RADIOACTIVE DATING METHODS

K-Ar Method:

The radioactive decay scheme involving the breakdown of potassium of mass 40 (^{40}K) to argon gas of mass 40 (^{40}Ar) formed the basis of the first widely used isotopic dating method. Since radiogenic argon-40 was first detected in 1938 by the American geophysicist Lyman T. Aldrich and A.O. Nier, the method has evolved into one of the most versatile and widely employed methods available. Potassium is one of the 10 most abundant elements that together make up 99 percent of Earth's crust and is therefore a major constituent of many rock-forming minerals. In fact, potassium-40 decays to both argon-40 and calcium-40, but, because argon is absent in most minerals while calcium is present, the argon produced is easier to detect and measure. Most of the argon in Earth's atmosphere has been created by the decay of potassium-40, as the argon-40 abundance is about 1,000 times higher than expected from cosmic abundances. Argon dating involves a different technology from all the other methods so far described, because argon exists as a gas at room temperature. Thus, it can be purified as it passes down a vacuum line by freezing out or reacting out certain contaminants. It is then introduced into a mass spectrometer through a series of manual or computer-controlled valves. Technical advances, including the introduction of the argon-40–argon-39 method and laser heating, that have improved the versatility of the method are described below.

In conventional potassium–argon dating, a potassium-bearing sample is split into two fractions: one is analyzed for its potassium content, while the other is fused in a vacuum to release the argon gas. After purification has been completed, a spike enriched in argon-38 is mixed in and the atomic abundance of the daughter product argon-40 is measured relative to the argon-38 added. The amount of the argon-36 present is then determined relative to argon-38 to provide an estimate of the background atmospheric correction. In this case, relatively large samples, which may include significant amounts of alteration, are analyzed. Since potassium is usually added by alteration, the daughter–parent ratio and the age might be too low.

A method designed to avoid such complexities was introduced by American geochronologist Craig M. Merrihue and English geochronologist Grenville Turner in 1966. In this technique, known as the argon-40–argon-39 method, both parent and daughter can be determined in the mass spectrometer as some of the potassium atoms in the sample are first converted to argon-39 in a nuclear reactor. In this way, the problem of measuring the potassium in inhomogeneous samples is eliminated and smaller amounts of material can be analyzed. An additional advantage then becomes possible. The sample can be heated in stages at different temperatures and the age calculated at each step. If alteration is evident, the invalid low-temperature age can be eliminated and a valid high-temperature age determined. In some cases, partly reset systems also may be detected.

As in all dating systems, the ages calculated can be affected by the presence of inherited daughter products. In a few cases, argon ages older than that of Earth which violate local relative age patterns have even been determined for the mineral biotite. Such situations occur mainly where old rocks have been locally heated, which released argon-40 into pore spaces at the same time that new minerals grew. Under favourable circumstances the isochron method may be helpful, but tests by other techniques may be required. For example, the rubidium–strontium method would give a valid isotopic age of the biotite sample with inherited argon.

As techniques evolved, argon background levels have been reduced and the method has become more and more sensitive. Capitalizing on this, it is now possible to measure the minute amount of argon released when a single spot on a crystal is heated by an intense laser beam. For geologically old potassium-rich materials, a single spot may produce sufficient gas for analysis, whereas single millimetre-sized grains (1 mm equals 0.04 inch) may be required in very young materials. Progressive refinement of the method has made new areas of research possible, and the ability to understand complexities encountered in earlier investigations has increased. In one study the age of volcanic ash as young as $215,000 \pm 4,000$ years and the presence of inherited older grains in another ash sample were thoroughly documented. This was done by melting single millimetre-sized grains with a laser and measuring individual argon-40–argon-39 ages with a highly sensitive gas mass spectrometer.

The potassium–argon method has provided a great deal of information about Earth's recent and ancient past. It has been instrumental, for example, in determining the ages of the stripes of alternating normally and reversely magnetized volcanic rocks that parallel the axis of the mid-oceanic ridges. In ancient shield areas large segments of crust that were uplifted and cooled at the same time—i.e., geologic provinces—have been identified by the potassium–argon method. The technique is highly responsive to thermal events in a relatively predictable fashion, so the cooling history of a region may be established.

Rb-Sr Method:

The radioactive decay of rubidium-87 (^{87}Rb) to strontium-87 (^{87}Sr) was the first widely used dating system that utilized the isochron method. Rubidium is a relatively abundant trace element in Earth's crust and can be found in many common rock-forming minerals in which it substitutes for the major element potassium. Because rubidium is concentrated in crustal rocks, the continents have a much higher abundance of the daughter isotope strontium-87 compared with the stable isotopes. This relative abundance is expressed as the ^{87}Sr/^{86}Sr ratio, where strontium-86 is chosen to represent the stable isotopes strontium-88, strontium-86, and strontium-84, which occur in constant proportions in natural materials. Thus, a precise measurement of the ^{87}Sr/^{86}Sr ratio in a modern volcano can be used to determine age if recycled older crust is present. A ratio for average continental crust of about 0.72 has been determined by

measuring strontium from clamshells from the major river systems. In contrast, Earth's most abundant lava rocks, which represent the mantle and make up the major oceanic ridges, have values between 0.703 and 0.705. This difference may appear small, but, considering that modern instruments can make the determination to a few parts in 70,000, it is quite significant. Dissolved strontium in the oceans today has a value of 0.709 that is dependent on the relative input from the continents and the ridges. In the geologic past, changes in the activity of these two sources produced varying $^{87}Sr/^{86}Sr$ ratios over time. Thus, if well-dated, unaltered fossil shells containing strontium from ancient seawater are analyzed, changes in this ratio with time can be observed and applied in reverse to estimate the time when fossils of unknown age were deposited.

Dating Simple Igneous Rocks

The rubidium–strontium pair is ideally suited for the isochron dating of igneous rocks. As a liquid rock cools, first one mineral and then another achieves saturation and precipitates, each extracting specific elements in the process. Strontium is extracted in many minerals that are formed early, whereas rubidium is gradually concentrated in the final liquid phase. At the time of crystallization, this produces a wide range in the Rb/Sr ratio in rocks that have identical $^{87}Sr/^{86}Sr$ ratios. On the isochron diagram shown in the figure above, the samples would plot initially at points R_1 to R_3 along a line representing the initial ratio designated $(^{87}Sr/^{86}Sr)_0$. Over geologic time, this ratio is increased in proportion to the $^{87}Rb/^{86}Sr$ ratio, as discussed earlier, and the line rotates with a slope equal to ($e\,t - 1$) that represents the time elapsed; thus, the present-day ratio $(^{87}Sr/^{86}Sr)p$ equals the initial ratio $(^{87}Sr/^{86}Sr)_0$ plus radiogenic additions, or $(^{87}Sr/^{86}Sr)p = (^{87}Sr/^{86}Sr)_0 + {}^{87}Rb/^{86}Sr\,(e\,t - 1)$. This equation is that of a straight line of the form $y = b + xm$, where $y = (^{87}Sr/^{86}Sr)p$, the value measured today; b represents $(^{87}Sr/^{86}Sr)_0$, the value initially present; x stands for the $^{87}Rb/^{86}Sr$ ratio; and m is the slope of the line ($e\,t - 1$).

In practice, rock samples weighing several kilograms each are collected from a suite of rocks that are believed to have been part of a single homogeneous liquid prior to solidification. The samples are crushed and homogenized to produce a fine representative rock powder from which a fraction of a gram is withdrawn and dissolved in the presence of appropriate isotopic traces, or spikes. Strontium and rubidium are extracted and loaded into the mass spectrometer, and the values appropriate to the x and y coordinates are calculated from the isotopic ratios measured. Once plotted as R1p (i.e., rock 1 present values), R2p, and R3p, the data are examined to assess how well they fit the required straight line. Using estimates of measurement precision, the crucial question of whether or not scatter outside of measurement error exists is addressed. Such scatter would constitute a geologic component, indicating that one or more of the underlying assumptions has been violated and that the age indicated is probably not valid. For an isochron to be valid, each sample tested must (1) have had the same initial ratio, (2) have been a closed system over geologic time, and (3) have the same age.

Well-preserved, unweathered rocks that crystallized rapidly and have not been subjected to major reheating events are most likely to give valid isochrons. Weathering is a disturbing

influence, as is leaching or exchange by hot crustal fluids, since many secondary minerals contain rubidium. Volcanic rocks are most susceptible to such changes because their minerals are fine-grained and unstable glass may be present. On the other hand, meteorites that have spent most of their time in the deep freeze of outer space can provide ideal samples.

Dating Minerals

Potassium-bearing minerals including several varieties of mica, are ideal for rubidium–strontium dating as they have abundant parent rubidium and a low abundance of initial strontium. In most cases, the changes in the $^{87}Sr/^{86}Sr$ ratio are so large that an initial value can be assumed without jeopardizing the accuracy of the results. When minerals with a low-rubidium or a high-strontium content are analyzed, the isochron-diagram approach can be used to provide an evaluation of the data. As discussed above, rubidium–strontium mineral ages need not be identical in a rock with a complex thermal history, so that results may be meaningful in terms of dating the last heating event but not in terms of the actual age of a rock.

Dating Metamorphic Rocks

Should a simple igneous body be subjected to an episode of heating or of deformation or of a combination of both, a well-documented special data pattern develops. With heat, daughter isotopes diffuse out of their host minerals but are incorporated into other minerals in the rock. Eventually the $^{87}Sr/^{86}Sr$ ratio in the minerals becomes identical. When the rock again cools, the minerals close and again accumulate daughter products to record the time since the second event. Remarkably, the isotopes remain within the rock sample analyzed, and so a suite of whole rocks can still provide a valid primary age. This situation is easily visualized on an isochron diagram, where a series of rocks plots on a steep line showing the primary age, but the minerals in each rock plot on a series of parallel lines that indicate the time since the heating event. If cooling is very slow, the minerals with the lowest blocking temperature, such as biotite mica, will fall below the upper end of the line.

A more dramatic presentation of this phenomenon is found when the changes in the $^{87}Sr/^{86}Sr$ ratios in a variety of minerals in a single rock are depicted as a function of geologic time. Here, an essentially rubidium-free, strontium-rich phase like apatite retains its initial $^{87}Sr/^{86}Sr$ ratio over time, whereas the value in such rubidium-rich, strontium-poor minerals as biotite increases rapidly with time. The rock itself gives the integrated, more gradual increase. At the time of heating, identical $^{87}Sr/^{86}Sr$ ratios are again achieved as described above, only to be followed by a second episode of isotopic divergence.

Approaches to this ideal case are commonly observed, but peculiar results are found in situations where the heating is minimal. If one assumes for a moment that only the mineral with the lowest blocking temperature loses its daughter isotope, it is easy to imagine that other low-temperature minerals formed at this time may acquire extremely high $^{87}Sr/^{86}Sr$ ratios. Epidote, a low-

temperature alteration mineral with a very high concentration of radiogenic strontium, has been found in rocks wherein biotite has lost strontium by diffusion. The rock itself has a much lower ratio, so that it did not take part in this exchange.

Advantage & Disadvantage:

Although rubidium–strontium dating is not as precise as the uranium–lead method, it was the first to be exploited and has provided much of the prevailing knowledge of Earth history. The procedures of sample preparation, chemical separation, and mass spectrometry are relatively easy to carry out, and datable minerals occur in most rocks. Precise ages can be obtained on high-level rocks (i.e., those closer to the surface) and meteorites, and imprecise but nevertheless valuable ages can be determined for rocks that have been strongly heated. The mobility of rubidium in deep-level crustal fluids and melts that can infiltrate other rocks during metamorphism as well as in fluids involved in weathering can complicate the results.

Samarium–neodymium Method

The radioactive decay of samarium of mass 147 (^{147}Sm) to neodymium of mass 143 (^{143}Nd) has been shown to be capable of providing useful isochron ages for certain geologic materials. Both parent and daughter belong to the rare-earth element group, which is itself the subject of numerous geologic investigations. All members of this group have similar chemical properties and charge, but differ significantly in size. Because of this, they are selectively removed as different minerals are precipitated from a melt. In the opposite sense, their relative abundance in a melt can indicate the presence of certain residual minerals during partial melting. Unlike rubidium, which is enriched over strontium in the crust, samarium is relatively enriched with respect to neodymium in the mantle. Consequently, a volcanic rock composed of melted crust would have elevated radiogenic strontium values and depressed radiogenic neodymium values with respect to the mantle. As a parent–daughter pair, samarium-147 and neodymium-143 are unique in that both have very similar chemical properties, and so loss by diffusion may be reduced. Their low concentrations in surface waters indicates that changes during low-temperature alteration and weathering are less likely. Their presence in certain minerals in water-deposited gold veins, however, does suggest mobility under certain conditions. In addition, their behaviour under high-temperature metamorphic conditions is as yet poorly documented.

The exploitation of the samarium–neodymium pair for dating only became possible when several technical difficulties were overcome. Procedures to separate these very similar elements and methods of measuring neodymium isotope ratios with uncertainties of only a few parts in 100,000 had to be developed.

In theory, the samarium–neodymium method is identical to the rubidium–strontium approach. Both use the isochron method to display and evaluate data. In the case of samarium–neodymium dating, however, the chemical similarity of parent and daughter adds another complication because fractionation during crystallization is extremely limited. This makes the isochrons short and adds further to the necessity for high precision. With modern analytical methods, however, uncertainties in measured ages have been reduced to 20 million years for the oldest rocks and meteorites. Mineral isochrons provide the best results.

The equation relating present-day neodymium isotopic abundance as the sum of the initial ratios and radiogenic additions is that of a straight line, as discussed earlier for rubidium–strontium.

In a successful application of the samarium–neodymium method to a sample of basalt from the Moon, the constituent minerals plagioclase, ilmenite, and pyroxene provide enough spread in the $^{147}Sm/^{143}Nd$ ratio to allow an age of 4,367 ± 11 million years to be calculated. Other successful examples have been reported where rocks with open rubidium–strontium systems have been shown to have closed samarium–neodymium systems. In other examples, the ages of rocks with insufficient rubidium for dating have been successfully determined. There is considerable promise for dating garnet, a common metamorphic mineral, because it is known to concentrate the parent isotope.

In general, the use of the samarium–neodymium method as a dating tool is limited by the fact that other methods (mainly the uranium–lead approach) are more precise and require fewer analyses. In the case of meteorites and lunar rocks where samples are limited and minerals for other dating methods are not available, the samarium–neodymium method can provide the best ages possible.


Uranium-Thorium-Lead (U-Th-Pb) Method:

Uranium (U) salts are highly soluble in meteoric water. Uranium concentrate in zircons.

The U-Th-Pb method/system is the most complicated of the major methods used in geochronology for two reasons:

i)   Three different parent isotopes are involved.
ii)   Each isotope goes through an extensive decay series before stable Pb isotope is formed. On the other hand it has been found that these complication can be used to gain additional information about the history of rocks and minerals.
      Three decay series of the system are:
      $^{238}U \longrightarrow {}^{206}Pb$
      $^{235}U \longrightarrow {}^{207}Pb$
      $^{232}Th \longrightarrow {}^{208}Pb$
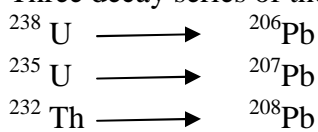
The occurrence of radio active daughter products in each decay series requires that age measurement be made only on material i.e. in equilibrium with its daughter products. The basic equation of the U-Th-Pb system used for age calculation are obtained from

$$N=N_0 (e^t-1)$$

Use of the above equation gives

$$^{206}Pb=^{238}U (e^{238t}-1) \qquad\qquad ....(i)$$

$$^{207}Pb=^{235}U (e^{235t}-1) \qquad\qquad ....(ii)$$

$$^{208}Pb=^{232}Th (e^{232t}-1) \qquad\qquad ....(iii)$$

Initial Pb can be calculated from the following equation:

$$^{206}Pb_{measure} = {}^{206}Pb_{initial} + {}^{238}U (e^{238t}-1) \qquad ....(iv)$$

$$^{207}Pb_{measure} = {}^{207}Pb_{initial} + {}^{235}U (e^{235t}-1) \qquad ....(v)$$

$$^{208}Pb_{measure} = {}^{232}Th_{initial} + {}^{232}Th (e^{232t}-1) \qquad ....(vi)$$

More accurate values can be obtained by measuring ratios of isotopes than by measuring their absolute abundances.

Since a non-radiogenic isotope of lead ^{204}Pb occur with the other isotope which divide the above equation by the abundance of this isotope to get the basic age equation of U-Th-Pb system.

$$(^{206}Pb/^{204}Pb)_{measure} = (^{206}Pb/^{204}Pb)_{initial} + (^{238}U/^{204}Pb)(e^{238t}-1) \qquad ....(vii)$$

$$(^{207}Pb/^{204}Pb)_{measure} = (^{207}Pb/^{204}Pb)_{initial} + (^{235U}/^{204}Pb)(e^{235t}-1) \qquad ....(viii)$$

$$(^{208}Pb/^{204}Pb)_{measure} = (^{232}Th/^{204}Pb)_{initial} + (^{232}Th/^{204}Pb)(e^{232t}-1) \qquad ....(ix)$$

The values for initial Pb are obtained by determining the isotope composition of Pb in the environment in the time of sample formation. One way of making the correction is to analyse Pb mineral such as galena in the same rock sample for geological setting. If no Pb bearing mineral is present with the sample the correction is often made by estimating the average oceanic Pb composition that existed at the approximate time that the sample formed.

The procedure clearly introduces an uncertainty in the calculating the sample. The first method analysing a co-existing Pb mineral can also provide an error. In the estimated age the isotopic composition of Pb has been found to vary somewhat even in different samples of same mineral from same locality. Another way to solve this problem is to use a mineral like zircon which contains so little initial Pb that a measurement of initial Pb is not needed. The major source of

error in using of age equation is uncertainty in the measurement of Pb isotope ratio. To obtain the age of a sample the appropriate isotope ratio are measured and these along with the known value of   allow solving of equation (iv,v,vi) for time of formation.

Beacause ^{235} U and ^{238} U at different rates a forth age equation can be developed from the ratio of the equation:

$$[(^{207}Pb/^{204}Pb)_{measure} - (^{207}Pb/^{204}Pb)_{initial}] / [(^{207}Pb/^{204}Pb)_{measure} - (^{207}Pb/^{204}Pb)_{initial}]$$

$$= (^{235U}/^{238}U)_{measure} \quad (e^{235t}-1/e^{238t}-1) \quad \dots\dots\dots\dots\dots\dots\dots\dots\dots\dots(x)$$

Use of this equation is referred to as the Pb-Pb method or 207-206 method.

The ratio of $(^{235U}/^{238}U)$ has a value at the present time of (1/137.88) and independent of the age and history of the source of the material.

Thus the early measurement requires getting an age using the equation (vii). This method also has the advantage that it will be least affected by any loss of Pb from a sample during geologic time, since Pb would probably be lost in the isotopic proportion in which it is present. If Pb loss did occur, age obtained using equation no (i, ii & iii) would be less than the true age. On the other hand these methods can be used as a check on each other and on the Pb-Pb method.

Analytical techniques allow measurement of the various isotope ratios to a precission of about ±1-2%. If no gain or loss of material has occurred the $^{238}U/^{206}Pb$, $^{235}U/^{207}Pb$, $^{232}Th/^{208}Pb$ and $^{207}Pb/^{206}Pb$ ages should agree (concordant ages). Gain or less of material can be caused by metamorphism or weathering (so only fresh samples should be analysed).

When two or more age determination don't agree, the results are said to be discordant. This frequently occurs in use of the U-Th-Pb system. Assuming careful sample collection, purification, chemical analysis and initial Pb correction this discordant relationship is probably due to gain or loss of parent or dauther isotopes. In terms of geochemical behaviour U & Th (lithophile) are quite different from chalcophile Pb. If Pb has been lost it is possible to use the data to obtain not only the age of the sample but also the time when Pb was lost, assuming that this was a rapid process.