# One Hundred Years of Isotope Geochronology, and Counting

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## ABSTRACT

In 1913, Frederick Soddy’s research on the fundamentals of radioactivity led to the discovery of “isotopes.” Later that same year, Arthur Holmes published his now famous booklet *The Age of the Earth*, in which he applied this new science of radioactivity to the quantification of geologic time. Combined, these two landmark events did much to establish the field of “isotope geochronology” – the science that underpins our knowledge of the absolute age of most Earth (and extraterrestrial) materials. In celebrating the centenary, this issue brings together modern perspectives on the continually evolving field of isotope geochronology – a discipline that reflects and responds to the demands of studies ranging from the early evolution of the Solar System to our understanding of Quaternary climate change, and the 4.5 billion years in between.

KEYWORDS**:** radioactivity, geochronology, isotopes, geologic time

## INSIGHTS GAINED FROM A CENTURY OF GEOCHRONOLOGY

To paraphrase Monty Python, what’s geochronology ever done for us? Quite a lot it turns out. The quantification of time is fundamental to our understanding of planetary evolution and the geologic processes that shape our own planet Earth. The origin and evolution of life on Earth is recorded in its sedimentary carapace, within stratigraphic successions that we sequence and order using radioisotopic dates. Geochronology informs our understanding of plate tectonic processes, their influence on the development of topography, and in turn the climate system. The integration of disparate geologic records via absolute dating illuminates the connections and feedbacks among the biological, climatic and tectonic components of the coupled Earth system. Their causal links to phenomena like biological mass extinctions and changes in atmospheric composition are also tested and revealed by radioisotopic dating. Geochronology has become a key tool of geological mapping and the discovery of mineral and energy resources upon which our society is built. And equally relevant is the role of chronology in understanding environments during the last tens to hundreds of thousands of years, an understanding that provides the context for anthropogenic climate change. Indeed, geochronology has done quite a lot for us.

The year 2013 marks the centenary of two landmark publications that laid the foundations of modern geochronology: (1) a book by Arthur Holmes entitled *The Age of the Earth* (Holmes 1913), and (2) a paper by Frederick Soddy on the concept of "radio elements chemically non-separable" which, at the suggestion of Dr. Margaret Todd, he termed "isotopes" (Soddy 1913). Soddy received the 1921 Nobel Prize in Chemistry for this work, which contributed to the burgeoning field of nuclear physics. Arthur Holmes' pioneering application of radioactivity to dating rocks and his prescient realization of the importance of a quantified geologic timescale instigated the quantitative study of the stratigraphic record, which continues to this day (Gradstein et al. 2012). This convergence in 1913 of physics and geology marks the birth of isotope geochronology, the field of the Earth sciences that exploits the radioactive decay of isotopes in minerals to quantify geologic time. While these centenaries deserve an auspicious marking, the current state of isotope geochronology also merits celebration.

Today, isotope geochronology underpins much of our knowledge of the absolute age of minerals and rocks, and the records they contain. In this issue of *Elements*, Schoene et al. (2013) lead off with a primer on precision and accuracy in geochronology and on the metrological foundations of radioisotopic dates. The resolving power of radioisotope geochronology is further explored in terms of temporal resolution by Schmitz and Kuiper and spatial resolution by Nemchin, Horstwood and Whitehouse. Schmitz and Kuiper (2013) address the special challenges of rock-clock calibration when increasingly precise radioisotopic ages impinge upon accuracy limits imposed by systematic errors and geological complexity. The tools with which radioisotopic dates are measured have also proliferated over the past few decades, and Nemchin et al. (2013) explore the high–spatial resolution methods that have opened windows onto geologic processes preserved at the micron scale in minerals. Our understanding of geologic history is heavily informed by radioisotopic dating methods, and the articles on cosmochronology by Amelin and Ireland (2013) and on Quaternary geochronology by Richards and Andersen (2013) explore the general and unique challenges in applying radioisotope geochronology to the extreme ends of the geologic timescale. The last article, on “revolution and evolution” in geochronology by Mattinson (2013) brings us full circle, reminding us not only of our early geochronological heritage but also the links in the chain to the present flourishing of the field.

## “ABSOLUTE AGES AREN'T EXACTLY?”

You would be forgiven for thinking that the analytical uncertainties on published radioisotopic dates would be sufficiently large to encompass the true geologic age in question. Yet research during the past decade and a half demonstrates that this often held assumption is not always true. For example, the estimated the age of the Cretaceous-Paleogene (K-Pg, Figure 1) boundary has shifted from 65.5 ± 0.3 Ma to 66.04 ± 0.05 Ma between publication of the 2004 and 2012 Geological Timescales (Gradstein et al. 2004; 2012). These evolving age estimates, significantly different at the stated level of confidence, reflect the refinement of radioisotopic dating methods - in this case the improved calibration of the reference mineral used for $^{40}$Ar/$^{39}$Ar dating (Kuiper et al., 2008). With the proliferation and increasing precision of radioisotopic dating in the last decades of the twentieth century, it has become increasingly common to combine geochronologic methods that use different parent and daughter isotopes, and data generated in different laboratories, in order to address complex problems. In a 1998 note, Paul Renne and others (Renne et al. 1998) highlighted the issues related to systematic uncertainties in geochronology and the fact that many published dates from one method could not be easily compared with other chronologies, thus greatly limiting their utility. Quantifying the coincidence of the Siberian Traps large igneous province with the end-Permian mass extinction is a great example of this dilemma: the extinction level has been dated using U–Pb zircon geochronology of silicic ash beds in stratigraphic sections that record the extinction of marine fauna, whereas the basaltic rocks of the Siberian Traps have largely been dated using the $^{40}$Ar/$^{39}$Ar system in feldspar (Renne et al. 1995). At what level of uncertainty can these two chronologies be compared and inference made about the cause of mass extinction?

The perspective provided by Renne et al. (1998) was that radioisotopic ages should include systematic sources of uncertainties that were often neglected in the past, greatly limiting the degree to which ages could be compared and the inferences about temporal associations that could be drawn. In response, the new millennium marked a watershed in the recent history of radioisotopic dating because, since then, a number of studies aimed at tackling accuracy and intercalibration have been initiated. These include the use of astrochronologic dating of tephra to improve the accuracy of $^{40}$Ar/$^{39}$Ar geochronology (Kuiper et al. 2008); the refinement of estimates of decay constants used in U–Th–Pb geochronology through diligent analysis of closed-system, secular equilibrium materials (Cheng et al. 2000); the accurate determination of previously assumed ‘constants’ such as the terrestrial $^{238}$U/$^{235}$U value (Hiess et al. 2012); and the combination of data from physical counting experiments and complementary U–Pb and $^{40}$Ar/$^{39}$Ar datasets to provide improved estimates of fundamental parameters in $^{40}$Ar/$^{39}$Ar geochronology (Renne et al. 2010). Together, these efforts are moving the various chronometers towards improved traceability and increased accuracy, a theme—the elimination of bias—that links all the articles in this issue of *Elements*.

## THE NEXT 100 YEARS OF GEOCHRONOLOGY

A crystal ball isn’t required to predict that high-precision geochronology will become increasingly precise or that high–spatial resolution techniques will allow us to analyse even smaller domains. These trends of the 20th century and the first decade of the new millennium will continue, with incremental improvements in technology and methodology.

More interesting perhaps are the directions in which synergies amongst analytical methods and chronometers will lead us. Whereas historical competition between different analytical methods and chronometers during their development has promoted significant scientific advancements, in recent years there has been an increasing realization that the strengths of one methodology can actually be used to inform the weaknesses of another – that often the best solution to a problem involves the tandem application of a number of methods. This could mean combining U–Pb, $^{40}$Ar/$^{39}$Ar and astrochronologic data to develop an age model for a stratigraphic succession, or using a rapid, in situ method to characterize the provenance of a sandstone followed by analysis of the youngest grains by high-precision techniques to confirm and refine the maximum depositional ages.

Other breakthroughs, perhaps more significant, will come from increased collaboration and changes in the ways geochronologists and their collaborators work together and share ideas within and across disciplines. These changes are already underway, and in the 'high-precision' community this has largely been driven by the EARTHTIME Initiative (www.earth-time.org) (see Schmitz and Kuiper 2013), in which scientists interested in the quantification of Earth history have come together to explore issues related to accuracy of the different chronometers, interlaboratory agreement, and the robust integration of geochronology, palaeontology and stratigraphy. While there are a number of tangible analytical outputs from the EARTHTIME Initiative (e.g. new reference materials, improved best practices, common software platforms for data reduction and analysis), the greatest outcome of this effort has been the evolution of our attitudes – collaboration is now contagious.

Finally, we close with a caveat. The breadth of topics within the field of geochronology is immense, and though we have attempted to gather perspectives on both fundamental issues and exemplar applications, we readily acknowledge our incomplete coverage of many areas of geochronology. For example, much of this issue deals with chronologies derived from the decay of the uranium isotopes—fitting, given our celebration of the pioneering contributions of Soddy and Holmes, but certainly not representative of the full spectrum of radioisotopic techniques now in the isotope geochemist's toolkit. While acknowledging these shortcomings, we hope that the articles in this issue will inspire the reader to further investigations of the myriad forms and applications of isotope geochronology.

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## GLOSSARY

This glossary explains some useful terms encountered in this issue, but we also refer you to past *Elements* articles that also cover the topic of geochronology (Harley and Kelly 2007)

**Accuracy** – The closeness of agreement between a measured quantity value and a true quantity value

**Decay constant ($\lambda$)** – The reciprocal value of the average lifetime of a radionuclide, which is the time over which a population of parent radionuclides is reduced by 1/e times its initial value. The half-life of a radionuclide is equal to $\ln(2)/\lambda$.

**Isotope dilution–thermal ionisation mass spectrometry (ID-TIMS)** – A method of isotopic analysis in which an artificial or enriched isotopic tracer is added to a dissolved sample (e.g. zircon) to make a homogeneous isotopic mixture, the isotopic composition of which is analysed using TIMS. This technique is currently the form of isotopic measurement with the highest precision and accuracy, but it requires complete dissolution of the sample.

**LA-ICPMS (laser ablation–inductively coupled plasma mass spectrometry)** – A microanalytical method that employs a focused laser beam to ablate material from samples. The ejected matter is ionised using a plasma before being passed through to a mass spectrometer.

**MSWD (mean squared weighted deviation)** – A goodness of fit statistic that compares the sum of the squares of the deviations of a set of measurements from their mean value to the corresponding sum of the variances of each measurement

**Precision** – The closeness of agreement between indications or measured quantity values obtained by replicate measurements on the same or similar objects under specified conditions

**Secondary ion mass spectrometry (SIMS)** – Also referred to as an ion microprobe or microscope, SIMS measures the chemical or isotopic composition of small sample volumes by focusing a beam of high-energy primary ions onto a polished sample surface, ablating atoms and molecules, and generating secondary ions that are analysed by mass spectrometry. The high spatial resolution offered by SIMS (commonly <30 μm wide and <1 μm deep during analysis of geological materials) allows in situ analysis of geological materials. The method is relatively non-destructive, allowing multiple analyses to be performed within single grains or zones within grains, but has lower analytical precision than ID-TIMS.

**Radioactive decay** – Nuclear reactions by which an atomic nucleus transforms via emission of ionising particles and electromagnetic radiation. Radioactive decay is a stochastic (i.e. random) process at the level of single atoms, in that it is impossible to predict when a given atom will decay. However, the probability that a given atom will decay is constant over time.

**Uncertainty (of measurements)** – A parameter characterising the dispersion of the quantity values being attributed to the subject of a measurement, which can include components arising from both random and systematic measurement errors. **Random errors** are those that in replicate measurements vary in an unpredictable manner; **systematic errors** are those that remain constant or vary in a predictable manner across replicate measurements.