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Radiometric chronology of the Moon and Mars

“How old is the Earth?” was a topic of scientific inquiry in the late nineteenth century. In the twentieth century the question became “How old are the Earth and other objects in the Solar System?” Related questions are: “How old is the Solar System?”; “How has the Earth changed over geologic time?”; and “How have the planetary bodies in the Solar System changed over time?” Also, “What has made Earth unique in our Solar System?” With the aid of spacecraft-acquired data and samples, and through the study of lunar and Martian meteorites, we are beginning to answer some of these questions as they relate to the Moon and Mars.

A century ago the age of the Earth was addressed by diverse approaches. These included calculations of how long it would take an initially hot Earth to lose its heat by thermal conduction and radiation to space; how long it would take the oceans to attain their current load of salt, assuming an estimated modern rate of weathering of surface rocks; and estimates of the rate of regression of the Moon away from the Earth. The ages obtained by such methods were often of the order of 10–100 Ma (million years). Unfortunately, these methods were based on faulty assumptions. For example, estimates of the age of the Earth based on observable geological processes failed to account for significant changes in the rate and nature of those processes acting over very long periods of time. Also, calculations of the thermal cooling of the Earth failed to consider the heat generated within the Earth by the natural radioactivity of potassium, uranium, and thorium.

The physical basis for determining the absolute ages of objects within our Solar System in the twentieth century is natural radioactivity, a phenomenon initially discovered in the closing years of the nineteenth century. A collection of radioactive atoms can be thought of as being like a clock, which is running at a constant and measurable speed. But unlike an ordinary clock which tells only the present time, the accumulated daughter products of radioactive decay give a measure of how long the radioactive clock has been running since it was initially “set.”

USING NATURAL RADIOACTIVITY TO TELL GEOLOGIC TIME

Historical background

The discovery of natural radioactivity by H. Becquerel (1896) set scientists on the path to quantitative definition of geologic time. In an instance of scientific serendipity, Becquerel found that photographic plates kept near uranium-bearing minerals became darkened. Marie Skłodowska Curie pursued the observation for her PhD dissertation, noting that both uranium and thorium were active, and that two minerals of uranium, pitchblende and chalcocite, had greater radioactivity than uranium itself (Curie 1898). Pursuing the great activity of pitchblende, she and her husband, Pierre Curie, isolated the “new” element polonium from this mineral (Curie and Curie 1898). Next, the Curies, with G. Bémont, also isolated radium from pitchblende (Curie *et al.* 1898). Although these shorter-lived daughter elements are far more radioactive than uranium, our interest here remains with uranium, their

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radioactive parent. Its decay period, or half-life, was soon found to extend over geologic time, and thus its radioactive decay was recognized as a possible basis for a geologic timescale (Rutherford 1906). For historical completeness, we note that Schmidt (1898) also discovered the radioactivity of thorium contemporaneously with M. Curie. Within a decade, two more long-lived naturally radioactive elements had been discovered which also could be used to tell geologic time: potassium (Campbell and Wood 1906, Campbell 1906) and rubidium (Campbell and Wood 1906, Campbell 1908). The radioactivity of a fourth element currently used for geologic age determinations, samarium, was discovered considerably later (Hevesey *et al.* 1933). Thus, the fundamental scientific discoveries leading to a quantitative geologic timescale were made near the beginning of the twentieth century.

The actual development of rigorous radiometric methods of telling geologic time occupied much of the first half of the century. Geochronology is the subject of a voluminous literature, and of a number of standard texts (e.g. Faure 1986). Here, we hope only to give enough background for the reader to gain an appreciation of the developments that permitted its application to the absolute chronology of the Moon and Mars. In preparing this overview, we rely heavily, but not exclusively, on “benchmark” papers assembled by Harper (1973), and his associated commentary.

The development of geochronology during the first three decades of the twentieth century was intimately intertwined with emerging views of the structure of the atom. The study of radioactive elements showed that atoms of the same chemical element could have different atomic weights. For example, we now know that “natural” uranium of atomic number 92 decays via α -particle emission with a very long half-life to the element of atomic number 90 (thorium), which, after two β -decays, becomes element 92 (uranium) again, but with a much shorter half-life than it had originally. However, its atomic mass is lighter by 4 mass units, the mass of the α -particle. This reasoning was expressed by Soddy (1913–14), who suggested the name isotopes for these two types of uranium. The name stems from the Greek *isos* (equal) and *topos* (place), meaning that two different kinds of atoms occupy the same place in the periodic table of the elements. J.J. Thomson also discovered that atoms of a stable element, neon, could have differing atomic weights (Thomson 1913). Later, F.W. Aston, a student of Thomson, discovered that many other elements also were composed of differing isotopes. Romer (1970) provides a historical account of the multiple contributions by many investigators to the “discovery” of isotopes.

A complete understanding of isotopes was not achieved, however, until the discovery of the neutron by Chadwick (1932). This discovery supported the view of the nucleus as composed of protons and neutrons. Atoms of a given element have a fixed number of protons, called the atomic number. However, atoms of a given element may have a

variable number of neutrons. The atomic mass of an atom is approximately equal to the total number of protons and neutrons it contains. These concepts differ from those of Soddy (1913–14) principally in that he envisioned the nucleus to consist of electrons plus protons, and that the algebraic sum of charges in the nucleus gave the atomic number. Nuclei having differing arithmetical sums of particles would have differing atomic masses, but could nevertheless share atomic numbers, constituting his definition of isotopes. Rutherford later suggested that protons and electrons in the nucleus could be so closely bound that they would in effect constitute a new particle, the neutron. This suggestion was confirmed by Chadwick’s work.

The modern term nuclide refers to an atom of specific atomic number and specific atomic mass. Radioactive decay results in conversion of a number, P , of radioactive parent nuclides into a number, D , of daughter nuclides. The daughter nuclide most often is an isotope of a different element than the parent, but sometimes branched-decay into more than one type of daughter nuclide also occurs. The activity, or decay rate, of P parent nuclides is

$$\frac{dP}{dt} = -\lambda P \quad (1)$$

where λ is the decay constant, the probability per unit time that a parent-nuclide will decay. The decay constant is related to the half-life, τ , the time interval required for half the parent nuclides to decay by

$$\lambda = \frac{(\ln 2)}{\tau} \quad (2)$$

The number of radiogenic daughter nuclides, D^* , produced in the time interval $(t-t_0)$ is given by the equation:

$$D^*(t) = P(t) [e^{\lambda(t-t_0)} - 1] \quad (3)$$

where t_0 is the time when the volume containing the parent nuclides became closed, and the daughter nuclides began to be retained, and t is the time when the numbers of parent and daughter nuclides are measured. In geochronology, the volume of interest is a rock or mineral, and $(t-t_0) = T$, the age of that rock or mineral.

It often is convenient to normalize $D^*(t)$ to the number of nuclides, N , of a non-radiogenic isotope of the same element as the daughter to obtain:

$$\frac{D^*(t)}{N} = \frac{P(t)[e^{\lambda(t-t_0)} - 1]}{N} \quad (4)$$

In natural systems, a number, D_0 , of daughter nuclides may be present at time t_0 . In this case, analytical measurements yield not $D^*(t)$, but $D(t) = D^*(t) + D_0$. Thus, in practice, eqn (4) is modified to

$$\frac{D(t)}{N} = \frac{D_0}{N} + \frac{P(t)[e^{\lambda(t-t_0)} - 1]}{N} \quad (5)$$

which contains the measured quantities directly. Although eqns (4) and (5) are simple modifications of eqn (3), determining which equation best described various real systems played a significant role in the development of geochronology.

Development of U–Pb dating

Not surprisingly, the initial application of the above concepts involved the α -decay of uranium and thorium (e.g. Rutherford 1906). Uranium and thorium decay define separate α -decay series ending with three stable isotopes of lead: ^{206}Pb , ^{207}Pb , and ^{208}Pb . A fourth, minor, stable isotope, ^{204}Pb , is non-radiogenic. The two stable elements resulting from uranium and thorium decay are thus lead and helium. Historically, this gave rise to the “chemical lead method” and the “helium method” of telling geologic time, because only chemical methods were initially available to measure the products of radioactive decay. Thus, both methods initially attempted to apply eqn (3) with the simplifying assumptions that (a) the daughter element was initially absent in the rock or mineral analyzed, and (b) the contribution of thorium decay could be ignored, since with purely chemical means there was no way of telling which portion of the helium or lead came from thorium. These considerations initially led to application of the U–Pb method only to uranium-rich ores and minerals.

Arthur Holmes, in writing the first of several treatises dealing with the age of the Earth (Holmes 1913), placed the helium and lead ages of the day into the geological timescale, placing the oldest geological era, the Archean, at 1400–1600 Ma ago according to the lead method. A younger age for the Archean of about 700 Ma was indicated by the helium method, but was attributed to long-term leakage of some helium from such ancient minerals, a potential problem anticipated by Rutherford (1906). Holmes (1913) wrote: “Radioactive minerals, for the geologist, are clocks wound up at the time of their origin. After a few years’ preliminary work, we now are confident that the means of reading these time-keepers is in our possession.” Not all geologists of the time agreed with him, and indeed chemists and physicists were still struggling to better understand the phenomenon of radioactivity itself. Much more effort would go into refinement of the methods of telling geologic time.

The possibility of mass spectrographic determination of the isotopic composition of lead was realized within the next decade, and led to significant refinements of the U–Pb method. Aston (1927) reported the first determination of the isotopic composition of lead in collaboration with C.S. Piggot of the Geophysical Laboratory, Washington. Aston’s instrument was called a mass spectrograph because it separated positively charged ions according to mass, in a manner similar to that in which a light prism separates sunlight into a spectrum of differing wavelengths, and because a

photographic plate was exposed to the impact of electrically accelerated ions. The latter caused ionization of the photographic emulsion on the plate proportional to the number of incident ions. In later instruments, the magnitude of the positive ion current was measured directly. Such instruments are called mass spectrometers and in modern geochronology are used exclusively in preference to mass spectrographs.

Piggot (1928) records how he wrote to Aston, in October 1926, with the suggestion that several problems encountered in the chemical lead method, including the poorly known rate of thorium decay, could be overcome by means of mass spectrograph analysis, which would allow the identification of those lead isotopes produced by uranium decay only. He also wrote that it was he who supplied Aston with the sample of lead tetramethyl used for the analysis reported in the 1927 *Nature* article, and that he was “working up” a sample of radiogenic lead from some very pure Norwegian bröggerite, a mineral containing considerable proportions of uranium and lead, but a very small proportion of thorium. From this sample he hoped to determine directly the uranium-to-lead ratio, “and thereby secure a reliable estimate of its age.” The next year, Aston (1929) reported the results of the isotopic analysis of the bröggerite with the comment: “These figures have been communicated to Mr Piggot, and when combined with the analyses of the mineral should enable its age to be fixed with considerable certainty.”

Fenner and Piggot (1929) later reported the age of the bröggerite as between 920 and 908 Ma as determined from the ^{206}Pb and $(^{206}\text{Pb} + ^{207}\text{Pb})$ abundances, respectively, and 1313 Ma as determined from the ^{208}Pb abundance. Rutherford (1929), in a companion paper to the earlier paper by Aston (1929), had assumed the age to be 1000 Ma. He focused instead on interpreting the spectrographic line corresponding to mass number 207, rather than the mineral age. Rutherford, like Aston (1929), interpreted mass 207 as the end product of actinium decay, and further inferred its ultimate source as an isotope of uranium, of mass 235, which he called actino-uranium. Rutherford estimated “the period of transformation of the new isotope” to be 3.4 Ga. He interpreted this period as an upper limit to the age of the Earth, noting that it was “about twice the age of the oldest known radioactive minerals.” In doing so, Rutherford (a) inferred the existence of undiscovered ^{235}U from the existence of ^{207}Pb , (b) estimated the half-life of ^{235}U , (c) utilized the knowledge that odd-mass isotopes are less abundant than the main even-mass ones to infer $^{235}\text{U}/^{238}\text{U} \leq 1$ at production, and (d) estimated an upper limit on the time of uranium decay, and by assumption on the age of the Earth, from the estimated present-day $^{235}\text{U}/^{238}\text{U}$ ratio. Rutherford’s estimate was within 35% of the age presently accepted, but contained several errors, including the

assumption that uranium was initially produced in the Sun. Furthermore, his estimate (a) used a present-day ^{235}U abundance that was more than twofold too low; and (b) used an estimated ratio of the decay constants for ^{235}U and ^{238}U , $\lambda_{235}/\lambda_{238} = 10.6$, which was too high by about 70%. This estimate nevertheless illustrates Rutherford's scientific insight.

The next advance in U–Pb dating was made without aid of a mass spectrograph. Rose and Stranathan (1936) determined the ratio of ^{207}Pb (“AcD”) to ^{206}Pb (“RaG”) for a number of radiogenic mineral leads from the hyperfine structure of their emission spectra. They assumed the actual progenitor of AcD was not known with certainty, calling it AcU to distinguish it from UI (^{238}U) and UII (^{234}U). They identified the probable mass of AcU as 235 or 239, most probably the former, following earlier suggestions (Russell 1924, Hahn 1925). Rose and Stranathan (1936) derived an expression for the age of the minerals as a function of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{235}\text{U}/^{238}\text{U}$, but not explicitly dependent on the Pb/U ratio; that is, they determined the “Pb–Pb” ages of the minerals, and showed them to be in reasonable agreement with the U–Pb ages. However, they incorrectly assumed $\lambda_{235}/\lambda_{238}$ to lie between 10 and 11, from the earlier suggestions of Rutherford and others. Moreover, the ages of their oldest minerals were about 1 Ga, and did not improve estimates of the age of the Earth.

In a pair of classic papers, Nier (1939a,b) simultaneously reclaimed U–Pb dating for mass spectrometry, and put the method on a sound footing by positively identifying AcU as ^{235}U and by refining the values of the half-lives of both ^{238}U and ^{235}U . He also measured the isotopic composition of Pb in some U-rich minerals. Figure 1 is reproduced from Nier (1939b), and shows the relative abundance of ^{207}Pb and ^{206}Pb in pitchblende from Katanga, Africa. This “mass spectrum” shows that the Pb in this mineral, which Nier (1939b) reported as containing 72.2% U, was entirely radiogenic, and produced from U decay only, being free of both “common” ^{204}Pb and of ^{208}Pb from ^{232}Th decay. From the known α -disintegration rate of bulk uranium, Nier derived decay constants for ^{238}U and ^{235}U , respectively, that were within 2% of currently accepted values of $1.551 \times 10^{-10} \text{ a}^{-1}$ and $9.85 \times 10^{-10} \text{ a}^{-1}$ (Jaffey *et al.* 1971). Furthermore, the corresponding ratio of decay constants that he used was within 1% of the currently accepted value of 6.35, and significantly different from previous estimates. Nier (1939b) calculated ages from the $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in the minerals he analyzed, and found that one uraninite from Manitoba, Canada, was 2200 Ma old, older than the then accepted age of the Earth.

Nier, a physicist, had entered the field of geochronology through work as a postdoctoral fellow at Harvard University in the early 1930s, and, after returning to the University of Minnesota, by building a mass spectrometer

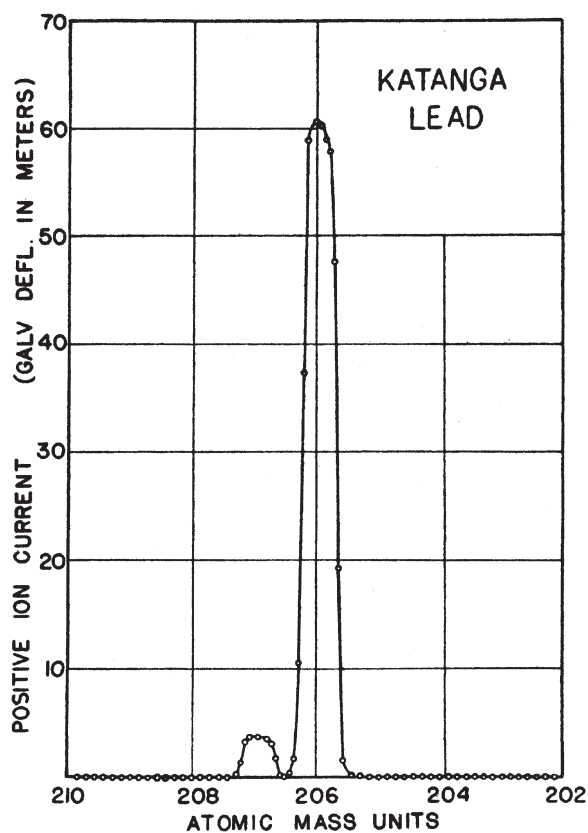


Figure 1 Mass spectrum showing the relative abundance of the isotopes ^{207}Pb and ^{206}Pb , daughter products of decay of ^{235}U and ^{238}U , in pitchblende from Katanga, Africa (Nier 1939b). The heights of the spectral peaks, and thus the abundances of the isotopes, are proportional to the positive ion current striking the ion-collecting electrode of a mass spectrometer. In this pioneering work, the positive ion current was measured with a ballistic galvanometer, as found in many elementary physics laboratories early in the twentieth century. The magnitude of the current was measured by the torsion of the galvanometer coil. A light beam was directed to a mirror attached to the coil, and the coil's torsion measured as meters of deflection of the reflected beam on an opposing laboratory wall (A.O.C. Nier, personal communication).

superior to other instruments of its day. Those interested in the historical development of mass spectrometry, the study of the isotopic abundances of the elements, and geochronology will find his short autobiographical sketch (Nier 1981) fascinating reading. His discovery of ^{235}U not only allowed it to be identified as the radioactive parent of ^{207}Pb , but also led to its identification as a fissionable uranium isotope (Nier *et al.* 1940). Nier often proudly referred to a handwritten note he had received from E. Fermi in October 1939, to the effect that “deciding whether the slow neutron fission (of uranium) is or is not due to the 235 isotope... is of considerable theoretical and possibly practical interest.”



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