as mica and K-feldspar. As a result, no Rb minerals occur in nature: that is, it is not a stoichiometric component of any mineral. Because of its incompatible nature, it is strongly concentrated in the Earth’s crust and depleted in its mantle.

Sr is an alkaline earth element (Group 2) with a valence of +2. The alkaline earths are also reasonably soluble in water and hydrous fluids, but not as soluble as the alkalis. Sr is therefore a moderately mobile element. Its ionic radius is 113 pm, which is still sufficiently large for it to be excluded from many minerals, and it is also an incompatible element, but not a highly incompatible one. It substitutes for Ca (ionic radius 99 pm) to varying degrees. It is quite comfortable in the Ca site in plagioclase, the solid/liquid partition\(^1\) coefficient being about 2. It seems to be considerably less comfortable in the Ca

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\(^1\)The solid-liquid partition (or distribution) coefficient is a useful parameter in igneous trace element geochemistry. It is defined simply as the equilibrium ratio of the concentration of the element in the solid phase (e.g., a mineral such
site in clinopyroxene; the Sr partition coefficient being only about 0.1. Thus in most igneous and high-grade metamorphic rocks, most Sr will be in plagioclase (which typically constitutes about 50% of mafic igneous rocks). Sr can also substitute for Ca in other minerals such as calcite, apatite, gypsum, titanite (CaTiSiO$_5$, also known as sphene), etc. Sr is also concentrated in the crust relative to the mantle, but not to the degree that Rb is.

The Rb/Sr in the Earth as a whole is in the range of 0.021-0.029; we do not know this ratio exactly. The ratio is lower in the mantle, and much higher in the crust. Mantle-derived rocks such as basalts also have low Rb/Sr ratios. Low ratios such as these violate condition 1 above; as a result, it is often difficult to obtain good Rb/Sr ages on mafic and ultramafic rocks. However, igneous differentiation tends to increase the Rb/Sr ratio because Sr is removed by fractional crystallization of plagioclase while Rb remains in the melt. In felsic or silicic igneous rocks, the Rb/Sr ratio often exceeds 1 (a Rb/Sr ratio of 1 corresponds to a $^{87}\text{Rb}/^{86}\text{Sr}$ ratio of 2.9, depending somewhat on the $^{87}\text{Sr}/^{88}\text{Sr}$ ratio). As a result, Rb/Sr dating can often be applied successfully to felsic igneous rocks. A large range in Rb/Sr ratio is also reasonably common. It may occur in whole rock samples when the whole rocks represent various members of a comagmatic differentiation suite, or in mineral samples when both K- and Ca-bearing minerals are present. Rb-Sr geochronology can also be applied to metamorphic rocks, provided K-bearing, Rb-rich minerals are present, as they typically are. Figure 2.11 shows an example isochron of a meteorite.

A serious disadvantage of the Rb-Sr system is the mobility of these elements, particularly Rb. Because of their solubilities, Rb and Sr are readily transported by fluids, and may be moved into or out of the system. Furthermore, some K-bearing minerals such as micas are comparatively reactive, in the sense that some or much of the Rb may be present in exchangeable sites. These minerals are also subject to metamorphic resetting or partial resetting at relatively low temperatures. Thus, Rb-Sr is a good system for dating acid igneous rocks where no intervening metamorphism or alteration has occurred, and for metamorphic rocks.

Rb-Sr dating can in special instances be applied to sedimentary rocks. Sedimentary rocks are generally difficult to date by any method because of the lack of the high-temperatures necessary for homogenization of initial Sr isotope ratios. But minerals crystallizing from a homogeneous solution, such as plagioclase) to the concentration in the magma. The partition coefficient provides a means of quantifying the term ‘incompatibility’: the lower the partition coefficient, the higher the incompatibility.

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2 A reasonable compositional model for the Earth is that of chondritic meteorites, which we consider representative of the concentrations of non-gaseous elements in the solar system. However, the Earth is demonstrably depleted in the more volatile of the non-gaseous elements, so that this model of the Earth is valid only for the more refractory elements. The alkalis, including are among the volatile elements, for which this model is not valid.

3 Mafic rocks are those rich in magnesium and iron (the term “mafic comes from “MAGnesium and Ferric or Ferrous (fer being the Latin root meaning iron). Ultramafic rocks are simply very rich in magnesium and iron. Basalt, the composition typical of many lavas, is mafic. The Earth’s mantle is composed of peridotite, an ultramafic rock.
Sr isotope ratios can, however, be used to date sediments in another way. Sr has a long residence time in the oceans, a consequence, in part, of its relatively high solubility. Consequently, it is uniformly mixed in the open ocean. As a result of that, its concentration and isotopic composition in the modern ocean is uniform. Its isotopic composition has, however, changed over geologic time. The change over the Phanerozoic is illustrated in Figure 2.12.

Since seawater $^{87}\text{Sr}/^{86}\text{Sr}$ is geographically uniform at any time yet varies through time, the isotopic composition of material precipitated from seawater will be a function of time. Sr is concentrated in calcite and aragonite, which many organisms, most notably mollusks, corals, and foraminifera, precipitate to form shells. By comparing the $^{87}\text{Sr}/^{86}\text{Sr}$ of a particular shell with the seawater curve in Figure 2.12, we can determine its age. This dating technique is called Sr isotope chronostratigraphy. There are, however, several caveats. First, $^{87}\text{Sr}/^{86}\text{Sr}$ is uniform only in the open ocean; it can vary in coastal areas due to continental inputs. Thus, for example, oyster shells would not be useful because oysters grow in brackish water. Second, while the ratio in a pristine shell should reflect the composition of the water it precipitates from, this ratio may change as a result of interaction with pore water. Finally, a given value of $^{87}\text{Sr}/^{86}\text{Sr}$ does not necessarily correspond to a unique age. For example, the value of 0.7080 occurred during Ordovician, Devonian, Mississippian, Permian, and Cenozoic time. Thus the age of the fossil being dated needs to be approximately known before Sr isotope chronostratigraphy can be applied usefully. Finally, the accuracy of this technique depends on how accurately the $^{87}\text{Sr}/^{86}\text{Sr}$ value of seawater is known for any given time. For much of the Cenozoic, particularly the late Cenozoic, these values are very well known. Consequently, Sr isotope chronostratigraphy provides useful and accurate ages for these times. Values are much less well known for the Paleozoic.

The change in seawater $^{87}\text{Sr}/^{86}\text{Sr}$ shown in Figure 2.12 has been very non-linear. Indeed, there have been times, such as the Permian and the Jurassic, when $^{87}\text{Sr}/^{86}\text{Sr}$ has actually decreased in seawater. This is perhaps initially surprising since the decay of $^{87}\text{R}$ to $^{86}\text{Sr}$ occurs at a constant rate. This reflects the open system nature of the oceans. Salts are continuously added and removed from seawater; consequently, the oceans inventory of Sr is constantly, albeit slowly, renewed. Thus the isotopic composition of seawater Sr reflects the isotopic composition of Sr added to seawater, i.e., the isotopic composition of the sources of Sr in seawater. We can broadly divide these sources into “continental” and “mantle”. The “continental” source is dominantly the riverine input, and secondarily wind-blown and glacially derived particles that dissolve or partly dissolve when the reach the sea. The isotopic composition of the continental source will vary with the nature of continental material undergoing erosion at any time as well as with the rate of erosion. The “mantle” source consists primarily of hydrothermal fluids of mid-ocean ridge hydrothermal systems. Secondary sources include erosion and weathering (both subareal and submarine) of young.
mantle-derived basalts. We'll discuss this further in Chapter 7.

2.5 The Sm-Nd System

\(^{147}\text{Sm}\) decays to \(^{143}\text{Nd}\) by alpha decay with a half-life of 106 Ga (\(\lambda = 6.54 \times 10^{-12}\) y\(^{-1}\)). Because the half-life is so long, the resulting variations in Nd isotopic composition are small and require precise measurement. Sm and Nd are both intermediate rare earth elements (Figure 2.13). The distinctive feature of the rare earth elements is that inner electron shells (specifically the 4f and 5d shells) are being filled as atomic number increases. Normally an electron is added to the outermost shell when atomic number increases. It is the outer electron shells that dictate the chemical behavior of elements. Since the outer electron shells of the rare earths have identical configurations, we would expect them to behave quite similarly. This is indeed the case. The rare earths generally have a +3 valence, the most important exceptions being Eu, which is +2 under some conditions, and Ce, which is +4 under some conditions. The primary chemical difference between the rare earth elements is the ionic radius, which shrinks systematically from 115 pm for La (\(A=57\)) to 93 pm for Lu (\(A=71\)). Since the rare earths form predominately ionic bonds with oxygen in the solid Earth, their ionic radius is a key factor in their geochemical behavior. Thus there is a systematic variation in their abundances in rocks, minerals, and solutions (see box on rare earth plots). The ionic radii of Sm and Nd, which are separated by Pm (an element that has no stable or long-lived isotope), differ by only 4 pm (Nd=108, Sm=104). The ionic radii and relatively high charge of the rare earths make them fairly unwelcome in many mineral lattices: they can be considered moderately incompatible, with Nd being slightly more incompatible than Sm. Ce is generally the most abundant rare earth and forms its own phase in rare instances. Some rare earths, particularly the heavier ones, are accommodated in lattice structures of common minerals; for example the partition coefficient of Lu in garnet is in the range of 4-10 (depending on the composition of the magma and the garnet). In mafic minerals, the lighter rare earths, which have the largest ionic radii, tend to be excluded more than the heavies, but in plagioclase, the heavies are the most excluded (though partition coefficients generally are not less than 0.1). The high valence state of the rare earths results in relatively strong bonds. This, together with their tendency to hydrolyze (that is, surround themselves with OH\(^-\) radicals), results in relatively low solubilities and low mobilities.

Although absolute concentrations vary significantly, the rare earths have very nearly the same relative

![Figure 2.13](image_url)
We'll discuss the issue of mass fractionation in a subsequent chapter.
variable $^{142}\text{Nd}/^{144}\text{Nd}$ ratios (e.g., Boyet et al., 2003, O'Neil et al., 2008). This implies the $^{147}\text{Sm}/^{144}\text{Nd}$ ratio of the Earth is about 6 to 8% higher than the chondritic one (about 0.208), corresponding to an $\varepsilon_{\text{Nd}}$ of about $+7$.

**Rare Earth Plots**

The systematic contraction in the ionic radii of the rare earth elements leads to systematic variation in their behavior. This is best illustrated by viewing their abundances on rare earth, or Masuda-Curryell, plots. The plots are constructed by first “normalizing” the concentrations of the rare earth, i.e., dividing but the concentration of the element in a standard. Generally, this standard is the abundance in chondritic meteorites, but other values are also used (for example, rare earths in sediments and seawater are often normalized to average shale). This normalizing process removes the sawtooth pattern that results from odd-even nuclear effects, and also the effect of decreasing concentration with atomic number. These concentration variations, illustrated in Figure 2.14, reflect differences in nuclear stability and the nucleosynthetic process, and therefore affect the abundances of rare earths in all matter. Removing these effects by normalization highlights differences in concentration due to geochemical processes. After normalizing, the log of the abundance of each element is plotted against atomic number, as is illustrated in Figure 2.15.

![Figure 2.14. Rare earth concentrations in the CI carbonaceous chondrite Orgueil.](image)

![Figure 2.15. A rare earth plot showing rare earth patterns for Orgueil, average upper continental crust, and average mid-ocean ridge basalt (MORB).](image)
Why the Earth should not have a chondritic Sm/Nd ratio is unclear. These two elements are very similar to each other in chemical behavior, having identical configurations of electrons in bonding orbitals, and are both refractory lithophile elements. Indeed, Nd and Sm have 50% condensation temperatures of 1602 and 1590 K, respectively. It is difficult to see how processes operating in the solar nebula could have fractionated these elements significantly. Two primary hypotheses have been proposed to explain this, both involve formation of an early primitive, incompatible element-enriched, and therefore low Sm/Nd, crust by crystallization of a terrestrial magma ocean. Boyet and Carlson (2006) suggested that this enriched crust (what they call the “Early Enriched Reservoir”) subsequently sunk to the deep mantle where it remains. The complimentary “Early Depleted Reservoir” is the part of the mantle sampled by volcanism and gave rise to the present continental crust. In this model, the bulk Earth does have chondritic Sm/Nd, although the ‘observable’ part does not.

Alternatively, Caro et al. (2008) and Caro and Bourdon (2010) proposed that the primitive incompatible element-enriched crust was lost from the Earth by “collisonal erosion”; as the Earth accreted from nebular material, very large impacts of protoplanetary bodies blasted the proto-crust into space. In support of this view, they point out that the Moon, itself thought to have formed when a large protoplanet impacted Earth, appears to have the same non-chondritic Sm/Nd as the Earth, as may Mars (although the case for non-chondritic Sm/Nd is weaker for Mars). A third proposed explanation is heterogeneous distribution of $^{142}\text{Nd}$ or, particularly, $^{144}\text{Sm}$ in the solar nebula. There is indeed some evidence of isotopic heterogeneity in the solar system and we will consider this in more detail in Chapter 5.

Figure 2.16 illustrates how $^{143}\text{Nd}/^{144}\text{Nd}$ has evolved in the Earth. If the Earth indeed has chondritic Sm/Nd, it evolves along the line labeled “CHUR”. If the $^{147}\text{Sm}/^{144}\text{Nd}$ is higher (0.208), it evolves along a steeper trajectory labeled “Bulk (Observable) Silicate Earth”. In either case, differentiation of the Earth into a light rare earth-enriched crust and light rare earth-depleted mantle results in the mantle evolving along a steeper (high Sm/Nd) trajectory, and crust evolving along a less steep one (low Sm/Nd). Converting $^{143}\text{Nd}/^{144}\text{Nd}$ to $\varepsilon_{\text{Nd}}$ (Figure 2.16b) the CHUR value remains constant at $\varepsilon_{\text{Nd}} = 0$ while the observable Earth evolves toward an $\varepsilon_{\text{Nd}}$ value of about +7. The mantle evolves toward even more positive $\varepsilon_{\text{Nd}}$ while the crust evolves toward negative $\varepsilon_{\text{Nd}}$.

Perhaps the greatest advantage of Sm/Nd is the lack of mobility of these elements. The Sm-Nd chronometer is therefore relatively robust with respect to alteration and weathering.
low-grade metamorphism. Thus the Sm-Nd system is often the system of choice for mafic rocks and for rocks that have experienced metamorphism or alteration. An additional advantage is relatively high closure temperatures for this system making it useful for dating peak metamorphism.

There also are several drawbacks to the use of the Sm-Nd system in geochronology. First, the half-life of $^{147}$Nd is relatively long, leading to relatively small variation in $^{143}$Nd/$^{144}$Nd and imprecise ages, particularly for young rocks. The second is the limited variation in Sm/Nd. As things turn out, however, Sm-Nd compliments Rb-Sr nicely. Sm/Nd variations tend to be largest in mafic and ultramafic rocks and smallest in acid rocks, exactly the opposite of Rb/Sr. One application that has been highly successful has been to use the Sm-Nd isotope system to date garnet bearing rocks. Garnets incorporate HREE over LREE as they grow, which lead to very high Sm/Nd ratio in these minerals. Therefore, garnet bearing rocks such as eclogites can be dated to relatively high precision with the Sm-Nd system. Figure 2.17 is an example of a Sm-Nd isochron of a garnet-bearing granite from the Qinling metamorphic belt in China (Cheng et al., 2011). The 394 Ma age is younger than the 434±7 Ma zircon age of the granite. The garnets likely formed from incongruent breakdown of biotite. The age reflects time the granite cooled through the closure Sm-Nd temperature, in this case some 40 million years after crystallization, suggesting it remained deeply buried.

2.5.1 Sm-Nd Model Ages and Crustal Residence Times

A general assumption about the Earth is that the continental crust has been created from the mantle by magmatism. When a piece of crust is first created, it will have the $^{143}$Nd/$^{144}$Nd ratio of the mantle, though it’s Sm/Nd ratio will be lower than that of the mantle (a consequence of Nd being more incompatible and partitioning more into the melt than Sm). Let’s make the simplistic assumption that the mantle has the same Nd isotopic history as CHUR. This means a piece of crust will have the same $^{143}$Nd/$^{144}$Nd as the mantle and as CHUR when it is created, i.e., $\varepsilon_{\text{Nd}} = 0$. If we know the present-day Sm/Nd and $^{143}$Nd/$^{144}$Nd ratio of this piece of crust, we can estimate its age. Figure 2.18 illustrates how this is done graphically; let’s see how this is done mathematically. What we want to find is the intersection of line describing the evolution of the sample and that describing the evolution of the mantle. To do so, we simply need to subtract one equation from the other.

The closed system isotopic evolution of any sample can be expressed as:

$$^{143}\text{Nd} / ^{144}\text{Nd}_{\text{sam}} = ^{143}\text{Nd} / ^{144}\text{Nd}_0 + ^{147}\text{Sm} / ^{144}\text{Nd}_{\text{sam}} (e^{\lambda t} - 1)$$  \hspace{1cm} 2.46
The chondritic evolution line is:

\[ \frac{^{143}Nd}{^{144}Nd}_{CHUR} = \frac{^{143}Nd}{^{144}Nd}_0 + \frac{^{147}Sm}{^{144}Nd}_{CHUR} \left( e^{\lambda t} - 1 \right) \]  \hspace{1cm} (2.47)

The CHUR model age of a system is the time elapsed, \( t = \tau \), since it had a chondritic \( \frac{^{143}Nd}{^{144}Nd} \) ratio, assuming the system has remained closed. We can find \( \tau \) by subtracting equation 2.47 from 2.46, which yields:

\[ \frac{^{143}Nd}{^{144}Nd}_{s} - \frac{^{143}Nd}{^{144}Nd}_{CHUR} = \frac{^{147}Sm}{^{144}Nd}_{s} - \frac{^{147}Sm}{^{144}Nd}_{CHUR} \left( e^{\lambda \tau} - 1 \right) \]  \hspace{1cm} (2.48)

Another way of thinking about this problem is to imagine a \( 
\frac{^{143}Nd}{^{144}Nd} \) vs. time plot: on that plot, we extrapolate the sample’s evolution curve back to the chondritic one. In terms of the above equations, this intersection occurs at \( \left( \frac{^{143}Nd}{^{144}Nd} \right)_s \).

Solving eqn. 2.48 for \( \tau \):

\[ \tau_{CHUR} = \frac{1}{\lambda} \ln \left( \frac{^{143}Nd/^{144}Nd_s - ^{143}Nd/^{144}Nd_{CHUR}}{^{147}Sm/^{144}Nd_s - ^{147}Sm/^{144}Nd_{CHUR}} + 1 \right) \]  \hspace{1cm} (2.49)

An age obtained in this way is called an \textit{Nd model age} (the model is that of chondritic evolution of the mantle), or a \textit{crustal residence age}, because it provides an estimate of how long this sample of Nd has been in the crust. Note that we explicitly assume the sample has remained a closed system, in the sense of no migration in or out of Sm or Nd. Because of the immobility of these elements, the assumption often holds, although generally only approximately.

We can obtain somewhat better model ages by making more a sophisticated assumption about the Nd evolution of the mantle. Since the crust is enriched in Nd relative to Sm, the mantle must be depleted in Nd relative to Sm (analyses of mantle-derived rocks confirm this) and the mantle should evolve along a line steeper than chondritic. Once we decide on Sm/Nd and present-day \( \frac{^{143}Nd}{^{144}Nd} \) for this ‘depleted-mantle’ (the latter can be estimated from the \( ^{143}Nd/^{144}Nd \) of MORB, mid-ocean ridge basalts), we can calculate a model age relative to the depleted mantle by substituting the depleted-mantle terms for the CHUR terms in 2.47 and 2.48.

To calculate the depleted mantle model age, \( \tau_{DM} \), we use the same approach, but this time we want the intersection of the sample evolution line and the depleted mantle evolution line. So equation 2.49 becomes:

\[ \tau_{DM} = \frac{1}{\lambda} \ln \left( \frac{^{143}Nd/^{144}Nd_{DM} - ^{143}Nd/^{144}Nd_{CHUR}}{^{147}Sm/^{144}Nd_{DM} - ^{147}Sm/^{144}Nd_{CHUR}} + 1 \right) \]  \hspace{1cm} (2.50)

Figure 2.18. Sm-Nd model ages. The \( 
\frac{^{143}Nd}{^{144}Nd} \) is extrapolated backward (slope depending on Sm/Nd) until it intersects a mantle or chondritic growth curve.
closed system evolution since the formation of the Earth, 4.55 Ga ago (i.e., a straight line on a $^{143}\text{Nd}/^{144}\text{Nd}$ vs. time plot). This evolution implies a $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.213.

Because the $\text{Sm}/\text{Nd}$ ratio is so little affected by weathering, and because these elements are so insoluble, $\text{Sm}/\text{Nd}$ ratios in fine-grained sediments do not generally differ much from the ratio in the precursor crystalline rock. Thus, the system has some power to ‘see through’ even the process of making sediment from crystalline rock. The result is we can even compute crustal residence times from Nd isotope ratio and Sm/Nd measurements of fine-grained sediments. This generally does not work for coarse-grained sediments though because they contain accessory minerals whose $\text{Sm}/\text{Nd}$ ratios can be quite different from that of the whole rock.

2.6 The Lu-Hf System

Lu is the heaviest rare earth element, with a valence of +3 and an ionic radius of 93 pm. It has two isotopes, $^{175}\text{Lu}$ (97.4%) and $^{176}\text{Lu}$ (2.6%). As an odd-odd nucleus, $^{176}\text{Lu}$ is unstable relative to both $^{176}\text{Yb}$ and $^{176}\text{Hf}$. However, there is some uncertainty as to whether the decay to $^{176}\text{Yb}$ occurs at all, and it certainly constitutes less than 3% of the decay. Hf is a member of the group IVB elements, which include Ti and Zr. As members of the same periodic group, the three elements show chemical similarity and this similarity is quite strong in the case of Zr and Hf. Hf has an ionic radius of 71 pm in six-fold coordination (0.83 in 8-fold coordination) and a valence of +4. The particularly strong similarity between Hf and Zr results in part from the similarity of ionic radii: the radius of $\text{Zr}^{4+}$ is 72 pm in six-fold and 84 pm in 8-fold coordination; the radius of $\text{Ti}^{4+}$ is much smaller: 61 pm. Lu can be considered a slightly to moderately incompatible element; Hf is moderately incompatible (its incompatibility is very similar to that of Sm).

The Lu-Hf system shares many of the advantages of the Sm-Nd system: both are relatively insoluble and immobile elements, both are refractory and hence we have reason to believe that the Lu/Hf ratio is the Earth should be the same as in chondrites. Indeed, we can define an $\epsilon_{\text{Hf}}$ value in a manner exactly analogous to the $\epsilon_{\text{Nd}}$:

$$\epsilon_{\text{Hf}} = \left[ \frac{(^{176}\text{Hf})_{\text{sample}} - (^{176}\text{Hf})_{\text{Chon}}}{(^{176}\text{Hf})_{\text{Chon}}} \right] \times 10000$$ 2.51

Isotopic analysis of Hf is made difficult by its extremely limited aqueous solubility and its nearly identical chemical behavior to Zr (indeed, its chemical similarity to Zr is one reason why Hf was the very last stable element to be discovered and isolated – it was discovered in X-ray spectra in 1923 and the metal first purified in 1925). Although laborious, standard techniques are available for Hf purification. An additional problem is that the temperatures required for ionization are extremely high; as a result the ionization efficiency by thermal ionization is low, making analysis difficult by this method. This problem has been overcome with the development of multiple-collector magnetic sector inductively coupled plasma mass spectrometers (MC-ICP-MS), in which the analyte is ionized in an Ar plasma rather than thermally. Secondary ion mass spectrometry, in which the Hf is ionized by an ion beam while being heated (hot SIMS), was also used with some success, but has now been abandoned in favor of MC-ICP-MS Hf analysis, which enjoys widespread use.

As the analytical problems with the Lu-Hf system were overcome, other problems emerged that needed to be resolved. Perhaps most importantly, there was a worrisome amount of uncertainty of the value of the decay constant. Determining the decay rate of a nuclide that decays as slowly as $^{176}\text{Lu}$ is not easy. As we noted earlier, there are several possible approaches. These approaches produced results that did not agree as well as one would hope. Counting experiments performed since 1975 have yielded a range of decay constants ranging from 1.70 x 10$^{-11}$ a$^{-1}$ to 1.93 x 10$^{-11}$ a$^{-1}$, a 14% range. The “calibration” approach has also produced a range of values. Tatsumoto et al. (1981) calculated a decay constant of 1.94 x 10$^{-11}$ a$^{-1}$ from a Lu-Hf isochron on eucrite meteorites assuming an age of 4.55 Ga. Scherer et al. (2001) performed a calibration experiment by obtaining U-Pb and Lu-Hf isochrons on 4 rocks suites ranging in age from 0.91 to 2.06 Ga and using the U-Pb ages to determine a decay constant for $^{176}\text{Lu}$ of
1.865±0.015 x 10^{-11} \text{ a}^{-1}. \text{Söderlund et al. (2004) calculated a decay constant of 1.867±0.008 x 10^{11} \text{ yr}^{-1} by comparing Lu-Hf and U-Pb isochrons of Proterozoic dolerites from Sweden and Finland. Bizzarro et al. (2003) determined a decay constant of 1.983 x 10^{-11} \text{ a}^{-1} from an isochron on chondritic and eucritic meteorites and an assumed age of 4.56 Ga. Although the Bizzaro age was based on an isochron which mixed different classes of meteorites with different histories, it seemed that one value of the decay constant applied to meteorites and another to terrestrial samples, which hardly seemed likely.}

Subsequent studies of meteorites appear to have resolved this issue in favor of the ‘terrestrial’ decay constant of Söderlund and Scherer (1.867 x 10^{11} \text{ yr}^{-1} is the currently accepted value). Amelin (2005) carried out a calibration study using phosphates (such as apatite) in the Acapulco and Richardton meteorites. Phosphates have the useful property that they concentrate both U and the rare earths, such as Lu while excluding Pb and Hf. The resulting high U/Pb and Lu/Hf ratios lead to good chronometers (unfortunately, phosphates are also rather soluble, hence isochrons are potentially easily disturbed, although they were not in this study). Comparing Lu-Hf isochrons with previously determined U-Pb ages of 4556.5±1.3 Ma and 4550.7±2.6 Ma, Amelin (2005) found decay constants of 1.864±0.016 x 10^{11} \text{ yr}^{-1} and 1.832±0.029 x 10^{11} \text{ yr}^{-1}, in good agreement with the previously determined decay constants from terrestrial samples. Subsequent work by Bouvier et al. (2008) found that the least thermally metamorphosed chondrites (petrologic classes 1-3) showed much less scatter on an Lu-Hf isochron plot than metamorphosed or “equilibrated” chondrites (Figure 2.19). Using only the most precise data and assuming an age of 4568.5 Ma, they calculated a ^{176}\text{Lu} decay constant of 1.884 (±0.060) x 10^{11} \text{ yr}^{-1}, in good agreement with the value obtained in studies of terrestrial rocks.

In addition to questions about the decay constant, there were also been questions about the ^{167}\text{Lu}/^{177}\text{Hf} ratio and the present and initial ^{176}\text{Hf}/^{177}\text{Hf} ratio of chondrites. A good part of the problem is that there is a 28% variation in the ^{167}\text{Lu}/^{177}\text{Hf} ratio in chondrites (compared to only 3% variation in the Sm/Nd ratio). Bouvier et al. (2008) found that when only the least thermally metamorphosed chondrites are considered the scatter in ^{167}\text{Lu}/^{177}\text{Hf} ratio reduces to only 3%, comparable to that observed for Sm/Nd. They argued the problem likely relates to the presence of phosphate phases in meteorites.
These can have very high $^{167}\text{Lu}/^{177}\text{Hf}$ ratios and easily mobilized and recrystallized during thermal metamorphism. Using only the least thermally metamorphosed chondrites, Bouvier et al. calculate a mean $^{176}\text{Lu}/^{177}\text{Hf}$ ratio of 0.0336±1 and a mean $^{176}\text{Hf}/^{177}\text{Hf} = 0.27978±0.00004$. However, the question of the initial $^{176}\text{Hf}/^{177}\text{Hf}$ of the solar system persists. For example, Bizzarro et al. (2012) reported a $^{176}\text{Lu}^{176}\text{Hf}$ internal isochron age of 4869 ± 34 Ma for a pristine achondritic meteorite (the angrite SAH99555), which had been precisely dated by U-Pb to 4564.58 ± 0.14 Ma. Thus the Lu-Hf age is roughly 300 Ma too old. Their isochron yields an initial $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.279685 ± 0.000019, 3.4 $\epsilon_{\text{Hf}}$ units lower than Bouvier et al.’s value, which they argue is the initial $\epsilon_{\text{Hf}}$ of the solar system. We’ll discuss this question in more detail in the context of events of the early solar system in further detail in Chapter 5. In this book we will continue to use the Bouvier et al. (2008) value of the chondritic $^{176}\text{Hf}/^{177}\text{Hf}$ for calculation of $\epsilon_{\text{Hf}}$. Nevertheless, there is some uncertainty in the $\epsilon_{\text{Hf}}$ of the silicate Earth, perhaps several epsilon units, just as there is for the $\epsilon_{\text{Nd}}$ of the silicate Earth.

The Lu-Hf system has several advantages, in principle at least, over the Sm-Nd system. First, because the half-life of $^{176}\text{Lu}$ is shorter than that of $^{147}\text{Sm}$ (37 Ga vs. 106 Ga) and because the range of Lu/Hf ratios in common rocks and minerals is greater than that of Sm/Nd, the variations in $^{176}\text{Hf}/^{177}\text{Hf}$ and $\epsilon_{\text{Hf}}$ are larger than of $^{143}\text{Nd}/^{144}\text{Nd}$ and $\epsilon_{\text{Nd}}$. Second, because of the chemical similarity of Hf to Zr, Hf is concentrated in zircon, a very robust mineral that also concentrates U and can be dated using the U-Pb system.

Figure 2.20. $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ in the Earth. The $\epsilon_{\text{Hf}}$ and $\epsilon_{\text{Nd}}$ in magmatic rocks of the continental and oceanic crust define the ‘terrestrial array’ ($\epsilon_{\text{Hf}} = 1.21+1.55\epsilon_{\text{Nd}}$; Vervoort and Blichert-Toft, 1999; Vervoort et al., 2011) Terrigenous sediments also lie on this array. Hydrothermal and hydrogenous sediments, including Mn-Fe crusts and and nodules, define a shallower array, called the seawater array by Albarède et al. (1998) described by the equation $\epsilon_{\text{Hf}} = 7.1+0.55\epsilon_{\text{Nd}}$ (Vervoort et al. (2011). From the database kindly provided by J. D. Vervoort.

60 December 4, 2013
The general similarity between the Lu-Hf system and the Sm-Nd system is demonstrated by Figure 2.20, which shows that $\varepsilon_{\text{Hf}}$ and $\varepsilon_{\text{Nd}}$ are well correlated in crustal rocks of all ages. It also shows that the variations in $\varepsilon_{\text{Hf}}$ are about half again as large as those of $\varepsilon_{\text{Nd}}$. The correlation holds for ‘terrigenous’, that is marine continent-derived sediments, but breaks down for ‘hydrogenous’ sediments that contain a significant component derived from seawater, which define a shallower ‘seawater array’. This results from two effects. The first is the ‘zircon effect’ (Patchett et al., 2004). When continental rocks are weathered, the rare earths, including Sm, Nd, and Lu concentrate in clays, but a significant fraction of unradiogenic Hf remains concentrated in zircons, which resist both chemical and mechanical weathering. The zircons tend to remain in coarser-grained sediments on the continents continental shelves, thus the Hf flux to the oceans from the continents is more radiogenic that the continents themselves. Secondly, Hf is extremely insoluble in stream and ocean water, but less so in hydrothermal solutions where it forms soluble complexes with fluorine (Bau and Koschinsky, 2006). As a result, the flux of radiogenic Hf to seawater from the oceanic crust is larger compared to the hydrothermal Nd flux (White et al., 2006). One consequence of the different behavior of Hf and Nd during weathering is that there would be little point to calculating Lu-Hf crustal residence times analogous to Sm-Nd residence times. We can, however, use initial $\varepsilon_{\text{Hf}}$ values of detrital zircons to trace crustal evolution. We will return to all of these topics in Chapter 7.

One important difference between Lu-Hf and Sm-Nd is that whereas Sm/Nd ratios usually do not change much in the weathering of a crystalline rock to form a sediment, Lu/Hf ratios do. In both cases, the elements are reasonably insoluble, and little is carried away by solution. Most of the rare earths end up in clays, but much of the Hf in felsic crystalline rocks of the continental crust is in zircon (ZrSiO$_4$), which, as we have already noted, is very resistant to both chemical and mechanical weathering. The clays are, of course, quite fine and can be carried great distances from their source. Zircon remains in the coarse (and hence less mobile) sand fraction. As a result, there are large differences between Lu/Hf ratios in fine and coarse sediments.

Figure 2.21 illustrates two recent examples of Lu-Hf geochronology. The first (Figure 2.21a) is a garnet-mica schist from Snow Peak in northern Idaho. Garnets strongly concentrate Lu, as well as the other heavy rare earths, while excluding Hf, making garnet-bearing rocks good targets for Lu-Hf geochronology, as they are for

![Figure 2.21](image-url)
Isotope Geochemistry

Chapter 2

Geochronology I

Sm-Nd geochronology. Nesheim et al. (2012) analyzed four garnet fractions and a whole rock, with the data defining an age of metamorphism 1314±2.3 Ma. The low MSWD indicates that all variation from the isochron can be explained by analytical error alone. The second example is blueschist facies metamorphic rocks from the Ring Mountain on the Tiburon Peninsula in California (which projects into San Francisco Bay). Blueschist facies metamorphic rocks are formed in the high pressure, low temperature regime of subduction zones and have been difficult to date by methods other than K-Ar. Among their characteristic minerals are glaucophane (Na₂Mg₃Al₂Si₈O₂₀(OH)₂), which gives blueschist facies rocks their characteristic blue color, and lawsonite, (CaAl₂Si₂O₇(OH)₂·H₂O). The latter can, in some cases, incorporate heavy rare earths such as Lu, while glaucophane preferentially incorporates Hf. The ages reflect closure of these to diffusion; the closure temperatures are not known but are probably high relative to the conditions typical of blueschist facies metamorphism. Mulcahy et al. (2009) analyzed lawsonite and glaucophane separates, as well as whole rock samples, and obtained the isochron shown in Figure 2.21b. In this case, the MSWD is rather high, indicating the misfit to the isochron is greater than expected from estimated analytical errors alone. This may be a consequence of open system behavior – the lawsonite formed under retrograde conditions while the rocks were being exhumed – or, in this case, inclusion of Hf rich phases within the separates, such as titanite. The age nevertheless agrees well with other ages from the Tiburon Peninsula, which range from 157 to 141 Ma.

2.7 THE RE-Os SYSTEM

2.7.1 The Re-Os Decay System

After early efforts by Hirt et al., (1963), the Re-Os system was largely ignored due to the analytical challenges it presented. The problems are two-fold: (1) Os is an extremely rare element, rarely present at concentrations above the part per billion level (and often much lower) and (2) Os metal is extremely refractory, evaporating and ionizing only at extremely high temperatures. This was been overcome through analysis of the negative ion of OsO₃⁻, which, in contrast to the metal, evaporates and ionizes at quite low temperature. This technique has proved to be extremely sensitive, making it possible to determine Os iso-
Isotope Geochemistry

Chapter 2

Geochronology I

tope ratios on extremely small amounts of Os (Creaser et al., 1991). Consequently, the Re-Os system has become a useful geochronological tool over the past two decades, although the applications are somewhat limited. Up to now, most of the elements of the decay systems we have discussed have been lithophile (derived from Greek words for rock and love) elements (the exception is Pb, which is chalcophile). Lithophile means simply that, given the choice, the element prefers a silicate or oxide phase (in fact a better term would be oxyphile) to a sulfide or metal phase. Chalcophile elements would choose the sulfide phase and siderophile elements would choose a metal phase given the same choices (a final group is the atmophile elements: those elements preferring a gas phase). Re and Os are both siderophile elements, though both also have some chalcophile tendencies. Their siderophile nature accounts for their low concentrations in the crust and mantle: most of the Earth's Re and Os are in the core. Os is one of the platinumoid, or platinum-group, elements (the second and third transition series members of Group VIII elements) which include Ru, Rh, Pd, and Ir and well as Os and Pt. Like the rare earths, these elements behave coherently, though their valences and ionic radii differ. The usual valence state of Os is +4 at the Earth's surface; its ionic radius is 0.69. The valence of Re is also +4; its ionic radius is 0.63. However, in the mantle and in magmas, these elements are likely in +1 or 0 valence states. Re is a moderately incompatible element whereas Os is highly compatible one: it partitions into a melt only very sparingly. Hence the crust has a much lower Os concentration than the mantle (the core, of course, should have a higher concentration than both).

The older convention for Os isotope ratios, established by Hirt et al. (1963) reports the isotope ratio as $\frac{^{187}\text{Os}}{^{188}\text{Os}}$ (normalized for fractionation to $\frac{^{186}\text{Os}}{^{188}\text{Os}}$ of 3.08271). The difficulty is with this normalization. It is that $^{186}$Os is itself radiogenic, being the product of $\alpha$-decay of $^{188}$Pt. $^{188}$Pt is sufficiently rare and its half-life sufficiently long (450 billion years) that in most cases the amount of radiogenic $^{186}$Os is insignificant. However, measurable amounts of radiogenic $^{186}$Os have been observed, as discussed below. This discovery prompted a shift in the convention and now all laboratories report Os isotope analyses as $\frac{^{187}\text{Os}}{^{188}\text{Os}}$. $^{186}$Os/$^{188}$Os ratios may be converted to $^{187}$Os/$^{188}$Os ratios by multiplying by 0.12035.

Figure 2.22 illustrates the evolution of Os isotope ratios in the crust and mantle. As expected from the difference in compatibilities of Re and Os, much higher $^{186}$Os/$^{188}$Os ratios are found in the crust than in the mantle. Interestingly, the Re/Os ratio of the mantle, and therefore presumably the silicate Earth, is nearly chondritic (Allègre and Luck, 1980), but unlike the Sm-Nd and Lu-Hf system, there is no theoretical expectation that it should be. This is a bit surprising if most of Re and Os have been extracted to the core. If the core and mantle are in equilibrium, then mantle concentrations will be determined by metal-silicate partition coefficients, which are large for both elements. Since the partition coefficients of these two elements are different, the ratio of the two in the mantle should be quite different from chondritic. The approximately chondritic Re/Os ratio of the mantle is, however, consistent with models in which core formation is complete before the Earth entirely accretes. In these models, the highly siderophile elements, such as Re and Os, are quantitatively extracted by core formation. The inventory of highly siderophile elements in the crust and mantle comes from the last 1% of material to accrete to the Earth, which occurs after core formation. An alternative explanation has been proposed by Snow and Schmidt (1998). They argue that the nearly chondritic Re-Os ratio of the mantle results from mixing of a small fraction of the outer core back into the mantle.

Since the silicate Earth appears to have a near-chondritic $^{187}$Os/$^{188}$Os ratio, it is useful to define a parameter analogous to $\varepsilon_{\text{Nd}}$ and $\varepsilon_{\text{Hf}}$ that measures the deviation from chondritic. Walker et al. (1989) defined $\gamma_{\text{Os}}$ as:

$$\gamma_{\text{Os}} = \frac{\left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{sample}} - \left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{Chon}}}{\left(\frac{^{187}\text{Os}}{^{188}\text{Os}}\right)_{\text{Chon}}} \times 100$$

(2.51)

(The present day chondritic $^{186}$Os/$^{188}$Os is taken to be 0.1270.) Thus the gamma parameter is exactly analogous to the epsilon one, but where the latter is deviations in parts per ten thousand, the former is percent deviations.

63 December 4, 2013
Since the mantle $^{187}\text{Os}/^{188}\text{Os}$ evolution curve is known, at least to a first approximation, an estimate of age, or model age, analogous to Sm-Nd model ages, can be obtained simply by comparing the measured $^{187}\text{Os}/^{188}\text{Os}$ ratio with the mantle evolution curve. Platinum metal deposits associated with mantle-derived ultramafic rocks would be one example of where such model ages could be obtained. The PGM’s (platinum group metals) occur as very fine (down to a µm or so) metal alloys and sulfides. Os occurs principally as osmiridium (OsIr) and laurite (Ru[Os,Ir]S$_2$). These minerals have Re/Os close to zero. As a result the $^{187}\text{Os}/^{188}\text{Os}$ ratio ceases to change once these minerals form (a model age would still be possible even if a small correction for radiogenic growth of $^{187}\text{Os}$ were necessary).

There has also been considerable interest in the Os isotope composition of seawater. The $^{187}\text{Os}/^{188}\text{Os}$ ratio of modern seawater is about 1.07. Like that of $^{87}\text{Sr}/^{86}\text{Sr}$, $^{187}\text{Os}/^{188}\text{Os}$ depends on the balance of continental fluxes (e.g., rivers, with $^{187}\text{Os}/^{188}\text{Os} \sim 1.4$) and oceanic crustal fluxes (e.g., hydrothermal activity, with $^{187}\text{Os}/^{188}\text{Os} \sim 0.13$). In addition, however, cosmic fluxes ($^{187}\text{Os}/^{188}\text{Os} \sim 0.13$), which include both cosmic dust, which continually settles through the atmosphere into the oceans, and large meteorite impacts, may be significant for Os. Variations in the proportions of these fluxes have resulted in systematic changes in the $^{187}\text{Os}/^{188}\text{Os}$ ratio through time. We’ll return to this topic and discuss these changes in Chapter 7.

### 2.7.2 Re-Os Geochronology

Because of the differences in compatibility, Re/Os variations are huge, at least by comparison to the other systems we have considered. The mantle has a Re/Os ratio on the order of 0.1 whereas the crustal materials can have Re/Os ratios of 100 or even more. The $^{187}\text{Os}/^{188}\text{Os}$ ratio of the mantle is about 0.128 whereas the crustal ratio is thought to be between 1.1 and 1.3. Despite these large variations, strictly geochronological applications of Re-Os are limited because of the very low concentrations of Os in most minerals. Yet in specialized circumstances, such as
iron meteorites, a variety of ore deposits, hydrocarbons, and for some ultramafic rocks such as komatiites (komatiites are very MgO-rich lavas that occur almost exclusively in the Archean, i.e., before 2.5 Ga), Re-Os geochronology has proved quite valuable. Figure 2.23 is an example of an isochron obtained on a komatiite from Monro Township in Ontario. Re is strongly concentrated in some sulfides and arsenides, making the system ideal for dating a variety of ore deposits, including sulfides and gold deposits (e.g., Arne et al., 2001). Let’s consider a few examples.

2.7.2.1 Re-Os Dating of Diamonds

One novel application of the Re-Os system is dating diamonds by dating sulfide inclusions within them. Since Re and Os are somewhat chalcophile, they can be concentrated in mantle sulfide minerals such as pyrrhotite (FeS), chalcopyrite (CuFeS$_2$), and pentlandite ((Fe,Ni)$_9$S$_8$). These minerals are sometimes found as small inclusions in diamond (Figure 2.24). Encapsulated in diamond, individual inclusions become closed systems and accumulate $^{187}$Os is proportion to the amount of $^{187}$Re they contain. Figure 2.25 shows a 2.9 Ga Re-Os isochron derived from inclusions in diamonds from the Kimberley mine in South Africa. Studies such as these have shown that diamond formation in the mantle occurs in discrete events, most likely related to subduction (Shirey et al., 2004).

2.7.2.2 Re-Os Dating of Hydrocarbons

There is perhaps no geologic material that is as essential to modern society as petroleum. Petroleum, however, consists almost exclusively of hydrocarbons, i.e., compounds of C and H, making its formation a challenge to date. Economic petroleum deposits can form if a series of conditions are met: an environment in which relatively high concentrations of organic matter are preserved in sediment as kerogen during deposition of the source rock; subsequent burial and conversion of the kerogen to hydrocarbons through gentle heating, and migration and concentration of the petroleum thus produced in a sufficiently porous reservoir rock. Through a variety of methods (some of which involve isotopic analysis), it is often possible to identify the source rock, and standard correlation techniques can determine the age of source rock deposition. The age of other steps in the process, particularly the timing of generation and migration, have been much harder to determine. Researchers have recently had some success in dating hydrocarbon migration using Re-Os.

Perhaps surprisingly, noble metals, and Re and Os in particular, can be present in relatively high concentrations in petroleum. Work by Selby et al. (2007) found that Re and Os are primarily present in asphaltene fraction of petroleum. Asphaltenes are heavy (molecular masses around 750u) polycyclic aromatic hydrocarbons. Although detailed studies have not been done, it seems likely that Re and Os are bound in porphyrins in the asphaltene fraction. Porphyrins are rings of pyrrole and pyrole groups (5-sided hydrocarbon rings containing N or NH) that can complex a metal ion in the center of the ring. Such organometallic complexes play vital biological roles. In the chlorophyll porphyrin, essential for harvesting photic energy in plants, Mg occupies this site; in the porphyrin structure that is part of the hemoglobin protein, essential for oxygen transport in blood, Fe occupies this site. Porphyrins in hydro-
carbon can have high concentrations (up to a ppm or so) of transition metals such as Ni, V, and Mo. Re concentrations in petroleum can be as high as 50 ppb, and it is more strongly concentrated than Os, whose concentration reaches only 300 ppt. Consequently, \(^{187}\text{Rb}/^{188}\text{Os}\) ratios can exceed 1000, and that in turn results in high \(^{187}\text{Os}/^{188}\text{Os}\) ratios.

Selby and Creaser (2005) used Re-Os to ‘date’ petroleum of the Western Canada Sedimentary Basin (WCSB). As may be seen in Figure 2.26, \textit{apparent} isochrons yield ages of 111 to 121 Ma, depending on which samples are included. We say “apparent” isochrons because the mean square weighted deviations (MSWD) is greater than 1, indicating that not all deviations from regression can be accounted for by analytical error. In other words, there is real \textit{geologic} variation from the isochron model. Selby and Creaser (2005) argue that, given the regional scale involved, this is more likely due to incomplete homogenization of the initial isotope ratio than to subsequent disturbances of Re/Os ratios. Precisely what event is being dated here is, however, somewhat unclear. Hydrocarbons in the WCSB are thought to have been derived from source rocks on the western side of the basin and then migrated east. It seems reasonable that hydrocarbon generation and migration could homogenize \(^{187}\text{Os}/^{188}\text{Os}\) ratios, although perhaps imperfectly, but it is unclear what mechanism produced the high \(^{187}\text{Re}/^{188}\text{Os}\) ratios observed. Selby and Creaser (2005) noted the high initial \(^{187}\text{Os}/^{188}\text{Os}\) compared to \(^{187}\text{Os}/^{188}\text{Os}\) in Mesozoic seawater suggests that the source rocks are of Paleozoic age.

Figure 2.26. A. Re-Os isochron diagram for 24 samples of oil from the WCSB. The slope when all data are included corresponds to an age of 116±27 Ma. A slightly older but more precise age is obtained when the Prevost data is excluded. B. Including just those samples whose calculated \(^{187}\text{Os}/^{188}\text{Os}\) at 110 Ma is 1.4 to 1.5 yields a yet more precise age of 111.6±5 Ma. C. Location map for samples. From Selby and Creaser (2005).
2.7.3 The $^{190}\text{Pt}-^{186}\text{Os}$ Decay

As noted earlier, $^{186}\text{Os}$ is the decay product of $^{190}\text{Pt}$. Significant amounts of radiogenic $^{186}\text{Os}$ were first observed by Walker et al. (1991) in copper ores from Sudbury, Ontario. The chondritic $^{186}\text{Os}/^{188}\text{Os}$ ratio is 0.119828±6; the value in most terrestrial materials is indistinguishable from this value. In Sudbury sulfide copper ore, however, Walker et al. (1991) measured a $^{186}\text{Os}/^{188}\text{Os}$ ratio of greater than 0.3. This is a result of the strongly chalcophile nature of Pt, and its consequent concentration in sulfides; Os by contrast, is only weakly chalcophile. More recently, Brandon et al. (1998) have reported measurable variations in the $^{186}\text{Os}/^{188}\text{Os}$ ratio in mantle materials. They found that most mantle materials have $^{186}\text{Os}/^{188}\text{Os}$ ratios indistinguishable from the chondritic value, but samples of komatiite (a rare ultramafic lava type) and a xenolith from Kilbourne Hole, Colorado had ratios as high as 0.119842. Excess $^{186}\text{Os}$ has also been found in some Hawaiian basalts, prompting the suggestion that the Hawaiian plume might contain a small core-derived component (Brandon et al., 1998).

REFERENCES AND SUGGESTIONS FOR FURTHER READING


Isotope Geochemistry

Chapter 2


Isotope Geochemistry

Chapter 2

Geochronology


Renne, P. R., Mundil, G. Balco, K. Min and K. R. Ludwig, 2010. Joint determination of $^{40}$K decay constants and $^{40}$Ar*/$^{40}$K for the Fish Canyon sanidine standard, and improved accuracy for $^{40}$Ar/$^{39}$Ar geochronology, Geochimica et Cosmochimica Acta, 74:5349-5367,10.1016/j.gca.2010.06.017.


Tetley, N. W. Geochronology by the $^{40}$Ar/$^{39}$Ar Method Using the HIFAR Reactor. PhD dissertation, Australian National University, Canberra.


**Problems**

1. Use Dodson’s equation (equation 2.37) to calculate the closure temperatures of biotite for the cases of a slowly cooled intrusion discussed in Section 2.3.1, namely at 10°/Ma and 100°/Ma. Use the data given in Figure 5.1, which corresponds to \( E_A = 196.8 \text{ kJ/mol} \) and \( D_0 = -0.00077 \text{ m}^2/\text{sec} \). Assume \( a = 140 \mu\text{m} \) and \( A = 27 \). The value of \( R \) is \( 8.314 \text{ J/K \cdot mol} \). If we were to do K-Ar dating on these biotites long after they cooled (say 100 Ma later), how much different would the two ages be assuming the intrusion cooled at these rates from an initial temperate of 600°C? (Hint, you can easily do this in Excel, either using the solver, or iterating manually following an initial guess of the closure temperature – you can base that on the discussion in the text. Be careful to use consistent units).

2. You measure the following K$_2$O and $^{40}$Ar on minerals from a small pluton. Calculate the age for each. What do you think the ages mean? Use the following:
   - branching ratio is 0.1157,
   - $\lambda_{Rb} = 0.58755 \times 10^{-10}$ yr$^{-1}$,
   - $\lambda_{total} = 5.5492 \times 10^{-10}$ yr$^{-1}$.
   (These are newly recommended values).
   - $^{40}$K/$K = 0.0001167$, atomic weight of K is 39.03983.

<table>
<thead>
<tr>
<th>K$_2$O (wt. %)</th>
<th>Radiogenic $^{40}$Ar, mole/g</th>
</tr>
</thead>
<tbody>
<tr>
<td>biotite</td>
<td>8.45</td>
</tr>
<tr>
<td>hornblende</td>
<td>0.6078</td>
</tr>
</tbody>
</table>

   Are the ages the same? If not, speculate on why not?

3. Use following data to answer this question:
   - $\lambda_{Rb} = 1.42 \times 10^{-11}$ yr$^{-1}$;
   - $^{86}$Sr/$^{88}$Sr: 0.11940;
   - $^{84}$Sr/$^{88}$Sr: 0.006756,
   - $^{85}$Rb/$^{87}$Rb = 2.59265, atomic weight of Rb: 85.46776
   - atomic masses of Sr:
     - $^{86}$Sr: 87.9056
     - $^{87}$Sr: 86.9088
     - $^{88}$Sr: 85.9092

December 4, 2013
Chapter 2

Geochronology I

Isotope Geochemistry

$^{84}\text{Sr}: 83.9134$

Calculate the abundances of the isotopes and atomic weight of Sr given that $^{87}\text{Sr}/^{86}\text{Sr} = 0.7045$.

4. The following $^{40}\text{Ar}^{*}/^{39}\text{Ar}$ ratios were measured in step heating of lunar Basalt 15555 from Hadley Rile. The flux monitor had an age of $1.062 \times 10^{9}$ yrs and its $^{40}\text{Ar}^{*}/^{39}\text{Ar}$ ratio after irradiation was 29.33. The $^{40}\text{K}/^{39}\text{K}$ ratio is 0.000125137. Calculate the age for each step and plot the ages versus percent of release. From this release spectrum, estimate the age of the sample.

<table>
<thead>
<tr>
<th>Cumulative % Ar released</th>
<th>$^{40}\text{Ar}^{*}/^{39}\text{Ar}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>58.14</td>
</tr>
<tr>
<td>10</td>
<td>61.34</td>
</tr>
<tr>
<td>27</td>
<td>72.77</td>
</tr>
<tr>
<td>61</td>
<td>80.15</td>
</tr>
<tr>
<td>79</td>
<td>83.32</td>
</tr>
<tr>
<td>100</td>
<td>79.80</td>
</tr>
</tbody>
</table>

5. The following data was obtained on 3 minerals from a pegmatite. Calculate the age of the rock using the isochron method (you may use conventional regression for this problem). The data and approach used in question 4 will prove useful.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Rb, ppm</th>
<th>Sr, ppm</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Muscovite</td>
<td>238.4</td>
<td>1.80</td>
<td>1.4125</td>
</tr>
<tr>
<td>Biotite</td>
<td>1080.9</td>
<td>12.8</td>
<td>1.1400</td>
</tr>
<tr>
<td>K-feldspar</td>
<td>121.9</td>
<td>75.5</td>
<td>0.7502</td>
</tr>
</tbody>
</table>

6. The following data were measured on phlogopites (P) and phlogopite leaches (LP) from a kimberlite from Rankin Inlet area of the Hudson Bay, Northwest Territories, Canada. What is the (1) the age of the rock (2) the uncertainty on the age, (3) the initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratio, and (4) the uncertainty on the initial ratio? The relative uncertainty on the $^{87}\text{Sr}/^{86}\text{Sr}$ is 0.005% and that of the $^{86}\text{Rb}/^{86}\text{Sr}$ is 1%. (Hint: this is best accomplished using the Isoplot.xla Excel add-in written by Ken Ludwig and available at http://bgc.org/isoplot_etc/isoplot.html).

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{86}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>46.77</td>
<td>0.848455</td>
</tr>
<tr>
<td>P2</td>
<td>40.41</td>
<td>0.828490</td>
</tr>
<tr>
<td>P3</td>
<td>34.73</td>
<td>0.810753</td>
</tr>
<tr>
<td>P4</td>
<td>33.78</td>
<td>0.807993</td>
</tr>
<tr>
<td>P5</td>
<td>0.1829</td>
<td>0.706272</td>
</tr>
<tr>
<td>P6</td>
<td>0.1373</td>
<td>0.705616</td>
</tr>
<tr>
<td>P7</td>
<td>1.742</td>
<td>0.710498</td>
</tr>
</tbody>
</table>

7. The following were measured on a coarse grained metagabbro from Cana Brava complex in central Brazil. Plot the data on an isochron diagram, calculate the age, errors on the age, and the initial $\varepsilon_{\text{Nd}}$ and the error on the initial. The errors on the $^{147}\text{Sm}/^{144}\text{Nd}$ are all 0.0001 (2 sigma absolute). Two sigma errors on the $^{143}\text{Nd}/^{144}\text{Nd}$ shown below are in the fifth digit.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$^{147}\text{Sm}/^{144}\text{Nd}$</th>
<th>$^{143}\text{Nd}/^{144}\text{Nd}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>pyroxene</td>
<td>0.1819</td>
<td>0.51234±2</td>
</tr>
<tr>
<td>plagioclase</td>
<td>0.0763</td>
<td>0.51183±4</td>
</tr>
</tbody>
</table>

December 4, 2013
Isotope Geochemistry

Chapter 2

Geochronology I

8. The following data apply to whole rocks and separated minerals of the Baltimore Gneiss. Interpret these data by means of suitable isochron diagrams. Determine dates and initial $^{87}\text{Sr}/^{86}\text{Sr}$ ratios and errors on both using simple linear regression. Speculate on the geologic history of these rocks and minerals.

<table>
<thead>
<tr>
<th></th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rock 1</td>
<td>2.244</td>
<td>0.7380</td>
</tr>
<tr>
<td>Rock 2</td>
<td>3.642</td>
<td>0.7612</td>
</tr>
<tr>
<td>Rock 3</td>
<td>6.59</td>
<td>0.7992</td>
</tr>
<tr>
<td>biotite</td>
<td>289.7</td>
<td>1.969</td>
</tr>
<tr>
<td>K feldspar</td>
<td>5.60</td>
<td>0.8010</td>
</tr>
<tr>
<td>plagioclase</td>
<td>0.528</td>
<td>0.7767</td>
</tr>
<tr>
<td>Rock 4</td>
<td>0.2313</td>
<td>0.7074</td>
</tr>
<tr>
<td>Rock 5</td>
<td>3.628</td>
<td>0.7573</td>
</tr>
<tr>
<td>biotite</td>
<td>116.4</td>
<td>1.2146</td>
</tr>
<tr>
<td>K feldspar</td>
<td>3.794</td>
<td>0.7633</td>
</tr>
<tr>
<td>plagioclase</td>
<td>0.2965</td>
<td>0.7461</td>
</tr>
</tbody>
</table>

9. The following data was obtained on a Egyptian diorite:

<table>
<thead>
<tr>
<th></th>
<th>$^{87}\text{Rb}/^{86}\text{Sr}$</th>
<th>$^{87}\text{Sr}/^{86}\text{Sr}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>plagioclase</td>
<td>0.05124</td>
<td>0.705505</td>
</tr>
<tr>
<td>amphibole</td>
<td>0.13912</td>
<td>0.706270</td>
</tr>
<tr>
<td>biotite</td>
<td>0.95322</td>
<td>0.713847</td>
</tr>
<tr>
<td>alkali feldspar</td>
<td>0.58489</td>
<td>0.710418</td>
</tr>
<tr>
<td>whole rock</td>
<td>0.33975</td>
<td>0.708154</td>
</tr>
</tbody>
</table>

Assume that the analytical error on the $^{87}\text{Sr}/^{86}\text{Sr}$ ratio was 0.006% and that the analytical error on the $^{87}\text{Rb}/^{86}\text{Sr}$ ratio was 0.1% in each case, and that these errors are uncorrelated. Use the two-error regression method to calculate the age and initial ratio and the errors on both.

(HINT: this is best accomplished using the Isoplot.xla Excel add-in.)

10. A sample of granite has $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ of 0.51196 and 0.12990, respectively. The present chondritic $^{143}\text{Nd}/^{144}\text{Nd}$ and $^{147}\text{Sm}/^{144}\text{Nd}$ are 0.512638 and 0.1967, respectively. The decay constant of $^{147}\text{Sm}$ is $6.54 \times 10^{-12} \text{a}^{-1}$. Calculate the $\tau_{\text{CHUR}}$, i.e., crustal residence time relative to a chondritic mantle, for this granite.

10. The following data were obtained on sulfide inclusions in diamonds from the Keffiefontein mine in South Africa. Calculate the age of the diamonds assuming all analyzed samples are cogenetic.

<table>
<thead>
<tr>
<th></th>
<th>$^{187}\text{Re}/^{188}\text{Os}$</th>
<th>$^{187}\text{Os}/^{188}\text{Os}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>K310</td>
<td>104</td>
<td>2.19</td>
</tr>
<tr>
<td>K309</td>
<td>5.24</td>
<td>0.346</td>
</tr>
<tr>
<td>K308</td>
<td>116</td>
<td>2.28</td>
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<tr>
<td>K307</td>
<td>6.31</td>
<td>0.411</td>
</tr>
<tr>
<td>K305</td>
<td>80.6</td>
<td>1.78</td>
</tr>
</tbody>
</table>