Learn About ...

URANIUM:

A RADIOACTIVE CLOCK

How old is the Earth, the solar system, or a piece of charcoal from an ancient campfire? Until the beginning of the 20th Century, geologists had no method by which to determine the absolute age of a material. The age of the earth was believed to be at most tens of millions of years. Not long after the discovery of radioactivity in 1896, scientists realized that radioactive decay constitutes a “clock” capable of measuring absolute geologic time. By 1907, the discovery that lead was the final product of uranium decay provided evidence that geologic age needed to be reckoned not in millions, but in billions of years.

Uranium occurs in numerous minerals, such as pitchblende ($UO_3 \cdot UO_2 \cdot PbO$) and carnotite ($K_2O \cdot 2U_2O_3 \cdot V_2O_5 \cdot 3H_2O$). It is not all that rare, being more plentiful in the Earth's crust than mercury or silver. The metal was first isolated in 1841 by the reduction of uranium(IV) chloride with potassium.

$$4\,K + UCl_4 \longrightarrow 4\,KCl + U$$

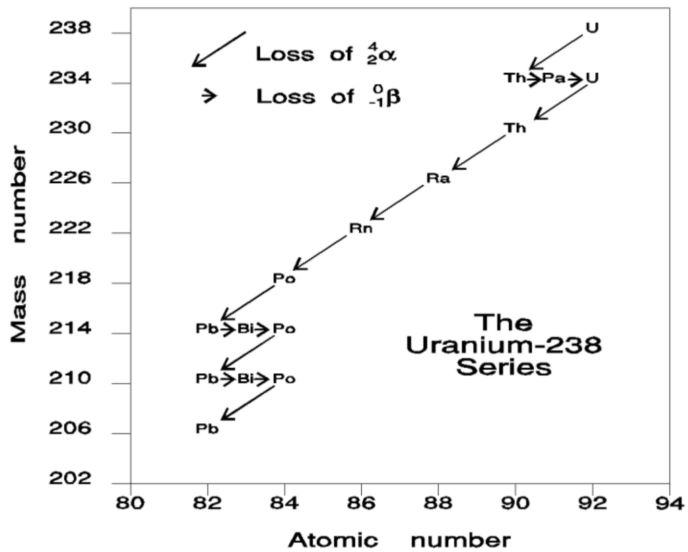
Uranium is sufficiently radioactive to expose a photographic plate in about an hour. Naturally occurring U contains 14 isotopes, all of which are radioactive. The three most abundant are U-238 (99.28%), U-235 (0.71%), and U-234 (0.006%). In contrast to chemical reactions, where the isotopes of an element behave similarly, in nuclear reactions isotopes behave quite differently. This reveals itself in the different half lives of these isotopes, and in the fact that among these three only U-235 undergoes fission.

The most abundant of the naturally occurring uranium isotopes decays by α emission to Th-234.

$$^{238}_{92}U \longrightarrow {}^{234}_{90}Th + {}^{4}_{2}He \qquad t_{1/2} = 4.5 \times 10^9 \text{ years}$$

The product of this reaction, Th-234, is also radioactive and undergoes β decay.

$$^{234}_{90}Th \longrightarrow {}^{234}_{91}Pa + {}^{0}_{-1}e \qquad t_{1/2} = 24 \text{ days}$$



Protactinium-234 also decays by emitting a β particle. These are only the beginning of a series of 14 nuclear decay steps. After the emission of eight α particles and six β particles, the isotope Pb-206 is produced. It is a stable isotope that does not disintegrate further. The complete process is called the uranium radioactive decay series. The intermediate isotopes are called “daughters.” The half lives of the daughters range from 1.6×10^{-4} seconds for Po-214 to 2.5×10^{5} years for U-234. Two other such radioactive series occur in nature. They start with U-235 and Th-232.

The uranium radioactive series has been used to estimate the age of the oldest rocks in the Earth's crust. The ratio of U-238 to Pb-206 in a rock changes slowly as the U-238 in the rock decays. Because the half life of U-238 is 20,000 times that of the next longest half life in the series, the rate of decay of U-238 is the rate-determining step in the conversion of U-238 to Pb-206.

The rate of radioactive decay is called activity (*A*) and is expressed in units of Curies, which are disintegrations per second. Activity is the change in the number of nuclei with time, that is,

$$A = -\frac{dN}{dt}$$

where *N* is the number of nuclei and *t* is time. Activity is proportional to the number of decaying nuclei. That is,

$$-\frac{dN}{dt} = kN$$

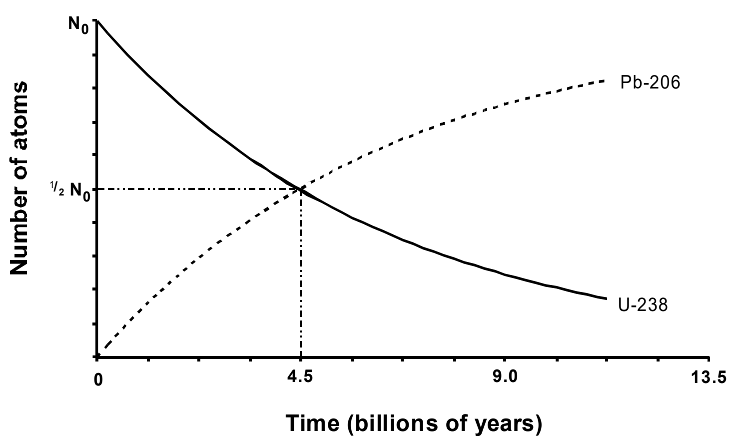
where *k* is a proportionality constant called the decay constant. This equation is the derivative form a first-order rate equation. The integrated form of a first-order rate equation is

$$\ln \frac{N}{N_0} = -kt$$

In this equation, N_0 is the number of radioactive atoms initially present in the sample, N is the number of these atoms in the sample after a length of time t has elapsed. The amount of time required for half of the nuclei in a sample of a radioactive isotope to decay is called the half life of the isotope. The integrated rate equation can be used to determine the relationship between the half life ($t_{½}$) and the decay constant, and that relationship is

$$t_{½} = \frac{0.693}{k}$$

The rate of decay of U-238 can be used to determine the age of a uranium-bearing rock. If the rock contained no Pb-206 when it was formed, then N_0 is equal to the sum of the number of atoms of U-238 and Pb-206. In the oldest uranium-bearing rocks, the ratio of U-238 to Pb-206 is about 1-to-1. Therefore, half of the original



U-238 has decayed to Pb-206 and the rock is as old as one half life of U-238.

At least two other radioactive clocks are used for dating geological time spans. These are the potassium to argon and rubidium to strontium transformations. Potassium-40 decays by electron capture to argon-40.

$${}^{40}_{19}\text{K} + {}^{0}_{-1}\text{e} \longrightarrow {}^{40}_{18}\text{Ar} \quad t_{½} = 1.3 \times 10^9 \text{ years}$$

In the rubidium-strontium transformation, Rb-87 emits a β particle to form Sr-87.

$$^{87}_{37}\text{Rb} \longrightarrow {}^{87}_{38}\text{Sr} + {}^{0}_{-1}\text{e} \qquad t_{½} = 5.7 \times 10^{10} \text{ years}$$

These radioactive clocks are more useful for dating rock samples than the uranium clock, because both potassium and rubidium are more widely distributed in rock samples than is uranium.

All radiochemical methods of dating have some uncertainties associated with them. Several assumptions must be made in determining an age. Perhaps the most significant assumption is the supposition that the sample was a closed system throughout its existence, that is, no parent or daughter isotope was gained or lost. Another assumption involves the amount of daughter isotope present at the formation of the sample. Generally, this is taken as zero for rare isotopes. The strongest evidence for the age of a sample is obtained when two different radiochemical dating methods produce the same result. Because the chemical properties of daughter products are so very different, any geological transformation of a rock sample will have quite different effects on the sample's daughter isotope contents. Potassium and rubidium frequently occur together in rock samples, making this pair particularly important for radiochemical dating.

Radiochemical dating of samples from the Earth's crust yield a maximum age of about 3.5×10^9 years. The Earth is believed to be older than this. The oldest meteorites and moon rocks are 4.5×10^9 years old. If these other members of the solar system were formed at the same time, then perhaps the Earth was also formed 4.5 billion years ago. The isotopic composition of lead supports this conclusion. Of the four lead isotopes, only Pb-204 is not produced by radioactive decay of parent U-328, U-235, or Th-232. Comparing the isotopic composition of lead in the Earth's crust to that of meteorites free of uranium and thorium indicates that about 4.5 billion years of U decay and Th decay would be required to produce the Pb isotope ratios found on Earth.