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How Old Is It? How Do We Know? A Review of Dating Methods – Part Two: Radiometric Dating: Mineral, Isochron and Concordia Methods

How Old Is It? How Do We Know? A Review of Dating Methods— Part Two: Radiometric Dating: Mineral, Isochron and Concordia Methods

Davis A. Young



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This second in a three-part series on dating methods reviews important radiometric dating methods that are applicable only to geological situations. The basic theory behind radiometric dating is outlined. Details of the ⁴⁰K-⁴⁰Ar, ⁸⁷Rb-⁸⁷Sr, ²³⁸U-²⁰⁶Pb, ⁸⁷Rb-⁸⁷Sr whole-rock isochron, ¹⁴⁷Sm-¹⁴³Nd whole-rock isochron, and U-Pb concordia methods are outlined and examples of results are provided.

We know that extremely large quantities of any radioactive isotope will disintegrate in accord with a radioactive decay law ...

ithin a decade of the discovery of radioactivity in 1896, the chemical elements uranium, radium, polonium, and thorium were recognized as radioactive; the basic theory, mechanisms, and mathematics of radioactive decay were established; decay rates of some radioactive chemical elements were determined; and the ages of two mineral specimens were calculated for the first time from their uranium and helium contents.1 Soon thereafter, isotopes were discovered, the decay constants of a few specific isotopes were determined, and mass spectroscopy was developed.2 Ever since these early heady days in the study of radioactivity, numerous radiometric dating methods have been proposed. Some methods were eventually discarded,3 but many others have not only withstood critical scrutiny but have been refined and improved.4

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Radiometric Dating

To understand how radiometric dating works, consider a crystal of pure rubidium chloride (RbCl). Rubidium (Rb) consists of 72.2% ⁸⁵Rb, an isotope that is not radioactive, and 27.8% ⁸⁷Rb, an isotope that is radioactive. A cubic crystal of RbCl with a volume of 1 cm³ contains approximately 10¹⁸ atoms of ⁸⁷Rb. Although we cannot predict exactly when any specific atom of ⁸⁷Rb will undergo spontaneous radioactive decay, we know that extremely large quantities of any radioactive isotope will disintegrate in accord with a radioactive decay law that is expressed by the equations:

$$dN/dt = -\lambda N$$
 (1)

$$N = N_0 e^{-\lambda t}$$
 (2)

where dN/dt is the rate of decay of a radioactive isotope, N is the present amount of a radioactive isotope (called the *parent*) in a sample, N_0 is the amount of parent isotope in the sample at the time of its formation, t is the age of the sample, and λ is the *decay constant* of the parent isotope. Equation (1) indicates that the decay rate, dN/dt, is proportional to the amount of radioactive isotope in a sample, an amount that decreases with time as indicated by the minus sign. Equation (2) is derived from equation (1) by rearrangement and integration. Decay constants (Table 1)

have now been measured by a variety of methods. To date, experimental evidence indicates that decay constants vary by no more than a very small fraction of one percent, if they vary at all.⁵ Decay constants are virtually independent of the chemical composition of compounds containing the radioactive isotope and of the effects of temperature, pressure, gamma radiation, x-rays, high energy particles, and electrical and magnetic fields. *No geologically or archeologically important radioactive isotope shows any significant variation in its decay constant*.

Closely related to the decay constant is the <code>half-life</code> (τ_{ν_2}) of a radioactive isotope, defined as the amount of time during which the amount of parent radioactive isotope in a sample decreases by one half. The amount of isotope into which the parent is transformed (the so-called <code>daughter</code>) increases as the parent decreases. If the amount of parent isotope in a sample equals half the original amount (N = $^{1/2}$ N₀), then the age equals one half-life (t = τ_{ν_2}). By substitution of these expressions into equation (2), we obtain

$$^{1/2}N_{0} = N_{0}e^{-\lambda\tau}$$
 (3)

an expression from which we can calculate that $\tau_{1/2} = 0.693/\lambda$. The half-life, therefore, is inversely proportional to the decay constant of a radioactive isotope. Table 1 also lists half-lives of several important radioactive isotopes.

Figure 1 graphically shows the amount of decay of parent and increase in amount of daughter isotopes in a sample containing no initial daughter as a function of the number of half-lives of the parent isotope that have elapsed. For example, after one half-life has elapsed, the amount of parent has decreased to one half of the original amount, and the amount of daughter has increased from zero to an amount equal to that of the parent. After two half-lives have elapsed, the amount of parent has decreased to one half of one half, that is, one quarter of the original amount. The amount of daughter will now be three times as much as that of the parent. After a third half-life has elapsed, the amount has decreased to one half of one quarter, that is, one eighth of the original amount, and so on.

Table 1. Decay Constants and Half-Lives of Some Geologically Important Radioactive Isotopes		
Radioactive Isotope	Decay Constant (years ⁻¹)	Half-Life (years)
¹⁴ C	0.1209 x 10 ⁻³	5730
⁴⁰ K	0.581 x 10 ⁻¹⁰	1.19 x 10 ¹⁰
⁸⁷ Rb	1.42 x 10 ⁻¹¹	48.8 x 10 ⁹
¹⁴⁷ Sm	0.654 x 10 ⁻¹²	1.06 x 10 ¹¹
²³² Th	4.9475 x 10 ⁻¹¹	14.01 x 10 ⁹
²³⁵ U	9.8485 x 10 ⁻¹⁰	0.7038 x 10 ⁹
²³⁸ U	1.55125 x 10 ⁻¹⁰	4.468 x 10 ⁹

Radioactive isotopes with extremely large half-lives and correspondingly low decay constants are useful in dating extremely old materials, because it takes a very long time for the parent isotope in a sample to diminish to extremely small amounts that would be difficult to analyze. Moreover, in a brief span of time, an insufficient amount of daughter isotope would be formed to permit its precise measurement. For example, ²³⁸U with a half-life of nearly 4.5 billion years is eminently suitable for dating minerals and rocks that are hundreds of millions to billions of years old. Isotopes with short half-lives and correspondingly larger decay constants are useful in dating very recent materials. Such isotopes cannot be used to date old material because the parent isotope decreases sufficiently rapidly that it may be virtually immeasurable in a matter of years. By way of example, 14C with a half-life of 5,730 years is suitable for dating materials that are only hundreds to a few tens of thousands of years old, but not millions of years.

To determine when a mineral or rock sample originally crystallized, the sample must have remained closed to both parent and daughter isotopes subsequent to its crystallization. In other words, neither parent nor daughter isotope should have entered into the sample from its environment or escaped from the sample into its environment during the course of the sample's post-crystallization history. If a quantity of parent isotope escaped from, or a quantity of daughter isotope entered into, a sample, then the calculated age would be higher than the actual age. Conversely, if a quantity of parent entered, or a quantity of daughter escaped from, the sample, the calculated age would be lower than the actual age. To improve the chances of dating a sample that acted as a closed system, geochronologists collect specimens that lack evidence of chemical weathering, are not extensively fractured, and are not associated with faults or shear zones. If the speci-

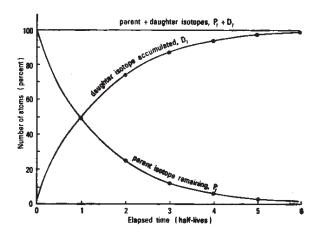
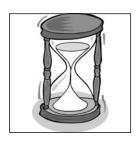


Figure 1. The decay of radioactive parent isotope and accompanying growth of daughter isotope in terms of half-life of the parent. Reproduced from Figure 3.2, p. 85 in G. B. Dalyrmple, *The Age of the Earth* (Stanford, CA: Stanford University Press, 1991) by permission of Stanford University Press; © 1991 by the Board of Trustees of the Leland Stanford Jr. University.



Consider a crystal of a potassium-rich mineral like potassium feldspar or biotite in a volcanic ash deposit or a rhyolitic lava flow. We can ordinarily date the mineral by the ${}^{40}K$ - ${}^{40}Ar$ method. *In this case,* the problem of knowing the initial isotope ratios or amounts is avoided because essentially no daughter isotope is initially present ...

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men acted as a closed system experiencing no gains or losses of the relevant isotopes, then the sum of parent and daughter in a sample at present must equal that sum at the time of formation. Thus, we may express the closed system condition by the equation

$$N + D = N_0 + D_0 (4)$$

where D is the present amount of daughter isotope in a sample at present and D_0 is the amount of daughter isotope in the sample at the time of formation. By rearranging equation (4) to the form $N = N_0 + D_0 - D$, substituting that form of equation (4) into equation (2), and further rearranging, we obtain

$$D = D_0 + N(e^{\lambda t} - 1)$$
 (5)

Equation (5) is the fundamental equation for radiometric dating methods that assume a closed system and for which concentrations of the relevant isotopes can either be measured directly or calculated from appropriate measurements. Because absolute numbers of atoms of some isotopes are difficult to measure, and because ratios of isotopes with very similar atomic masses can be measured accurately and precisely with a mass spectrometer, equation (5) may be modified while preserving the equality of both sides of the equation by dividing each side by the identical amount of a stable non-radiogenic isotope (d) of the same element as the daughter isotope. A stable non-radiogenic isotope is not radioactive, and it is either not produced by decay of a radioactive isotope at all or else it is produced at an exceedingly slow rate by a radioactive isotope with a half-life that far exceeds the age of the universe. For example, in rubidium-strontium (Rb-Sr) dating, 86Sr in a sample will serve as the stable non-radiogenic (see equation 8). For purposes of isotope analysis, ⁸⁷Sr/⁸⁶Sr ratios are measured. The amount of the stable non-radiogenic isotope in the sample does not change through time in a closed system so that the amount of the stable non-radiogenic isotope in the sample now is the same as it was when the sample was formed ($d = d_0$). Thus, when we divide both sides of equation (5) by d, we obtain

$$D/d = D_0/d_0 + (N/d) (e^{\lambda t} - 1)$$
 (6)

This is a perfectly valid general equation for the radioactive decay of a specific isotope within a closed system.

How do we use this equation to obtain the age of a sample? We can measure both the present-day ratios of D/d and N/d in a sample, and we know the value of the decay constant. But that leaves us with two unknowns, t, the age of the sample, and D_0/d_0 . To calculate the age of the sample, therefore, we must also know D_0/d_0 , the ratio of daughter isotope and the stable non-radiogenic isotope in the sample at the time of its origin. But if no analyst was present when a mineral was formed millions of years ago, how can we possibly know the value of the initial ratio? We shall soon see.

Mineral Dating

Let's now look at some examples of various dating methods. In the process, we will see how the determination of original isotope ratios is addressed. Consider a crystal of a potassium-rich mineral like potassium feldspar or biotite in a volcanic ash deposit or a rhyolitic lava flow. We can ordinarily date the mineral by the 40K-40Ar method. In this case, the problem of knowing the initial isotope ratios or amounts is avoided because essentially no daughter isotope is initially present (${}^{40}Ar_0 = 0$)⁶. Very little radiogenic daughter 40 Ar is incorporated into most minerals when they crystallize because argon is an inert gas that is typically excluded from their crystal structures. Known exceptions are avoided in routine K-Ar dating. Any ⁴⁰Ar already present in a cooling magma is also likely to be degassed during eruption or trapped in glass. Most 40K atoms decay to 40 Ca by β emission, but a small percentage of 40K atoms decays to 40Ar by electron capture.⁷ The operative equation based on equation (5) is

40
Ar = 40 Ar₀ + $(\lambda_{ec}/\lambda)^{40}$ K $(e^{\lambda t} - 1)$ (7)

where λ_{ec}/λ is the fraction of decays to ^{40}Ar by electron capture. As noted, we assume that $^{40}Ar_0$ = 0. ^{40}K is determined by measuring the total K concentration in the mineral by flame photometry or x-ray fluorescence and multiplying by 0.01167, the $^{40}K/$ total K ratio in all K-bearing materials. The concentration of radiogenic ^{40}Ar is calculated from argon isotope ratios that are measured by mass spectrometry.

The K-Ar method is also useful for dating biotite, muscovite, hornblende, and feldspar in coarse-grained igneous rock bodies such as granite or gabbro that solidify far beneath Earth's surface. The coarse grains of such rocks result from the very slow cooling of

magma in the subsurface. The rocks continue to cool very slowly after crystallization. As these rocks cool, 40Ar produced by radioactive decay of 40K easily diffuses out of the mineral structure in which it originally forms thanks to intense thermal vibration of atoms at high temperature. Consequently, an insignificant amount of Ar accumulates in minerals at very high temperatures. Not until the rock cools to a so-called closure (or blocking) temperature does a mineral begin to retain 40Ar atoms that were generated by 40K decay, because the atoms are no longer vibrating with sufficient energy to diffuse out of the mineral grains in significant quantities. Therefore, K-Ar ages of minerals in plutonic igneous rocks generally represent cooling ages that are somewhat younger than the age of original crystallization. Normally the cooling ages of different minerals in the same igneous rock body differ from one another because the closure temperatures for Ar retention are different in different minerals.9

As examples of K-Ar ages, potassium feldspar crystals in pumice fragments from the Bishop Tuff in California, a volcanic ash deposit, consistently yield ages of approximately 725,000 years. ¹⁰ K-Ar ages on biotite crystals from the Mount Givens Granodiorite and El Capitan Granite in the Sierra Nevada of California are 84, 86, and 89 million years for the former and 92 and 94 million years for the latter. ¹¹

Geochronologists formerly dated feldspar and the K-bearing mica minerals biotite, muscovite, and lepidolite by the ${}^{87}\text{Rb}/{}^{87}\text{Sr}$ method. By substitution of ${}^{87}\text{Rb}$ for N, ${}^{87}\text{Sr}$ for D, ${}^{87}\text{Sr}$ for D₀, and ${}^{86}\text{Sr}$ for d and d₀ into equation (6), we obtain

87
Sr/ 86 Sr = (87 Sr/ 86 Sr)₀ + (87 Rb/ 86 Sr) (2 t - 1) (8)

87Sr/86Sr is determined by mass spectrometry, and ⁸⁷Rb/⁸⁶Sr is calculated from the measured Rb/Sr ratio and relative abundances of 87Rb/total Rb and 86Sr/total Sr, the latter determined by mass spectrometric measurements of several Sr isotope ratios. Again, how can we determine the original Sr isotope ratio? To address the problem, geochronologists commonly assumed an initial (87Sr/86Sr)₀ ratio such as 0.704, a ratio that is commonly found in recently erupted oceanic lava flows. Because the initial ratio was assumed, the resulting ages were not as reliable as desired. In addition, Rb and Sr are sufficiently mobile elements that the closed system condition is not always met. As a result, this method is rarely if ever used today. Zircon grains, which are especially resistant to both chemical and physical weathering, are commonly dated by the U-Pb method. 13 Via a long chain of decays, ²³⁸U ultimately decays to ²⁰⁶Pb, and ²⁰⁴Pb is used as the stable non-radiogenic isotope. By substitution of 238 U for N, 206 Pb for D, 206 Pb₀ for D₀, and 204 Pb for d and d₀ into equation (6), we obtain

$$^{206}\text{Pb}/^{204}\text{Pb} = (^{206}\text{Pb}/^{204}\text{Pb})_0 + (^{238}\text{U}/^{204}\text{Pb}) (e^{\lambda t} - 1)$$
 (9)

The ²⁰⁶Pb/²⁰⁴Pb ratio in zircon grains is typically measured by mass spectrometry. ¹⁴ ²³⁸U/²⁰⁴Pb is calculated from mea-

sured ²³⁸U/total U and ²⁰⁴Pb/total Pb ratios. But how do we find the original lead ratio, (206Pb/204Pb)₀? Consider that zircon (ZrSiO₄) invariably contains some U because U⁴⁺ ions are sufficiently similar in size to Zr4+ ions that they can substitute for Zr during crystallization of zircon. In contrast, Pb²⁺ has a significantly different charge and is too large to substitute for Zr⁴⁺. Consequently, the initial lead content of most zircons would have been inconsequential. The original Pb isotope ratio term (206Pb/204Pb)₀ can, therefore, normally be ignored. But what if we attempt to date a mineral other than zircon? Other U-bearing minerals, such as uraninite, may contain some initial Pb. How do we assess the initial Pb isotope ratio in such cases? Here we may reasonably assume that the initial lead isotope ratio was identical to the lead isotope ratio in minerals such as feldspar and galena that coexist in the same rock with the mineral we wish to date. We can do this because both feldspar and galena lack radioactive uranium and would not have produced any 206Pb during their history. Consequently, the initial ²⁰⁶Pb/²⁰⁴Pb ratio would not increase through time.

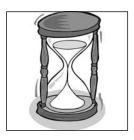
As examples of ²³⁸U/²⁰⁶Pb dating, zircon from the Mount Givens Granodiorite in the Sierra Nevada yielded ages of 87.9 and 87.6 million years, and zircons from the El Capital Granite in Yosemite National Park have ages of 102.8 and 96.9 million years.¹⁵ Note that these U-Pb ages are higher than the K-Ar ages mentioned above, a finding that is consistent with the idea that the U-Pb data represent crystallization ages and the K-Ar data represent cooling ages.

Isochron Methods

To obtain crystallization ages, geochronologists also commonly employ the graphical isochron and concordia methods. We begin with the isochron method. The ⁸⁷Rb/⁸⁷Sr and ¹⁴⁷Sm/¹⁴³Nd decay systems are particularly amenable to treatment by the isochron method. With ⁸⁷Rb/⁸⁷Sr as an example, let's rearrange equation (8) slightly by switching the terms on the right side to obtain

87
Sr/ 86 Sr = (87 Rb/ 86 Sr) ($e^{\lambda t} - 1$) + (87 Sr/ 86 Sr)₀ (10)

This equation has the same form as the equation for a straight line: y = mx + b. Thus, if we plot a straight line on a diagram with ⁸⁷Sr/⁸⁶Sr as the vertical y-axis (ordinate) versus 87Rb/86Sr as the horizontal x-axis (abscissa), $(^{87}\text{Sr}/^{86}\text{Sr})_0$ is the y-intercept, b, and $(e^{\lambda t} - 1)$ is the slope, m, of the straight line (Figure 2). Notice that the slope of the straight line for equation (10) is a function of t, the age of a sample containing Rb and Sr. Obviously then it would be nice to generate a straight line based on information about Rb and Sr so that we could obtain an age from the slope of the line. How do we do that? We produce this line is by determining the present 87Sr/86Sr and 87Rb/86Sr ratios of several rock samples from an igneous intrusion or a mass of metamorphic rocks such as gneiss and then plotting these ratios on a diagram of ⁸⁷Sr/⁸⁶Sr versus ⁸⁷Rb/⁸⁶Sr. The straight line that is generally obtained is termed



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a *whole-rock isochron*. Attainment of a straight line plot from the analytical data suggests that the rocks we analyzed were essentially closed to Rb and Sr diffusion and that all samples had the same initial ratio at the time of igneous or metamorphic crystallization.

To understand why the whole-rock isochron method works and why we might obtain a straight line that yields age information, let's try to visualize the major geologic process of magmatic crystallization. Envision a mass of magma, that is, intensely hot molten (normally silicate) rock, in Earth's crust that contains trace amounts of 87Rb, ⁸⁷Sr, and ⁸⁶Sr. Different isotopes of a chemical element are likely to fractionate during geologic processes such as evaporation, crystallization from magma, or diffusion in a temperature gradient in a magma if the masses of the isotopes differ from one another significantly. For example, hydrogen isotopes strongly fractionate during evaporation of water on Earth's surface. Light hydrogen (1H) atoms are preferentially incorporated into water vapor whereas heavy hydrogen atoms known as deuterium (2H) are preferentially incorporated into liquid water. As a result, the ¹H/²H ratio in water vapor that coexists with liquid water is much higher than the ¹H/²H ratio in the liquid water. This strong isotopic fractionation occurs because of the great difference in mass between the two isotopes of hydrogen. A heavy hydrogen isotope is twice as massive as a light hydrogen isotope.

In contrast, the atomic masses of 87Sr and ⁸⁶Sr are very similar. Because a ⁸⁷Sr atom is only 1.2% heavier than a 86Sr atom, Sr isotopes should fractionate only very slightly during geologic processes. Therefore, the ratio of these two isotopes should normally have much the same value throughout a body of cooling magma. As the magma cools, minerals eventually begin to crystallize. Each mineral has a different chemical composition and crystal structure. Rb1+ ions readily substitute for K1+ ions in growing crystals because the two ions have similar sizes (ionic radii) and identical electrical charges, and Sr2+ ions likewise substitute for Ca2+ ions. There will be variation in 87Rb/86Sr ratios throughout the newly crystallized igneous rock mass because of variation in mineral abundances. For example, K-rich and Ca-poor domains of a magma body will crystallize to rocks with high

⁸⁷Rb/⁸⁶Sr initial ratios, and K-poor and Ca-rich domains will produce rocks with low ⁸⁷Rb/⁸⁶Sr initial ratios. If we could analyze the isotope ratios of several chunks of rock as soon as the magma crystallized and plot the results on an isochron diagram, we would normally obtain a virtually horizontal line (Figure 2). The slope of a horizontal straight line is zero, indicating a zero age for a suite of rocks that have just crystallized.

As the granite becomes older, ⁸⁷Rb in each volume of rock spontaneously decays to ⁸⁷Sr. The ⁸⁷Rb/⁸⁶Sr ratio of each volume of granite decreases and the 87Sr/86Sr ratio increases in each sample through time because ⁸⁷Sr is being added to the rock by decay of 87Rb. Data points on the isochron diagram would shift their positions as shown by the lines with arrows in Figure 2. All data points would shift through time along paths with the same slope. Points representing rock samples with the highest initial 87Rb/86Sr ratios would shift the most because they have higher 87Rb contents, and a greater amount of ⁸⁷Rb decays into a greater amount of ⁸⁷Sr. As the granite body ages, the farther the data points would shift. Through time, the isochron would pivot around the y-intercept, (87Sr/86Sr)0, and the slope of the isochron would become steeper, indicating that the rocks are getting older. Although we cannot observe this shift in position of the

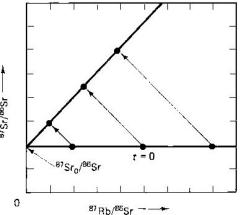


Figure 2. Idealized Rb-Sr isochron diagram illustrating the isotopic development of three samples in time. All samples had the same initial strontium isotope ratio at the time of formation. The isotope composition of each sample moves along lines with arrows having a slope of -1 as 87 Rb decays to 87 Sr. The slope of the isochron is ($e^{\lambda t}-1$). The initial Sr isotope ratio can be ascertained from intersection of the isochron with the abscissa. Reproduced from Fig. 12.6, p. 386 in Steven M. Richardson and Harry Y. McSween, Jr., *Geochemistry: Pathways and Processes* (Englewood Cliffs, NJ: Prentice Hall, 1989) by permission of Harry Y. McSween, Jr.

isochron in real time (we have not lived long enough!), we can obtain information about the age of the granite from knowledge of the isotope ratios that we analyze today. From the diagram, we can calculate the time of crystallization of the granite from the slope of the whole-rock isochron, find the initial ⁸⁷Sr/⁸⁶Sr ratio from the y-intercept, and infer lack of significant diffusion of Rb or Sr from strong co-linearity of points. Significant scatter of analytical data points suggests that there may have been substantial diffusion and that the age calculated from the slope of a poorly defined isochron is somewhat suspect. Some variation in initial Sr isotope ratio may also produce slight scatter of data points that nonetheless define a straight line with reasonably good fit.

As an example, a Rb-Sr whole-rock isochron for the Stolzburg pluton in the Barberton Mountains of South Africa, indicates a probable crystallization age of 3.48 billion years (Figure 3).¹⁷ The slight scatter of data points in this isochron plot suggests possible minor diffusion or slight variation in initial Sr isotope ratios. As another example, a remarkably tightly constrained whole-rock Rb-Sr isochron for 38 samples of several different stony meteorites indicates a meteorite crystallization age of 4.498 billion years (Figure 4).¹⁸

Internal or mineral isochrons are constructed from isotopic analyses of individual minerals that have been extracted from a single large rock sample. Such isochrons sometimes include an analysis of the whole-rock sample. Internal isochrons are especially useful for determining crystallization ages of individual meteorite fragments and fragments of returned lunar samples. Figure 5 shows an internal isochron from a lunar basalt fragment that indicates an age of 3.09 billion years.¹⁹

Conceivably, straight lines on an isochron diagram could be generated simply by mixing two magmas in vari-

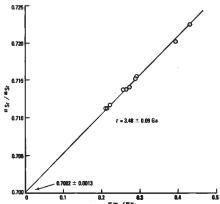


Figure 3. Rb-Sr whole-rock isochron from samples of Stolzburg Pluton, Barberton Mountains, South Africa. Reproduced from Figure 3, p. 67 in "Geochronologic and Sr-isotopic Studies of Certain Units in the Barberton Granite-Greenstone Terrane, South Africa" by J. M. Barton, Jr., L. J. Robb, C. R. Anhaeusser, and D. A. Van Nierop in Contributions to the Geology of the Barberton Mountain Land: National Geodynamics Programme Barberton Project, Special Publication no. 09. C. R. Anhaeusser, ed. (Johannesburg: Geological Society of South Africa, 1983): 63–72 by permission of Professor J. M. Barton for the Geological Society of South Africa.

ous proportions and allowing them to crystallize. If so, the resulting straight line would tell us nothing about the age of the rocks. The vast majority of straight lines of an isochron plot, however, cannot be explained by simple mixing for several reasons. We mention only two. For example, evidence of extensive magma mixing can generally be detected from variations in chemical composition of an igneous rock body as well as from field evidence. For most igneous rock bodies, however, field and chemical evidence of significant mixing of two or more magmas is lacking. In addition, the mixing hypothesis fails to account for the very wide range of values of Sr isotope ratios that have been observed on all isochron diagrams of igneous rocks.

The Sm-Nd decay is also amenable to treatment by isochron methods. Sm-Nd isochrons have an advantage over Rb-Sr isochrons in that rare-earth elements (REE) like Sm and Nd are relatively immobile during geologic heating events, and, therefore, are unlikely to diffuse into or out of rocks. As a result, the isotope ratios of these elements are not significantly changed during geologic disturbances such as metamorphism. Evidence of the original crystallization age of an igneous intrusion, therefore, is normally preserved even though that body may have been metamorphosed subsequently. This characteristic feature means that Sm-Nd whole-rock isochron dating is especially important for dating exceptionally old rocks in the one to four billion year range. As an example, Sm-Nd whole-rock isochron data obtained from metamorphosed volcanic rocks in the Barberton Mountains indicate an age of 3.53 billion years (Figure 6).²⁰

Several additional isochron methods have been developed in recent decades based on the β decay of ^{138}La to ^{138}Ce , of ^{187}Re to ^{187}Os , and of ^{176}Lu to $^{176}\text{Hf}.^{21}$ Although none of these methods is as widely useful as Sm-Nd or Rb-Sr, they offer promise in the investigation of igneous rocks rich in iron-magnesium minerals, iron meteorites,

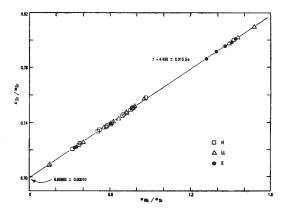
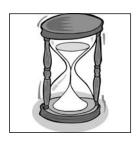


Figure 4. Rb-Sr whole-rock isochron of 38 samples of undisturbed chondritic meteorites. Reproduced from Figure 4, p. 414 in "Absolute Age of Formation of Chondrites Studied by the 87Rb-87Sr Method" by J. F. Minster, J. L. Birck, and C. J. Allégre, *Nature* 300, no. 5891 (1982): 414–9; by permission of Nature Publishing Group.



The concordia method, another powerful graphical method, was developed to deal with [the] problems of lead loss and discordance among ages obtained for the same sample by different U-Th-Ph

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or certain ore samples – geological materials that are not so readily datable by the Rb-Sr and Sm-Nd isochron method.

The Concordia Method

The concordia method, another powerful graphical method, is very useful in evaluating radiometric data for the U-Th-Pb system. U- and Th-bearing minerals can be dated by analyzing 238U and its ultimate daughter product ²⁰⁶Pb, ²³⁵U and its ultimate daughter product ²⁰⁷Pb, and ²³²Th and its ultimate daughter product ²⁰⁸Pb. In addition, the leadlead method provides another calculation that is based on the ratio of radiogenic ²⁰⁷Pb to radiogenic ²⁰⁶Pb.²² There are, therefore, four independent methods for calculating the time of crystallization of a U-Th-bearing mineral such as zircon in an igneous rock body. The difficulty is that most U-Th-Pb analyses of the same sample yield discordant, i.e., different, ages by the four different methods because lead can be lost from U-bearing minerals either by slow continuous leakage or in discontinuous episodes, most likely caused by heating. The Pb/Pb method typically yields higher ages than those obtained by the other three methods. The reason is that the ²⁰⁷Pb/²⁰⁶Pb ratio of any lead that is lost from a U-bearing sample should be virtually the same as the isotope ratio of lead that is retained in the sample. The masses of the two Pb isotopes are so similar that there would be negligible isotope fractionation during lead loss. Because the age in this method is calculated from the ²⁰⁷Pb/²⁰⁶Pb ratio, a reliable age should be obtained even

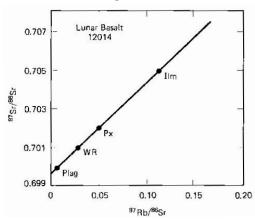


Figure 5. Rb-Sr internal isochron for lunar basalt 12014. WR = whole rock, ilm = ilmenite, px = pyroxene, and plag = plagioclase feldspar. The age determined from the slope is 3.09 billion years. Reproduced from Fig. 12.7, p. 387 in Richardson and McSween, *Geochemistry* by permission of Harry Y. McSween, Jr.

if some lead is lost. In the other three methods, however, if lead is lost at all, a mineral will yield a spuriously young age because a daughter isotope, either ²⁰⁸Pb, ²⁰⁷Pb, or ²⁰⁶Pb, is lost, and the ages are based on the ratios of ²³⁸U/²⁰⁶Pb, ²³⁵U/²⁰⁷Pb, or ²³²Th/²⁰⁸Pb.

The concordia method was developed to deal with these problems of lead loss and discordance among ages obtained for the same sample by different U-Th-Pb methods.23 The most important concordia diagram plots ²⁰⁶Pb/²³⁸U (y-axis) versus 207 Pb/ 235 U (x-axis). The diagram (Figure 7) includes a curve, termed concordia, that shows how the values of these two ratios change continuously over time for any hypothetical sample that has been completely closed to U and Pb and for which all of the Pb is radiogenically derived from U decay. Because both ²³⁸U and ²³⁵U decrease and ²⁰⁶Pb and ²⁰⁷Pb increase through time due to radioactive decay, the 206Pb/238U and ²⁰⁷Pb/²³⁵U ratios must both increase in a closed system, resulting in the positive slope of concordia.

Now suppose that a U-bearing zircon is analyzed for U and Pb, that any necessary correction is made for original Pb isotopes in the sample, that the appropriate Pb/U ratios are plotted on the diagram, and that the data point for the sample analysis plots exactly on concordia. A reasonable conclusion would be that the position of the point on concordia indicates the crystallization age of

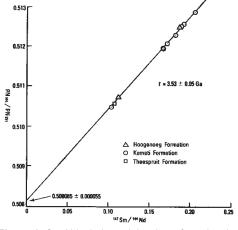


Figure 6. Sm-Nd whole-rock isochron for volcanic rocks from the Onverwacht Group, Barberton Mountains, South Africa. Reproduced from Figure 2, p. 299 in "Sm-Nd Dating of Onverwacht Group Volcanics, Southern Africa" by P. J. Hamilton, N. M. Evenson, R. K. O'Nions, H. S. Smith, and A. J. Erlank, *Nature* 279 (24 May 1979): 298–300 by permission of the Nature Publishing Group.

methods.

the zircon. In many studies, however, data points obtained from several analyses of a suite of zircons from a rock body define a straight line, called discordia that intersects concordia at two points (Figure 7). Even if no data points lie on concordia, the upper intercept of discordia indicates the time of original crystallization of the zircons, and the lower intercept of the straight line with concordia presumably indicates a time of disturbance when Pb was lost in varying amounts from the analyzed zircons. If lead had been lost from individual zircons during some geologic event in the past, their Pb/U ratios would decrease, and the more lead that they lost, the lower their Pb/U ratios would become even though the ratio of lead isotopes $(^{207}\text{Pb}/^{206}\text{Pb})$ would not change. If the zircons were analyzed immediately after an episode of lead loss, the data points would define a line intersecting the origin where both Pb/U ratios are zero. Any zircon that lost all of its lead (Pb = 0) would plot at the origin because the Pb/U ratios would both be zero. After the episode of lead loss is over, the radioactive decay of U continues and accumulation of Pb in the zircons resumes, and both Pb/U ratios of all zircons begin to increase again. Through time, the straight line representing the time of lead loss rotates into the position defined by the zircon analyses at present (Figure 7). In this scenario, we obtain the original crystallization age and the age of lead loss episode.

There are other instances in which lead may have been lost continuously or in two or more discrete episodes of lead loss. These cases are much more complex and will not be treated here. Suffice it to say, however, that the concordia method demonstrates that, for U-Th-Pb systems, the closed system condition does not always have to be met to make use of it for dating purposes.

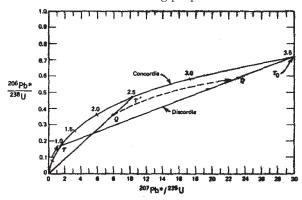


Figure 7. Schematic U-Pb concordia diagram illustrating episodic lead loss at time τ' when the system was 2.5 billion years old. Because of varying degrees of lead loss, the Pb isotope composition of various samples moved toward the origin. Point Q represents one sample that suffered partial Pb loss. A sample that lost all of its Pb would be represented by a point at the origin. Following the time of Pb loss to the present, a period of 1.0 billion years, discordia would rotate into position $\tau\text{--}\tau'$. Discordia indicates that the samples originally crystallized 3.5 billion years ago and that the episode of Pb loss occurred 1.0 billion years ago. Reproduced from Fig. 18.5, p. 292 in G. Faure, *Principles of Isotope Geology*, 2d ed. (New York: John Wiley and Sons, 1986) by permission of John Wiley and Sons, Inc.

As examples of the concordia method, consider the following. Zircon separates from the Duffer Formation in Western Australia (Figure 8) define a discordia that intersects concordia at 3.45 billion years. ²⁴ Five zircon separates from the Gamitagama Lake Complex, an igneous intrusion in southern Canada, define an excellent straight-line discordia that intersects concordia at 2.67 billion years, and five zircons from another intrusion, the nearby Kasubeck Creek Granodiorite, also define a very good straight line that intersects concordia at 2.67 billion years.²⁵ These ages are close to those of volcanic rocks in the area. One additional example concerns the Qôrqut Granite from western Greenland.²⁶ Seventeen zircon separates define a very good straight line discordia that intersects concordia at 2.53 billion years, whereas zircons from the Amitsoq gneisses that were intruded by the granite give an intersection age of 3.595 billion years.

Geologists now have at their disposal a wide array of radiometric methods that are capable of yielding highly reliable information about the ages of igneous crystallization, metamorphic recrystallization, cooling, lead-loss, and other events for many kinds of samples provided that the methods are used in conjunction with careful sample collection, precise analysis, understanding of the geologic conditions that affected the samples being dated, and judicious interpretation of the geologic significance of the age that is obtained.

My final article, to appear in the September 2007 issue, will examine thermochronometric methods as well as methods based on the radioactive decay of cosmogenically produced isotopes. It will conclude with a brief reflection on the theological implications of belief in a very ancient Earth.

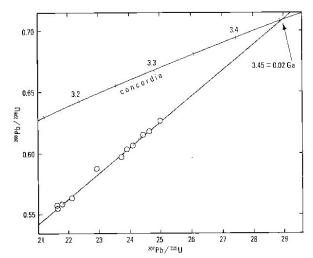


Figure 8. U-Pb concordia diagram plotting analyses of zircons separated from rocks of the Duffer Formation, Pilbara Supergroup, Western Australia. The zircon analyses define an excellent discordia indicating an original crystallization age of 3.45 billion years. Reproduced from Figure 2 in R. T. Pidgeon, "3450-m.y.-old Volcanics in the Archaean Layered Greenstone Succession of the Pilbara Block, Western Australia," *Earth and Planetary Science Letters* 37, no 3 (January 1978): 421–8 by permission of Elsevier Publishing.

Article

How Old Is It? How Do We Know? A Review of Dating Methods – Part Two: Radiometric Dating: Mineral, Isochron and Concordia Methods

Notes

¹Henri Becquerel discovered radioactivity in 1896 while working with uranium compounds. Marie and Pierre Curie discovered the radioactive nature of the chemical elements thorium, radium, and polonium, and Pierre Curie coined the term "radioactivity." In 1903, Ernest Rutherford and Frederick Soddy worked out the general theory and mathematics of radioactive decay, recognized the mechanisms of α and β particle emission, and postulated that helium is an important by-product of radioactive decay. Two years later, Rutherford calculated the ages of two mineral samples from measurements of their uranium and helium contents.

²In 1907, Bertram Boltwood separated "ionium," a substance chemically indistinguishable from thorium but with a different atomic mass. In 1912, Soddy applied the term "isotope" to such apparently different forms of the same chemical element, and J. J. Thomson provided experimental confirmation of the existence of isotopes. In 1919, Frederick Aston constructed the first mass spectrograph and by 1927 had determined the isotope composition of more than fifty chemical elements.

³For a discussion of some of the earlier, but now abandoned, methods see Henry Faul, ed., *Nuclear Geology: A Symposium on Nuclear Phenomena in the Earth Sciences* (New York: John Wiley and Sons, 1954).

⁴For details on geologically important radiometric dating systems, see Gunter Faure and Teresa M. Mensing, *Isotopes: Principles and Applications*, 3d ed. (Hoboken, NJ: Wiley, 2005) and Alan P. Dickin, *Radiogenic Isotope Geology* (Cambridge: Cambridge University Press, 1997). Also of great value are the summaries in G. Brent Dalrymple, *The Age of the Earth* (Stanford, CA: Stanford University Press, 1991) and G. Brent Dalrymple, *Ancient Earth, Ancient Skies: The Age of Earth and Its Cosmic Surroundings* (Stanford, CA: Stanford University Press, 2004).

⁵For reviews of experimental studies of changes in rates of radioactive decay, see G. T. Emery, "Perturbation of Nuclear Decay Rates," *Annual Review of Nuclear Science* 22 (1972): 165–202 and H.-P. Hahn, H. J. Born, and J. I. Kim, "Survey on the Rate Perturbation of Nuclear Decay," *Radiochimica Acta* 23 (1976): 23–37. As early as 1903, Rutherford and Soddy performed experiments under a wide range of chemical and physical conditions and detected no change in rates of radioactive decay.

⁶On K-Ar dating, see G. Brent Dalyrmyple and Marvin A. Lanphere, *Potassium-Argon Dating: Principles, Techniques, and Applications to Geochronology* (San Francisco: W. H. Freeman, 1969). See also chapter 6 in Faure and Mensing, *Isotopes: Principles and Applications*.

⁷In β decay, a neutron of a radioactive isotope such as ⁴⁰K is transformed to a proton plus an electron (β particle) which is emitted from the nucleus. As a result, the atomic number (Z) of a daughter isotope such Ca (Z = 20) is one more than that of the parent K (Z = 19) whereas the atomic mass remains the same (40) because the sum of protons and neutrons remains constant, a neutron being replaced by a proton. In electron capture, an electron in an inner shell is captured by the nucleus. The combination of electron with a proton creates a neutron. As a result, the atomic number of the daughter is reduced by one with the loss of the proton but the atomic mass remains the same as the proton is replaced by a neutron. Thus, ⁴⁰Ar produced by decay of ⁴⁰K due to electron capture has Z = 18.

In mass spectrometry, isotopes of interest in either gaseous or solid samples are ionized. The beam of positively charged ions is deflected by a magnetic field as it is passed through a curved electromagnet. The radius of curvature of beam paths of each isotope is dependent on isotopic mass. The paths of heavier isotopes are deflected less than those of lighter isotopes. The magnetically separated ion beams are focused onto a collecting cup where beam intensities are measured. Mass spectrometric analysis of isotope ion beams is carried out in a near vacuum. Older mass spectrographs measured isotope abundances photographically.

⁹The K-Ar closure (blocking) temperature of biotite is approximately 325°C and that of hornblende is approximately 475°C.

The closure temperatures are a function of the rate of cooling and grain size of the mineral. In actuality, as a K-bearing mineral cools, it passes through a temperature range during which Ar retentivity increases until below the closure temperature the Ar retention is 100%.

¹⁰G. Brent Dalrymple, "K-Ar Ages of the Friant Pumice Member of the Turlock Lake Formation, the Bishop Tuff and the Tuff of Reds Meadow, Central California," *New Mexico Bureau of Mines and Mineral Resources, Isochron/West*, no. 28 (1980): 3–5.

¹¹T. W. Stern, P. C. Bateman, B. A. Morgan, M. F. Newell, and D. L. Peck, "Isotopic U-Pb Ages of Zircon from the Granitoids of the Central Sierra Nevada," California United States Geological Survey Professional Paper 1185 (1981).

¹²For fundamentals of Rb-Sr dating, see Louis H. Ahrens, "Measuring Geologic Time by the Strontium Method," *Geological Society of America Bulletin* 60 (1949): 217–66.

¹³For details of the U-Pb method, see Chapter 10 in Faure and Mensing, *Isotopes: Principles and Applications*.

¹⁴Small mineral grains such as tiny zircon crystals can be analyzed with the aid of a Sensitive High-Resolution Ion Microprobe (SHRIMP), an instrument that bombards a mineral surface with high-energy ions that cause atoms to be sputtered from the surface of the sample. These atoms are then analyzed by mass spectrometry.

¹⁵Stern, et al., Isotopic U-Pb Ages of Zircon from the Granitoids of the Central Sierra Nevada, California.

¹⁶For details on the Rb-Sr and Sm-Nd isochron methods, see chapters 5 and 9 in Faure and Mensing, Isotopes: Principles and Applications.

¹⁷J. M. Barton, Jr., L. J. Robb, C. R. Anhaeusser, and D. A. Van Nierop, "Geochronologic and Sr-Isotopic Studies of Certain Units in the Barberton Granite-Greenstone Terrane, South Africa," in C. R. Anhaeusser, ed., *Contributions to the Geology of the Barberton Mountain Land* (The Geological Society of South Africa Special Publication No. 9, 1983), 63–72.

¹⁸J.-F. Minster, J.-L. Birck, and C. J. Allègre, "Absolute Age of Formation of Chondrites Studied by the ⁸⁷Rb-⁸⁷Sr Method," *Nature* 300 (1982): 414–9.

¹⁹L. E. Nyquist, C.-Y. Shih, J. L. Wooden, B. M. Bansal, and H. Wisemann, "The Sr and Nd Isotopic Record of Apollo 12 Basalts: Implications for Lunar Geochemical Evolution," *Proceedings of the* 10th Lunar and Planetary Science Conference (1979): 77–114.

²⁰P. J. Hamilton, N. M. Evensen, R. K. O'Nions, H. S. Smith, and A. J. Erlank, "Sm-Nd Dating of Onverwacht Group Volcanics, Southern Africa," *Nature* 279 (1979): 298–300.

²¹On the Lu-Hf, Re-Os, and La-Ca methods, see chapters 12–14 in Faure and Mensing, *Isotopes: Principles and Applications*.

²²On various U-Th-Pb methods, see Chapters 10 and 11 in Faure and Mensing, *Isotopes: Principles and Applications*. Both the U and Th decay chains include α and β decays. An α particle consists of two protons and two neutrons, in essence the nucleus of a helium atom. Consequently, helium is an important by-product of both U and Th decay. The initial step in the decay chain of ²³⁸U is the decay of ²³⁸U to ²³⁴Th in which the atomic number of the daughter is two less than that of the parent (90 vs. 92) because of the loss of two protons, and the atomic mass decreases by four (234 from 238) because of the loss of two protons and two neutrons.

²³George Wetherill, "Discordant Uranium-Lead Ages," *Transactions* of the American Geophysical Union 37 (1956): 320–36.

²⁴R. T. Pidgeon, "3450-m.y.-old Volcanics in the Archaean Layered Greenstone Succession of the Pilbara Block, Western Australia," Earth and Planetary Science Letters 37 (1978): 421–8.

²⁵T. E. Krogh and A. Turek, "Precise U-Pb Zircon Ages from the Gamitagama Greenstone Belt, Southern Superior Province," *Canadian Journal of Earth Sciences* 19 (1982): 859–67.

²⁶H. Baadsgaard, "Further U-Pb dates on Zircons from the Early Precambrian Rocks of the Godthaabsfjord Area, West Greenland," *Earth and Planetary Science Letters* 33 (1976): 261–7.