

Geological Time (Geochronology)

Summary of materials relating to course ESS 461 "Geological Time"
taught at the University of Washington, Winter 2010, by John O. Stone PhD
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Introduction

I compiled this summary to assist in learning some of the material relevant to the study of Geochronology, the subject of University of Washington course ESS 461, as presented in winter 2010. Geochronology is a technical subject, more mathematical than many, and drawing on nuclear physics, sophisticated inorganic chemistry, mass spectrometry (including accelerator mass spectrometry), and other advanced technologies. However, it is an important discipline because, like evolution, relativity, and cosmology, it dramatically affects how we view the world and our place in it. I hope that my summary will be of benefit to others starting to learn more about this fascinating subject.

This course was taught by Professor John O. Stone (Assoc. Prof., Earth and Space Sciences, hereafter "JOS"). I appreciate Professor Stone's teaching, expertise, and willingness to allow me to audit his course. I also

appreciate the time spent by Professor Bruce Nelson¹, who showed us around his mass spectrometry lab at the UW, and Prof. James Feathers, who gave us a tour of his UW Luminescence Lab² (where OSL and TL dating of archeological specimens is performed).

I am a retired physician and claim no expertise in this field (although my background in physics and nuclear medicine was helpful). The materials here represent selected key concepts assembled from various Web sources, the lecture notes, the two recommended textbooks, the other assigned materials, and various original papers in the scientific literature. No assumptions are made regarding the ultimate authoritativeness of Web sources utilized, particularly Wikipedia. Note that links (URLs) shown in footnotes are “live” and can be followed by clicking on them in PDF documents such as this. The cited sources and URLs are current as of winter 2010, but I will not be updating this material or the URLs as they go out of date. I have tried to indicate where I do not fully understand the subject matter presented.

The terminology of geologic time and age includes the following abbreviations³ (the word “ago” is often implied):

y	year
a	annum (year)
ka	kilo-annum = 1000 years = 10^3 y
Ma	mega-annum = million years = 1,000,000 y = 10^6 y
Ga	giga-annum = 1 USA billion years = 10^9 y
Ta	tera-annum = 1 USA trillion years = 10^{12} y
BP	before the present
CE	Common Era (i.e., AD)
BCE	before the Common Era (i.e., BC)
m.y.	Time duration in millions of years

Impressive Latin phrases sometimes used in relation to limits on dates and intervals include:

- *terminus ante quem*: the date before which an artifact or feature must have been deposited or written
 - *terminus post quem* (TPQ): the date after which an artifact or feature must have been deposited or written
 - *terminus ad quem*: the latest possible date of an interval, period, era, etc.; the ending point or goal
 - *terminus a quo*: the earliest possible date of an interval, period, era, etc.; the starting point or origin
- (Note that “TAQ” is an ambiguous abbreviation.)

Useful websites

Geological Time ESS461 Course Website (John O. Stone):

http://faculty.washington.edu/stn/ess_461/index.shtml

Charts of the Nuclides including Radionuclides:

Korean Atomic Energy Research Institute (KAERI): <http://atom.kaeri.re.kr/> [arranged in sections]

Brookhaven National Lab: <http://www.nndc.bnl.gov/chart/> [must zoom in to level 1 for details]

Cosmogenic Isotope Laboratory (John O. Stone, Dir.): <http://depts.washington.edu/cosmolab/>

Geological Time Scale: <http://pubs.usgs.gov/fs/2007/3015/>

USGS: <http://pubs.usgs.gov/fs/2007/3015/fs2007-3015.pdf>

International Commission on Stratigraphy: <http://www.stratigraphy.org/upload/ISChart2009.pdf>

Physical Constants and Conversions: <http://physics.nist.gov/cuu/Constants/index.html>

Physical Units Conversion and Calculations:

<http://online.unitconverterpro.com/>

http://www.chemie.fu-berlin.de/chemistry/general/units_en.html

<http://keisan.casio.com/has10/Free.cgi> high precision numbers calculator

Quaternary Isotope Laboratory (Minze Stuiver, former director): <http://depts.washington.edu/qil/>

¹ <http://earthweb.ess.washington.edu/dwp/people/profile.php?name=nelson--bruce>

² <http://depts.washington.edu/lumines/>

³ Geological Time terminology:

• <http://pubs.usgs.gov/fs/2007/3015/>

• <http://en.wikipedia.org/wiki/Annum>

Course description (excerpted from JOS website):

The following course description helps to convey some of the topics relevant to this field (although we did not actually cover all of them):

“... The main aim is to survey the clever methods used to tell geological time; as we go we'll put some precise numbers on significant events in the history of the Earth, the solar system and the cosmos. Along the way we'll encounter many other interesting topics: Radioisotope tracers, and how they're used to measure geochemical reaction rates. Thermochronology - how leaky radioisotope systems, that don't keep accurate time, are used to measure the thermal history of the crust...”

“Most of the class is devoted to radiometric dating methods, so we begin with a quick look at nuclear structure and stability, the chart of the nuclides and the various forms of radioactivity”⁴

Topics also include

“(Simple) mathematical description of radioactive decay and daughter isotope growth. Requirements for an accurate geochronometer. Basic assumptions underlying all radiometric dating methods. Simple parent-daughter systems. Systems involving a continuously produced parent isotope or a disappearing daughter isotope.

Chemical and isotopic measurements - Chemical analyses. Decay counting methods. Mass spectrometry. Atom counting methods. Isotope dilution. Errors, accuracy and precision.

Isotopic decay methods - Radiocarbon dating and applications to archeology...

Radioactive parent - stable daughter systems. Workhorse methods of geochronology: K-Ar and $^{40}\text{Ar}/^{39}\text{Ar}$ dating, ^{87}Rb - ^{87}Sr , ^{147}Sm - ^{143}Nd , U-Th-Pb-He methods. Fission-tracks - geochronology by microscope. The timescale for human evolution. Dating magnetic reversals to measure rates of continental drift. Earth's oldest rocks. Earth's oldest minerals. Age of the Earth, meteorites and the solar system.

Radioactive decay chains. Uranium-series methods. Dating carbonates. Isotopic disequilibrium in volcanic rocks. Radon in your basement. Measuring deposition rates with ^{210}Pb .

Trapped charge methods - Thermoluminescence, optically-stimulated luminescence, electron spin resonance.

‘Geomorphic’ dating - Cosmic ray exposure dating. Erosion rate measurements. Cosmogenic nuclide and luminescence methods for burial dating.

Thermochronology - Temperature-sensitive systems (leaky geochronometers). Radiation damage, He and Ar diffusion, fission tracks and track annealing. Time-temperature histories. Uplift, erosion and geothermal evolution of mountain belts.

Chemical kinetic methods - Amino acid racemisation, weathering rinds, obsidian hydration. Optical isomers, chirality, and racemisation. Kinetics. Paleotemperatures from amino acid data. [We did not cover these topics.]

Layer counting and correlation methods - Ice core chronologies from oxygen and hydrogen isotope records. Dendrochronology, varve counting, stratigraphic and geochemical ‘pattern matching’. High-resolution Quaternary climate history, Milankovitch theory, orbital periods and ‘tuned’ chronologies.” [We did not cover these topics.]

Recommended textbooks

(1) G Faure and T Mensing. *Isotopes: Principles and Applications*, 2005, Wiley [QE501.4.N9 F38 2005]. JOS: “A good solid textbook, written specifically for our purposes.” The third edition of Faure's original [1977] *Principles of Isotope Geology*.

MCM: This is a very thorough textbook aimed at geological applications. Hereafter called *Faure05*.

(2) G Brent Dalrymple. *The Age of the Earth*. 1991 [QE508 .D28 1991] “...focuses on the age of the solar system, meteorites, the moon and the ancient history of the Earth.”

MCM: This is a finely detailed book with emphasis on techniques for dating the age of the Earth. It therefore provides little on shorter lived radioisotopes such as ^{14}C . It was prepared in part as a well-argued resource

⁴ http://faculty.washington.edu/stn/ess_461/information.shtml

made available to counter Creationist dating claims. Some of the information, which was mostly gathered in the mid-1980s, is getting a little out-of-date—for instance, he is unaware of the Chicxulub crater. Hereafter called *Dalrymple91*.

Age of the Earth: Early Estimates

“...Other naturalists used these hypotheses to construct a history of Earth, though their timelines were inexact as they did not know how long it took to lay down stratigraphic layers. In 1830, the geologist **Charles Lyell**, developing ideas found in Scottish natural philosopher **James Hutton**, popularized the concept that the features of Earth were in perpetual change, eroding and reforming continuously, and the rate of this change was roughly constant. This was a challenge to the traditional view, which saw the history of Earth as static, with changes brought about by intermittent catastrophes. Many naturalists were influenced by Lyell to become ‘**uniformitarians**’ who believed that changes were constant and uniform...”

“In 1862, the physicist William Thomson (who later became **Lord Kelvin**) of Glasgow published calculations that fixed the age of Earth at between **20 million and 400 million years**. [MCM: same range stated in *Dalrymple91* p. 38] He assumed that Earth had formed as a completely molten object, and determined the amount of time it would take for the near-surface to cool to its present temperature. His calculations did not account for convection inside the Earth, which allows more heat to escape from the interior to warm rocks near the surface...”

“Geologists had trouble accepting such a short age for Earth. Biologists could accept that Earth might have a finite age, but even 100 million years seemed much too short to be plausible. **Charles Darwin**, who had studied Lyell's work, had proposed his theory of the evolution of organisms by natural selection, a process whose combination of random heritable variation and cumulative selection implies great expanses of time...”

“In a lecture in 1869, Darwin's great advocate, Thomas H. Huxley, attacked Thomson's [Kelvin's] calculations, suggesting they appeared precise in themselves but were based on faulty assumptions. The German physicist Hermann von Helmholtz (in 1856) and the Canadian astronomer Simon Newcomb (in 1892) contributed their own calculations of **22 and 18 million years** respectively to the debate: they independently calculated the amount of time it would take for the Sun to condense down to its current diameter and brightness from the nebula of gas and dust from which it was born. Their values were consistent with Thomson's calculations. However, they assumed that the Sun was only glowing from the heat of its gravitational contraction. The process of solar nuclear fusion was not yet known to science.”⁵

Biblical chronology (Ussher, Lightfoot)

The Ussher chronology⁶ “is a 17th-century chronology of the history of the world formulated from a literal reading of the Bible by James Ussher, the Anglican Archbishop of Armagh (in what is now Northern Ireland). The chronology is sometimes associated with Young Earth Creationism, which holds that the universe was created only a few millennia ago.

Ussher's work, more properly known as the *Annales veteris testamenti, a prima mundi origine deducti* (Annals of the Old Testament, deduced from the first origins of the world), was his contribution to the long-running theological debate on the age of the Earth. This was a major concern of many Christian scholars over the centuries.

The chronology is sometimes called the Ussher-Lightfoot chronology because John Lightfoot published a similar chronology in 1642–1644. This, however, is a misnomer, as the chronology is based on Ussher's work alone and not that of Lightfoot. Ussher deduced that the first day of creation began at nightfall preceding Sunday October 23, **4004 BC**, in the proleptic Julian calendar, near the autumnal equinox. Lightfoot similarly deduced that Creation began at nightfall near the autumnal equinox, but in the year **3929 BC**.” [MCM: *Dalrymple91* lists Lightfoot's age as **3928 BC**.]

⁵ http://en.wikipedia.org/wiki/Age_of_the_Earth

⁶ http://en.wikipedia.org/wiki/Ussher_chronology

Estimate by sedimentation rates (Benoît de Maillet)

Benoît de Maillet⁷ (Saint-Mihiel, 12 April 1656 – Marseille, 30 January 1738) was a well-travelled French diplomat and natural historian. He was French consul general at Cairo, and overseer in the Levant. He formulated an evolutionary hypothesis to explain the origin of the earth and its contents... His main work, *Telliamed*, [advanced] an ultraneptunian theory of the Earth, and was to a large extent based on field geology discerned during trips throughout Egypt and other Mediterranean countries. It is based essentially on processes today known as **sedimentation**, excluding all other geological or geomorphological agents except some minor aspects of weathering. The work therefore seems modern as it touches sedimentation, but fantastical when touching other fields. Maillet observed, but did not always understand, all the major types of rocks forming the Earth's crust... From the observation of fossilized shells embedded in sedimentary rocks on mountains high above sea level, de Maillet recognized the true nature of fossils. Not appreciating that the land might rise, he concluded that the earth had originally been entirely covered by water (a theory of René Descartes), which had since been steadily lost into the vortex. Maillet derived a rate of fall of sea level, of about three inches per century, from sites where former ports were now above sea level. Working back to the highest mountains, he reached a figure of **2.4 billion years** for the age of the earth, so he thought it quite reasonable to accept that at least 2 billion years had passed since the earth was covered with water."

MCM: This was the first estimate yielding a much greater age than Christian theology provided.

Astronomical estimate of the age of Earth (George Darwin)

George Darwin, 2nd son of Charles Darwin and an astronomer, estimated the age of the Earth based on tidal moon-Earth interactions, etc, and came up with **>56 Ma** for the age of the Earth.⁸

Ocean salinity estimate of the age of Earth (John Joly)

In 1899 – 1901, **John Joly** calculated the rate of delivery of salt to the ocean. River water has only small concentrations of salts. He considered the volume of river water flowing into the sea, the salinity of the larger rivers, the volume of the ocean etc. Based on current salinity, he calculated an Age of Earth of **90 – 100 million years**. However, he could not account for recycled salt, salt incorporated into clay minerals, salt deposits, etc.⁹

Earliest radiometric estimates of the age of Earth (Rutherford, Boltwood)

"Discovery of radioactivity by **Henri Becquerel** in **1896**. In 1905, **Rutherford and Boltwood** used radioactive decay to measure the age of rocks and minerals. Uranium decay produces He, leading to a date of **500 million years**.¹⁰" [MCM: same age is stated in Dalrymple 91 p. 71]

In 1907, Boltwood concluded that lead was the stable end product of the decay of uranium. He published the age of samples of rock based on Uranium-Lead dating, calculating ages in specimens ranging from **410 to 2200 Ma**.¹¹

Modern Radiometric and Other Dating Techniques

Overview

"By measuring the amount of Radioactive decay of a radioactive isotope with a known half-life, geologists can establish the absolute age of the parent material. A number of radioactive isotopes are used for this purpose, and depending on the rate of decay, are used for dating different geological periods. More slowly decaying isotopes are useful for longer periods of time, but less accurate in absolute years. With the exception of the radiocarbon method, most of these techniques are actually based on measuring an increase in the abundance

⁷ http://en.wikipedia.org/wiki/Beno%C3%AEt_de_Maillet

⁸ Dalrymple 1991 p. 51

⁹ Dalrymple 1991 p. 54

¹⁰ <http://facstaff.gpc.edu/~pgore/geology/geo102/age.htm>

¹¹ Dalrymple 1991 p. 74

of a radiogenic isotope, which is the decay-product of the radioactive parent isotope. Two or more radiometric methods can be used in concert to achieve more robust results. Most radiometric methods are suitable for geological time only, but some such as the radiocarbon method and the $^{40}\text{Ar}/^{39}\text{Ar}$ dating method can be extended into the time of early human life and into recorded history.”¹²

Commonly-used modern techniques in radiometric dating

[Items 1 – 4 are largely derived from or quoted from here¹³.]

(1) *Radiocarbon ^{14}C dating.* This technique measures the decay of ^{14}C in organic material and can be best applied to samples younger than about 50,000 years.

(2) *Uranium–lead and Lead–lead dating.* This technique measures the ratio of two lead isotopes (^{206}Pb and ^{207}Pb) arising from the decay of ^{235}U and ^{238}U in a mineral or rock. “Often applied to the trace mineral zircon in igneous rocks, this method is one of the two most commonly used (along with argon–argon dating) for geologic dating. Uranium–lead dating is applied to samples older than about 1 million years.”

(3) *Uranium–thorium dating.* “This technique is used to date speleothems, corals, carbonates, and fossil bones. Its range is from a few years to about 700,000 years.”

(4) *Potassium–argon and argon–argon dating.* These techniques date metamorphic, igneous and volcanic rocks. They are also used to date volcanic ash layers within or overlying paleoanthropologic sites.” The younger [smallest] age limit of the argon–argon method is a few thousand years.”¹⁴

MCM: The precise half-lives and decay constants for some of these longer-lived radioisotopes are somewhat uncertain and varying values have been reported which affect estimates of age. For example, Rb-87 values are controversial and may require revision. Because materials in this document have been taken from multiple sources, there is some inevitable inconsistency in values used for particular radioisotopes.

The age equation:¹⁵

“The mathematical expression that relates radioactive decay to geologic time, is

$$D_t = D_0 + P_t (e^{\lambda t} - 1)$$

where

t = age of the sample (expressed in suitably chosen time units such as years),

D_t = number of atoms or amount of the radiogenic stable daughter isotope in the sample at time t,

D_0 = number of atoms or amount of the daughter stable isotope in the original composition (at t = 0),

P_t = number of atoms or amount of the parent radioisotope in the sample at time t, and

λ = the decay constant for the parent radioisotope, equal to $\ln(2) / t_{1/2}$.

where $t_{1/2}$ is expressed in the same time units as t.

In its simplest form, this can be rearranged to yield the age t:

$$t = \left(\frac{1}{\lambda}\right) \ln \left[\frac{D_t - D_0}{P_t} + 1 \right]$$

This formula must be corrected if there are alternate branching decay paths or multiple daughters, and more advanced techniques such as use of isochrons may also be needed if D_0 is significant and unknown.

Uranium–lead and lead–lead dating

Overview: Uranium [^{92}U] to lead [^{82}Pb] dating is one of the oldest and most refined of the radiometric dating schemes, yielding age ranges of about 1 million years to over 4.5 billion years, and with precisions in the 0.1% to 1% range.¹⁶ These methods usually rely on two separate decay chains, the series from **^{238}U to ^{206}Pb** (the

¹² <http://en.wikipedia.org/wiki/Geochronology>

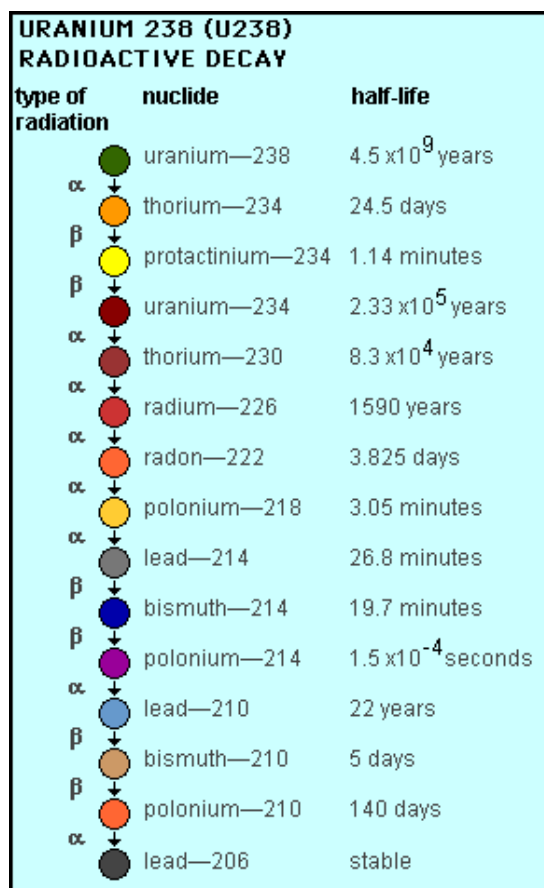
¹³ <http://en.wikipedia.org/wiki/Geochronology>

¹⁴ <http://en.wikipedia.org/wiki/Geochronology>

¹⁵ http://en.wikipedia.org/wiki/Radiometric_dating

¹⁶ http://en.wikipedia.org/wiki/Uranium-lead_dating

“uranium series”), with a half-life of 4.468 Ga ($\lambda_{U238} = 1.5514 \times 10^{-10} \text{ y}^{-1}$)¹⁷, and the series from ²³⁵U to ²⁰⁷Pb (the “actinium series”), with a shorter half-life of 0.704 Ga ($\lambda_{U235} = 9.846 \times 10^{-10} \text{ y}^{-1}$). These decay series occur via a series of alpha and beta decays. For ²³⁸U, the chain is as follows:



[This compact diagram of the decay scheme is from <http://www.atral.com/U2381.html>.

The half-lives shown are only approximate. For more current half-life data, see http://en.wikipedia.org/wiki/Uranium-238#Radium_series_.28aka_Uranium_series.29]

“Uranium-lead dating is usually performed on the mineral *zircon* (ZrSiO_4), though it can be used on other minerals such as monazite, titanite, and baddeleyite. Zircon incorporates uranium and thorium atoms into its crystalline structure, but strongly rejects lead. Therefore we can assume that the entire lead content of the zircon is radiogenic [i.e., arose in the specimen solely through radioactive decay]... Uranium-lead dating techniques have also been applied to other minerals such as calcite/aragonite and other carbonate minerals. These minerals often produce lower precision ages than igneous and metamorphic minerals traditionally used for age dating, but are more common in the geologic record.”¹⁸

The term *Uranium-lead dating* often involves both decay schemes in a graph called a *concordia diagram*, using the decay of ²³⁸U and ²³⁵U radioisotopes. However, a single decay scheme (usually ²³⁸U to ²⁰⁶Pb) may be used to yield a **U-Pb isochron**, like the rubidium-strontium and other isochron dating methods described below. Ages can also be determined by analysis of Pb isotope ratios alone, the *lead-lead method*, which makes use of ²³⁸U and ²³⁵U decay chains.

U-Pb concordia and discordia dating: This technique was pioneered by G. W. Wetherill¹⁹ Unlike the simple isochron technique (see below), this method makes use of the radioactive decay of two different isotopes of Uranium. Under conditions where the zircon has remained “closed”, so that no initial lead was present and no lead loss or entry into the rock has occurred since formation, the age of a zircon can be calculated independently from the two equations:

¹⁷ <http://www.nndc.bnl.gov/chart/chartNuc.jsp>

¹⁸ http://en.wikipedia.org/wiki/Uranium-lead_dating

¹⁹ Dalrymple 91 p. 115 – 119

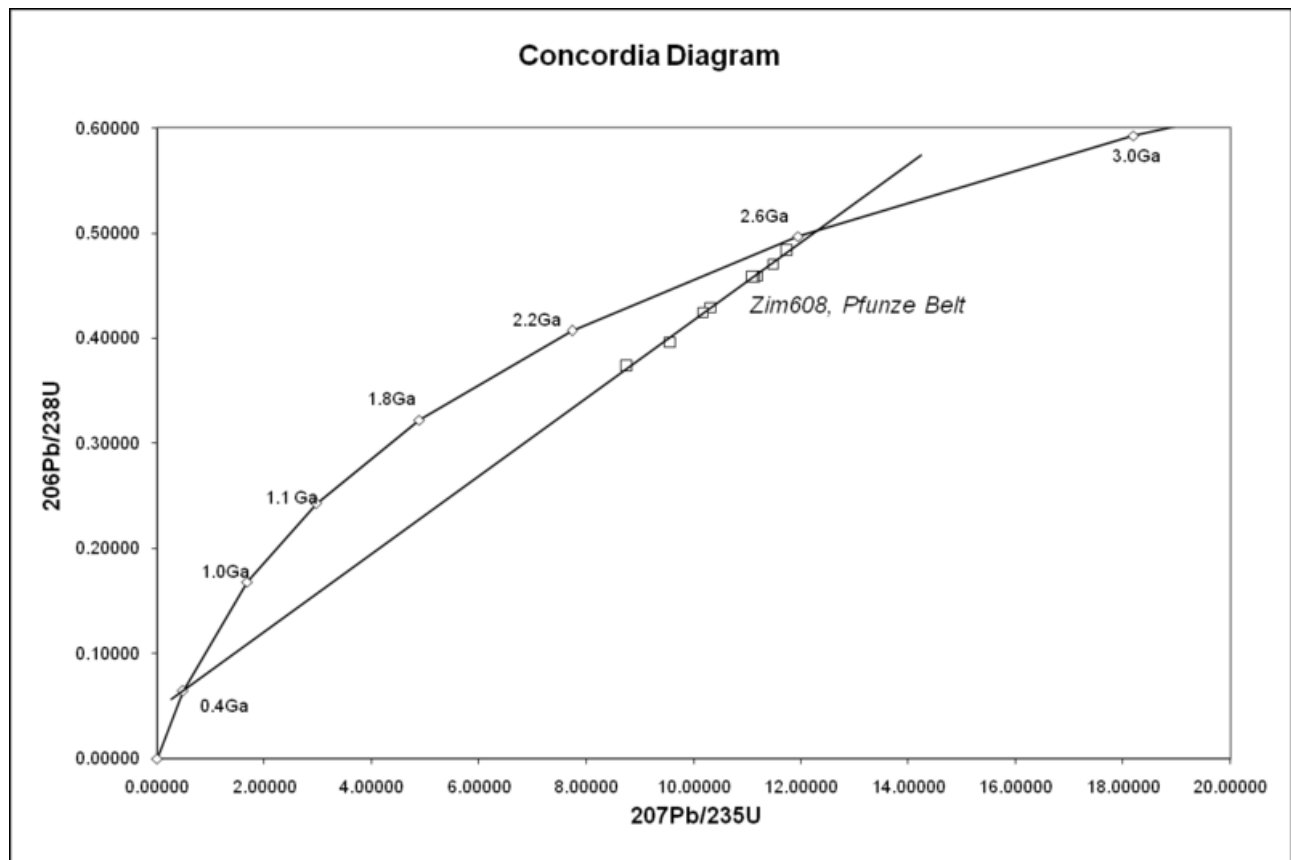
$$\frac{{}^{206}\text{Pb}}{{}^{238}\text{U}} = e^{(\lambda_{238}t)} - 1$$

and

$$\frac{{}^{207}\text{Pb}}{{}^{235}\text{U}} = e^{(\lambda_{235}t)} - 1$$

The concordia diagram (*concordia*) is the locus of points yielding equal (concordant) ages by the two ratios, ${}^{207}\text{Pb}/{}^{235}\text{U}$ and ${}^{206}\text{Pb}/{}^{238}\text{U}$ and for which there has been no loss of lead (the system has remained closed). The age is the last time the U-Pb clock was “reset”. The horizontal axis is ${}^{207}\text{Pb}/{}^{235}\text{U}$. The concordia diagram, a parametric relationship arising from the two equations in t , has a steadily decreasing slope with increasing age. Although this shape may initially seem unintuitive, graphing in Excel helps to demonstrate that the ratio ${}^{207}\text{Pb}/{}^{235}\text{U}$ is always changing by a larger multiplicative factor than does ${}^{206}\text{Pb}/{}^{238}\text{U}$ for equal increments in age t . (See spreadsheet examples.)

Consider a specimen of 4.2 Ga (an age corresponding to the concordia point P). When Pb is lost at 2 Ga, the various subsamples (perhaps differing minerals) from this rock are found to yield values off concordia and lying along a straight line. This line is called *discordia*, also termed an *errochron*, and it connects point P with the concordia point corresponding to 2.0 Ga. This graphical behavior arises because the two isotopes of lead are lost in the same proportion as their relative composition at P. Determination that the requisite multiple specimens fall on the discordia straight line provides a consistency check and indication of lead loss at a particular time. Despite the lead loss, the method still yields the true age at P, provided the points are colinear: (See diagram and caption explanation to follow.)



Concordia analysis for specimens from the Pfunze Belt, Zimbabwe.

All the samples (squares) show loss of lead isotopes at about 0.4 Ga, so they fall on a *discordia* straight line, but the upper (older) intercept of the discordia line with the *concordia* curve gives the correct age of the rock, about 2.6 Ga.

[from http://en.wikipedia.org/wiki/File:Pfunze_belt_concordia.png]

Lead-lead Isochron dating: In this technique, U values are eliminated, but primordial lead ratios must be included. The radiogenic daughter Pb isotopes ${}^{206}\text{Pb}$ and ${}^{207}\text{Pb}$ are measured and normalized by dividing by

the stable non-radiogenic isotope, ^{204}Pb . The presence of initial Pb in zircon etc. can be detected and corrected for by measuring the ^{204}Pb .²⁰

The relevant equations²¹ (where P = present activity, I = initial activity) are

$$\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_P = \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_I + \left(\frac{^{235}\text{U}}{^{204}\text{Pb}}\right)(e^{\lambda_{235}t} - 1)$$

$$\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_P = \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_I + \left(\frac{^{238}\text{U}}{^{204}\text{Pb}}\right)(e^{\lambda_{238}t} - 1)$$

$$\left[\frac{\left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_P - \left(\frac{^{207}\text{Pb}}{^{204}\text{Pb}}\right)_I}{\left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_P - \left(\frac{^{206}\text{Pb}}{^{204}\text{Pb}}\right)_I}\right] = \left(\frac{1}{137.88}\right)\left(\frac{e^{\lambda_{235}t} - 1}{e^{\lambda_{238}t} - 1}\right)$$

express present and initial values of $^{207}\text{Pb}/^{204}\text{Pb}$ and $^{206}\text{Pb}/^{204}\text{Pb}$ as a function of age and decay constants. These define a family of straight lines with slopes that can be used to compute the age. The lines all pass through a point P which represents the composition of the initial Pb in the system and may be seen to “rotate” counterclockwise about point P with increasing age. Unlike in the simple isochron method, P is not defined by an intersection with one of the graph coordinates, but the age is determined solely by the slope of the line.

Best estimates of the age of the Earth, meteorites, the Moon, and the Solar System

Claire Patterson pioneered use of the lead-lead isochron dating method to make some of the earliest accurate estimates of the ages of ancient meteorites and of the Earth.²² Although in 1956 he was using older values of decay constants, he obtained an age for 5 meteorites (from Canyon Diablo in AZ, Nuevo Laredo in Mexico, Henbury in Australia, etc.) of 4.55 ± 0.07 Ga. He also studied the lead isotopic composition in ocean sediment, which he believed was representative of pooled terrestrial lead, and found essentially the same age. Specifically, he found that the oceanic sediment lead value fell on the meteoritic lead isochron, and that therefore the age of the Earth (or at least the “time since the Earth attained its present mass”) was the same as the meteoritic age. The meteoritic/Earth isochron came to be called the *geochron*.

According to Dalrymple91, the best estimate for **the age of the Earth is 4.54 Ga**, a value which is “based on a single-stage model for the evolution of lead isotopes in the Earth using data from a few ancient lead ores and from one special iron meteorite, Canyon Diablo.”²³ (This is the asteroid/meteoroid whose impact formed “Meteor Crater” in Arizona.)

The USGS states in 2007: “The ages measured for Earth's oldest rocks and oldest crystals show that the Earth is at least 4.3 billion years in age but do not reveal the exact age of Earth's formation. The best age for the Earth (4.54 Ga) is based on old, presumed single-stage leads coupled with the Pb ratios in troilite from iron meteorites, specifically the Canyon Diablo meteorite. In addition, mineral grains (zircon) with U-Pb ages of 4.4 Ga have recently been reported from sedimentary rocks in west-central Australia.”²⁴

The oldest moon rocks have been found to have similar ages, and Dalrymple91 concludes, “The radiometric data, including both rock and model ages, show clearly that **the Moon is at least 4.5 Ga in age.**”²⁵ The

²⁰ Dalrymple91 p. 119 – 121.

²¹ Pb-Pb dating equations:

• Dalrymple91 p. 120

• http://en.wikipedia.org/wiki/Lead-lead_dating [source of equations images]

²² Patterson C. “Age of meteorites and the earth” *Geochimica et Cosmochimica Acta*. Volume 10, Issue 4, October 1956, Pages 230-237

See also extensive discussion in Dalrymple91, Chapters 4, 5, 6, and 7.

²³ Dalrymple91 p. 356

²⁴ <http://pubs.usgs.gov/gip/geotime/age.html>

²⁵ Dalrymple91 p. 119 – 121.

USGS states, “the oldest dated moon rocks, however, have ages **between 4.4 and 4.5 [Ga]** and provide a minimum age for the formation of our nearest planetary neighbor. Thousands of meteorites, which are fragments of asteroids that fall to Earth, have been recovered. These primitive objects provide the best ages for the time of formation of the Solar System. There are more than 70 meteorites, of different types, whose ages have been measured using radiometric dating techniques. The results show that **the meteorites, and therefore the Solar System, formed between 4.53 and 4.58 [Ga] ago.**”²⁶

These ages are of course in harmony with the “current calculations of 11 to 13 [Ga] for the age of the Milky Way Galaxy (based on the stage of evolution of globular cluster stars) and the age of 10 to 15 [Ga] for the age of the Universe (based on the recession of distant galaxies)”.²⁷

Uranium–thorium and other disequilibrium intermediate radioisotope daughter dating

When a decay chain is involved, such as with ^{238}U , the kinetics governing the buildup and decay of the various intermediate radioactive daughter isotopes (e.g., $^{234}\text{U} \rightarrow ^{230}\text{Th}$, $^{222}\text{Rn} \rightarrow ^{218}\text{Po}$, or $^{210}\text{Pb} \rightarrow ^{210}\text{Po}$) are described by the *Bateman's equations*²⁸. Although there is no true equilibrium when unstable daughters are being measured (thus a “disequilibrium” or “dysequilibrium” is present), the system may for a time manifest a *transient equilibrium* or a *secular equilibrium*. (When the daughter has a longer half-life than the parent, there may be no equilibrium of any type.)

A *secular equilibrium* exists when the quantity of a [daughter] radioactive isotope remains constant over a period of time because its production rate (from decay of a long-lived parent isotope) is equal to its own decay rate.²⁹ When a state of equilibrium is reached, the activity of the radioactive daughter is determined by the activity of the parent. “For practical purposes, saturation [maximum activity of the daughter] is reached in approximately five half-lives [of the parent] when the activity [of the daughter] is more than 96% of the saturation value.”³⁰

A *transient equilibrium* exists when a temporary equilibrium-like state is reached by a parent–daughter radioisotope pair for which the half-life of the parent is only a little more or a few times longer than the half-life of the daughter. The activity of the daughter (in Bq) exceeds somewhat the activity of the parent during the period of transient equilibrium, and the daughter appears to decay with the half-life of the parent, as does the total activity (from decay of daughter + parent). A well-known example of transient equilibrium is the ^{99}Mo generator (^{99}Mo has $t_{1/2} = 67$ hours), which produces $^{99\text{m}}\text{Tc}$ ($^{99\text{m}}\text{Tc}$ is metastable and has $t_{1/2} = 6$ hours) for nuclear medicine diagnostic procedures. Such a generator is sometimes called a *cow* because the daughter $^{99\text{m}}\text{Tc}$ is milked at regular intervals.³¹ (I made extensive use of generator-produced $^{99\text{m}}\text{Tc}$ as a nuclear medicine physician.)

Corals may be dated with the $^{238}\text{U} \rightarrow ^{234}\text{Th} \rightarrow ^{234}\text{U} \rightarrow ^{230}\text{Th}$ *disequilibrium method*. This method makes use of the fact that U is highly soluble and persistent in sea water, whereas Th is rapidly scavenged by adsorption or other processes binding it to sinking (precipitating) particles, and therefore it virtually completely precipitates to the ocean floor sediment³². (The excess ^{230}Th in sediment is termed “parentless” because it formed in seawater from a parent that is not also precipitated in the sediment. The rate of sedimentation of excess or parentless ^{230}Th has been quite constant over the last 300 ka, according to a graph provided by JOS and derived from data of Mangini 1986.) ^{234}U is readily incorporated into coral aragonite (a form of CaCO_3) as a calcium substitute in the same ratio as that of $^{234}\text{U}/\text{Ca}$ in sea water. Aragonites formed by corals are assumed to be essentially ^{230}Th -free at formation, but ^{230}Th accumulates in the coral's aragonite crystals from ^{234}U decay and cannot escape the crystal structure. Coral dating with this method can be used as far back as

²⁶ <http://pubs.usgs.gov/gip/geotime/age.html>

²⁷ *ibid.*

²⁸ Cetnar J. “General solution of Bateman equations for nuclear transmutations” *Annals of Nuclear Energy*. Volume 33, Issue 7, May 2006, Pages 640–645

²⁹ http://en.wikipedia.org/wiki/Secular_equilibrium

³⁰ <http://www.sprawls.org/ppmi2/RADIOACT/#Secular%20Equilibrium>

³¹ Transient equilibrium of radioisotopes:

• http://en.wikipedia.org/wiki/Transient_equilibrium and

• <http://www.sprawls.org/ppmi2/RADIOACT/#Transient%20Equilibrium>

³² Santschi PH, et al “Thorium speciation in seawater”. *Marine Chemistry* 100 (2006) 250–268.

<http://ocean.otr.usm.edu/~w607661/.../2006/Santschi%20et%20al%202006.pdf>

about 400 ka³³, limited ultimately by the half-life³⁴ of the radioactive daughter ²³⁰Th of 75,400 y. The calibration of the radiocarbon curve (calendar age vs. conventional age) has been extended for ages older than the oldest for which dendrochronology applies (thus extending at least to 15 – 20 ka and possibly beyond 30 ka) by means of corals dated with this technique. (See here³⁵ for example.) This technique has also been applied to speleothems such as stalactites and stalagmites.

Rubidium-strontium dating using the isochron technique

This method³⁶ is based on the beta (negatron) decay of rubidium-87 (⁸⁷₃₇Rb, Z=37) to strontium-87 (⁸⁷₃₈Sr, Z=38). This natural radioisotope has a very long half-life of 48.8x10⁹ (or 48.1 Ga³⁷ or 47.5 Ga³⁸) and with $\lambda = 1.42 \times 10^{-11} \text{ y}^{-1}$ (a value corresponding with 48.8 y and adopted by international convention but needing revision³⁹). “This scheme is used to date old igneous and metamorphic rocks, and has also been used to date lunar samples. Closure temperatures are so high that they are not a concern. Rubidium-strontium dating is not as precise as the uranium-lead method, with errors of 30 to 50 million years for a 3-billion-year-old sample.”⁴⁰

The isotopes of Rb include ⁸⁵Rb (72.17%, stable) and ⁸⁷Rb (27.835%⁴¹, radioactive). The stable isotopes of Sr include ⁸⁴Sr (0.56%), ⁸⁶Sr (9.87%), ⁸⁷Sr (7.04%), and ⁸⁸Sr (82.53%). Most rocks contain daughter ⁸⁷Sr from the outset. Rb is an *alkali metal* in Group I (1)⁴² of the periodic table (a group which includes lithium (Li), sodium (Na), potassium (K), rubidium (Rb), cesium (Cs), and francium (Fr)). It is substituted for Na and K as a trace element in many minerals and rocks. Sr is a *alkaline earth metal* in Group IIA (2)⁴³ of the periodic table, a group which includes beryllium (Be), magnesium (Mg), calcium (Ca), strontium (Sr), barium (Ba) and radium (Ra). It is also found in trace amounts, substituting for Ca.

Because it is rare for rocks to lack Sr on formation, it is not generally possible to apply the simple decay equation to computing ages with Rb-Sr. Instead, the isochron⁴⁴ method is required. This technique, in the right circumstances, circumvents the problem of not knowing the initial daughter amount, and also provides a self-check for determining whether the specimens tested are likely to have the same age. It is used on a “suite” of minerals of different mineral composition derived from whole-rock specimens assumed to be cogenetic (having arisen at the same time). The key to this technique is the normalization of values or parent ⁸⁷Rb and radiogenic daughter ⁸⁷Sr with respect to the stable non-radiogenic isotope ⁸⁶Sr, which has an abundance roughly similar to ⁸⁷Sr. The assumption is that ⁸⁷Sr/⁸⁶Sr will be the same for all starting samples of the cogenetic specimens. The ratio of ⁸⁷Sr/⁸⁶Sr at the starting time $t = 0$ (rock/mineral formation) is therefore assumed to be constant. (If this assumption proves to be invalid, this fact will become apparent.)

A plot of ⁸⁷Sr/⁸⁶Sr plotted against ⁸⁷Rb/⁸⁶Sr for the multiple specimens ideally will yield points falling on a straight line on regression fitting. The theoretical formula is

$$\left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)_t = \left(\frac{{}^{87}\text{Sr}}{{}^{86}\text{Sr}}\right)_0 + (e^{\lambda t} - 1) \left(\frac{{}^{87}\text{Rb}}{{}^{86}\text{Sr}}\right)_t$$

which has the form of a linear equation, $y = b + mx$.

³³ http://en.wikipedia.org/wiki/Uranium-thorium_dating

³⁴ <http://www.nndc.bnl.gov/chart/chartNuc.jsp>

³⁵ Yokoyama Y et al. “Last Ice Age millennial scale climate changes recorded in Huon Peninsula Corals”. Radiocarbon, Vol 42, Nr 3, 2000, p 383–401.

³⁶ Faure05 p. 75 ff; Dalrymple91 p. 102 ff.

³⁷ <http://www.nndc.bnl.gov/chart/chartNuc.jsp>

³⁸ <http://atom.kaeri.re.kr/ton/nuc3.html>

³⁹ Dickin AP *Radioisotope Geology 2nd Ed.*, 2005, p. 43

⁴⁰ http://en.wikipedia.org/wiki/Radiometric_dating

⁴¹ <http://atom.kaeri.re.kr/ton/nuc3.html>

⁴² http://en.wikipedia.org/wiki/Alkali_metal

⁴³ http://en.wikipedia.org/wiki/Alkaline_earth_metal

⁴⁴ • Dalrymple91 p. 102 ff.

• <http://www.talkorigins.org/faqs/isochron-dating.html>

This line is called an *isochron* because its points represent specimens all arising at the same time and place. Similar “simple” isochrons are also used for Sm-Nd⁴⁵ (Samarium and Neodymium), ¹⁷⁶Lu-¹⁷⁶Hf (Lutetium and Hafnium), and ¹⁸⁷Re-¹⁸⁷Os⁴⁶ (Rhenium and Osmium) dating systems. “Points that fall on an isochron, therefore, can confidently be interpreted as indicating the time of last isotopic homogenization.” (Dalrymple91 p. 108) The slope of this line is ($e^{\lambda t} - 1$) so that the age t can be readily derived from the slope. The steeper the slope, the older the specimens.⁴⁷ The intercept on the ordinate axis gives the relative starting daughter amount ⁸⁷Sr/⁸⁶Sr. If the points do not lie on a straight line, the specimens are not cogenetic or have not been closed but instead have been “disturbed” by partial melting, migration, etc., and a single age determination does not apply.

A Rb-Sr isochron diagram shown by JOS comes from a 1982 article⁴⁸ by Minster et al. It is for whole-rock chondrites⁴⁹ (meteorites), and demonstrates consistent ages of about 4498±15 Ma. The authors note the possibility of remaining uncertainty in the decay constant λ for ⁸⁷Rb, a revision of which would be needed to match the dating provided by U-Th-Pb methods (4555 Ma).

Potassium-argon and argon-argon dating methods

⁴⁰K – ⁴⁰Ar Method: Potassium-40 (⁴⁰₁₉K) is a long-lived natural radioisotope, and has a natural abundance of about 0.01% of overall K. Its overall half-life is 1.277x10⁹ years⁵⁰ (or 1.248x10⁹ y⁵¹), with an overall (combined) $\lambda_{\text{tot}} = \lambda_{\text{ec}} + \lambda_{\beta^-} = 5.54 \times 10^{-10} \text{ y}^{-1}$. Dating using this isotope is applicable to the oldest rocks. “Radioactive ⁴⁰K is common in micas, feldspars, and hornblendes, though the closure temperature is fairly low in these materials, about 125°C (mica) to 450°C (hornblende).”⁵² Radioactive ⁴⁰K has decay branches to ⁴⁰₁₈Ar (via electron capture, branch ratio=10.72% or 10.48%, $\lambda_{\text{ec}} = 0.581 \times 10^{-10} \text{ y}^{-1}$, and ⁴⁰₂₀Ca (via negatron beta decay, branch ratio=89.28% or 89.52%, $\lambda_{\beta^-} = 4.962 \times 10^{-10} \text{ y}^{-1}$).^{53 54} The Ca branch is not used because of the natural abundance of this isotope.

To a first approximation, the age of the rock, assuming that there was no initial ⁴⁰Ar, may be calculated⁵⁵ as

$$T = \left\{ \frac{1}{(\lambda_{\text{ec}} + \lambda_{\beta^-})} \right\} \ln \left\{ \left(\frac{{}^{40}\text{Ar}}{{}^{40}\text{K}} \right) \times \left(\frac{\lambda_{\text{ec}} + \lambda_{\beta^-}}{\lambda_{\text{ec}}} \right) + 1 \right\}$$

where T = age of specimen in years since it was last melted

⁴⁰K = parent ⁴⁰K remaining in the specimen

⁴⁰Ar = daughter (radiogenic) ⁴⁰Ar present in specimen

λ_{ec} = decay constant for electron capture branch to ⁴⁰₁₈Ar

λ_{β^-} = decay constant for beta decay branch to ⁴⁰₂₀Ca

⁴⁵ http://en.wikipedia.org/wiki/Samarium-neodymium_dating

⁴⁶ http://en.wikipedia.org/wiki/Rhenium-osmium_dating

⁴⁷ <http://www.talkorigins.org/faqs/isochron-dating/AnimatedIsochron.html> (a good animated demo)

⁴⁸ Minster J-F, et al. “Absolute age of formation of chondrites studied by the ⁸⁷Rb-⁸⁷Sr method”. *Nature* 300, 414 - 419 (02 December 1982)

“The ⁸⁷Rb-⁸⁷Sr isochrons for H-, E- and LL-, chondrites are undistinguishable from each other. The joint isochron yields an age of 4,498±15 Myr if the rubidium decay constant λ ⁸⁷Rb=1.42x10⁻¹¹ y⁻¹, and a strontium initial ratio ⁸⁷Rb/⁸⁷Sr = 0.69885±0.00010. For the age to agree with U-Th-Pb data, λ ⁸⁷Rb would have to be changed to 1.402±0.008x10⁻¹¹ yr⁻¹”

⁴⁹ <http://en.wikipedia.org/wiki/Chondrite>

⁵⁰ <http://atom.kaeri.re.kr/ton/nuc3.html>

⁵¹ <http://www.nndc.bnl.gov/chart/reCenter.jsp?z=19&n=21>

⁵² http://en.wikipedia.org/wiki/Radiometric_dating

⁵³ • <http://www.nndc.bnl.gov/chart/chartNuc.jsp> for branch ratios

• Dalrymple91 p. 80 for λ ⁴⁰K

⁵⁴ <http://adsabs.harvard.edu/abs/2008AGUFM.V13A2097J>

⁵⁵ Dalrymple91 p. 93

This simplifies to⁵⁶

$$T = \{1.804 \times 10^9\} \ln \left\{ \frac{{}^{40}\text{Ar}}{{}^{40}\text{K}} + 1 \right\}$$

A correction must be made for atmospheric argon present.

This technique assumes a closed system (no daughter ${}^{40}\text{Ar}$ escapes and none has entered the rock), no fractionation of K isotopes has occurred except by radioactive decay, etc. These assumptions may not always prove valid.⁵⁷ The requirement to make separate chemical measurements of K and Ar lead to accuracy and precision of no greater than $\pm 1\%$.

${}^{40}\text{Ar} - {}^{39}\text{Ar}$ Method: The “argon-argon” or ${}^{40}\text{Ar} - {}^{39}\text{Ar}$ method⁵⁸ has largely supplanted the original ${}^{40}\text{K} - {}^{40}\text{Ar}$ method, although it requires a reactor and accelerator mass spectrometry (AMS). The specimens are irradiated with fast neutrons in a reactor (along with a known “monitor” sample simultaneously irradiated under the same conditions). This converts some of the commonest stable potassium, ${}^{39}\text{K}$ (abundance 93.26%), to a “spike” of the relatively short-lived radioisotope, ${}^{39}\text{Ar}$ (half-life = 269 y). The AMS technique employed ignores K (obviating a splitting of the specimen into separate chemical analytic pathways) and measures only argon isotopes, namely ${}^{36}\text{Ar}$, ${}^{39}\text{Ar}$, and ${}^{40}\text{Ar}$. After applying multiple complex corrections for atmospheric Ar and reactor-produced contaminants, the ${}^{39}\text{Ar}$ somehow serves as a proxy for ${}^{40}\text{K}$, and an isochron (correlation diagram) can be obtained by plotting ${}^{40}\text{Ar}/{}^{36}\text{Ar}$ against ${}^{39}\text{Ar}/{}^{36}\text{Ar}$. The various specimens will fall along the isochron if the specimens are cogenetic and have been closed and not disturbed by excessive heating since formation.

The age of the specimens may be derived from the slope of this isochron, using

$$T (y) = 1.804 \times 10^9 \ln \left(J \times \frac{{}^{40}\text{Ar}}{{}^{39}\text{Ar}} + 1 \right)$$

where J = an empirical constant (“neutron flux parameter”) determined by reactor geometry etc. and analysis of the known “monitor” sample.

Note that the slope of the isochron is proportional to $\frac{{}^{40}\text{Ar}}{{}^{39}\text{Ar}}$.

This method is much more accurate and precise than the original ${}^{40}\text{K} - {}^{40}\text{Ar}$ method, and can be used with smaller samples (nanogram amounts of ${}^{40}\text{Ar}$), even of recent age.

Thermal Geochronology: Another advantage of ${}^{40}\text{Ar} - {}^{39}\text{Ar}$ dating is the ability to measure argon evolved while heating at progressively higher specimen temperatures. This can be performed in a furnace or by lasers, the latter allowing the testing of very small sample regions. The individual ages from each heating step are then graphically plotted on an age spectrum or an isochron. Rocks or specimens that have not been disturbed or contaminated (often mineral components with higher melting points) fall along the isochron, whereas those with lower melting points may not. The least disturbed portion of specimens may be found in the interior of crystals, from which Ar has had the least opportunity to escape or enter. This technique is useful for deducing the time course of metamorphic and igneous rocks. For example,

“Laser incremental heating of sanidine [a high temperature form of potassium feldspar] from the pumice deposited by the Plinian eruption of Vesuvius in 79 A.D. yielded a ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ isochron age of 1925 ± 94 years ago. Close agreement with the Gregorian calendar-based age of 1918 years ago demonstrates that the ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ method can be reliably extended into the temporal range of recorded history. Excess ${}^{40}\text{Ar}$ is present in the sanidine in concentrations that would cause significant errors if ignored in dating Holocene samples.”⁵⁹

⁵⁶ Dalrymple 91 p. 93

⁵⁷ <http://geoinfo.nmt.edu/labs/argon/methods/home.html>

⁵⁸ http://en.wikipedia.org/wiki/Argon%E2%80%9339argon_dating

⁵⁹ P. R. Renne, et al. “Calibration Against Pliny the Younger ${}^{40}\text{Ar}/{}^{39}\text{Ar}$ Dating into the Historical Realm” *Science* 277, 1279 (1997)

The history of metamorphism in the Himalayan convergence zone⁶⁰ has been reconstructed using this type of dating (so-called *Argon Age Spectrum* analysis) combined with ⁸⁷Rb-⁸⁷Sr dating. This analysis makes use of the formation and metamorphism of various K-containing minerals at differing temperatures and pressures, such as biotite, potassium feldspar, muscovite, and amphibole. The K is substituted for by Rb... (I am regrettably hampered by a lack of experience in mineralogy and cannot discuss this in any detail.)

Dating of the ancient meteorite Menow is illustrated by Dalrymple⁹¹ p. 114 using the Argon Age Spectrum. Some of this meteorite's components were disturbed and partially lost their argon at about 2.5 Ga, but a plateau of higher Argon content is seen in the argon age spectrum released at highest temperatures, yielding an age of 4.48 Ga.

See further comments pertaining to Thermal Geochronology by using fission tracks below.

Radiocarbon (¹⁴C) dating

Introduction: ¹⁴C is continuously created in the upper atmosphere through collisions of thermal neutrons with nitrogen [¹⁴N]. These neutrons are most abundant at altitudes of 9 to 15 km.⁶¹ They arise as spallation products by cosmic rays (charged particles) impacting primarily on N and O nuclei, causing an "air shower" of lighter particles including neutrons. The ¹⁴C ends up in atmospheric carbon dioxide (¹⁴CO₂), where it makes up typically only 1 part per trillion of the total carbon⁶².

The atmospheric CO₂ equilibrates with surface water in lakes and oceans, but other reservoirs of carbon may be depleted to varying degrees in ¹⁴C.

Plants acquire ¹⁴C through incorporation of ¹⁴CO₂ during photosynthesis, and animals acquire it from consumption of these plants and animals that have eaten plants. When an organism dies, it ceases taking in any more ¹⁴C, and the existing ¹⁴C decays with a half-life of 5730 years ± 40 y. The proportion of ¹⁴C left when the remains of the organism are examined provides an indication of the time elapsed since its death. The ¹⁴C dating limit lies around ~50 ka according to JOS—somewhat less than 10 half-lives.

The method makes several assumptions, several of which require modification for optimal calibration. The rate of creation of atmospheric ¹⁴C is only to a first approximation constant—it has in fact varied, especially according to the intensity of solar wind and therefore of lower energy cosmic ray impacts. Local eruptions of volcanoes or other events that give off large amounts of carbon dioxide can dilute and reduce local concentrations of ¹⁴C. The releases of fossil carbon dioxide into the biosphere as a consequence of industrialization and fossil fuel burning have also depressed the proportion of ¹⁴C by a few percent (see Suess effect, below). In addition the amount of ¹⁴C was increased substantially by above-ground nuclear bomb tests that were conducted from 1945 until the early 1960s.⁶³

To reduce the impact of contamination of specimens by recent ¹⁴C, etc., it is preferable to extract and count the ¹⁴C of specific stable molecules (such as *cellulose* and the bone protein *osteocalcin*) from the specimen, rather than counting bulk specimens containing unstable or contaminated molecules (such as bone hydroxyapatite and collagen, etc.) (JOS; Faure⁰⁵ p. 625) Some structures such as coral reefs are particularly difficult to date.

Conventional ¹⁴C age = ¹⁴C BP: Carbon-14 [¹⁴C] has a true half-life of **5,730 years** ± 40 y, equivalent to a decay constant $\lambda = 1.209 \times 10^{-4} \text{ y}^{-1}$. The true *specific activity* of pure ¹⁴C is 4460 mCi/g, but the specific activity of natural carbon (including stable isotopes ¹²C and ¹³C) is assumed for conventional dating to be **13.6 dpm per g**. (This is the 1950 value utilized by Libby.) The value 13.6 dpm per g translates to 0.227 dps [becquerel or Bq] or 6.126×10^{-9} mCi per g. The ¹⁴C content is currently best measured by accelerator mass spectroscopy (AMS, also called tandem accelerator mass spectroscopy) but originally was measured by counting of radioactive decays in an ionization chamber or liquid scintillation detector. The AMS techniques improve sensitivity by a factor of 1000 or so compared to decay counting, and are widely employed now to quantitate

⁶⁰ Robinson DM et al. "Tectonic evolution of the Himalayan thrust belt in western Nepal: Implications for channel flow models". *Geological Society of America Bulletin* July 2006 v. 118 no. 7-8 p. 865-885. This is given as an example, but I have not read this complex article in any detail.

⁶¹ http://en.wikipedia.org/wiki/Radiocarbon_dating

⁶² <http://en.wikipedia.org/wiki/Carbon-14>

⁶³ http://en.wikipedia.org/wiki/Radiocarbon_dating

trace quantities of many radioactive and stable isotopes. According to Stuiver and Polach 1977⁶⁴, by convention, the original Libby half-life of **5568 y** (having decay constant $\lambda = 1.244 \times 10^{-4}$) is used to create a “conventional radiocarbon age” expressed in years before the present (BP, adjusted so that the “present” is 1950). The sample activity $A_{\text{SN:1950}}$ is compared to the activity of the absolute international standard $A_{\text{ON:1950}}$ (derived from an oxalic acid standard), both of which have been normalized to 1950 and for the relative quantity or fractionation of ^{13}C (expressed as $\delta^{13}\text{C}$). The conventional age t (^{14}C BP, in years before 1950) is given from these quantities by

$$t = -8033 \ln(A_{\text{SN:1950}} / A_{\text{ON:1950}})$$

Calibrated ^{14}C age = cal BP: This *conventional radiocarbon age* must be calibrated against a correction curve based on tree ring dating (dendrochronology) or, for older ages, dating by other means using marine corals and sediments, etc.⁶⁵ For ages greater than a few hundred years, the correction for wood yields calibrated dates (“cal BP”) that are older than the conventional age (“ ^{14}C BP”). For example, a sample of wood that has conventional age ^{14}C BP = 11,500 years has a cal BP \approx 13,300 y⁶⁶. This suggests that the atmospheric ^{14}C activity (at the time of “growth” of the source tree) was higher than the current value, thus making the sample appear younger. This discrepancy is said to arise from a variety of geophysical and astronomical causes⁶⁷.

Solar activity effect on ^{14}C production: The production of ^{14}C is related to solar activity and cosmic ray bombardment. Increased solar activity and solar wind results in a reduction of lower energy cosmic rays reaching the earth's atmosphere and reduces ^{14}C production. The overall *cosmic ray intensity and resulting ^{14}C production vary inversely* with respect to the general level of solar activity. The atmospheric ^{14}C concentration is lower during sunspot maxima and higher during sunspot minima. “A reconstruction of the past 10,000 years shows that the ^{14}C production [in tree rings] was much higher during the mid-Holocene 7,000 years ago and decreased until 1,000 years ago. In addition to variations in solar activity, the long term trends in ^{14}C production are influenced by changes in the Earth's geomagnetic field and by changes in carbon cycling within the biosphere (particularly those associated with changes in the extent of vegetation since the last ice age).”⁶⁸ The period of the *Maunder Minimum* (about 1645 – 1715 CE) was a prolonged sunspot minimum accompanied by increased ^{14}C production, yielding low conventional ^{14}C BP ages.

Adjustment of cal BP for reservoirs and/or age:⁶⁹ The $\delta^{14}\text{C}$ for a sample is the ratio of the *age-corrected* sample activity to the *absolute international standard activity*, minus 1, all times 1000. Like $\delta^{13}\text{C}$, this ratio is expressed in parts per mil (‰, also spelled *per mille* or *permil*), rather than in years. The age correction includes a term x for the year of growth, which is the unknown in geochronological dating and therefore confusing.

The quantity $\Delta^{14}\text{C}$, as defined in Stuiver 1977, is also reported in parts per mil (‰), and adjusts $\delta^{14}\text{C}$ for $\delta^{13}\text{C}$ to a standard level. Although the terminology and uses of these adjustments remain quite confusing to me, and I don't claim to have mastered this remarkably complex topic, $\Delta^{14}\text{C}$ is apparently used to adjust cal BP for varying fractionations of ^{14}C arising at various site-specific or regional “reservoirs”. Examples include certain marine environments, which may be relatively depleted of ^{14}C due to deep currents (see below). Examples of corrections for site-specific reservoirs are presented in INTCAL09 Table 1⁷⁰, INTCAL04 Table 1⁷¹, and INTCAL98 fig. 2⁷², etc.

⁶⁴ Stuiver M and Polach HA. “Reporting Of ^{14}C Data” *Radiocarbon*, Vol. 19, No. 3, 1977, P. 355-363 <http://www.radiocarbon.org/Pubs/Stuiver/Stuiver-Polach.pdf>. Hereafter called Stuiver 1977.

⁶⁵ JOS; Wikipedia; Faure05; INTCAL98; INTCAL04; INTCAL09; etc.

⁶⁶ Reimer PJ et al, “INTCAL09 and MARINE09 Radiocarbon Age Calibration Curves, 0–50,000 Years Cal BP” *Radiocarbon*, Vol 51, Nr 4, 2009, p 1111–1150. Hereafter called “INTCAL09”.

⁶⁷ Faure05 p. 618

⁶⁸ http://en.wikipedia.org/wiki/Solar_variation

⁶⁹ Stuiver 1977

⁷⁰ Reimer PJ et al, “INTCAL09 and MARINE09 Radiocarbon Age Calibration Curves, 0–50,000 Years Cal BP” *Radiocarbon*, Vol 51, Nr 4, 2009, p 1111–1150. Hereafter called “INTCAL09”

⁷¹ Reimer PJ et al. “Intcal04 Terrestrial Radiocarbon Age Calibration, 0–26 Cal Kyr BP”. *Radiocarbon*, Vol 46, Nr 3, 2004, p 1029–1058. Hereafter called “INTCAL04”

⁷² Stuiver M et al, “INTCAL98 Radiocarbon Age Calibration, 24,000-0 cal BP 1998” *Radiocarbon*, VOL. 40, No. 3, 1998, P.1041-1083. Hereafter called INTCAL98. Download at

Figure 4 in INTCAL09⁷³ (see graph to follow) appears to show a general or “international” $\Delta^{14}\text{C}$ value for age-correction applying to the range 0 – 50,000 ^{14}C BP. I have not yet determined whether or how one can derive cal BP from this $\Delta^{14}\text{C}$ and the conventional ^{14}C BP. The INTCAL09 data graphed in figure 4 combines terrestrial (tree ring) and marine data. The Marine04⁷⁴ data set deals specifically with marine reservoirs.

Because the calibration curves are not uniformly monotonic, a single value of conventional ^{14}C BP may correspond to several cal BP ages, yielding a wider than usual error range in the cal BP. This applies for instance to the cal BP age determination for the cold climate period termed the *Younger Dryas*, which dates to 12,900-11,500 cal BP.⁷⁵

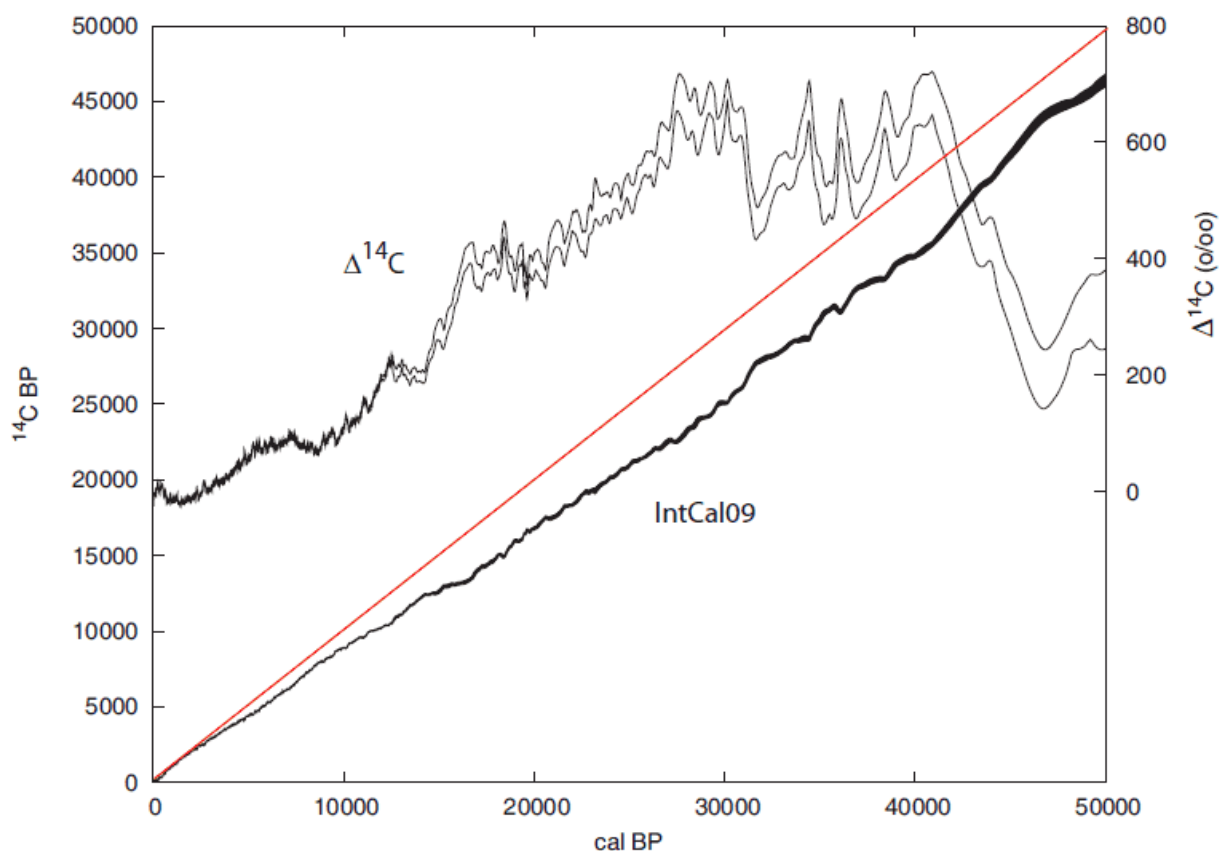


Figure 4 IntCal09 calibration curve and age-corrected $\Delta^{14}\text{C}$ (‰) with 1-standard deviation envelopes

Red line (added by MCM) is the line of identity between conventional ^{14}C BP and cal BP.

Calibrated cal BP's are mostly greater than conventional ^{14}C BP's⁷⁶

Isotope ^{13}C – ^{12}C fractionation standard: The standard of comparison used in computing $\delta^{13}\text{C}$ is the level of ^{13}C in PDB=*Peedee Belemnite* carbon. Belemnite refers to an extinct cephalopod. Their bullet-shaped “guards” are made of carbon-containing calcite. These were deposited in great numbers in the Peedee Formation, a Late Cretaceous marine deposit in South Carolina.⁷⁷ The original fossil-derived standard has

http://digitalcommons.library.arizona.edu/objectviewer?o=http%3A%2F%2Fradiocarbon.library.arizona.edu%2FVolume40%2FNumber3%2Fazu_radiocarbon_v40_n3_1041_1083_v.pdf

⁷³ INTCAL09 p. 1139

⁷⁴ Hughen KA et al. “MARINE04 Marine Radiocarbon Age Calibration, 0–26 Cal Kyr BP”. *Radiocarbon*, Vol 46, Nr 3, 2004, p 1059–1086. Hereafter called MARINE04.

⁷⁵ http://en.wikipedia.org/wiki/Younger_Dryas

⁷⁶ INTCAL p. 1139, modified by MCM.

⁷⁷ Stable Carbon 13 Ratio, $\delta^{13}\text{C}$, PDB (Vienna VPDB), Belemnites, etc.:

• Vienna Pee Dee Belemnite (VPDB, the secondary standard) has value of $^{13}\text{C}/^{12}\text{C} = R = 0.0112372$. This is

been supplanted by the synthetic Vienna PDB standard (VPDB) because of fossil depletion. The typical abundance of ^{13}C is 1.1% compared to 98.9% for ^{12}C . Stuiver 1977 states, "It is strongly desirable that all workers report $\delta^{13}\text{C}$ values, either measured or estimated relative to PDB. By convention, the ^{13}C isotopic fractionation in all samples, irrespective of environment, is taken into account by normalizing to -25 per mil [‰] with respect to PDB, the postulated mean value of terrestrial wood"⁷⁸. He provides a formula⁷⁹ for the sample activity normalized to this $\delta^{13}\text{C}$. I believe this process is intended to compensate for the relative depletion by fractionation of ^{14}C , which is expected to be twice as great as that of ^{13}C —this adjustment typically makes the estimated age older.⁸⁰

Plant and animals *fractionate* (take up at different rates) the naturally occurring carbon isotopes, namely ^{12}C , ^{13}C , and ^{14}C . Terrestrial plants that use the C4 photosynthetic pathway discriminate less than terrestrial C3 photosynthetic plants, thus C4 plants have less negative (less ^{13}C -depleted) $\delta^{13}\text{C}$. (CAM photosynthetic plants have a wider range of $\delta^{13}\text{C}$ values.) Typical $\delta^{13}\text{C}$ values (relative to PDB) are as follows (see multiple footnote references, plus Faure05 p. 620):

C3 plants	-21‰ to -35‰ (includes most common garden plants, potatoes, wheat)
C4 plants	-10‰ to -14‰ (includes corn, sugar cane, grasses, Brassicaceae)
CAM plants	-10 to -31‰ (Cacti, succulents, etc.)
Eukaryotic algae	-10‰ to -25 ‰ (Faure05 p. 755, visual estimated from graph)
Peat and humus	-21‰ to -35‰
Coal ⁸¹	-23 to -25‰ (derived from C3 plant cellulose per Faure05 p. 762)
Petroleum	-18 to -34‰ (derives from lipid fraction unlike coal, per Faure05 p. 762)
Marine organic matter	-18 to -22‰
Collagen from bone	-18 to -20‰
Marine calcite (precipitated)	+2 to -2‰
CO ₂ atmospheric	-7 to -9‰
PDB standard	+0‰ by definition

Suess effect: The Suess effect is a change, usually a decrease, in the ratio of the atmospheric concentrations of the heavier naturally occurring isotopes of carbon (^{13}C and ^{14}C) by the admixture of large amounts of CO₂

defined as the standard for which $\delta^{13}\text{C} = 0$ ‰. "Materials with ratios of $^{13}\text{C}/^{12}\text{C} > 0.0112372$ have positive delta [$\delta^{13}\text{C}$] values, and those with ratios of $^{13}\text{C}/^{12}\text{C} < 0.0112372$ have negative delta values." [with MCM corrections]

<http://www4.nau.edu/cpsil/isotopes.htm>

Plant discrimination affecting $\delta^{13}\text{C}$:

- "The standard established for carbon-13 work was the Pee Dee Belemnite or (PDB) and was based on a Cretaceous marine fossil, Belemnitella americana, which was from the Pee Dee Formation in South Carolina. This material had an anomalously high $^{13}\text{C}:^{12}\text{C}$ ratio and was established as ^{13}C value of zero [i.e., $\delta^{13}\text{C} = 0$]. Use of this standard gives most natural materials a negative $\delta^{13}\text{C}$. The PDB material has been exhausted and the standard replaced by secondary standards."

<http://en.wikipedia.org/wiki/%CE%9413C>

- "...Terrestrial C4 plants discriminate less than terrestrial C3 plants [thus have less negative or ^{13}C depleted $\delta^{13}\text{C}$], with $\delta^{13}\text{C}$ values [for C4 plants] in the range -10‰ to -14‰ compared to -21‰ to -35‰ for C3 plants... R_{std} [the standard ratio used in the denominator of $\delta^{13}\text{C}$] is the $^{13}\text{C}:^{12}\text{C}$ ratio of the standard, calcium carbonate in a fossil belemnite from the Cretaceous Pee Dee formation with a $^{13}\text{C}:^{12}\text{C}$ ratio of 0.011237."

<http://www.springerlink.com/content/r3v57008n1423740/fulltext.pdf>

Maberly SC et al. "Discrimination between ^{12}C and ^{13}C by marine plants". *Oecologia* (1992) 91 : 481-492. Physiologic mechanism for the greater ^{13}C depletion (more negative $\delta^{13}\text{C}$) by C3 plants compared to C4 or CAM plants:

<http://www.mcgoodwin.net/pages/plantphysuw425.pdf> page 44

Belemnites:

<http://en.wikipedia.org/wiki/Belemnitella>

⁷⁸ Stuiver 1977, p. 356

⁷⁹ Stuiver 1977, p. 362

⁸⁰ Faure05 p. 620

⁸¹ Keogh RA et al "Stable Carbon Isotope Analysis of Products from Coal/Tar Sand Bitumen Coprocessing". *Energy & Fuels* 1991,5,322-327

that is depleted in one or both of these isotopes and that arises from the burning of fossil fuels and deforestation.

¹⁴C Suess Effect: The term *Suess Effect* originally referred only to dilution of atmospheric ¹⁴C (as ¹⁴CO₂), termed the “¹⁴C Suess Effect”, arising from burning fossil fuels. This CO₂ contains no ¹⁴C because of the great age of the fossil fuel. The term was extended to effects on other reservoirs of carbon such as the oceans and soils. The effect is named for the Austrian chemist Hans Suess, who noted its influence on the accuracy of radiocarbon dating.⁸² Incidentally, carbon introduced into the atmosphere by volcanism is depleted in ¹⁴C but has a normal ratio of the stable isotopes.

¹³C Suess Effect: The concept of a Suess Effect was also extended to dilution of ¹³C in atmospheric CO₂ and in other reservoirs of carbon, also by the burning of fossil fuels. Most fossil carbon is relatively depleted in ¹³C because it is derived largely from C3-photosynthetic plants (see footnotes). The atmospheric value of δ¹³C has declined (become more negative) by more than 1.5 – 2‰ to approximately -8‰ compared to the pre-industrial era in the early 18C.⁸³

Ocean currents and deep water reservoirs: It takes up to 1600 years in some locations for water to complete a *thermohaline circulation* cycle⁸⁴ whereby surface ocean water (that starts out equilibrated with atmospheric ¹⁴CO₂) sinks to deep water reservoirs, travels long horizontal distances, and eventually returns to the surface. During this time, the water becomes somewhat ¹⁴C depleted due to radioactive decay, and organisms that live in such depleted zones will also be depleted of ¹⁴C and yield conventional ¹⁴C BP ages that are older than their true age.

Atmospheric nuclear weapons testing: This topic is of interest because it affects ¹⁴C dating and also because nuclear weapons testing has increased human risk from contamination. Weapons testing dramatically increased the δ¹⁴C in both hemispheres. The peak value of δ¹⁴C occurred around the time of the institution of the Partial Test Ban Treaty⁸⁵ (10 Oct. 1963), and since then the value of δ¹⁴C has declined to near but still well above the 1950 value.⁸⁶

⁸² http://en.wikipedia.org/wiki/Suess_effect

⁸³ Verburg P. “The need to correct for the Suess effect in the application of δ¹³C in sediment of autotrophic Lake Tanganyika, as a productivity proxy in the Anthropocene”. *Journal of Paleolimnology*. Volume 37, Number 4 / May, 2007. See p. 599 for the author’s equation for correcting for δ¹³C.

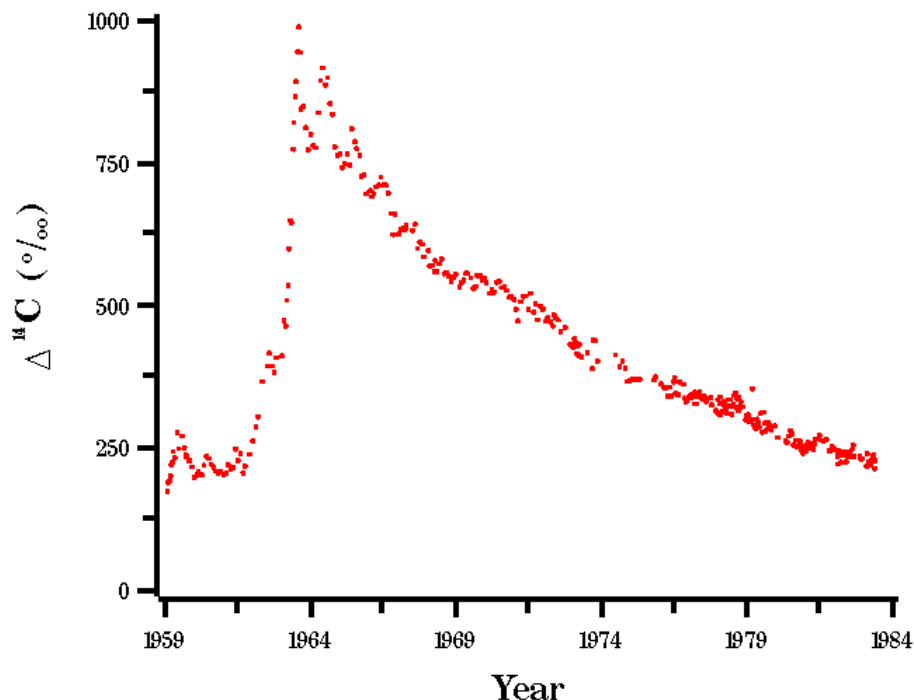
⁸⁴ http://en.wikipedia.org/wiki/Thermohaline_circulation

⁸⁵ http://en.wikipedia.org/wiki/Partial_Test_Ban_Treaty

⁸⁶ Atmospheric Nuclear Testing and ¹⁴C Spike:

- http://en.wikipedia.org/wiki/Carbon-14#Formation_during_nuclear_tests
- http://en.wikipedia.org/wiki/File:Radiocarbon_dating_calibration.svg [graph]
- <http://cdiac.esd.ornl.gov/trends/co2/graphics/cent-vegr.gif> [graph from next URL]
- <http://cdiac.esd.ornl.gov/trends/co2/cent-verm.html>

Vermunt, Austria



Source: I. Levin, B. Kromer, H. Schoch-Fischer, M. Bruns, M. Minnich, D. Berdau, J.C. Vogel, and K.O. Minnich (University of Heidelberg)
<http://cdiac.esd.ornl.gov/trends/co2/cent-verm.html>

Medical radiotoxicity of ^{14}C : ^{14}C has low external radiotoxicity but is an internal hazard.⁸⁷ “Carbon-14 is a weak beta particle emitter, with a low level of activity due to its long half-life. It presents a unique hazard however since, unlike other isotopes, it is incorporated directly into genetic material as a permanent part throughout the body. This means that it presents a hazard out of proportion to the received radiation dose as normally calculated.”⁸⁸

Other radioisotopic dating techniques

The isochron technique is described with Rubidium-strontium dating.

Samarium-neodymium dating method: This involves the alpha-decay of ^{147}Sm to ^{143}Nd with a half life of 1.06×10^{11} years.⁸⁹ http://en.wikipedia.org/wiki/Radiometric_dating%5d

Uranium-thorium dating method: A relatively short-range dating technique is based on the decay of uranium-234 into thorium-230, a substance with a half-life of about 80,000 years. It is accompanied by a sister process, in which uranium-235 decays into protactinium-231, which has a half-life of 34,300 years.

While uranium is water-soluble, thorium and protactinium are not, and so they are selectively precipitated into ocean-floor sediments, from which their ratios are measured.⁹⁰ The scheme has a range of several hundred thousand years.

Thermoluminescence (TL) and optically-stimulated luminescence (OSL) dating

Thermoluminescence (TL) dating: Thermoluminescence is a form of luminescence that is exhibited by certain crystalline materials which have been previously exposed to ionizing radiation. (See also the closely related OSL dating, below.) For geologic dating, the substances evaluated include quartz and feldspar (see

⁸⁷ <http://uq.edu.au/ohs/pdfs/C14datasheet.pdf>

⁸⁸ <http://nuclearweaponarchive.org/Nwfaq/Nfaq5.html#nfaq5.6>

⁸⁹ http://en.wikipedia.org/wiki/Radiometric_dating

⁹⁰ http://en.wikipedia.org/wiki/Radiometric_dating

further discussion under OSL dating). These materials trap energy as excited metastable centers (lattice defects consisting of electrons and holes trapped in the normally forbidden region between the valence and conduction bands) which can be quite stable over time provided the substance is not heated or exposed to light. However, the trapped energy is released from recombination and emitted as light upon heating of the material, allowing quantitation of previous radiation exposure. The amount of luminescence emitted (expressed by the area measured under the “glow curve” detected with a sensitive photomultiplier upon heating typically to 200–400 °C) is proportional to the cumulative dose of radiation received since the last episode of heating.

In thermoluminescence and OSL dating, buried objects such as ceramic pottery that have been heated in the past can be dated, since the ionizing radiation dose received (from radioactive elements, mostly ^{238}U , ^{232}Th , and ^{40}K , as alpha and beta radiation in the specimen and as gamma rays from the nearby soil, or from cosmic rays) is roughly proportional to age. The radiation dosage for geologic specimens may be in the range of 1–2 Gy ka⁻¹ (as illustrated in an example given by JOS).

The age equation is expressed as:

$$\text{Age (ka)} = D_e \text{ (Gy)} / D_R \text{ (Gy/ka)}$$

where D_e is the equivalent dose in grays (1 Gy, a unit of absorbed dose = 1 J/kg = 100 rads), and D_R is the average dose rate over time. The *equivalent dose* is the amount of laboratory radiation dose that is necessary to account for the measured natural luminescence signal. “Luminescence is not as precise as some dating methods, but errors between 5 and 10 percent are commonly obtained.”⁹¹

Thermoluminescence is a common geochronology tool for dating pottery or other fired archeological materials, as heating depletes the metastable centers and thereby “resets” the clock to zero (a process also referred to as “bleaching”). The sensitivity of the particular specimen to radiation may be estimated by laboratory exposure to a known amount of acute radiation, such as 662 keV gamma rays from a ^{137}Cs source. The method involves several uncertainties and potentially confounding factors: spontaneous decay or release of metastable states including from partial heating or exposure to light, nonlinear radiation dose response and saturation of trapping centers, different radiation responses from slow versus rapid irradiation rates, variation in sensitivity of excitation and penetration depth with radiation energy and type, incomplete initial “bleaching”, destructive effects of heating (or optical stimulation), variations in dosage from variations in pore water, etc.⁹²

I had the privilege as a college student of working with early LiF thermoluminescence dosimetry in a radiation therapy research setting.⁹³

Optically stimulated luminescence (OSL) dating: This is closely related to TL, but makes use of focally directed heating of the specimen using infrared, optical, or ultraviolet wavelength exposure, with measurement of the luminescence given off as with TL. The specimen illuminated can be of a much smaller area and volume than with TL, often consisting of individual crystal grains, so that those which are the actual source of the luminescence may be interrogated.

Quartz can be useful to measure, if present in adequate amounts, because of the stability (lack of fading) of its trapping centers. It also tends to be uranium and thorium free, thus lacking intrinsic alpha radiation. The complexity of dealing with the contribution from exogenous alpha radiation can be reduced by etching away the outer 20–30 microns of the grains.

Potassium feldspars have higher luminescence than quartz. They are self-dosing from substantial ^{40}K content, which lacks alpha radiation and reduces the effects of variations in surrounding interstitial water, thus somewhat simplifying dosimetry. In addition, feldspars allow infrared OSL, whereas quartz does not. However, the trapping centers are less stable than quartz. [I have not reviewed in detail the complex and

⁹¹ <http://depts.washington.edu/lumines/aboutluminescence.doc>

⁹² • Course lecture and handouts

• <http://en.wikipedia.org/wiki/Thermoluminescence>

• Shigeo Shionoya and William Yen, ed., *Phosphor handbook*, Phosphor Research Society, 1999

⁹³ Crosby E, Boone M, Almond P, Worsnop BR, McGoodwin MC, and Shalek JR, “Use of Lithium Fluoride Dosimeters for In Vivo Measurement of Transmission Through Bone and Lung”. *Luminescence Dosimetry*, Proc. of Intl. Conf. on Luminescence Dosimetry, Stanford, California June 21-23, 1965, p. 380, publ. April 1967 as *AEC Symposium Series 8*.

somewhat confusing aspects of estimating radiation dosages from various types of radiation in OSL and TL dating.^{94,95]}

The optical stimulation OS may be administered in short pulses, immediately after which the luminescence is measured, or the OS may be administered simultaneously while measuring the stimulated luminescence. In the latter, the luminescence is typically of higher photon energy than the photons used for stimulation, and filters may also be employed to minimize interference. The OSL sensitivity of the specimen to radiation is estimated by experimental exposure, as above.

Fission track dating

This technique is less accurate or misleading for absolute dating compared to other radioisotopic methods above, but is employed especially to determine thermal history (*thermochronology*). It makes use of the occasional spontaneous fission (SF) occurring with natural ^{238}U decay. “The fission-track dating technique is widely used in understanding the thermal evolution of the upper crust, especially in mountain belts.”⁹⁶

“This scheme has application over a wide range of geologic dates. For dates up to a few million years micas, tektites (glass fragments from volcanic eruptions), and meteorites are best used. Older materials can be dated using zircon, apatite, titanite, epidote and garnet which have a variable amount of uranium content. Because the fission tracks are healed by temperatures over about 200°C the technique has limitations as well as benefits. The technique has potential applications for detailing the thermal history of a deposit.”⁹⁷

The fission probability per decay⁹⁸ for ^{238}U is only 5.4×10^{-7} (compared to 7.0×10^{-11} for the much less common ^{235}U) but over long periods of time these decays occur sufficiently often to deposit latent fission tracks along which there is crystal structure disruption from the passage of heavy fission fragments. Typically for these fission fragments, one daughter nucleus has a mass of about 90 to 100 u and the other 130 to 140 u⁹⁹. The analytical process involves sectioning the appropriate crystals, usually zircon or apatite, then etching the surface to make the fission tracks visible, then examining the crystal under a calibrated optical microscope to count track numbers and lengths. The method is quite operator-dependent and subject to observer biases (so a sample standard should also be counted). It is also complicated by the facts that the etchant may not reach tracks that do not extend to the surface of the sectioned crystal, the tracks can have any orientation in the 3-dimensional geometry of the crystals, and the etching response may vary with track orientation in the anisotropic crystal. The counting process has been partially automated in some labs

Typical fission track lengths are 15 – 20 microns or less. Annealing temperatures relax the strains induced by the SF and destroy, shorten, or diminish the conspicuity of the fission tracks. Annealing occurs in apatite at about 120°C , so FT dating is useful in determining when such specimens were last heated to this temperature. JOS showed an example in core samples from a hot sedimentary basin (the Otway Basin in Australia). Tracks in apatite were numerous and of lengths of 15 microns near the surface (never heated, great apparent FT age), whereas at depths of 2000 – 3000 m, the tracks shortened to 4 – 8 microns (and yielded much lower apparent though spurious age determination due to the annealing). Statistical analysis of the distribution of fission track lengths (e.g., sharp peak, peak with tail, and bimodal distributions) can be used to work out the cooling history of specimens.

The method requires knowing the Uranium content. “To determine the uranium content, several methods have been used. One method is by neutron irradiation, where the sample is irradiated with thermal neutrons in a nuclear reactor, with an external detector, such as mica, affixed to the grain surface. The neutron irradiation induces fission of ^{235}U in the sample, and the resulting induced tracks are used to determine the uranium content of the sample because the $^{235}\text{U} : ^{238}\text{U}$ ratio is well known and assumed constant in nature. To determine the number of induced fission events that occurred during neutron irradiation an external detector is attached to the sample and both sample and detector are simultaneously irradiated by thermal

⁹⁴ Wintle AG. “Luminescence dating: laboratory procedures and protocols” *Radiation Measurements*. Volume 27, Issues 5-6, Pages 769-817 (5 December 1997)

⁹⁵ Duller GAT. “Behavioural studies of stimulated luminescence from feldspars” *Radiation Measurements*. Volume 27, Issues 5-6, Pages 663-694 (5 December 1997)

⁹⁶ http://en.wikipedia.org/wiki/Fission_track_dating

⁹⁷ http://en.wikipedia.org/wiki/Radiometric_dating

⁹⁸ http://en.wikipedia.org/wiki/Spontaneous_fission

⁹⁹ http://en.wikipedia.org/wiki/Nuclear_fission

neutrons [in a reactor]. The external detector is typically a low-uranium mica flake, but plastics such as CR-39 [an allyl diglycol carbonate plastic that is sensitive to radiation] have also been used. The resulting induced fission of the ^{235}U in the sample creates induced tracks in the overlying external detector, which are later revealed by chemical etching. The ratio of spontaneous to induced tracks is proportional to the age. Another method of determining uranium concentration is through LA-ICPMS [Laser Ablation Inductively Coupled Plasma Mass Spectrometry], a technique where the crystal is hit with a laser beam and ablated, and then the material is passed through a mass spectrometer.¹⁰⁰

Cosmogenic radioisotope dating

This technique takes advantage of the spontaneous generation of exotic radionuclides by cosmic rays. It is a major interest of JOS, who directs the Cosmogenic Isotope Laboratory¹⁰¹ at the UW. But we were able to spend only a short time on this fascinating topic, and like the method itself, I have only scratched the surface and hope to penetrate someday to a greater depth.

The cosmic rays bombarding our upper atmosphere are extraterrestrial in origin and induce showers of products (see above with ^{14}C dating). Their initial energies are as high as 10^{20} eV. Most (90%) are protons, some are alpha particles (~10%), and a few are heavier ions or gamma ray photons.¹⁰² Their peak interactions in the atmosphere occur at about 15 – 20 km, but spallation products (neutrons, protons, pions, muons, etc.) continue to the ground level. According to JOS, the atmosphere presents a cross-sectional areal or columnar density of about 1000 g cm^{-2} , which is about 10 primary collisions thick (the average collision occurs after traversing 100 g cm^{-2}), so very few primary cosmic rays reach the ground without intervening collisions and generation of “secondary cosmic rays” (the various spallation products). The cosmogenic isotopes that are of greatest interest (produced mostly by neutron and proton nuclear collisions, but also by some of the muons) include ^{14}C , ^{10}Be , ^{26}Al , and ^{36}Cl , all at very low concentrations. It is fortuitous—as JOS jokes, almost like “divine intervention”, as with ^{235}U and ^{238}U dating—that two of these radioisotopes so produced are well-preserved and have favorable chemistry and half-lives.

Some of the relevant isotopes, their generation reactions^{103,104,105,106}, and their half-lives include (here t and u are neutrons or protons):

^{10}Be	$^{14}\text{N}(\text{n}, \text{p} + \alpha)^{10}\text{Be}$ or $^{16}\text{O}(\text{t}, 7\text{u})^{10}\text{Be}$	$t_{1/2} = 1.51 \times 10^6 \text{ y}$
^{26}Al	$^{28}\text{Si}(\text{n}, \text{p} + 2\text{n})^{26}\text{Al}$	$t_{1/2} = 7.17 \times 10^5 \text{ y}$
^{36}Cl	$^{40}\text{Ca}(\mu^-, \alpha)^{36}\text{Cl}$	$t_{1/2} = 3.01 \times 10^5 \text{ y}$

These cosmogenic radionuclides (CR) are generated in rock that is within about 2 m of the surface. A freshly exposed surface not previously exposed to cosmic rays starts with zero CR activity, and the activity gradually rises to a saturation level where cosmogenic synthesis is balanced by decay. Dating is not possible when such an equilibrium has been reached, but for lower levels of the CR, the date since exposure can be estimated from the buildup equation:

$$t = -\frac{1}{\lambda} \ln \left(1 - \frac{\lambda N}{P} \right)$$

where λ is the decay constant,

P is the corrected production rate (adjusted for factors affecting focal cosmogenic radiation flux including latitude, longitude, depth attenuation in the specimen, angle of exposure to cosmic rays when applied to a steep scarp or other geometries, etc.), and

N is the current measured activity.

The activities produced are quite small—for example, only 5 atoms ^{10}Be per gram of quartz per year. Therefore, detection of these trace quantities requires very careful chemical preparation and accelerator mass spectrometry.

¹⁰⁰ http://en.wikipedia.org/wiki/Fission_track_dating

¹⁰¹ <http://depts.washington.edu/cosmolab/>

¹⁰² http://en.wikipedia.org/wiki/Cosmic_ray

¹⁰³ <http://en.wikipedia.org/wiki/Beryllium-10>

¹⁰⁴ <http://en.wikipedia.org/wiki/Aluminium-26>

¹⁰⁵ http://depts.washington.edu/cosmolab/pubs/Mu98_abs.html

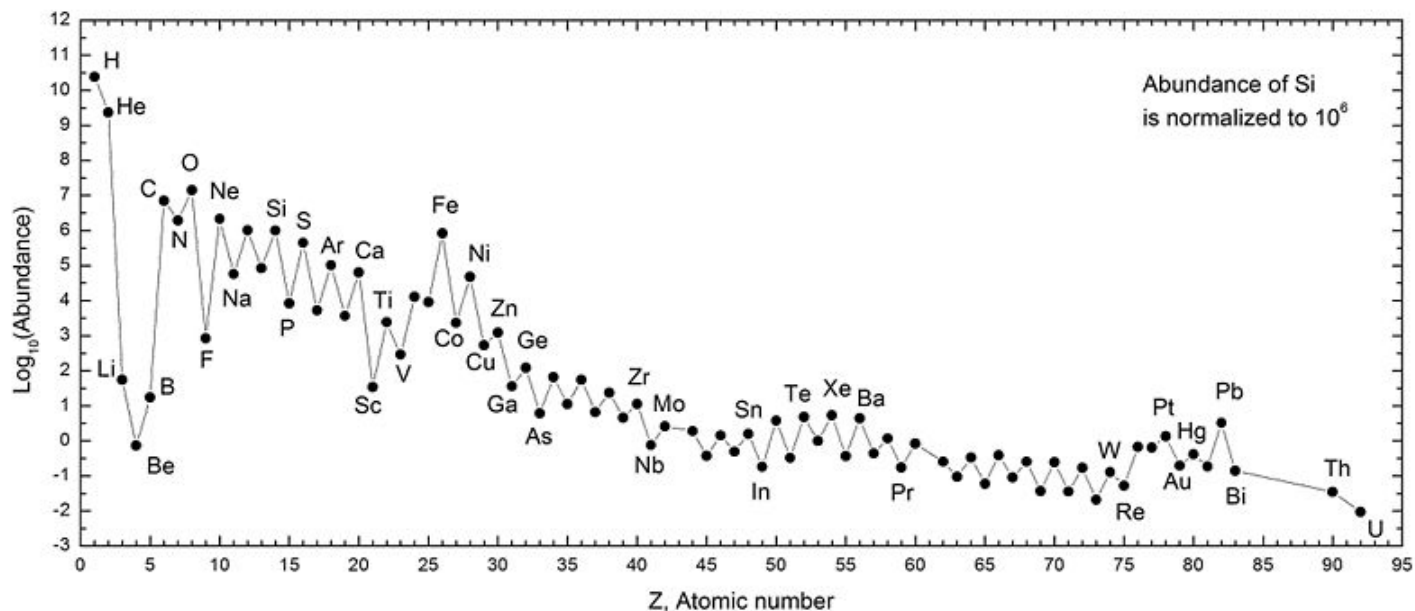
¹⁰⁶ <http://en.wikipedia.org/wiki/Chlorine-36>

Miscellaneous Topics and Terminology

Arranged alphabetically

Abundances of elements in the solar system (chart)

Image from here¹⁰⁷, normalized to a relative abundance for Silicon of 10^6 . Note the greater abundance of even Z elements presumably reflecting .



Advection

“Advection, in chemistry and engineering, is a transport mechanism of a substance or a conserved property with a fluid in motion. The fluid motion in advection is described mathematically as a vector field, and the material transported is typically described as a scalar concentration of substance, which is contained in the fluid. An example of advection is the transport of pollutants or silt in a river. The motion of the water carries these impurities downstream. Another commonly advected property is heat, and here the fluid may be water, air, or any other heat-containing fluid material. Any substance, or conserved property (such as heat) can be advected, in a similar way, in any fluid...In meteorology and physical oceanography, advection often refers to the transport of some property of the atmosphere or ocean, such as heat, humidity (see moisture) or salinity. Meteorological or oceanographic advection follows isobaric surfaces and is therefore predominantly horizontal.”¹⁰⁸

Atomic, nuclear, and particle units and measurements

See also Excel calculations file GeolTimeCalcs_MCM_ESS461.xls

Angstrom:

The ångström or angstrom (symbol Å) is 0.1 nanometer = 0.1 nm = 1×10^{-10} meters. It is approximately the size of a hydrogen atom.

¹⁰⁷ <http://en.wikipedia.org/wiki/File:SolarSystemAbundances.jpg> using data from Katharina Lodders (2003). "Solar System Abundances And Condensation Temperatures Of The Elements". *The Astrophysical Journal* 591: 1220-1247

See also http://en.wikipedia.org/wiki/Abundance_of_the_chemical_elements

See also <http://presolar.wustl.edu/work/abundances.html> for table of relative abundance of stable isotopes

¹⁰⁸ <http://en.wikipedia.org/wiki/Advection>

Atom Size:

The diameter of atoms¹⁰⁹ vary with definition but are about

H: 100 pm = 100,000 fm = 100×10^{-12} m

U: 375 pm = 375,000 fm = 375×10^{-12} m

Nuclear Size:

The diameter of nuclei¹¹⁰ vary depending on definition but are about

¹H: 1.6 fm = 1.6×10^{-15} m = 1/31250 the atom diameter

U: 15 fm = 15×10^{-15} m = 1/23000 the atom diameter

Atom to Nucleus Diameter and Volume Ratios:

The ratio of the diameter of the overall atom to its nucleus is approximately:

H: 62,000

U: 25,000

The ratio of the volume of the overall atom to its nucleus [MCM calculation] is approximately:

H: 2×10^{14}

U: 2×10^{13}

Speed of Light in Vacuum (c):

299,792,458 m/s by SI definition of the meter¹¹¹

Atomic Mass Unit (u or AMU):¹¹² The unified atomic mass unit or atomic mass unit (u), or dalton (Da) or, sometimes, universal mass unit (u), is a unit of mass used to express atomic and molecular masses. It is the approximate mass of a hydrogen atom, a proton, or a neutron. The precise definition is that the atomic mass unit (u) is one twelfth of the mass of an isolated atom of carbon-12 (¹²C) at rest and in its ground state [including electrons]:

1 AMU = $1.660538782 \times 10^{-27}$ kg

1 AMU = $1.49241783 \times 10^{-10}$ J (Energy equivalence by $E = mc^2$)

1 AMU = 931.494028 MeV (Energy equivalence by $E = mc^2$, also shown confusingly as “MeV/c²”)

Electron Mass:¹¹³

$9.10938215 \times 10^{-31}$ kg

$5.48579909 \times 10^{-4}$ u [atomic mass unit]

0.51099891 MeV (Energy equivalence by $E = mc^2$, also shown as “MeV/c²”)

Proton Mass:¹¹⁴

$1.67262164 \times 10^{-27}$ kg

1.007276467 u [atomic mass unit]

938.272013 MeV (Energy equivalence by $E = mc^2$, also shown as “MeV/c²”)

Neutron Mass:¹¹⁵

$1.67492721 \times 10^{-27}$ kg

1.008664916 u [atomic mass unit]

939.565346 MeV (Energy equivalence by $E = mc^2$, also shown as “MeV/c²”)

¹²C Atom Mass (resting bound state of 6P, 6N, 6e):¹¹⁶

$1.99264654 \times 10^{-26}$ kg

¹⁰⁹ http://en.wikipedia.org/wiki/Atomic_radii_of_the_elements_%28data_page%29

¹¹⁰ http://en.wikipedia.org/wiki/Atomic_nucleus

¹¹¹ http://en.wikipedia.org/wiki/Speed_of_light

¹¹² Atomic Mass Unit:

- <http://physics.nist.gov/cuu/Constants/index.html>
- MCM Excel calculations file GeolTimeCalcs_MCM_ESS461.xls

¹¹³ <http://physics.nist.gov/cuu/Constants/index.html>

¹¹⁴ <http://physics.nist.gov/cuu/Constants/index.html>

¹¹⁵ <http://physics.nist.gov/cuu/Constants/index.html>

¹¹⁶ Atomic Mass:

- <http://physics.nist.gov/cuu/Constants/index.html>
- MCM direct calculations

12.0 u [atomic mass unit, by definition]

11177.93 MeV (Energy equivalence by $E = mc^2$, also shown as “MeV/c²”)

Mass Deficit of ¹²C:¹¹⁷

1.64293333x10⁻²⁸ kg

9.89397759x10⁻⁰² u [atomic mass unit]

92.161810 MeV (Energy equivalence by $E = mc^2$, also shown as “MeV/c²”)

0.824% of mass of sum of components

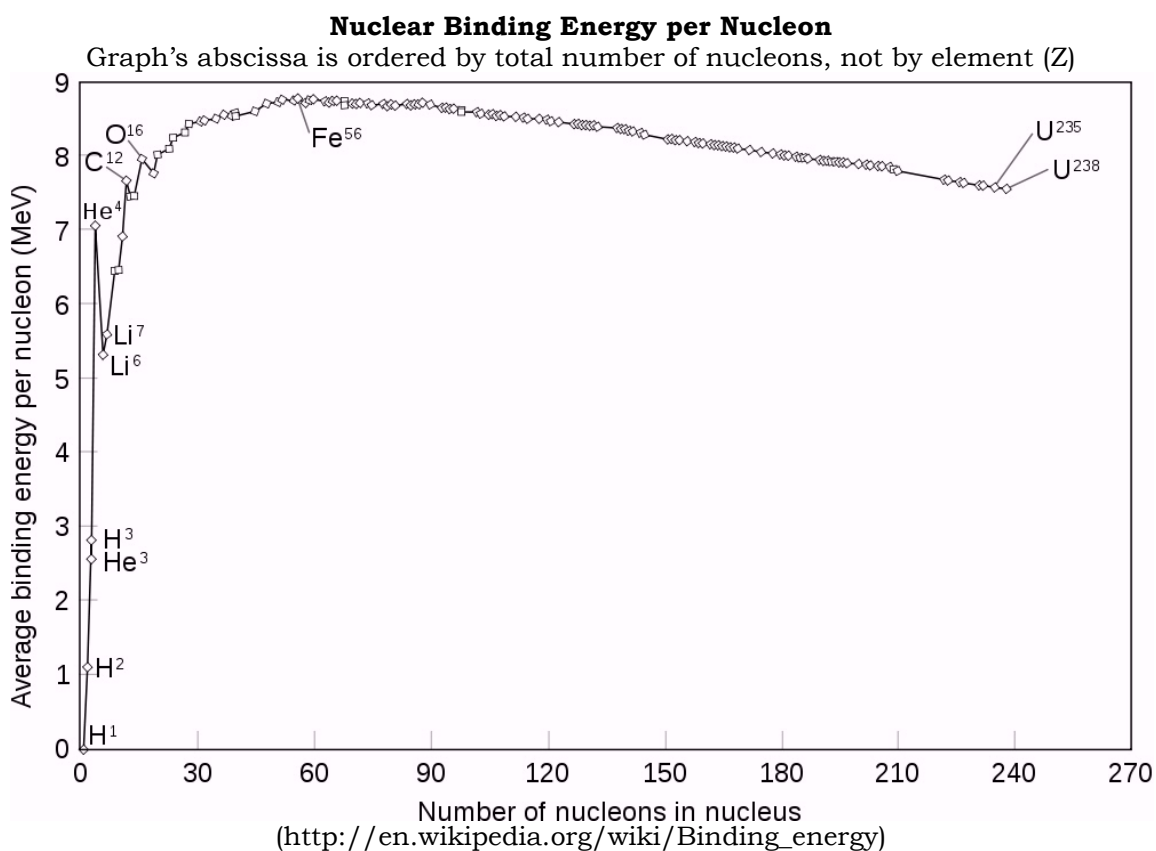
Decay rates: Becquerel and mCi

1 disintegration per second (dps) = 1 becquerel (Bq)

1 milliCurie (mCi) = 37000000 dps = 3.7 x 10⁷ dps

1 Curie (Ci) = 3.7 x 10¹⁰ dps

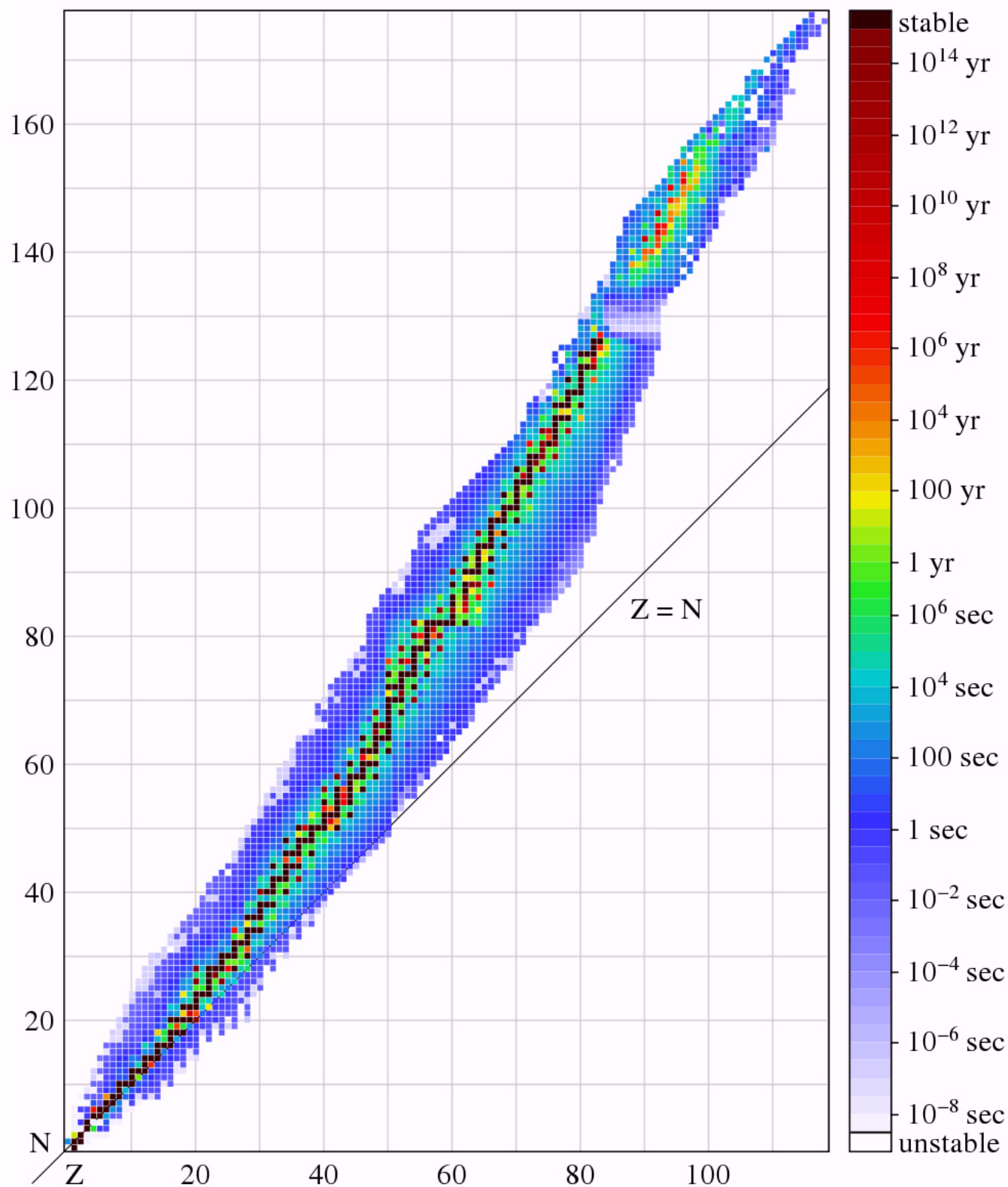
Isotopic binding energy and stability



¹¹⁷ Mass Deficit:

- <http://physics.nist.gov/cuu/Constants/index.html>
- MCM direct calculations]

Isotope Stability and Half-Lives



http://en.wikipedia.org/wiki/List_of_elements_by_stability_of_isotopes

Modes of radioactive decay

[Notes from Wikipedia, multiple pages, unless otherwise noted]

N = Number of Neutrons, Z = Number of Protons (Atomic Number),
A = Number of Nucleons (Atomic Mass Number)

Decay involving nucleon emission (changing A and Z and/or N)

Alpha decay α : “Alpha decay is by far the most common form of cluster decay where the parent atom ejects a defined daughter collection of nucleons, leaving another defined product behind (in nuclear fission, a number of different pairs of daughters of approximately equal size are formed). Alpha decay is the most likely cluster decay because of the combined extremely high binding energy and relatively small mass of the helium-4 product nucleus (the alpha particle).”¹¹⁸

Proton emission P: “Proton emission is not seen in naturally-occurring isotopes. Proton emission can occur from high-lying excited states in a nucleus following a beta decay, in which case the process is known as beta-delayed proton emission, or can occur from the ground state (or a low-lying isomer) of very proton-rich nuclei, in which case the process is very similar to alpha decay.”¹¹⁹

Double Proton emission: In 2002, the simultaneous emission of **two protons** was observed from the nucleus Iron-45 ... In 2005 it was experimentally determined that Zinc-54 can also undergo double proton decay.¹²⁰

Neutron emission N: “is a type of radioactive decay of atoms containing excess neutrons, in which a neutron is simply ejected from the nucleus. Ex. helium-5 and beryllium-13. Many heavy isotopes, most notably californium-252, emit neutrons among the products of a different radioactive decay process, spontaneous fission.”¹²¹

Spontaneous fission SF: “is a form of radioactive decay characteristic of very heavy isotopes. It is theoretically possible for any atomic nucleus whose mass is greater than or equal to 100 atomic mass units (u), i.e. elements near ruthenium. In practice, however, spontaneous fission is only energetically feasible for atomic masses above 230 u (elements near thorium). The elements most susceptible to spontaneous fission are the high-atomic-number actinide elements, such as mendelevium and lawrencium, and the trans-actinide elements, such as rutherfordium.”¹²²

Cluster decay: “is a type of nuclear decay in which a radioactive atom emits a cluster of neutrons and protons *heavier* than an alpha particle. This type of decay happens only in nuclides which decay predominantly by alpha decay, and occurs only a small percentage of the time in all cases. Cluster decay is limited to heavy atoms which have enough nuclear energy to expel a portion of its nucleus.”¹²³

Decay involving beta decay (changing Z but not A or N)

Beta decay: a beta particle (an electron or a positron) is emitted. With electron emission, it is referred to as beta minus (β^-) decay, while in the case of a positron emission as beta plus (β^+). Kinetic energy of beta particles has continuous spectrum ranging from 0 to maximal available energy (Q)... Some nuclei can undergo double beta decay ($\beta\beta$ decay) where the charge of the nucleus changes by two units.

Beta Negative Decay (Negatron) β^- : “In β^- decay, the weak interaction converts a neutron (n) into a proton (p) while emitting an electron (e^-) and an antineutrino ($\bar{\nu}_e$). In *Double beta [negative] decay*, a nucleus emits two electrons and two antineutrinos.”¹²⁴

Positron emission β^+ (Beta Positive decay): “In β^+ decay, energy is used to convert a proton into a neutron, a positron (e^+) and a neutrino (ν_e). Unlike β^- , β^+ decay cannot occur in isolation, because it requires energy, the mass of the neutron being greater than the mass of the proton. β^+ decay can only happen inside nuclei when the value of the binding energy of the mother nucleus is greater than that of the daughter

¹¹⁸ http://en.wikipedia.org/wiki/Alpha_decay

¹¹⁹ http://en.wikipedia.org/wiki/Proton_emission

¹²⁰ http://en.wikipedia.org/wiki/Double_proton_emission

¹²¹ http://en.wikipedia.org/wiki/Neutron_emission

¹²² http://en.wikipedia.org/wiki/Spontaneous_fission

¹²³ http://en.wikipedia.org/wiki/Cluster_decay

¹²⁴ http://en.wikipedia.org/wiki/Beta_decay

nucleus. The difference between these energies goes into the reaction of converting a proton into a neutron, a positron and a neutrino and into the kinetic energy of these particles.”¹²⁵

Electron capture EC (K-Capture): In all the cases where β^+ decay is allowed energetically (and the proton is a part of a nucleus with electron shells), it is accompanied by the electron capture process, when an atomic electron is captured by a nucleus with the emission of a neutrino: But if the energy difference between initial and final states is less than $2m_e c^2$, then β^+ decay is not energetically possible, and electron capture is the sole decay mode. This decay is also called K-capture, because the 'inner most' electron of an atom belongs to the K-shell of the electronic configuration of the atom and this has the highest probability to interact with the nucleus. *Double electron capture* can also occur—two of the orbital electrons are captured by two protons in the nucleus, forming two neutrons.¹²⁶

Decay involving transitions between isomeric states (no change in A, N, or Z)

Isomer: In physics pertaining to nuclei, isomers are any of two or more nuclei having the same mass number [A] and atomic number [Z] and that have different radioactive properties and can exist in any of several energy states for a measurable period of time.¹²⁷

Isomeric transition: “is a radioactive decay process in which the nucleus begins in an excited meta state (e.g. following the emission of an alpha or beta particle). The extra energy in the nucleus is released by the emission of a gamma ray, returning the nucleus to the ground state. This process is therefore similar to a gamma emission but differs in that it involves excited meta-states. The gamma-ray may transfer its energy directly to one of the most tightly bound electrons causing it to be ejected from the atom, a process termed photoelectric effect.”¹²⁸

Internal conversion: “is a radioactive decay process where an excited nucleus interacts with an electron in one of the lower atomic orbitals, causing the electron to be emitted from the atom. Thus, in an internal conversion process, a high-energy electron is emitted from the radioactive atom, but without beta decay taking place. For this reason, the high-speed electrons from internal conversion are not beta particles (which have a variable energy) whereas the IC electrons have a well defined energy. Since no beta decay takes place in internal conversion, the element atomic number does not change and no neutrino is emitted.”¹²⁹

Radioactive decay equations and parameters λ , τ , and $t_{1/2}$

Statistical law of radioactivity (per JOS): “The probability that a radioactive atom will decay in a given time interval is constant and not influenced by the past history or present circumstances of the atom.”

The decay rate is a nearly immutable nuclear process, minimally sensitive to the physical and chemical environment of the atom. Temperature, pressure, chemical state, physical state, magnetic fields, etc have minimal perceptible effect on the decay rate. Therefore, radioactive clocks keep exceptionally good time. [MCM: Slight deviations based on chemical state for various types of radioactive decay are discussed in Dalrymple91.]

Expressed as a differential equation, this statistical law is given by

$$\frac{dN}{dt} = -\lambda N$$

where N = number of radioactive atoms remaining at a given time t
 λ = decay constant characteristic of the radionuclide

From the statistical law, we can show that if the initial number of parent atoms is N_0 at time 0, then the number remaining N at time t is:¹³⁰

¹²⁵ http://en.wikipedia.org/wiki/Beta-Positive_decay

¹²⁶ http://en.wikipedia.org/wiki/Electron_capture

¹²⁷ http://en.wikipedia.org/wiki/Nuclear_isomer

¹²⁸ http://en.wikipedia.org/wiki/Isomeric_transition

¹²⁹ http://en.wikipedia.org/wiki/Internal_conversion

¹³⁰ Radioactive Decay:

• JOS lab notes

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

Or equivalently, the fraction remaining, N/N_0 , at time t is

$$\frac{N}{N_0} = e^{-\lambda t}$$

This is the exponential law of radioactive decay—no matter what the initial abundance of a radioactive species, both the number of atoms and the radioactivity decline exponentially with time. λ in these equations is referred to as the *decay constant*. λ is described as the probability that any individual atom will decay in a given time interval [see MCM clarifications below.] Commonly, λ is specified in units of yr^{-1} or "per year", though for short-lived radioactive atoms, you might see units of day^{-1} , min^{-1} or even sec^{-1} . In a population of atoms large enough to smooth out the random variations in individual atomic lifetimes, λ is the fraction of atoms that will decay in a given time interval (provided the time interval is very short in comparison to the half-life), as shown by the equivalent formula:

$$\lambda = -\frac{1}{N} \frac{dN}{dt}$$

λ^{131} is exactly the reciprocal of the time in which the population decreases by a factor of $1/e$ where $e = 2.71828182845904523536$ and $1/e = 0.3678794411714423215955$. The quantity $\tau = 1/\lambda$ is called the *mean lifetime*, and is the time in which the population decreases by a factor of $1/e$. The *half-life* $t_{1/2}$ is defined as the time in which the population decreases by $1/2$, and is given by

$$t_{1/2} = \frac{\ln(2)}{\lambda} = \tau \ln(2)$$

where $\ln(2) = 0.6931471805599453094172$.

Second (unit of time defined)

"The second¹³² (SI symbol: s), sometimes abbreviated sec., is the name of a unit of time, and is the International System of Units (SI) base unit of time...

Early definitions of the second were based on the motion of the earth: 24 hours in a day meant that the second could be defined as $1/86400$ of the average time required for the earth to complete one rotation about its axis. However, nineteenth- and twentieth-century astronomical observations revealed that this average time is lengthening, and thus the motion of the earth is no longer considered a suitable standard for definition. With the advent of atomic clocks, it became feasible to define the second based on fundamental properties of nature. Since 1967, the second has been defined to be:

The duration of 9,192,631,770 periods of the radiation corresponding to the transition between the two hyperfine levels of the ground state of the cesium 133 atom."

Uranium toxicity: Hazards of military use of depleted uranium and tungsten alloys

This is a digression entirely unrelated to geochronology, but is an important Uranium-related topic of some interest with regard to our increasingly widespread use of these highly persistent environmental contaminants on foreign soils.

D. E. McClain; A. C. Miller; J. F. Kalinich. "Status of Health Concerns about Military Use of Depleted Uranium and Surrogate Metals in Armor-Penetrating Munitions" fr. Armed Forces Radiobiology Research Inst Bethesda MD. Presentation made June 2005 to NATO:¹³³

• http://en.wikipedia.org/wiki/Radioactive_decay

• http://en.wikipedia.org/wiki/Exponential_decay

¹³¹ Radioactive Decay Calculations:

• http://en.wikipedia.org/wiki/Exponential_decay

• <http://keisan.casio.com/has10/Free.cgi> (calculator with high precision numbers)

¹³² <http://en.wikipedia.org/wiki/Second>

¹³³ http://www.afri.usuhs.mil/www/outreach/pdf/mcclain_NATO_2005.pdf

See also <http://www.wise-uranium.org/dgvd.html>

Abstract: "The use of depleted uranium in armor-penetrating munitions remains a source of controversy because of the numerous unanswered questions about its long-term health effects. Although there are no conclusive epidemiological data correlating depleted uranium exposure to specific health effects, studies using cultured cells and laboratory rodents continue to suggest the possibility of genetic, reproductive, and neurological effects from chronic exposure. Until issues of concern are resolved with further research, the use of depleted uranium by the military will continue to be controversial. Meanwhile, there are military programs to find substitutes for depleted uranium in munitions. Although a wide variety of alloys are being evaluated by munitions developers, certain alloys of tungsten have been developed that demonstrate properties very close to the ones that make depleted uranium useful in armor-penetrating munitions. One hundred and fifty years of industrial experience suggest that tungsten and tungsten alloys are not a significant health risk except in certain industrial exposure scenarios. However, recent research has shown that some of the most promising militarily relevant alloys of tungsten exhibit unexpected long-term toxicities as embedded shrapnel. Rats implanted in their leg muscles with pellets made from a particular alloy of tungsten, nickel, and cobalt, considered a promising surrogate for depleted uranium in munitions, develop aggressive rhabdomyosarcomas within 6 months of implantation that metastasize to the lung and necessitate euthanasia of the animals. One hundred percent of the tungsten alloy-implanted rats were affected. Immune system changes independent of tumor development were also observed. These findings amplify the need to investigate substances of questionable toxicity early in munitions development, especially with regards to the unusual kinds and levels of exposure that might be expected by the military."¹³⁴

¹³⁴ <http://oai.dtic.mil/oai/oai?verb=getRecord&metadataPrefix=html&identifier=ADA438738>