CHAPTER 1

Introduction

Occasionally debates arise and hands are wrung about what parts of a scientific discipline really distinguish it from others. Geoscientists often find themselves trying to define the unique perspectives or essential skills at the heart of their field as if failure to properly indoctrinate students in them might put the entire profession at risk. Without commenting on the wisdom of such disciplinary exceptionalism, a reasonable person asked to engage in it could, after some thought, suggest that if there is something distinctive about Earth science, it might have something to do with time. Naturalistic thinking about the evolution and workings of the Earth have been around for centuries if not millennia, and considerations of time at scales far surpassing human experience are a central and obligatory part of any serious endeavor in this area. The facility to deal easily with enormous timescales is such an ingrained part of Earth and planetary science that occasional meditative realizations of even the most hardened scientists are sometimes required to remind them that our ability to envision geologic time accurately and precisely has been in some ways hard won. Before quantitative measurements were available of the durations of time separating events of the past from the present, and of the rates of geologic processes, practically all attempts to understand Earth were, to paraphrase a key historical figure in geochronology (Lord Kelvin), meagre and of a most unsatisfactory kind. Quantitative geochronology as a concept, and especially radioisotopic geochronology as a field in and of itself, revolutionized our understanding of the Earth and planets. More importantly, geochronology continues to be one of, if not the most, important foundation and means of exploration in modern geoscience.

The tools and applications of geochronology find use in a variety of fields besides Earth and planetary science, including archeology, evolutionary ecology, and environmental studies. But the impact of geochronology on Earth science was fundamentally transformative. For one thing, it laid out the boundary conditions for reconstructing the history of the planet and quantitative understanding of the significance of ongoing physical processes like erosion, sedimentation, magmatism, and deformation. It also established, for the first time, a realistic temporal context of existence—not just of life as we know it, but for the recognizable planetary environment that hosts life. This is because the timescales of Earth history and Earth processes (including biotic evolution at that scale) require a fundamentally different temporal perspective than human experience (much less historical records) can offer. While some important geologic and evolutionary processes happen over very short timescales and require chronometers with commensurate sensitivity, many of the most challenging and important observations we make about the Earth reflect processes that occur either very slowly or very rarely, relative to the perspective of humans as individuals, civilizations, or even species. Modern radioisotopic techniques span vast timescales from seconds to billions of years, finding application in problems ranging from the age and pace of individual volcanic eruptions to condensation of the solar nebula and ongoing planetary accretion. The transformative power of geochronology comes from its capacity to expand our understanding beyond the reach of the pathetically short timescales of intuitive human or social perspectives.

1.1 GEO AND CHRONOLOGIES

Extending the timescale of our understanding does not mean just establishing a chronology of events that occurred earlier than historical records or generational folklore allow. It goes without saying that establishing pre-historical records of changes on and in Earth and other planets is practically useful: knowing when a volcano erupted or a nearby fault last ruptured or the age of an extinction or diversification event may be important. Establishing historical chronologies of tectonic events is clearly necessary for practical purposes. But a list of dates or sequence of regional events is of limited value in and of itself, and does little to represent geochronology as way of

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exploring how the planet works using time as an organizing principle or mode of inquiry.

For one thing, there is the question of how to define an event. At one level the question of the age of the Earth is simple, and has been the focus of countless studies since human curiosity began. Modern perspectives on the problem however, shifted years ago from simplistic numerical answers of around 4.56 Ga, to more sophisticated ones that raise issues of how to assign a single age to a protracted evolutionary process complicated by questions of the initial uniformity of and chemical fractionation in the solar nebula, and timescales of accretion, mass loss, and differentiation. Many other questions in Earth and planetary science have evolved similarly as understanding deepened. Continuing efforts to understand the geologic record are no longer satisfied with just knowing "the age" of a particular event such as the Permo-Triassic boundary, the Paleocene–Eocene Thermal Maximum (PETM), or meltwater pulse 1A, but now we need to know the duration, pace, and number of perturbations composing an event, and the detailed sequence and timing of resulting effects. Geochronology has been central to all of these as not only the intended accuracy and precision, but also the essence of the question, changed. Geochronology shows that "events" are not only finite and messy, but manifestations of more interesting phenomena in themselves.

Also, while some scientists see geochronology as a useful tool for addressing pre-defined geologic problems, using geochronology is not the same thing as doing it. The power of geochronology arises from innovative approaches. There is no single template for this, but one could make an argument for at least two types of creative geochronology. The first is adapting new geochemical, physical, or analytical insight or technology to addressing suitable geologic problems. Fission-track dating was developed after methods for observing cosmic ray tracks in insulators were extended to tracks produced by natural radiation sources *in situ* [*Fleischer and Price,* 1964]. Inductively coupled plasma mass spectrometry and its pairing with laser ablation sample introduction both changed isotope geochemistry and geochronology in key ways [e.g., *Halliday et al.,* 1998; *Lee and Halliday,* 1995; *Kosler et al.,* 2008]. K–Ar dating was adapted into one of the most precise and powerful geochronological techniques ever developed ($^{40}Ar/^{39}Ar$ dating) using fast neutron irradiation to create proxies of parent nuclides of the same element and chemical behavior as the daughter nuclides [*Merrihue and Turner*, 1966]. And of course the first radioisotopic date itself was calculated as a marginalia to a nuclear physics study much more concerned with "radioactive transmutations" than with determining the age of anything [*Rutherford*, 1906].

Second, and as is true in many other fields, some impactful advances in geochronology have come not from deliberate engineering but more as refusals to ignore complications. Solutions to such problems often hold potential for illuminating unknown unknowns, which may then be trained to address previously unsolvable problems. When a particular technique appears to "not work" for answering the question originally posed, it may be time to ask why the answer is unexpected and what can be learned from it by reframing the question. Thermochronology, for example, owes a great deal of its modern utility to this sort of lemons-to-lemonade evolution, as the diffusive loss of daughter products was initially considered a debilitating limitation of noble-gas-based techniques [e.g., *Strutt*, 1906] but is now recognized as its defining strength, as increasingly complex as it appears to be [e.g., *Shuster et al.*, 2006; *Guenthner et al.*, 2013].

This is all to say that geochronology is not just a "tool" serving other fields, but is a field unto itself, and one that originates the new ideas and approaches that allow for advances in the areas to which it is applied. Geochronology generates the innovative ways to use nuclear physics and geochemistry to understand natural processes, often by using initially problematic aspects of these systems, and adapting them to questions that initially may not have been asked. It was not until long after we started wondering about the age of the Earth that we started to appreciate questions about the duration of events, stratigraphic boundaries, and diachroneity. And it was not until we developed quantitative tools (serendipitously, in many cases) for measuring dates and rates in new ways that we began to realize the value of understanding many more nuanced time-related problems, like rates of erosion, sedimentation, crystallization, or groundwater flow, the degree to which these processes are steady or episodic, and the scale at which these questions even make sense.

There is no denying geochronology's utility for addressing some of the most fundamental and, in many cases, simple questions in Earth and planetary science. This is true in both a historical sense, as geochronology provided key foundations for geoscience progress over the century, as well as in a continuing sense, as it continues to provide simple formation and cooling ages essential to many geologic studies. So it is reasonable to begin here with a review of the history of geochronology in the context of its original mothers of its necessity: the age of the Earth and, soon thereafter, ages of stratigraphic boundaries. The last part of this chapter then returns to the broader topic of geochronology—the discipline and its objectives and significance—with the hope that the perspective of the historical review drives these home.

1.2 THE AGES OF THE AGE OF THE EARTH

It is impossible to know when humans or perhaps their predecessors first started posing questions about the age of the Earth, but it seems likely that it has been a central focus of human contemplation for millennia. The scope and context of the question has likely changed, and in fact continues to evolve as our resolution of the early days of the solar system improves [*Bouvier and Wadhwa*, 2010; *Brennecka et al.*, 2010]. Ancient Greek and Hindu philosophies explained the age of the "world" in terms of infinite or cyclical ages, the latter punctuated by revolutions of destruction and rebirth, a theme that may originate from the rise and fall of human civilizations, but which may also have been inferred by observant early naturalists from the rock record's evidence for episodes of upheaval and deformation followed by quiescence and slow accumulation.

Propositions for noncyclical and finite ages have also been around since ancient times. Early estimates for a finite age of the Earth (or "world"), which typically have more religious than philosophical origins, tended to converge on timescales in the thousands of years. These included Zoroasters 17th century BCE estimate of 12,000 years, and numerous estimates based on scrutiny of details in the Christian bible. No less than eight well established bible-based estimates for the age of the Earth are known from 169 and 1650 CE, bookended by the Syrian saint Theophilus of Antioch and the famous "scholarship" of James Ussher. All of these invoke ages between 5000 and 9000 years, and all but one are within a narrower range of 5500–7500 years.

The convergence of many "world" chronologies in the range of a few thousand years ago to millennial timescales is an interesting target of speculation. The 1000-year timescales may arise from being just beyond the reach of multigenerational memory of oral histories, but not so far as to seem unreasonable or intuitively incomprehensible. This timescale also is commensurate with the rise and fall of some of the most persistent political empires and cultural dynasties, as well as the timescale of the development of recorded human history. In any case, the eventual recognition that the age of the Earth was not infinite but is actually a million times greater than a few thousand years represented a slow-moving but important change in human perception. That the planet has a deep history of such immensity that it practically challenges our ability to conceive of it, and that it predates humans' presence by more than three orders of magnitude, has been called the fourth great revolution in human cognition [*Rudwick*, 2014].

Although not scientific in modern senses, some scholars consider early attempts to estimate the age of the Earth using biblical records historically important. Many of these essentially counted the number of human generations since the birth of Abraham. Like other pre-Enlightenment scholars who mixed religious and scientific approaches, Johannes Kepler combined biblical accounts with astronomy to arrive at very similar ~6000 ka ages for the Earth as late as the early 17th century. One of the best known of these biblically based, but astronomically laced, deductions is that of the Bishop James Ussher, who in the middle of the 17th century presented the results of his scholarship proposing the beginning of the Earth to be 22 October 4004 BCE. The "9:00 a.m." often associated with Ussher's estimate actually comes from a separate but similar account from a contemporary scholar, John Lightfoot, who put the beginning at the autumnal equinox of 3928 BCE. Incidentally, these results are a good example of the difference between accuracy and precision: Lightfoot's extremely precise time-of-day estimate was a full 76 years younger than Ussher's, and both were obviously lacking much more in the way of accuracy. Readers interested in these early examples are directed to more thorough accounts in G. Brent Dalrymple's "*The Age of the Earth*" [1994] and references therein.

Some historians of the evolution of thinking about the age of the Earth have suggested that early Christian accounts represent respectable nascent attempts to at least take the question seriously and start to frame the problem and possible solutions to it in an analytical and evidentiary way, even if the basis of the evidence was not scientific. Historian Martin Rudwick, in "*Earth's Deep History*" [2014], for example, calls Ussher's work "rigorous," and claims that it does not deserve the ridicule it commonly endures. It may indeed have been a rigorous examination of a document; less clear is the rigor of the documentation of the generations, much less their initiation as a proxy for the birth of the planet. But it may be true that Ussher's studies (and those of a few others) were not exactly sycophantic religious repetition then, but actually somewhat at odds with prevailing eternalism, the idea that the Earth has existed literally forever, at least insofar as humans are capable of understanding, and which to many seemed more reasonable and potentially reconcilable with biblical teachings. Thus Ussher's work and that of others might be considered the beginning of attempts to have a serious think about how old the Earth *could* be, using the scholarly resources available at the time. Rudwick argues that these efforts, while based largely on scripture, are continuous with later scientific attempts, which arose from the same progressive effort to understand the world. To that extent, it may be true that early studies by Ussher and others are distinguished from those of modern creationists (including proponents of intelligent design), whose absurdities are not honest attempts to comprehend anything and do not represent even primitive roots of any kind of legitimate understanding.

But before Ussher gets too much credit, his analysis was based on a religious text that represented the political, economic, and cultural authority of the time, so he probably did not lose sleep worrying whether his "rigorous" scholarship might put him in very real danger at the hands of the Christian power structure, as Galileo and others had only a few years earlier. So although Ussher's work may be detailed and arguably historically important, and may represent an early attempt to challenge the idea of equally nonscientific "eternalism," it does not rank with intellectually honest and courageous work of secular pioneers of the time who risked, and in many cases paid, the price of censure or far worse for crossing church authorities. In any case, the real challenge to human thinking (and, as it turns out, the scientific truth) though, is far different from both the relatively simple perspectives that either the Earth is eternal or its history is basically conceivable in terms of human generations. The far stranger truth is that the Earth is incredibly old, but has a finite age. Indeed it is the fact that it was born a knowable number of years ago in a relatively short period of time which we can know with somewhat startling precision that raises even more questions.

Although some 17th century scholarship on the age of the Earth mixed astronomical observations or theory with "textual" constraints, the Enlightenment brought new ideas about rates of natural processes and actual geologic observations to bear on the question. One important figure in this vein was French diplomat and amateur naturalist Benoit de Maillet. In the early 17th century he constructed a theory for the age of the Earth told through an ingenious parable designed to avoid directly antagonizing the powerful Christian church (undermining Rudwick's claims that the Christian theocracy was no barrier to free thought at the time). Speaking through his fictional Indian philosopher Telliamed (his surname backwards), he combined measurements of rates of regional sea level decline with the height of high mountains and a Cartesian assumption (common at the time) that the earliest Earth was completely covered by ocean and that water was continuously lost through Descartes' mysterious vortices. This led him to the conclusion that the highest terrain must have been covered in water more than two billion years ago, providing a minimum age for the age of the Earth. Although the initial condition and steady decline of sea level is clearly absurd, de Maillet's analysis deserves credit for combining geologic observations and uniformitarian arguments to derive an estimated duration and therefore age constraint.

Other notable 18th and early 19th century attempts to constrain the age of the Earth also followed the general approach of combining a process occurring at an assumed rate with an initial condition of some sort. A popular one was cooling of an initially molten or at least extremely hot Earth. Although as far as we know, Isaac Newton did not directly wade into the debate over the age of the Earth, in the late 17th century he calculated cooling times for planetary bodies and speculated about cooling durations of comets that passed close to the Sun. His contemporary Gottfried Leibniz also speculated about the origins of topography as resulting from differential contraction during cooling of the initially molten Earth. Neither Newton nor Leibniz used cooling timescales to actually estimate ages of planetary or solar bodies, perhaps because they recognized the potential complexities involved, this of course became a popular sport a few hundred years later, in the late 19th century. But long before the famous calculations of physicist William Thomson helped earn him the title of Lord Kelvin, similar experiments and calculations of the provocative natural historian George-Louis LeClerc helped earn him the title Comte de Buffon.

Buffon wrote his major work on the origin of the Earth, "*Époques de la Nature*," in 1778. By this time, advances in natural history had established evidence that Earth history was not static or eternal, but that the planet had changed progressively over time. This included recognition, attributed at least partially to Nicolas Steno, that sedimentary rocks lower in stratigraphic sequences, and hence older, contained macroscopic fossils that appeared to be morphologically simpler than the rocks above them. And in fact the oldest rocks contained no identifiable fossils at all. Progressive change over time, rather than strict steady-state concepts of Earth history, was an important basis of Buffon's (and others') thinking. Although he recognized uniformitarian principles, for example as represented in erosion and deposition, he did not extend these to a simple eternalist vision of the Earth as many other contemporary thinkers, including the purported founder of modern geology, James Hutton, whose strong Christian convictions pervaded his avoidance of questions on the age of the planet, as in "[the Earth shows] no vestige of a beginning, no prospect of an end."

In fact, Buffon's publication "*Nature's Epochs*" ventured to estimate both ends of Earth's history that Hutton said were unknowable. Although many aspects of Buffon's analysis were highly speculative, such as the origin of the Earth (and other planets) by impact of a large comet with the Sun, his work was some of the first to apply basic physics and experiments to the question. Recognizing, as many did by that time, that temperatures beneath the Earth's surface generally increase with depth, Buffon combined this with the then well-accepted idea that the primeval Earth was entirely molten, and set about to experimentally determine the duration of time required to cool an Earth-size body to present surface temperatures. Using cooling times of cast iron balls of varying size at initially high temperatures, he extrapolated his experimental results to determine a minimum age for the Earth on the order of 100 ka. Buffon considered this likely far too low, for reasons that are not entirely obvious but probably related to his recognition that stratigraphic thicknesses required longer timescales if achieved by typical erosion and deposition rates, an apparent problem that was to plague the issue of the age of the Earth for the next ~150 years.

Buffon's cooling timescale experiments, which were built on those of Newton, Liebniz, and others before him, also foreshadowed some of the well-recognized thinking of one of the 19th century's most celebrated scientists, William Thomson, later named Lord Kelvin, whose influence and subsequent arguments have been documented well by *Burchfield* [1975], *Stacey* [2000], and in many other places. Beginning with the same convenient initial condition that the Earth began as a uniformly very hot sphere that cooled gradually with time, simple thermal diffusion arguments led to the basic conclusion that the current surface temperature and near-surface geothermal gradient required something on the order of 100 Ma [*Kelvin*, 1863], a number that he later revised to 20 Ma. Although it was widely recognized as heuristic, and well known that any internal advection would change the result to some degree, this estimate stood as the most reasonable and definitely the most authoritative estimate for more many decades. It also put most geologists (and the few evolutionary biologists of the time), who felt that the Earth must be far older based on observed timescales of ongoing processes, at odds with much of the scientific establishment for the next several decades.

The common account of the reason Kelvin's estimate was so far off is that it came from failure to account for the contribution of radioactive decay to Earth's internal heat. In reality this additional heat is not very significant to the basic result, and its incorporation would not have changed things significantly. The true explanation of the erroneous result is its failure to incorporate the much more effective advective, instead of conductive, transport of heat from throughout Earth's interior to the thin crustal layer where the thermal gradient used in Kelvin's calculations was measured. A far more influential reason that most of the scientific community chose to accept the physicists' estimates over the longer views of geologists came from Kelvin's work on the estimated age of the Sun. Using similar approaches, Kelvin had argued that the Sun could only contain enough heat after initial formation to remain as hot as it now is for no more than about 20 Ma. Assuming that the Earth itself was unlikely to predate the Sun, this placed a strong upper bound on the age of the Earth. Even the discovery of radioactive decay of naturally occurring nuclides near the turn of the century would not change the basics of this argument, as nuclear fusion was not recognized until the 1920s or 1930s, extending the debate and undercurrent of animosity between geologists and physics for several more decades.

Among the many geologists resistant to Kelvin's constraints was then University of Chicago professor Thomas Crowder Chamberlin. Also recognized for proposing that changing CO_2 concentrations in the atmosphere may be responsible for climate change, he suggested that Kelvin's timescale was too short to reconcile with geologic evidence and that there must be another source of heat within the Earth. From this debate comes one of his well cited quotations:

> "*The fascinating impressiveness of rigorous mathematical analysis, with its atmosphere of precision and elegance, should not blind us to the defects of the premise that condition the process.*" [*Chamberlin*, 1899]

Ironically, it would be the physicists again, including a Kiwi by the name of Ernest Rutherford known for the quote, "*All science is physics or stamp collecting,*" who would all underscore Chamberlin's quote by not only helping find the additional heat source but also creating the means for accurate and increasingly precise quantification of the real age of the Earth.

Several other approaches to estimate the age of the Earth were also taken near the end of the 19th century and beginning of the 20th. One of the more productive, at least in terms of numbers of papers, was based on ocean salinity. As described by *Dalrymple* [1994] the "salt accumulation clock" method was first proposed by Edmund Halley (of comet fame), who reasoned as early as 1715 that comparing the total salt content of the ocean to the amount delivered by rivers could provide an estimate of the age of the ocean and, to the extent that the Earth has always had an ocean (and that it began as freshwater…), the Earth itself. Between 1876 and 1909 T. Mellard Reade and later John Joly, as well as others, picked up the approach and derived estimates falling between 25 and 150 Ma, with later estimates tending to inch upwards. The fact that the approach yielded answers converging on something similar to Kelvin's calculation based on heat flow probably aided its apparent legitimacy. But as we recognize now, even if delivery rates of ions to the ocean from rivers (and groundwater, as we now also know is an important source) were to stay constant with time, the ratio of the total amount of any ion in the oceans to this rate does not necessarily produce a time that corresponds to an initial concentration of zero. Analogous to the problem of coupled production and diffusion in open-system thermochronometers, the ratio of current inventory to current rate of accumulation does not account for fluctuations in both through time. In addition to the likelihood that the ocean was not born fresh, it is also subject to loss of its dissolved load at a rate that may vary itself over time. The apparent age may therefore be better thought of as a something approximating the residence time, which for the major ions (Na, Cl, Mg, SO_4) that were the primary focus of these studies, are about 12–130 Ma.

The golden years of the late 19th century for speculative calculations bearing on the age of the Earth also saw estimates based on orbital physics. Around 1879, George Darwin, second son of Charles and most famous for the fission model of the origin of the Moon and creation of the Pacific Ocean basin, developed a complicated set of geophysical arguments involving dissipation of tidal friction and its effect on slowing Earth–Moon rotation, coming up with a minimum estimate of around 56 Ma. This line of investigation was shared by several others including Lord Kelvin himself, who constrained the problem to an age less than about 1 Ga.

Probably few approaches of the pre-radioactivity era received more attention as avenues for estimating geologic time than accumulation rates of sediments or sedimentary rocks. According to *Dunbar* [1949] the great historian Herodotus (484–425 BCE) attempted to understand durations through observing sediment deposition during flooding of the Nile. Extrapolating individual flood events to the sediment pile in the Nile delta he inferred that buildup of the sediment there must have taken thousands of years. He also discusses calculations of durations of time from a statue of Ramses II (about 3200 years old) buried beneath about 2.7 m of sediment, and the burial of a clearly much older burned brick about 12 m beneath the surface. He observed that this made sense with the observed deposition rate from the area of about 9 cm/century, suggesting a sensible uniformitarian approach could at least extend back several thousand years.

One of the most detailed and influential attempts to constrain the magnitude of geologic time was Charles Walcott's 1893 paper in the Journal of Geology. His opening lines characterize the debate at the time:

> "*OF ALL subjects of speculative geology few are more attractive or more uncertain in positive results than geologic time. The physicists have drawn the lines closer and closer until the geologist is told that he must bring his estimates of the age of the earth within a limit of from ten to thirty millions of years. The geologist masses his observations and replies that more time is required, and suggests to the physicist that there may be an error somewhere in his data or the method of his treatment.*"

Walcott divided sedimentary strata of the US Cordillera into clastic and chemical precipitated rocks (in this case limestones). But rather than use arguably more direct estimates of depositional rates extrapolated from short timescales of modern observations as Herodotus did, he employed relatively complex

Period.	Time Duration.
Cenozoic, including Pleistocene - -	2,900,000 years
Mesozoic - - - - - - - -	7,240,000 "
Paleozoic - - - - - - -	17,500,000 "
Algonkian - - - - - - -	17,500,000 "
Archean - - - - - - -	10,000,000(?)"

Fig. 1.1. Estimated durations of time assigned to each geological era by Walcott based on stratigraphic accumulation (and erosion rate) estimates and observations from the US Cordillera. (Source: *Walcott* [1893].)

arguments about rates and areas of erosion providing the raw materials for deposition. Comparing these with thicknesses of stratigraphic units in each of the paleontologically defined eras, he came up with estimates shown in Fig. 1.1 (The Algonkian is essentially the same as the modern Proterozoic). Although the durations are obviously grossly low, it is interesting that the ratios of their apparent durations (except for the Archean and Algonkian, for which there was little sedimentary record in the region that Walcott could observe) are similar to those recognized now.

After Walcott's introduction, cited above, that contrasted geologic versus physics-based approaches, it is somewhat ironic that his estimate for the total duration of Earth history was not very different from that of Kelvin's. Many other estimates based on sediment accumulation were also published in the latest 19th and earliest 20th centuries, and although there were a few exceptions, by far most of them consistently estimated durations and total ages roughly 10 to 100 times too short. While some of this may owe to apparent legitimacy arising from similarities to physics-based methods, it is also undoubtedly an inevitable outcome of failure to properly account for unconformities, recycling, varying depositional (and erosional) rates, the fact that individual basins neither survive nor receive sediments for all of Earth history, and the increasing paucity of the preserved stratigraphic record for progressively older units. Although most of these limitations were recognized, their magnitude was obviously difficult to constrain, so when assumptions were made that yielded final results of the same order of magnitude as previous ones, those were probably considered the most reasonable.

In some ways, the relatively young field of geology of the late 19th to early 20th centuries was not held back by an inability to assign numerical ages to stratigraphic boundaries, deformation episodes, milestones of biotic evolution, or even the age of the planet. Armed with Nicolas Steno's principles of superposition and stratigraphic correlations, Cuvier's extinctions as marked by disappearances of fossil assemblages, and the ability to interpret orogenic episodes, there was a lot that could be done to interpret histories of subsidence, uplift, magmatism, deformation, and the regional extents and relationships of such processes. By 1870s, eras separated by biotic or lithologic differences were well defined (e.g., LeConte, 1879), including the Archaean (or Eozoic), Paleozoic, Mesozoic, Cenozoic, and the most recent era, the Psychozoic (which captures the defining characteristic of human degradation of our planet's habitability somewhat more eloquently than Anthropocene). The business of reconstructing the geologic history of the planet could, apparently, go on with only relative dating and some, at least relative, sense of the amount of time represented in each era.

But pre-geochronology geology floated in time and compressed Earth history the farther back in time one looked, underestimating the true extent of the planet's age by about 100 fold. This was at least partly due to the fact that the geologic record that was interpretable without geochronology was restricted to stratigraphic correlations of sedimentary rocks, particularly those bearing fossils. Correlations and interpretations of Precambrian rocks were difficult if not impossible without geochronology, and igneous and metamorphic units lacking constraints from related sedimentary rocks could be just about any age in any part of the world. Pre-20th century geologists recognized that there was a Precambrian history to the Earth, but the early "Geologic Timescale" basically ignored it. This is somewhat ironic not only because it excludes the vast majority of Earth history but also because the Precambrian–Cambrian boundary represents one of the most significant orogenic, biotic, and sedimentary events to affect the planet. Something huge happened at this time, but there was almost no way to date it or recognize how much time lay before it. In fact, because the Precambrian–Cambrian boundary represented a very widespread if not global event of very limited duration compared to the duration represented by the younger stratified rocks above it, it is an example of one of the completely undated but well-recognized geologic "revolutions" that proved useful for regional and global correlations and establishing the floating Geologic Timescale. According to *Williams* [1893],

> "*As the period of each dynasty in ancient history is marked by continuity in the successive steps of progress of the country, of the acts of the people and of the forms of government, and the change of dynasties is marked by a breaking of this continuity, by* revolutions *and readjustment of affairs, so in geological history the grand systems represent periods of continuity of deposition for the regions in which they were formed, separated from one another by grand revolutions interrupting the regularity of deposition, disturbing by folding, faulting and sometimes metamorphosing the older strata upon which the following strata rest unconformably and for the beginnings of a new system.*"

Geologic revolutions of the late 19th century included the close of the "Archean" revolution, now recognized as end of the Precambrian, as well as the Appalachian revolution (also recognized in Europe by other names), the Palisades revolution of the Jurassic–Triassic, the Rocky Mountain revolution (which was extended over what might now be a disturbingly long period of time, Cretaceous to Miocene, and also apparently distance, as lumped in causally were also the Pyrenees and the Himalaya), and the Miocene Cascadian revolution in flood basalts of the Pacific Northwest. Of course all of these periods were floating in temporal space. The clear and practically instinctive association of numerical ages to geologic periods or eras that we enjoy now did not exist then, and these revolutions could have been millions to tens to hundreds of millions of years old.

By Dunbar's time in the early 20th century, after the discovery of radioactivity but before geochronology had a serious influence on mainstream geologic thinking, revolution concepts were still important bases of understanding, though they had been tweaked a bit. The Rocky Mountain disturbance had been separated into the Nevadan, peaking in the Late Jurassic, the Laramide, near the Cretaceous–Paleogene boundary, the Palisades had been relegated to a "disturbance," the Appalachian was seen to postdate two earlier disturbances, the Acadian and Taconian, and several revolutions were recognized within the Precambrian, the Penokean, Algoman, and Laurentian.

As useful as the concept of geologic revolutions were, most them were not nearly as global or even superregional as typically envisioned, and to a large degree reflected regional tectonic processes largely restricted to the stomping grounds of their investigators. Ironically, the arguably most globally preserved revolution, the Precambrian-Cambrian boundary, did not really rise to the status of a revolution because it represented such a fundamental shift in the rock record as to make it different from all the others. In any case, as late as the early 20th century there was general acceptance that very widespread "events" punctuated the stratigraphic record and therefore Earth history. Although few if any of these retain their nearly global significance, they do point out that even prior to the advent of geochronology there was a great deal known about the geologic record of the last ~542 Ma, even if it was entirely floating in time. Though reliable numerical ages were a long way off and the methods of estimating durations were primitive, some semi-quantitative constraints on the relative amounts of time represented by geologic periods were also available. J.D. Dana did this by assigning sedimentary thicknesses a standard unit of time, and proposing that an equivalent thickness of limestone (which was supposedly much slower to accumulate) represented 5 times the duration of other sedimentary rocks. Williams and LeConte extended this to the idea of the geochrone as a unit of time useful for correlations and fundamental counting tool. As an aside it was also Williams who in 1893 was the first to propose the term geochronology, with a somewhat puzzling emphasis to modern ears that the time concerned is not human-centric:

> "*In all these studies in which the geological time-scale is applied to the evolution of the earth and its inhabitants, the time concerned is not human chronology but is what may be called geochronology.*"

In some ways the geochrone is not a complete anachronism but is still used today. But instead of referencing time to a particular thickness of sedimentary rocks (e.g., the Eocene section in a specific place, as proposed by Williams), it is the orbital period of the Earth around the Sun, 1 year, or 365.256363004 days, or in SI units, 31558149.8 s.

Geochrones, geologic revolutions, and stratigraphic correlations allowed a great deal of Earth history to be reconstructed. The fact that the resulting structure was floating in time did not seem to be of paramount importance, and in fact even the significance of assigning numerical constraints to dates and rates of geologic events and processes any older than a few thousand years was often considered (as it still is by some practically-minded stratigraphers) as wading into a kind of speculative philosophy not unlike asking what existed prior to the big bang.

As late as the 1889 fifth edition of *Elements of Geology*, the renowned Joseph LeConte wrote:

> "*Previous to even the dimmest and most imperfect records of the history of the earth there is, as already said, an infinite abyss of the unrecorded. This, however, hardly belongs strictly to geology, but rather to cosmic philosophy. We approach it not by written records, but by means of more or less probable general scientific reasoning.*"

and

> "*Thus the history of the earth, recorded in stratified rocks, stretches out in apparently endless vista. And still beyond this, beyond the recorded history, is the infinite unknown abyss of the unrecorded. The domain of Geology is nothing less than (to us) inconceivable or infinite time.*"

Meanwhile, a few enterprising German and French scientists in the field that had underestimated the age of the Earth for so long were busy in labs doing experiments whose sometimes serendipitous results would move these questions from philosophy to hard science and begin a scientific and in some ways cultural revolution.

1.3 RADIOACTIVITY

In a universe with only slightly different physics, a conceivable combination of circumstances like the availability of still extant radioactive parent nuclides, the happenstances of trace element partitioning in common minerals, and the achievable precision of mass spectrometers might conspire to make radioisotopic geochronology impossible or at least much more difficult than it is. An almost uncomfortably small number of parent-daughter decay systems (Table 1.1) have decay constants and parent-daughter partitioning that make them geochronologically useful. And an almost absurdly large amount of what is known about the age of the Earth and terrestrial rocks in general comes from the U–Pb system alone. The parent isotopes of this system, ^{235}U and ^{238}U, have already lost 98.5% and 50%, respectively, of their abundance since the beginning of the solar system, and the technique is most often applied to a mineral, zircon, that constitutes only a fraction of a percent in certain rock types. If it weren't for nuclear transmutation and its manifestations in minerals with particular properties, except for the distant limits from astronomers and lifetimes of main-sequence stars, we may still be arguing

Table 1.1 Geochronologically useful radioactive decay systems

Parent/daughter (system)	Reaction or key daughters	Decay constant (a^{-1})	Half-life (a)	Daughter ratio typically measured
$^{147}Sm/^{143}Nd$	$^{147}_{62}Sm \rightarrow ^{143}_{60}Nd + ^{4}_{2}He$	6.54×10^{-12}	1.06×10^{11}	$^{143}Nd/^{144}Nd$
$^{238}U/^{206}Pb$	$^{238}_{92}U \rightarrow ^{206}_{82}Pb + 8^{4}_{2}He$	1.55×10^{-10}	4.47×10^{9}	$^{206}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$
$^{235}U/^{207}Pb$	$^{235}_{92}U \rightarrow ^{207}_{82}Pb + 7^{4}_{2}He$	9.85×10^{-10}	7.07×10^{8}	$^{207}Pb/^{204}Pb$, $^{207}Pb/^{206}Pb$
$^{232}Th/^{208}Pb$	$^{232}_{91}Th \rightarrow ^{208}_{82}Pb + 6^{4}_{2}He$	4.95×10^{-11}	1.4×10^{10}	$^{208}Pb/^{204}Pb$
(U–Th–Sm)/He	Sum of four above			$^{4}He/^{3}He$
$^{87}Rb/^{87}Sr$	$^{87}_{37}Rb \rightarrow ^{87}_{38}Sr + ^{0}_{-1}\beta$	1.42×10^{-11}	4.88×10^{9}	$^{87}Sr/^{86}Sr$
$^{187}Re/^{187}Os$	$^{187}_{75}Re \rightarrow ^{187}_{76}Os + ^{0}_{-1}\beta$	1.67×10^{-11}	4.16×10^{10}	$^{187}Os/^{188}Os$
$^{40}K/^{40}Ca$	$^{40}_{19}K \rightarrow ^{40}_{20}Ca + ^{0}_{-1}\beta$	4.96×10^{-10}	1.25×10^{9}	$^{40}Ca/^{44}Ca$
$^{40}K/^{40}Ar$		0.581×10^{-10}	1.25×10^{9}	$^{40}Ar/^{36}Ar$
^{238}U/fission	Variable daughters + fission track	8.45×10^{-17}	8.20×10^{15}	Track density/^{238}U
$^{138}La/^{138}Ce$	$^{138}_{57}La \rightarrow ^{138}_{58}Ce + ^{0}_{-1}\beta$	6.80×10^{-12}	1.02×10^{11}	$^{138}Ce/^{136}Ce$
$^{138}La/^{138}Ba$	$^{138}_{57}La \rightarrow ^{138}_{56}Ba + ^{0}_{+1}\beta$	6.80×10^{-12}	1.02×10^{11}	
$^{176}Lu/^{176}Hf$	$^{176}_{57}Lu \rightarrow ^{176}_{56}Hf + ^{0}_{-1}\beta + v$	1.87×10^{-11}	3.71×10^{10}	$^{176}Lu/^{177}Hf$
^{238}U series	Commonly used daughters: ^{234}U, ^{230}Th, ^{226}Ra, ^{210}Pb, ^{210}Po	$0.01–2.82 \times 10^{-6}$	1.00×10^{2} to 2.46×10^{5}	($^{234}U/^{238}U$), ($^{230}Th/^{238}U$), ($^{226}Ra/^{230}Th$), ($^{210}Pb/^{226}Ra$), ($^{210}Po/^{226}Ra$)
^{235}U series	Commonly used daughters: ^{231}Pa, ^{227}Ac	$0.03–2.12 \times 10^{-5}$	$22.8–3.28 \times 10^{4}$	($^{231}Pa/^{235}U$), ($^{227}Ac/^{231}Pa$)
^{232}Th series	Commonly used daughters: ^{228}Th, ^{228}Ra	0.12–0.36	1.92–5.75	($^{228}Th/^{232}Th$), ($^{228}Ra/^{232}Th$)

about the age of the Earth and solar system, or relegating such discussions to cosmic-philosophy as was common less than one hundred years ago. But fortunately, there are sufficient numbers of geochronologically useful decay systems, undecayed parents, and minerals available to us.

The first graying of the dawn of the nuclear era is usually associated with Wilhelm Conrad Roentgen's discovery of X-rays in Wurzburg, Germany in 1895. Although not due to natural radioactivity, his discovery of radiation that had the ability to penetrate most solids (c.f., the X-ray image of Roentgen's wife's hand complete with wedding ring) set the stage for an even more serendipitous and portentous discovery in the next year. In spring of 1896 Henri Becquerel performed a series of experiments in which he determined that uranium-bearing salts had the ability to darken photographic plates. His own iconic figure features a fuzzy image of two rectangular dark spots on a plate, corresponding to photographic impressions left by two plates coated in uranium-bearing salt; one of the rectangles shows a lighter region corresponding to a Maltese cross that Becquerel placed between the salt and photographic plates to demonstrate the lesser penetration through the iron (Fig. 1.2). Interestingly, very similar experiments had actually been done and observations made about 40 years before this, by a French photographic inventor with the impressively lengthy name Claude Félix Abel Niépce de Saint-Victor, who noted that uranium produces "a radiation that is invisible to our eyes." In fact, Henri Becquerel's father Edmond had written about these observations in his book about light published in 1868.

Less serendipitous and more deliberate systematic explorations into natural radioactivity and a series of foundational discoveries

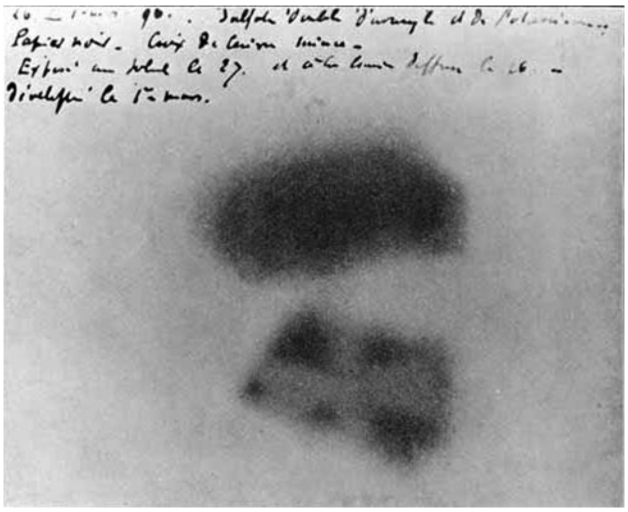

Fig. 1.2. Henri Becquerel's 1896 image of a photographic plate exposed by natural radiation from uranium-bearing salts. The lower of the two shows the shadow of an iron Maltese cross placed between the sample and the plate. (Source: https://en.wikipedia.org/wiki/Henri_Becquerel#/media/File:Becquerel_plate.jpg)

by Marie, and later Pierre, Curie soon followed Becquerel's work. Marie Curie measured electrical charge on the air surrounding uranium, and observed that its extent depended only on the amount of uranium present, leading to a hypothesis that uranium's radiation came from the atom, not molecules. She also observed that other U-bearing minerals were far more radioactive than uranium, leading to the insight that other elements must also be radioactive. Although she is often credited with discovering that Th is also radioactive, this was actually published in Berlin two months before by Gerhard Carl Schmidt. However, her more important insight, that uranium minerals contain small amounts of much more radioactive elements, soon led her and Pierre to large-scale chemical separations of constituents of uraninite (pitchblende), and the discovery of polonium and radium and recognition of their highly radioactive nature. In 1903 Marie and Pierre Curie (Fig. 1.3) and Henri Becquerel won the Nobel Prize in Physics; Marie also won a second prize in 1911 for her work on radium; their daughter Irène Joliot-Curie also won the Nobel in 1935 for discovery of artificial (neutron-bombardment induced) radioactivity.

The Curie's work on radioactivity accelerated progress on natural radioactivity at the turn of the century. In 1899 the Kiwi physicist Ernest Rutherford (Fig. 1.4) distinguished two types of radiation with different penetrating powers that he termed alpha and beta. He also discovered that thorium produced a gas, or "emanation" as he called it, that was itself radioactive, and that the activity of this gas followed a law whose differential form is $dN/dt = -\lambda N$, establishing the concept of the radioactive decay constant and half-life, which he determined for Th-emanation (now known to be ^{220}Ra) as 60 s (not far from today's accepted value of 55.6 s). In the process he also noticed that Th-emanation itself eventually produced another radioactive substance, which we now recognize as ^{212}Pb.

Working together between 1900 and 1903, *Rutherford and Soddy* [1903a,b] further characterized other intermediate daughter products of the U- and Th-series (as did several other workers of the time), suggested that He could be a decay product of radium, and they developed the "atomic theory of disintegration" that proposed radiation as a byproduct of "spontaneous transformation" of atoms of one element into those of another. They also delineated part of the first U- and Th-series decay series chain, and mathematically described its behavior (Fig. 1.5);

Fig. 1.3. The 1903 Nobel Prize winners Marie and Pierre Curie as depicted on the French 500-Franc note. (*See insert for color representation of the figure*.)

Fig. 1.4. The 1908 Nobel Prize winner Ernest Rutherford as depicted on the New Zealand 100-dollar note. (Source: https://commons.wikimedia.org/wiki/File:100Neuseeland-Dollar_vorderseite_21585256953_02d6c65788_o.jpg. Used under CC BY SA 3.0.). (*See insert for color representation of the figure*.)

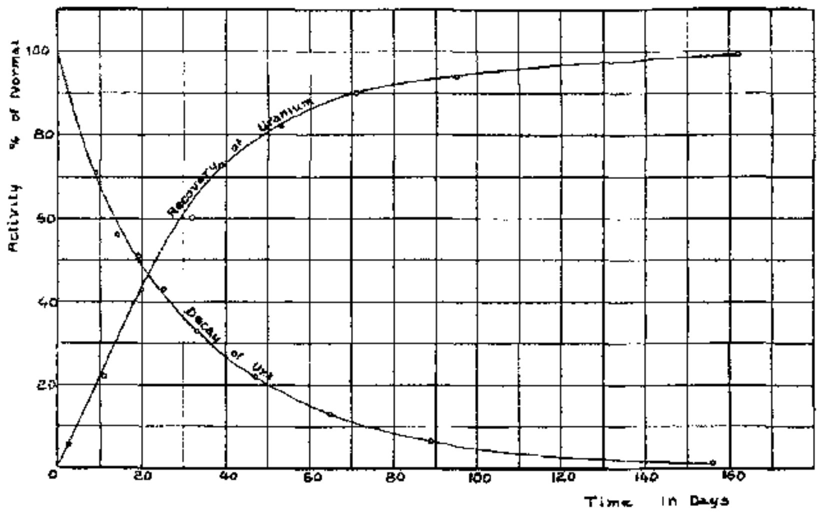

Fig. 1.5. Original figure from *Rutherford and Soddy* [1903b]. The curve showing an increase with time is the beta-activity of uranium from which a then unknown substance called uranium-X (now recognized as ^{234}Th) had been chemically removed, and the decreasing curve is the activity of the separated uranium-X. Through this experiment Rutherford and Soddy estimated the half-life of U-X (^{234}Th) as 22 days (now known to be 24.10 days) and recognized the beginning of the ^{238}U decay chain. (Source: *Rutherford* [1903]. Reproduced with permission of Taylor & Francis.)

this was followed up in a more complete way by *Harry Bateman* [1910], who laid out the differential equations and solutions for chained decay systems.

The year 1905 is sometimes referred to as the *annus mirabilis* for publication of Albert Einstein's four foundational physics papers, including the one with the famous equation relating nuclear energy, mass, and the speed of light. But it also was not a bad year for the study of radioactivity and geochronology. New Haven chemist Bertram Boltwood noted that Pb was likely a decay product of U, and in a series of lectures at the World's Fair in St. Louis and also at Yale, Rutherford presented a calculation of the first radioisotopic age. He described the calculation in a 1905 publication. Because the rate of He production directly from U was not known, but the Ra to He production was, Rutherford combined an assumption of U–Ra secular equilibrium with He and U concentrations, measured previously by William Ramsay and Morris Travers, on a sample of fergusonite, a Nb–Ta oxide, to obtain an apparent age of about 40 Ma [*Rutherford*, 1905]. In his book *Radioactive Transformations* [1906] he uses a different Ra to He production rate to obtain an age on the same sample of about 500 Ma, which he noted was likely a minimum as some of the He may have escaped. In the same work he also calculated 500 Ma for a uranium-bearing mineral from Glastonbury, Connecticut analyzed by W.F. Hillebrand. For some reason these calculations were undertaken assuming a simple linear relationship between the U (Ra) and He concentrations and Ra decay rate, even though Rutherford was aware of, and in fact derived with Soddy, the mathematical descriptions of radioactive decay and growth several years earlier.

Interestingly, in his 1906 book Rutherford also described W.F. Hillebrand's observations that U/He (though Hillebrand thought, as others prior to about 1902, that the inert gas in U-bearing samples was N_2, not He) ratios appeared to be fairly constant for "primary" minerals in certain locations but different from U/He ratios of similar minerals in other places. Given that Rutherford recognized the likelihood that some fraction of radiogenic He is lost from samples over time, the attention he pays to this observation suggests that he recognized the potential of the U–He system to represent something about regional geologic histories.

Although the accuracy, precision, and exact geologic significance of these first radioisotopic ages are not clear, their symbolic scientific importance was huge. Simple as they were, they were literally the first time humans resolved the timing of *something* in deep time using fundamental physical foundations relying only on uniformitarianism of decay constants. The ages came with a kind of cosmic insight that had been missing from centuries of "scholarly reasoning," wishful thinking, semi-quantitative heurism, and floating timescales. The fact that two almost arbitrary mineral samples from different places yielded ages about an order of magnitude older than prevailing estimates for the age of the entire Earth must have suggested to some that either the physics was missing something and the method was completely useless, or that physics had just provided something like a Promethean lens with which to understand the Earth and universe in an entirely new and powerful way.

Also in 1905, and in rapid succession over the next few years, Robert John Strutt (later the 4th Baron Rayleigh) published a large number of analyses and calculated ages of minerals and related materials based on the relative concentrations of He, U and Th, the latter which Strutt recognized as also producing radiogenic He. Strutt noticed that (U–Th)/He ages of specimens thought to be from the same geologic stratum in different places yielded different apparent ages, and that many samples lost He at room temperatures at rates approaching, and in some cases higher than, their production rates. This He "leakage" rendered the method largely unusable for the tasks of the day, which were to establish the age of the Earth and to place reliable numerical estimates on key parts of the geologic timescale.

Around the same time, Bertram Boltwood, a prolific scientific penpal of Ernest Rutherford [*Badash*, 1969], carried out experiments showing that Pb was likely the end-product of decay of U. Using the reasoning that the number of decays of U to Ra was the same as the number of decays of Ra to Pb (i.e., secular equilibrium), Boltwood calculated an apparent decay rate of U (around 1×10^{-10} a^{-1}), and combined this with measured U/Pb ratios in a series of minerals from a variety of areas, coming up with ages ranging from 410 Ma (for a sample from Glastonbury, Connecticut) to 2.2 Ga. If Rutherford's initial ages were in essence thermochronologic ages, Boltwood's were the first real geochronologic age estimates, insofar as they came closer to estimating formation rather than potential cooling ages.

Recognizing that Pb provided a more promising daughter product than He for measuring formation ages, one of Strutt's most famous students, Arthur Holmes, began a long series of studies carefully characterizing U/Pb ratios and apparent ages of a wide variety of samples strategically chosen from various parts of the geologic timescale. Initial results, published in 1911, carried a lot of promise for the new U/Pb dating method, showing regionally and stratigraphically consistent ages (Fig. 1.6).

Somewhat surprisingly, given geologists' decades of kvetching that physicists had the age of the Earth far too young, radioisotopic geochronology did not catch on quickly in geology. Once ages of many minerals were starting to look one to two orders of magnitude older than mainstream physicists' estimates, it was the geologists who generally became skeptical of the whole approach. Many proposed variable decay rates as a most probable culprit. Two US Geological Survey geologists led the skepticism prominently. *George Becker* [1908] measured U/Pb ratios of altered uranium minerals in Texas, finding apparent ages in some cases older than 10 Ga, prompting him to reiterate earlier arguments based on oceanic sodium accumulation and terrestrial "refrigeration" (à la Kelvin) that made these new estimates essentially untenable [*Becker*, 1910]. Even as late as 1924, the famous geochemist Frank Wigglesworth Clarke (with Henry Washington) cast copious doubt on radioisotope methods because they appeared to be so discordant with earlier methods that seemed

The Association of Lead with Uranium in Rock-Minerals.

Geological period.	Pb/U.	Millions of years.
Carboniferous	0·041	340
Devonian	0·045	370
Pre-carboniferous	0·050	410
Silurian or Ordovician	0·053	430
Pre-Cambrian—		
a. Sweden	0·125	1025
	0·155	1270
b. United States	0·160	1310
	0·175	1435
c. Ceylon	0·20	1640

Fig. 1.6. Table of early U/Pb ages. (Source: *Holmes* [1911].)

to converge in the much more "reasonable" tens to (maximum!) hundred Ma age range.

Although dating based on radioactive decay had a long way to go before mainstream acceptance, it was pursued in the early 20th century by a number of pioneering geologists with clever ways of estimating ages from U/Pb chemical dating. In 1917, Joseph Barrell made the first real attempts at delineating the boundaries between the main geologic eras, in his poetic and prescient publication "Rhythms and the measurement of geologic time." Aside from discussing what we now call Milankovitch cycles and climatic influences on sedimentation, he came pretty darn close (especially considering the tools and data available) to the currently recognized era boundaries: Cenozoic–Mesozoic at 55–65 Ma, Mesozoic–Phanerozoic at 135–180 Ma, and Phanerozoic–Precambrian at 360–540 Ma.

Attempts to use radioactivity to hone in on the age of the Earth itself started to approach at least the right order of magnitude, for the right reasons, with Henry Russell, an astronomer, who used relative concentrations of radioactive and radiogenic elements in the Earth's crust. His best estimates came up with a maximum age of about 8 Ga from U, Th, and Pb concentrations, and a minimum of about 1.1 Ga, from the oldest U/Pb age on minerals that he considered reliable.

As the era of radioactive "chemical" dating came to a close near the end of the 1920s, the geochronologic giant Arthur Holmes redid Russell's calculations, using U, Th, and Pb concentrations in the crust to estimate a most likely age of 1–3 Ga for the Earth [*Holmes and Lawson*, 1927]. He also amassed a good deal of previous data to delineate ages for various parts of the geologic timescale, and compared estimates from various methods.

With increasing convergence of an increasing number of calculations pointing to ages in the 1–3 Ga age range, and with the official authoritative blessing of an National Research Council committee report appointed by the National Academy of Sciences in 1931, the question of the age of the Earth appeared to have been solved (though not to all geologists, by any means) to at least an order of magnitude, and probably a factor of a few.

In the middle part of the 20th century, further progress in geochronology received a huge boost from the proliferation of mass spectrometry, begetting truly radioisotopic geochronologic methods. The recognition that some elements comprised atoms with more than one mass is generally attributed to Frederick Soddy. The name isotope referred to the fact that two different types of an element occupy the same place in the periodic table, and is said to have been suggested to him by novelist and medical doctor Margaret Todd during a dinner party in Glasgow. An example of the observations behind this insight go at least as far back as Boltwood's 1906 notes that a decay product of uranium, then called ionium and now known to be ^{230}Th, was chemically identical to thorium (i.e., ^{232}Th).

Ernest Rutherford's former advisor, J.J. Thomson, is generally given credit as the first one to separate isotopes of an element by mass spectrometry, identifying ^{20}Ne and ^{22}Ne in 1913. Another student of Thomson's, Francis Aston, built a mass spectrometer for the purpose of separating nuclides based on mass-to-charge ratios, and he identified multiple isotopes of Cl, Br, and Kr, earning a Nobel Prize in 1921. By 1929 Aston had measured the isotopic composition of radiogenic Pb in a Norwegian sample of broggerite (Th-bearing uraninite) and showed it to have much higher proportions of ^{206}Pb and ^{207}Pb than common Pb. Besides attributing the ^{206}Pb to U decay, he noted that the ^{207}Pb must have come from a precursor with an atomic mass of about 231, naming this element protactinium (actinium had actually been discovered much earlier, by DeBieren in 1899). Immediately following Aston's discovery, Fenner and Piggot were the first to use radioisotopic compositions of an element to calculate ages, combining the ^{206}Pb–^{207}Pb and ^{208}Pb abundances with the U and Th contents of the same sample analyzed by Aston, to obtain apparently discordant ages of 908 and 1310 Ma for the U–Pb and Th–Pb systems, respectively.

Also in 1929, Rutherford proposed that the parent of Aston's protactinium (actino-uranium) was likely to be a uranium isotope with a mass number of 235. After estimating the decay constant of the new element, he calculated the amount of time that would be required to reduce an assumed $^{235}U/^{238}U$ value of unity (as a heuristic assumption for an initial value in the solar nebula) to the present value, which he estimated as about 0.28%. His answer, which he presumed provided a constraint on the time since the Earth separated from the Sun, was 3.4 Ga (although using the now more accurately known constants this becomes 5.9 Ga). Rutherford noted that this was approximately twice as old as previous U/Pb age determinations on any terrestrial sample. This was the first constraint on the age of the Earth from isotopic compositions. (As an aside, in the same paper, Rutherford then used a contemporary accepted age estimate for the Sun (of seven trillion years), to infer that the Sun must have been able to produce uranium at least as recently as about 4 Ga, and probably still does today…).

Dramatic improvements in mass spectrometry occurred through the 1930s and 1940s, driven largely by concerns quite different from determining the age of the Earth and its rocks, primarily nuclear physics and the Manhattan Project. Applications to Pb isotopic compositions led quickly to generally converging estimates of the age of the Earth in the 2–4 Ga range. Alfred Nier, at the University of Minnesota, measured Pb isotopic compositions of both Pb ores (low U/Pb) and uraniferous (high U/Pb) samples from a variety of locations. Besides calculating ages of many samples that supported the existence of minerals with ages older than several billion years, he proposed that Pb isotopic variations could arise from separation of materials from primordial Pb into reservoirs with a range of U/Pb ratios over time. In 1942, E.K. Gerling, who also pioneered interpretation of diffusion kinetics of noble gas thermochronometry well ahead of his time, used this approach and Nier's measurements to develop some of the first Pb-dating approaches that became widespread in subsequent decades. Using a combination of minerals dominated by radiogenic and ore Pb, he used complex but prescient arguments to establish durations of time required to generate Pb isotopic differences, including a minimum estimate of 3.94 Ga for the Earth.

Somewhat similar approaches to estimating durations required for generating Pb isotope differences were also taken, independently, by Holmes and Houtermann through the 1940s and 1950s, obtaining constraints generally pointing to 3–4 Ga ages. As technically robust as many of the analyses were, and as insightful and useful as they were for understanding common Pb behavior in the crust, they required assumptions about source homogeneity, isolation of reservoirs, and durations of "events" that separated these reservoirs that limit their ability to accurately constrain the age of the Earth beyond the prevailing convergence of approximately 3–4 Ga.

Clair Patterson's famous 1956 paper "*Age of meteorites and the Earth*," was similar but introduced a significant variation on the Pb isotope riff, introducing the age of meteorites into the question. In an elegant two-figure paper, Patterson combined primitive Pb isotopic compositions of meteoritic (Canyon Diablo) troilite with that of several other meteorites. He showed that these meteorites form a single isochron consistent with

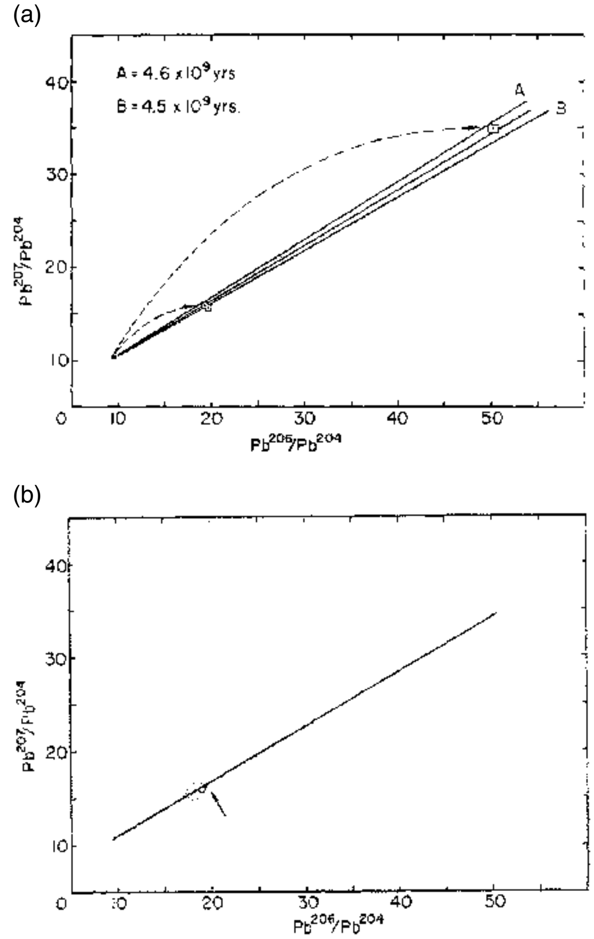

Fig. 1.7. (a) Pb-isotopic compositions of five meteorites. The least radiogenic point (near 10,10) represents troillite analyses from two different metallic meteorites; the other three points are from stony meteorites. The central line is the regression through the meteorite points; A and B represent isochrons with ages shown in legend. Curved dashed lines represent the evolution of Pb-isotopic compositions with time inferred for closed-system sources derived from the same reservoir as the troillite point. (b) The reference meteorite isochron compared with the Pb isotopic composition of oceanic sediment (unfilled circle) and a selection of recently formed galena ores (dashed field). (Source: Figures 1 and 2 from *Patterson* [1956]. Reproduced with permission of Elsevier.)

fractionation of U and Pb about 4.550 ± 0.070 Ga and closed system behavior since then (Fig. 1.7). Rather than comparing this isochron with numerous terrestrial samples, he then argued that a convenient proxy for the bulk common Pb composition of Earth could be estimated by oceanic sediment, which was rather close to many galena ores. Patterson may have been motivated to use oceanic sediment, distant from anthropogenic sources, partly because of his other work demonstrating the widespread Pb contamination of natural environments from burning of leaded gasoline. Although we now understand that even natural Pb-isotopic compositions of oceanic sediment vary more widely than the small range represented by Patterson, however fortuitous his sample choice was, the basic idea was not flawed. As long as one accepted the cogenetic nature of the Earth and the meteorites he chose for this study, and the approximation of his oceanic sediment for the Pb isotopic composition of the bulk Earth, the question of the age of the planet was at least close to settled.

Since Patterson's time, older terrestrial rocks and minerals have been discovered and dated precisely and accurately and have provided important geological understanding. Examples include early Archean units in Greenland and the Acasta gneisses of northern Canada [e.g., *Moorbath et al.*, 1975; *Bowring et al.*, 1989], and the well-known Jack Hills detrital zircons of western Australia, some of which yield concordant ages as old as 4.4 Ga [*Compston and Pidgeon*, 1986; *Wilde et al.*, 2001]. As far as determining the age of the Earth, the problem is no longer inadequate chronometers, but instead recognizing that the formation of the Earth was not an instantaneous event, not even on the scale of chronological resolution provided by radioisotopic geochronometers. The circa 4.567 Ga crystallization ages of some components of meteorites can now be determined with precisions of tens of thousands of years, but Earth growth likely took tens of millions of years. The processes involved in growing the Earth were sufficiently energetic that they continually reset the radioactive clocks in ways that are not yet well understood. As a result, most attempts to determine a singular age for the Earth, such as Patterson's, provide, at best, something approximating an average age for the interval of Earth growth. While "four and a half billion years" likely will remain a valid answer for the general age of the Earth, we can now ask this question in more detail. For example, when did Earth acquire its bulk composition, when did it form its core and atmosphere, and when did it form its first crust? Much like how the principle of superposition allowed resolution of the processes involved in the growth of sedimentary deposits, the precision obtainable with modern geochronometers is allowing the decoding of the processes involved in the growth of the Earth as a planet.

1.4 THE OBJECTIVES AND SIGNIFICANCE OF GEOCHRONOLOGY

Much of the preceding review focuses on the ability of geochronology to address ostensibly simple problems like the age of the Earth and of stratigraphic boundaries, and the history of those challenges as if they were linear pursuits with clear endings defined by sufficiently small error bars on a single number. It is true that the age of the Earth and of the punctuations in its biotic evolution are of great importance. As Martin Rudwick, and Steven J. Gould before him, suggested, the discovery of deep time and the historical evolution of the Earth and its inhabitants requires a cognitive expansion in human perspective beyond the generations, revolutions, and rises and falls of civilization, and therefore another displacement of humanity as the center of the universe, in this case with respect to time.

But as important as these questions are, geochronology is not just about determining the age of the Earth, marking precise mileposts on the geologic timescale, or even simply dating more geologic "things." If it were it would be an anachronism, minimizing its significance by its own progress—an exercise of increasingly specific, local, or minute geologic features. Simple questions posed as problems for hyperprecise dating raise the question of just how abrupt or well-defined events or processes are in the first place and so how precisely they could ever be known. Fortunately, questions that start out as easily posed usually do not end up that way. The Earth did not instantaneously appear, but was accreted over time, possibly with significant episodic mass loss, not to mention differentiation episodes; all these continue today, complicating questions of when. Similarly, stratigraphic boundaries are almost certainly diachronous to some degree, and the question of how diachronous they are may be at least as interesting as their regionally averaged age. For example, one could imagine that the K–P boundary may be diachronous over hours, whereas others defined by evidence for biostratigraphic changes that are less catastrophic may be over millions of years. The most interesting questions may have fundamental temporal aspects, but they are not solved by determining a single number with units of time.

Besides questions of instantaneousness and diachroneity, geochronology as a science in its own right comes from questions about not just dates, but also durations, rates, frequencies, and fluxes of geologic and planetary processes. Time is a fundamental characteristic of any natural process, and in many cases a timescale of some kind may be the most important part of understanding the process. For example, in struggling with the question of geochrones and stratigraphic durations, geologists of the pre-radioactivity era struggled with much more fundamental and physically enlightening questions: how long does erosion take; how long does sedimentation take? Why does it vary and what does that tell us? How long does it take to build a volcano, crystallize a pluton, or for groundwater to move through an aquifer? How steady or episodic are these processes and so over what timescales and length scales do these rates actually have a useful answer? Are these even reasonable questions with clear answers of the kind we are asking, or are these processes more complex than recognized by our simple questions? For example is groundwater transport far more complicated than can be expressed by a simple velocity, or will the attempt to answer the question lead to insights about episodicity of fluxes, mixing with ancient or multi-sourced fluids, dewatering and sorption with subsurface minerals, etc.? Although it is sometimes used this way, the objective of geochronology is not simply to estimate or deduce simple ages with which to label predefined geologic features as if the only thing left to understand is their birthdays. Geochronologic studies may start with simple questions, but most the power comes from harnessing the versatility of radioisotopic decay in analytically and interpretationally innovative ways. This often means resisting the temptation to declare that a geochronologic investigation "did not work." Unexpected geochronologic results are often interpreted as method failure, but the history of geochronology itself shows that these are often the most important results, leading to critical insights into the behavior of the radioisotopic systems or the geologic processes themselves.

One simple interpretation of a date is closure of the sample (a crystal, rock, fluid, etc.) to gain or loss of parent and daughter nuclides (or "daughter" damage effects). In many cases this may be reasonably argued to correspond to closure, especially for systems involving relatively immobile parent and daughter elements and single crystals or parts of crystals. Some consider this "geochronology" in the strict traditional sense—dating the age of formation of a phase. But geochronology could also refer to the collective activities of constraining other types of ages, rates, durations, and thermal histories, and processes with a key temporal aspect.

In other cases, age interpretations benefit from the consideration of open system behavior of either the parent or the daughter subsequent to formation of the sample. In most cases it is the daughter that is more easily lost, and this leads to great utility in thermochronology, U-series, and cosmogenic methods, as the chapters in this book demonstrate. Preferential loss of a daughter product is not a coincidence: typically the most useful systems are those in which the parent/daughter ratio is high, and if this is true the parent "fits" well into the crystallographic structure relative to the daughter, most likely because of its ionic radius and charge, and is therefore partitioned into it. In contrast the daughter is less welcome in the structure and more likely to be lost if opportunity or disturbance (typically thermal) arises. Therefore when we talk about closure we mostly mean cessation of loss of daughter products. But there are exceptions to this: Lu/Hf in garnet for example: although Lu partitions into garnet more than Hf, Lu has a higher diffusivity so may migrate out during high-T events.

Open-system behavior of radioisotopic systems is often associated with migration of daughter products by thermally activated diffusion (or annealing). Thermochronologic applications resulting from this have a wide range of uses in both low and high temperature settings. In some cases, geochronologic ages may be associated with neither formation nor temperature change, but other kinds of processes. Exposure or burial ages, for example, are commonly the target of cosmogenic nuclide and luminescence or ESR studies. Compositional changes, such as diagenetic uptake of parent nuclides accompanying fossilization, hydrothermal activity, or the timing of comminution are targeted by some types of U-series or ESR dating. In many cases, geochronologic approaches do not yield a simple date, but instead some other kind of temporal constraint. In many cosmogenic or low-temperature thermochronologic studies, for example, ages themselves carry little meaning other than through their relationships among samples, which can yield spatial or temporal patterns of erosion. Many U-series studies provide not dates, but minimum or maximum durations of time since material transfer, phase changes, transport, or other processes that fractionate intermediate daughter products. Some groundwater studies of He and H isotopes aim for constraints not on dates but rates of movement through underground reservoirs. Sedimentation rates have traditionally been the target of ^{230}Th excesses in deep-sea sediment.

Highly directed applications of geochronology to specific objectives have a long and successful history: e.g., determining the age of the Earth, ultraprecise stratigraphic dates, and astrochronologic calibrations. Deliberate and strategic method developments also have a distinguished track record: e.g., the engineering of ^{40}Ar/^{39}Ar dating, ^{4}He/^{3}He diffusion experiments, intercalibration of decay constants, and precise measurements of cosmogenic production rates. But some of the most important results of geochronology have been exploratory or even serendipitous, even if our professional propensity to recast our findings as resulting from carefully designed strategic plans make this hard to recognize. Few other approaches in geoscience have the ability to yield surprising results with minimal effort. Relatively straightforward techniques for measuring ages can be easily and widely applied in exploratory ways, rather than highly considered or routine conventional ways. In context, exploratory geochronology has the potential to relatively easily reveal insights that we did not know we did not know, especially when datasets are conscientiously combined, in the manner of abductive discovery advocated by *Hazen* [2014].

Discovery in geochronology also comes from exploring physical and chemical behavior of the chronometric systems. Our actual mechanistic understanding of how parent and daughter elements (or features) behave in minerals lags far behind our geologic applications. The lag is not in the basic physics of decay and decay constants, which are well known. Rather, many aspects of our understanding of the isotopic systems that we use are highly heuristic models based on relatively simple observations of complex systems. While we make many assumptions about daughter (and parent) nuclide partitioning and behavior in (usually ideal, perfect lattices of) crystals, in reality our mechanistic understanding of nuclide behavior at the atomic scale and the effects of defects are quite primitive. New discoveries of radioactive and radiogenic nuclide behavior at the atomic scale are revealing how complex these systems can be, but also what incredible archives of planetary history these complications can reveal [e.g. *Kusiak et al.,* 2015; *Valley et al.*, 2015]. Surprising but powerful insights also come from the behavior of parents and daughters in cases where interphase partitioning, intragranular media, or fluids impart unexpected behavior [e.g., *Camacho et al.*, 2005]. Innovative geochronology of the terrestrial planets, an endeavor that is evolving from analysis of accidentally launched samples [e.g. *Shuster and Weiss*, 2005; *Zhou et al.*, 2013] to more deliberate sample return and dating *in situ* [*Farley et al.*, 2014], also holds great promise for experimenting, exploring, and discovering.

This book contains chapters on many (but not all) of the tools of the trade of geochronology, a field that has become incredibly diverse and powerful since Williams proposed the term in 1893. The chapters aim to provide a blend of history, theory, nuts and bolts, and applications, all in a modern outlook that raises questions and nudges towards innovation, for the various techniques.

What ties these chapters and techniques together is the underlying question of dates and rates. As geochronology has expanded and the applications and approaches have become so varied and versatile that many modern objectives are much more nuanced than simple formation ages, the common themes of radioisotopic decay and growth (along with nucleogenic and cosmogenic production), and the desire for more precise, accurate, and innovative approaches to understanding dates and rates of natural processes have created a kind of disciplinary cohesion that underscores the fundamental importance of time in Earth and planetary science. Although the approaches and applications in these chapters may be diverse and at least superficially distinct, even besides the isotopic bases, they have in common that they are keys to discovering, quantitatively, when and how fast. To paraphrase Lord Kelvin again, when you can measure that, and express it in numbers, you know something about it. Without the temporal context of time, your knowledge is of a meagre and unsatisfactory kind.

1.5 REFERENCES

Badash, L. (1969) Rutherford and Boltwood: Letters on Radioactivity. Yale University Press, 378 pp.

Barrell, J. (1917) Rhythms and the measurements of geologic time. *Geological Society of America Bulletin* **28** (1), 745–904.

Bateman, H. (1910) The solution of a system of differential equations occurring in the theory of radioactive transformations. *Proceedings of the Cambridge Philosophical Society* **15** (part V), 423–427.

Becker, G. F. (1908) Relations of radioactivity to cosmogony and geology. *Geological Society of America Bulletin* **19** (1), 113–146.

Becker, G. F. (1910) *The Age of the Earth*, Vol. **56**. Smithsonian institution.

Bouvier, A. and Wadhwa. M. (2010) The age of the Solar System redefined by the oldest Pb–Pb age of a meteoritic inclusion. *Nature Geoscience* **3**(9), 637–641.

Bowring, S. A., Williams, I. S., and Compston, W. (1989) 3.96 Ga gneisses from the Slave Province, Northwest Territories, Canada. *Geology* **17**(11), 971–975.

Brennecka, G. A., Weyer, S., Wadhwa, M., Janney, P. E., Zipfel, J., and Anbar, A. D. (2010) $^{238}U/^{235}U$ variations in meteorites: extant ^{247}Cm and implications for Pb–Pb dating. *Science* **327** (5964), 449–451.

Buffon, G.-L. L. (1778) *Les Époques de la nature: 1778.* Paleo.

Burchfield, J. D. (1975) *Lord Kelvin and the Age of the Earth.* Science History, New York.

Camacho, A., Lee, J. K. W., Bastiaan J. Hensen, B. J., and Braun, J. (2005) Short-lived orogenic cycles and the eclogitization of cold crust by spasmodic hot fluids. *Nature* **435**(7046), 1191–1196.

Chamberlin, T. C. (1899) On Lord Kelvin's address on the age of the Earth as an abode fitted for life. *Annual Report*, 223–246. Smithsoniam Institution, Washington, DC.

Clarke, F. W. and Washington, H. S. (1924) *The Composition of the Earth's Crust*, Vol. **127**. US Government Printing Office, Washington, DC.

Compston, W. T. and Pidgeon, R. T. (1986) Jack Hills, evidence of more very old detrital zircons in Western Australia. *Nature* **321**(6072), 766–769.

Dalrymple, G. B. (1994) *The Age of the Earth.* Stanford University Press, 474 pp.

Dunbar, C. O. (1949) *Historical Geology.* New York, 567 pp.

Farley, K. A., Malespin, C., Mahaffy, P., *et al.* (2014) *In situ* radiometric and exposure age dating of the Martian surface. *Science* **343**(6169), 1247166.

Fleischer, R. L. and Price, P. B. (1964) Techniques for geological dating of minerals by chemical etching of fission fragment tracks. *Geochimica et Cosmochimica Acta* **28**(10), 1705–1714.

Gerling, E. K. (1942) Age of the earth according to radioactivity data. In *Doklady (Proc Russian Acad Sci)*, **34**, pp. 259–261.

Guenthner, W. R., Reiners, P. W., Ketcham, R. A., Nasdala, L., and Giester, G. (2013) Helium diffusion in natural zircon: radiation damage, anisotropy, and the interpretation of zircon (U–Th)/He thermochronology. *American Journal of Science* **313**(3), 145–198.

Halliday, A. N., Lee, D-C., Christensen, J. N., *et al.* (1998) Applications of multiple collector-ICPMS to cosmochemistry, geochemistry, and paleoceanography. *Geochimica et Cosmochimica Acta* **62**, 6 919–940.

Hazen, R. M. (2014) Data-driven abductive discovery in mineralogy. *American Mineralogist* **99**(11–12), 2165–2170.

Holmes, A. (1911) The association of lead with uranium in rock-minerals, and its application to the measurement of geological time. *Proceedings of the Royal Society of London, Series A* **85**, 248–256.

Holmes, A. and Lawson, R. W. (1927) Factors involved in the calculation of radioactive minerals. *American Journal of Science* **76**, 327–344.

Kelvin, Lord. (1863) Dynamical problem regarding elastic spheroid shell; on the rigidity of the Earth. *Philosophical Transactions of the Royal Society of London, Treatise on Natural Philosophy* **2**, 837.

Kosler, J. (2008) Laser ablation sampling strategies for concentration and isotope ratio analyses by ICP-MS. *Laser Ablation ICP-MS in the Earth Sciences: Current Practices and Outstanding Issues* **40**, 79–92.

Kusiak, M. A., Dunkley, D. J., Wirth, R., Whitehouse, M. J., Wilde, S. A., and Marquardt, K. (2015) Metallic lead nanospheres discovered in ancient zircons. *Proceedings of the National Academy of Sciences* **112**(16), 4958–4963.

Lee, D-C. and Halliday, A. N. (1995) Hafnium–tungsten chronometry and the timing of terrestrial core formation. *Geochimica et Cosmochimica Acta* **62**, 919–940.

LeConte, J. (1879) Elements of Geology*:* a Text-book for Colleges and for the General Reader. D. Appleton and Company, New York.

Merrihue, C. and Turner, G. (1966) Potassium-argon dating by activation with fast neutrons. *Journal of Geophysical Research* **71**(11), 2852–2857.

Moorbath, S., O'nions, R. K., and Pankhurst, R. J. (1975) The evolution of early Precambrian crustal rocks at Isua, West Greenland—geochemical and isotopic evidence. *Earth and Planetary Science Letters* **27**(2), 229–239.

Patterson, C. (1956) Age of meteorites and the Earth. *Geochimica et Cosmochimica Acta* **10**(4), 230–237.

Rudwick, M. J. S. (2014) *Earth's Deep History: How it was Discovered and Why it Matters*. University of Chicago Press.

Rutherford, E. (1905) Present problems in radioactivity. *Popular Science Monthly* **67**.

Rutherford, E. (1906) *Radioactive Transformations*. Yale University Press.

Rutherford, E. (1929) Origin of actinium and age of the Earth. *Nature* **123**, 313–314.

Rutherford, E. and Soddy, F. (1903a) Radioactive change. *Philosophical Magazine* **5**, 576–591.

Rutherford, E. and Soddy, F. (1903b) XLIII. The radioactivity of uranium. *Philosophical Magazine* **6**, 441–445.

Shuster, D. L. and Weiss, B. P. (2005) Martian surface paleotemperatures from thermochronology of meteorites. *Science* **309**(5734), 594–600.

Shuster, D. L., Flowers, R. M., and Farley, K. A. (2006) The influence of natural radiation damage on helium diffusion kinetics in apatite. *Earth and Planetary Science Letters* **249**(3) 148–161.

Stacey, F. D. (2000) Kelvin's age of the earth paradox revisited. *Journal of Geophysical Research: Solid Earth (1978–2012)* **105**(B6), 13155–13158.

Strutt, R. J. (1905) On the radio-active minerals. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **76**(508), 88–101.

Strutt, R. J. (1906) On the distribution of radium in the earth's crust. *Proceedings of the Royal Society of London. Series A, Containing Papers of a Mathematical and Physical Character* **78**(522), 150–153.

Valley, J. W., Reinhard, D. A., Aaron J. Cavosie, A. J., *et al.* (2015) Presidential Address. Nano- and micro-geochronology in Hadean and Archean zircons by atom-probe tomography and SIMS: new tools for old minerals. *American Mineralogist* **100**(7), 1355–1377.

Walcott, C. D. (1893) Geologic time, as indicated by the sedimentary rocks of North America. *The Journal of Geology* **1**(7), 639–676.

Wilde, S.A., Valley, J. W., Peck, W. H., and Graham, C. M. (2001) Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. *Nature* **409**(6817), 175–178.

Williams, H. S. (1893) Studies for students: the elements of the geological time-scale. *The Journal of Geology* **1**(3), 283–295.

Zhou, Q., Herd, C. D. K., Yin, Q-Z., *et al.* (2013) Geochronology of the Martian meteorite Zagami revealed by U–Pb ion probe dating of accessory minerals. *Earth and Planetary Science Letters* **374**, 156–163.