Uranium Series Dating
of Natural Materials

Radioactive Decay

*The transformation of elements into different
isotopes due to radioactivity over time*

The discovery of radioactive elements besides Uranium at the dawn of the 20th century by scientists, including Marie Currie, ushered in the realization that radioactive elements changed form when they decayed, becoming a new isotope (an element with the same number of protons, but a different number of neutrons than its typical form). This discovery paved the way for scientists to measure precisely how long it took each "parent" isotope to decay into its "daughter" isotope. This unique feature of radioactive decay allowed natural geologic and biological materials that contained certain radioactive elements to be dated (the age of the material could be determined) using the concentrations of radioactive parent and daughter isotopes in a sample. Knowing the concentrations of parent and daughter, along with the rate of decay, the time that has passed since the material formed can be calculated[2,4].

The Uranium Series

*The sequence of parent-daughter transformations
that result from the initial decay of ^{238}U*

Uranium naturally decays into a sequence of 17 daughter isotopes from its most abundant natral isotope ^{238}U. Each transformation along the series occurs at a unique rate, often refferd to by the parent isotopes half-life (the time it takes for half of the parent isotope to decay into its daugher isotope). Different sections of the U- series are useful for different materials depending on the age and type of material being dated. The different sections and corresponding methods used include Uranium-Uranium dating, Uranium-Thorium dating, and Uranium-Lead dating.
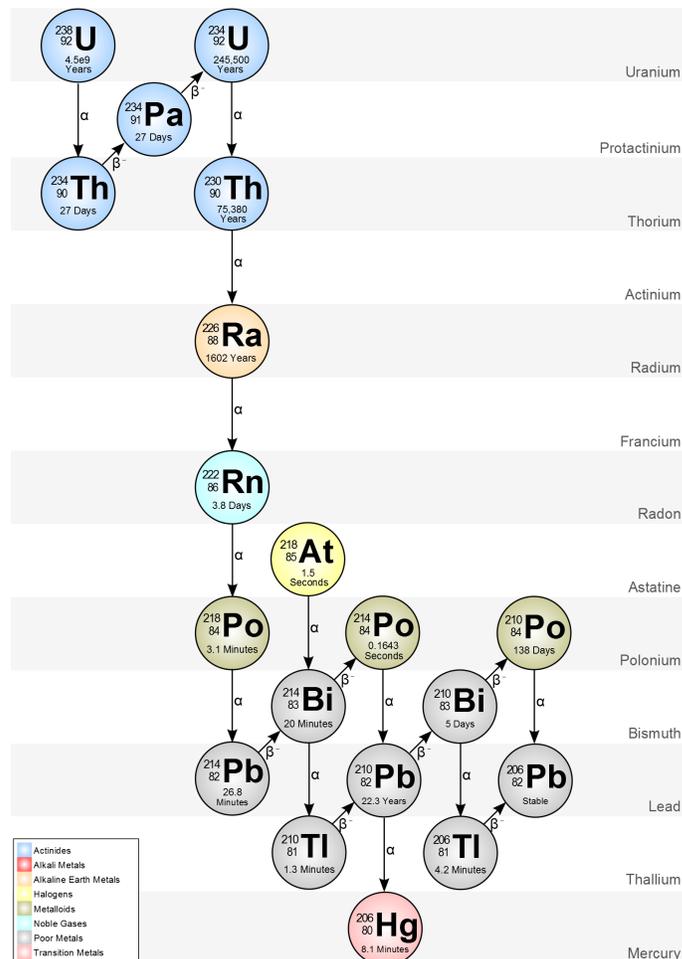

Figure 1: Schematic of the U-series decay chain from ^{238}U to the stable, non-radioactive ^{206}Pb. Note that many daughters are radioactive. http://bit.ly/2frNcSC

Uranium-Uranium dating uses the decay of ^{238}U into ^{234}U (through ^{234}Th & ^{234}Pa with half-lives of ~30 days) with a half-life of around 4.5 billion years.

^{238}U to ^{234}U dating is useful for materials that are very old (greater than 500,000 years old), such as deep sea sediments. This portion of the U-series is particularly valuable in dating very old calcium carbonate deposits in the ocean and limestones[5,7].

Uranium-Thorium dating uses the decay of ^{234}U to ^{230}Th, with a half-life of 245,000 years. This portion of the U-series is especially useful for dating

materials like stalagmites, coral reefs, and calcium carbonate depositing sponges and algae that are older than 50,000 years (the cut off for carbon dating) and less than 500,000 years[1].

Uranium-Lead dating uses the decay of ^{238}U into ^{206}Pb (through the rest of the U-series) with a half-life of around 4.5 billion years. ^{238}U to ^{206}Pb dating is useful for materials that approach the age of the solar system, and the universe itself (between 1 million years and the age of the solar system). This portion of the U-series is often used along with the complimentary decay of ^{235}U into ^{207}Pb to date very old materials, such as primordial zircons and meteorites that fell to Earth[2].

Measuring Uranium

Determining concentrations of U and its daughters

Uranium-series dating owes its utility to the ability of scientists to precisely measure concentrations of U and its daughter isotopes in the small quantities they are found in natural materials in. Initial Uranium measurements were accomplished using the emission products of radioactive decay (alpha particles and gamma rays). These techniques, known as alpha and gamma spectrometry, use the characteristics of the energy spectrum of Gamma ray emissions and Alpha particle energies to calculate the concentration of radioactive materials within a substance that are emitting them through radioactive decay[2]. These types of measurements were among the first developed to measure isotopes in the U-series with high enough precision to date materials and were integral in the original development of U-series dating methods.

After the mid 20th century, improvements in mass spectrometry (the measurement of ionized isotopes based on their unique mass and electrical charge as they pass through a curved tube past a magnet) made highly precise measurements of U-series isotopes even more robust. Alongside the Apollo Lunar missions, Dr. Gerald Wasserberg and his students and colleagues at the California Institute of Technology developed improved mass spectrometry techniques to measure and apply

the U-series to date rocks from the moon as well as meteorites and old rocks on the Earth[2,4]. The efforts of Dr. Wasserberg and his students propelled high-precision mass spectrometry to the forefront of U-series and geochemical dating techniques. While mass spectrometry has advanced substantially, alpha and gamma spectrometry are still used to study and understand the U-series and other radioactive isotopes from a variety of settings.
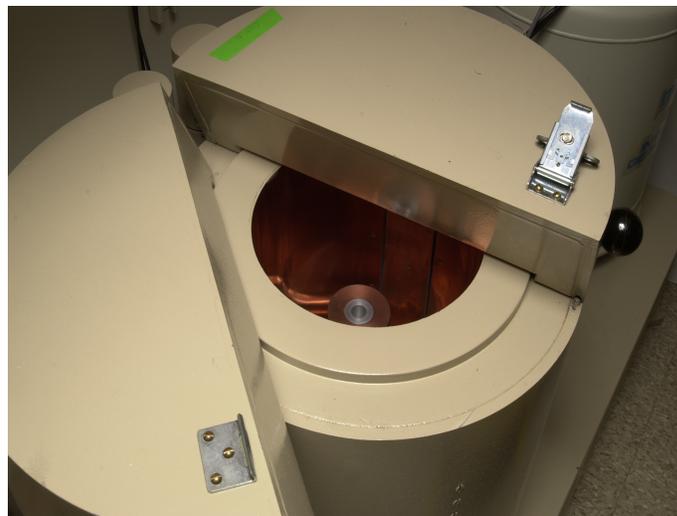

Figure 2: Inside the shielding of a gamma spectrometer. In gamma spectrometry, the sensor and sample must be shielded from outside sources of gamma radiation to prevent contamination of the measured gamma spectrum. http://on.doi.gov/2fP1bjv

Figure 3: A mass spectrometer (multicollector, Inductively coupled plasma ion source). http://bit.ly/2fP2hM4

Secular Equilibrium

As a radioactive parent and its radioactive daughter both decay, eventually the daughters rate of production decay reach parity

In a situation where a radioactive isotope decays into a stable, non-radioactive daughter (for example ^{238}U to ^{206}Pb) age can be determined by the concentration of the daughter isotope that has resulted from decay since the material formed. However, for most of the U-series, the parent decays into a daughter isotope that is also radioactive, and itself decays. The point at which the rate of production of the daughter isotope (from the decay of its parent isotope) is equal to the decay of the daughter isotope is known as secular equilibrium. While this is a more complex decay situation, dates can still be calculated by examining the how far from parity the effective concentrations of parent and daughter isotope are [1,2,3]. Secular equilibrium is important for many of the dating methods using portions of the U-series, as all daughter isotopes in the U-series with the exception of ^{206}Pb are themselves radioactive. Specifically, Uranium-Uranium and Uranium-Thorium dating rely on secular equilibrium to accurately date materials the methods are applied on. Portions of the U-series that do eventually reach secular equilibrium become effectively un-dateable with that portion of the series.

Dating Assumptions

Different assumptions must be made in order to apply U-series dating methods.

Important assumptions are made in order to date materials using the U-series methods. These assumptions aren't the same between methods and are important to test and ensure they are valid when dating any particular sample. All U-series methods assume that the dated material has remained an essentially closed system (new isotopes have not entered except by decay).

Uranium-Uranium dating-requires assumption of ^{238}U to ^{234}U ratio at the time a sample formed[2,5].

Uranium-Thorium dating-requires assumption of no initial ^{230}Th when it first formed (that all ^{230}Th is from the decay of ^{234}U). In aqueous and marine settings, this is often reasonable in carbonates precipitated out of water due to the solubility of U and the virtual insolubility of Th in typical natural waters[1,2,9].

Uranium-Lead dating-requires assumption of no initial ^{207}Pb or ^{206}Pb (that all ^{207}Pb and ^{206}Pb is from radioactive decay). In zircon crystals, this is often reasonable as zircons readily incorporate U and Th but strongly reject lead incorporation[3,6].

Violation of these assumptions can invalidate dates obtained using these methods, so careful screening is advisable prior to dating.
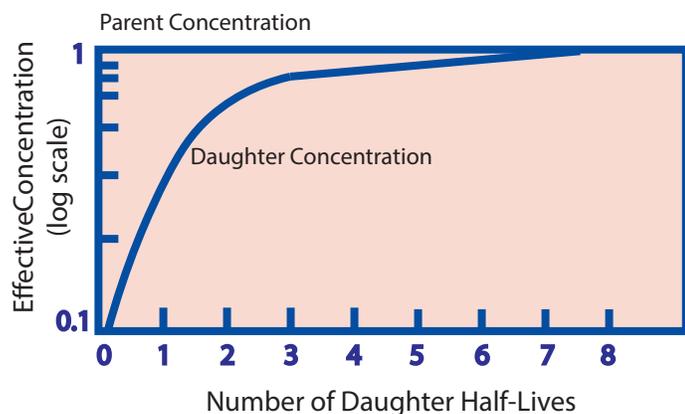

Figure 4: Graph of effective daughter isotope concentration over successive half lives. around 8 half lives, the daughter reaches secular equilibrium with the parent.

Figure 5: Photomicrograph of a zircon crystal (0.25mm). Zircons are great materials for U-Pb dating due to their strong Pb rejection. http://bit.ly/2eUXE0Y

U-series Dating Applications

U-series dating has become a valuable chronology building tool in many varied fields.

Uranium-series dating has been used in many fields to help constrain the ages of very old materials. Two examples that are particularly interesting, are the determination of the age of the Earth, and the determination of the age of a fossil hominid. These examples illustrate the power of U-series dating in speaking to our place in the world, elucidating the age of the planet we call home, and the age of our own evolutionary "family tree".

The age of the Earth- In the mid-20th century, a young Clair Patterson was working feverishly as a graduate student and researcher first at U. Chicago, then the California Institute of Technology. Clair's efforts were directed at one goal; using the U-series to calculate the age of the Earth. In 1956, after years of clean-lab protocols, contamination prevention, and method refinement, Clair got his age. 4.54 billion years, the age of the Earth Clair determined using a piece of the Diablo Canyon meteorite using ratios of ^{207}Pb and ^{206}Pb, an ingenious modification of the typical U-U series method[8].

The age of the Liujiang hominid- In the early 21st century, Guanjun Shen was working as a young researcher at Nanjing Normal University, in China. Shen was approached by a time-worn paleoanthropologist with a problem. Professor Phillip Tobias was working at a cave site in China, and a unique fossil hominid was discovered. The remains themselves were undoubtedly altered, and of little use for dating, however, calcite had been deposited from flowing waters in strata overlying the fossil hominid. These calcite deposits could hold the key to putting at least a minimum age on the fossil hominid, and testing hypotheses about the time when it lived. 111,000 -139,000 years old, the most likely age range Shen calculated using U-Th dating. This made the Liujiang man the oldest hominid yet discovered in Asia[9].

Figure 7: Etched cross-section of a fragment of the Canyon Diablo meteorite. The meteoritic Widmanstätten structure is visible in the etched face. http://bit.ly/2eVfOQd

Figure 8: Skull of the Liujiang hominid. Age constraint was obtained for this specimen using U-Th dating on calcite deposits around the fossil. http://bit.ly/2ga6DBp

References

1) Bard, E., Hamelin, B., & Fairbanks, R. G. (1990). U-Th ages obtained by mass spectrometry in corals from Barbados: sea level during the past 130, 000 years. Nature, 346(6283), 456-458.

2) Bourdon, B., Turner, S., Henderson, G. M., & Lundstrom, C. C. (2003). Introduction to U-series geochemistry. Reviews in Mineralogy and Geochemistry, 52(1), 1-21.

3) Crowley, J. L., Schoene, B., & Bowring, S. A. (2007). U-Pb dating of zircon in the Bishop Tuff at the millennial scale. Geology, 35(12), 1123-1126.

4) Elias, S. (2006). Encyclopedia of Quaternary science. Elsevier.

5) Hellstrom, J., Woodhead, J., Drysdale, R., Couchoud, I., & Zanchetta, G. (2008, April). U-Th, U-Pb and UU dating of the Corchia Cave speleothems: a continuous 1 Ma chronology. In Geophysical Research Abstracts (Vol. 10).

6) Košler, J., Fonneland, H., Sylvester, P., Tubrett, M., & Pedersen, R. B. (2002). U–Pb dating of detrital zircons for sediment provenance studies—a comparison of laser ablation ICPMS and SIMS techniques. Chemical Geology, 182(2), 605-618.

7) Parrish, Randall R. "U-Pb dating of monazite and its application to geological problems." Canadian Journal of Earth Sciences 27.11 (1990): 1431-1450.

8) Patterson, C. (1956). Age of meteorites and the earth. Geochimica et Cosmochimica Acta, 10(4), 230-237.

9) Shen, G., Wang, W., Wang, Q., Zhao, J., Collerson, K., Zhou, C., & Tobias, P. V. (2002). U-Series dating of Liujiang hominid site in Guangxi, Southern China . Journal of Human Evolution, 43(6), 817-829.