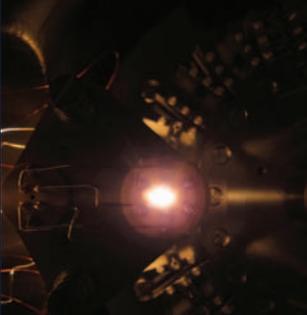


Precision and Accuracy in Geochronology

Blair Schoene¹, Daniel J. Condon², Leah Morgan³, and Noah McLean²

1811-5209/13/0009-0019\$2.50 DOI: 10.2113/gselements.9.1.19



Where isotope ratios are born: a sample filament in the source end of a thermal ionization mass spectrometer

Geochronology in Earth and Solar System science is increasingly in demand, and this demand is not only for more results, but for more precise, more accurate, and more easily interpreted temporal constraints. Because modern research often requires multiple dating methods, scrupulous inter- and intramethod calibration in absolute time is required. However, improved precision has highlighted systematic analytical biases and uncovered geologic complexity that affects mineral dates. At the same time, both enhanced spatial resolution through microbeam geochronology and creative uses of disparate data sets to inform age interpretations have helped explain complexities in age data. Quantifying random and systematic sources of instrumental and geological uncertainty is vital, and requires transparency in methodology, data reduction, and reporting. Community efforts toward inter- and intracalibration of chronometers will continue to help achieve the highest possible resolving power for integrative geochronology.

KEYWORDS: precision, accuracy, geochronology, intercalibration, uncertainty, U–Pb, ⁴⁰Ar/³⁹Ar

The uncertainty of a date is as important as the date itself.

—Ludwig (2003a)

THE IMPORTANCE OF PRECISION AND ACCURACY

Few, if any, scientific disciplines publish numerical data that are accepted by nonexperts and propagated through the literature as extensively as geochronology. Radioisotopic dates are used to constrain the age of a wide variety of rocks and minerals, from 4.4-billion-year-old zircon grains to volcanic eruptive products and corals only a few tens to hundreds of years old. Driven by increasingly intricate geological questions and a more complete geologic timescale, more precise and accurate time constraints are required through integrating multiple analyses from different laboratories using different decay schemes. Of paramount importance, therefore, is that reported dates are of adequate precision and accuracy to answer the question asked. But how do we distinguish precision from accuracy in geochronology, and how do we use these terms quantitatively? In this article we outline “where radioisotopic dates

come from”—their foundation in metrology, mass spectrometry, chemistry, and physics—and show how measurement and geologic uncertainty propagate into age interpretations.

Radioisotopic methods capitalize on the radioactive decay of parent to daughter nuclides. Though the sources of uncertainty and the calculation of dates vary for each dating method, we highlight below some key generic themes common to many dating methods. Terminology is important, and often the terms *precision*, *accuracy*, and *uncertainty* are used loosely in the geological literature even though strict definitions are used in the metrology and analytical chemistry communities (e.g. Potts 2012). Definitions for precision, accuracy, and uncertainty are

given in a Glossary (page 17), and FIGURE 1 illustrates their common usage in geochronology. Precision is one component of uncertainty and indicates the degree to which measurements are repeatable and reproducible. Accuracy, another component of uncertainty, expresses how close a measurement comes to the true value (FIG. 1).

When considering uncertainties in radioisotope geochronology, it is useful to differentiate between “systematic” and “random” uncertainties. Systematic uncertainties are constant or skew results in a predictable way such that they affect accuracy. The best example of systematic uncertainties comes from decay constants. In contrast, random uncertainties vary in an unpredictable manner, usually with an assumed Gaussian distribution, and include analytical uncertainties in isotope ratio mass spectrometry. With unlimited time and amount of sample, repeat measurements could reduce random uncertainties to zero, but systematic effects would remain.

Differentiating between random and systematic uncertainties is important, because we want to confidently answer the question “Are these two dates really different from one another?” For example, to quantify the time difference between two samples dated by one method, say U–Pb, we can ignore decay constant uncertainties because they would bias both ages in the same predictable manner. If however, we wanted to compare two dates, one Rb–Sr and one ⁴⁰Ar/³⁹Ar, we would have to incorporate the decay constant uncertainties of both systems so as not to mistake interchronometer bias for a real age difference (see Box 1).

1 Department of Geosciences, Princeton University
Princeton, New Jersey 08544, USA
E-mail: bschoene@princeton.edu

2 NERC Isotope Geosciences Laboratory, British Geological Survey
Keyworth, Nottinghamshire, NG12 5GG, UK

3 Scottish Universities Environmental Research Centre
East Kilbride, G75 0QF, UK

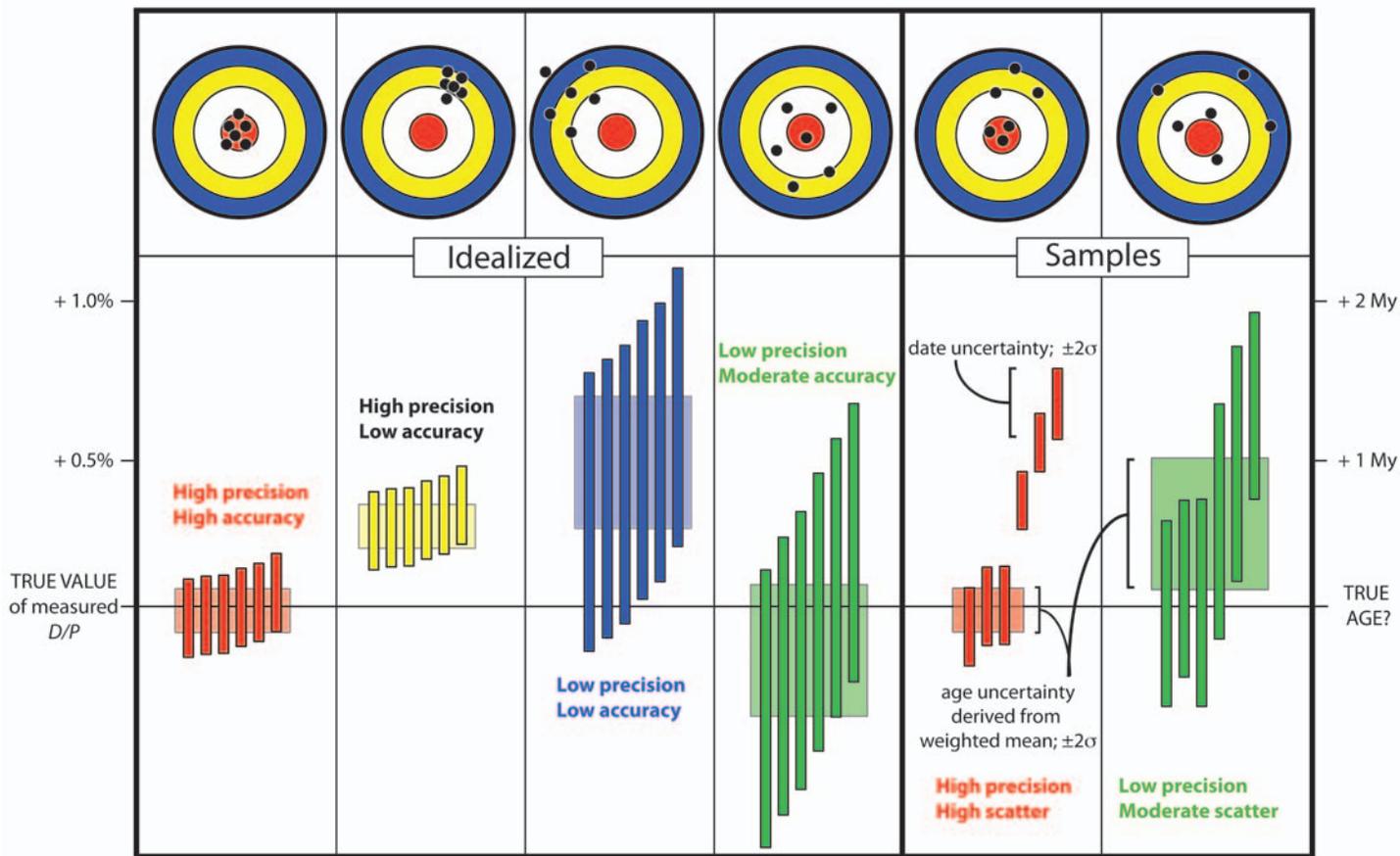


FIGURE 1 What is the difference between precision and accuracy? This schematic plot illustrates variably accurate and precise data sets. The top panel is a series of bull's-eye targets typical of those used to illustrate precision and accuracy. Below them are plots more typical of those used in geochronology studies, which show ratios or dates versus analysis number. The colored bars represent single analyses, and the height of the bar reflects the 2-sigma uncertainty for that analysis. The y-axis is in percent of the true daughter to parent ratio (D/P) on the left and in millions of years on the right. The partly transparent boxes behind groups of analyses represent a weighted-mean value for that group, with the box height equivalent to ± 2 -sigma uncertainty.

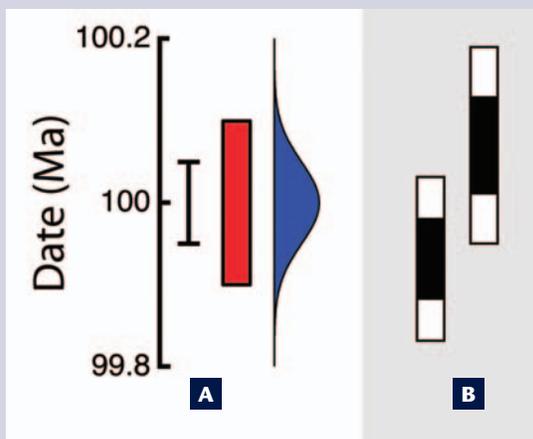
Field observations can be used to establish relative time constraints for geologic events through stratigraphic analysis or from crosscutting relationships. Geochronology, however, provides what are often referred to as “absolute” time constraints. Absolute dates are ones that can be traced to the International System of Units (i.e. SI units, such as kilogram, second, and becquerel) through a series of metrological experiments (traceability). This allows quantification of systematic uncertainties and permits comparison of radioisotopic dates to chronologies based upon independent temporal proxies. For example, U–Th dates that are calibrated against metrologically traceable standards and the U and Th decay constants (see below) can be meaningfully compared to independently derived models of solar insolation as a means to assess potential cause and effect between drivers of ice-sheet volume change and sea level (e.g. Cutler et al. 2003).

Many geochronologists distinguish the terms *date* and *age*. A date is a number calculated using measured isotopic ratios and the decay equation, and a date becomes an age when geologic significance is attached to that number.

Correctly reporting a date as an age thus depends on accurate interpretation of radioisotopic data, which is not easy given the complicated nature of geologic processes. Over the past several decades, analyses employing new technology with increased spatial resolution have revealed intramineral isotopic variability important for interpreting mineral dates. Recognition of millimeter- to micrometer-scale isotopic variation has inspired microsampling (e.g. microdrilling) and in situ “microbeam” techniques (primarily SIMS and LA-ICP-MS; Nemchin et al. 2013 this issue). These methods offer the potential for more informed sampling and coupling with geochemical and textural data and thus contribute to more accurate age interpretations. During this same period of time, precision in some lower spatial-resolution techniques (i.e. those that require manual manipulation and/or dissolution) has improved from several percent to less than a permil on single dates (e.g. ± 3 Ma to ± 100 ka for a 100 Ma sample). As a result, systematic biases now often dominate uncertainty in comparisons between dating methods and between laboratories. Improving the values of physical constants such as decay constants and verifying measured unknowns by analysis of reference materials have become increasingly important.

The task of comparing and integrating dates from different dating methods thus requires incorporation of geochemical and isotopic data with stratigraphic and field data. In other words, understanding complex geologic systems entails relating each date to a process, which results in exciting interplay among scientists from nearly all realms of the geosciences.

Box 1 What Is an Error Bar?



An error bar, or confidence interval, illustrates a range of possible values for a measured parameter such as a date. It is a visualization of the uncertainty of the measured parameter, and it should always be presented along with an estimate of the probability that the parameter falls within the bounds given. **(A)** Most high-precision geochronologic data are normally distributed, as shown here in blue, and the confidence level of the error bar corresponds to the area under the curve between the bounds of the error bar. For instance, the true value of the date has about a 68% chance of lying within a one-dimensional $\pm 1\sigma$ error bar, depicted as a black line, and about a 95% chance of lying within a $\pm 2\sigma$ error bar, depicted as a red bar. While error bars are a simple, succinct way of depicting data, the reader should imagine the shape of the distribution they imply. Thus, there is a higher probability that the true value lies near the center of the error bar than near its limits, and importantly there is a finite probability that the true value lies outside the error bar. The latter outcome is expected about 32% of the time for a correctly estimated $\pm 1\sigma$ error bar and about 5% of the time for a $\pm 2\sigma$ error bar, and does not imply that the measurement is “wrong.” **(B)** Both random (analytical) and systematic uncertainties may be displayed in the same error bar. In the two analyses depicted, the smaller black bar represents the analytical uncertainty for each analysis, while the larger white bar encompasses the combined random and systematic uncertainties. In the case where the two analyses are from the same dating method (i.e. Lu–Hf, Re–Os, U–Pb, etc.) and the systematic contribution is from decay constants only, the white portion of the error bar need not be considered: there is a high probability that these two dates are different. The situation changes, however, if the two analyses are from different isotopic systems. In this case, although the analyses agree poorly within analytical uncertainties (black), they agree well when the systematic uncertainties associated with their different decay constants are considered (white): the dates must be considered indistinguishable (see Renne et al. 1998).

DETERMINING PARENT/DAUGHTER ISOTOPE RATIOS: MASS SPECTROMETRY

A date (t) for a mineral or rock can be calculated using the age equation if one determines the atomic ratio of a stable daughter isotope relative to its radioactive parent isotope (D/P) and if one knows the parent isotope's decay constant (λ).

$$\text{Age equation: } \left(\frac{D}{P}\right) = \exp(\lambda t) - 1$$

These two inputs, and their accuracy and precision, control the accuracy and precision of radioisotopic dates. Determining the ratio of daughter products to their parent isotopes is the field of isotope ratio mass spectrometry and isotope geochemistry, and the principles and methods for achieving this are covered in many textbooks (e.g. Faure and Mensing 2005).

In brief, determining accurate D/P ratios using isotope ratio mass spectrometry is complicated for several reasons, including: (1) differential ionization of isotopes from

different elements (i.e. U and Pb, Re and Os); (2) fractionation of the D/P ratio during ion exchange chemistry (employed to purify an element prior to mass spectrometry); (3) mass-dependent fractionation of different isotopes during mass spectrometry; (4) correction for nonradiogenic D ; that is, the measured sample may contain not only the daughter isotope derived from the decay of the parent but also D that was within the material when it formed and/or was introduced during sample processing in the laboratory; and (5) traceability of age standards employed by some methods (e.g. $^{40}\text{Ar}/^{39}\text{Ar}$). Each of these factors can contribute to inaccurate dates, depending on the nature of the material being analyzed, the type of mass spectrometer, and the radioisotopic method being used.

Tracing D/P back to first principles measurements can be done accurately provided systematic and random uncertainties are carefully accounted for. In order to effectively eliminate fractionation of D/P during chemical purification of a sample and/or isotope ratio mass spectrometry, *isotope dilution* is employed. This involves adding to the sample synthetic or highly enriched tracer isotopes of the D and P elements, with a precisely determined ratio, prior to any procedures that could result in D/P fractionation (the tracer isotopes are denoted below as T_D and T_P ; for example, ^{205}Pb and ^{233}U , which do not exist in nature, are often added to a sample targeted for U–Pb dating). As the sample is processed and D/P fractionates in the laboratory, T_D/T_P also fractionates in exactly the same way. Therefore knowledge of T_D/T_P allows determination of D/P , even if the isotope ratio measurements of D and P are carried out using different methods and/or at different times. A critical link in the traceability chain is the calibration of these tracers, and this is done in a similar manner, this time treating T_D and T_P as unknowns and mixing them with a gravimetric reference solution (Wasserburg et al. 1981; Cheng et al. 2000). These solutions are made by dissolving large amounts of precisely and accurately weighed high-purity reference material (typically salts or metals) of the D and P elements such that their elemental ratio is known through concentrations traceable to the kilogram.

Isotope dilution requires the tracer isotopes to be mixed and equilibrated with the sample; therefore, this approach cannot be used with analytical methods that directly analyze a solid material, such as the in situ microbeam methods that employ a laser or ion beam to remove material from a solid sample. These methods derive their accuracy by determining D/P relative to a standard material, commonly a mineral that has a homogeneous and known D/P . Thus, “relative dating” methodologies depend on a reference material whose D/P can be known by isotope dilution (e.g. Wiedenbeck et al. 1995).

FROM ISOTOPE RATIOS TO TIME: DECAY CONSTANTS

The absolute accuracy of radioisotopic geochronometers universally depends on the decay constant of the parent isotope in the age equation. Some systems rely on decay constants for multiple isotopes; others rely on branched decays, where a single parent isotope has multiple daughter isotopes. Other physical constants are important in some decay schemes, in particular natural isotopic ratios. For example, U–Pb dating often relies, in part, on assuming a natural and constant $^{238}\text{U}/^{235}\text{U}$ ratio, while the $^{40}\text{Ar}/^{39}\text{Ar}$ system relies on the atmospheric $^{40}\text{Ar}/^{36}\text{Ar}$ ratio to differentiate radiogenic ^{40}Ar from atmospheric ^{40}Ar and also depends on the natural $^{40}\text{K}/^{39}\text{K}$ ratio.

Determining decay constants is a nontrivial task, and several methods can be used. Direct determination by activity counting (measuring the energy resulting from radioactive decay as a function of time; e.g. Beckinsale and Gale 1969; Jaffey et al. 1971) and ingrowth experiments using isotopically enriched materials (measuring the moles of D produced relative to P over a known length of time; e.g. Rotenberg et al. 2012) have been used to measure λ with traceability to standard units. Due to the long half-life of most radioactive isotopes useful in geochronology, these experiments are difficult and measurements of different decay constants may have order-of-magnitude differences in their experimental uncertainties.

An alternative approach is intercalibration, where the accuracy of one system can be exported to another system by selecting minerals or rocks that (1) are amenable to high-precision geochronology using multiple methods and (2) are relatable to a set of processes that occurred at the same time, for example, crystallization of two minerals immediately prior to a volcanic eruption or rapid crystallization and cooling beneath Earth's surface. The result is that one can compare dates from different techniques (e.g. U–Pb on zircon and $^{40}\text{Ar}/^{39}\text{Ar}$ on sanidine) with uncertainties that are smaller than those in the decay constant experiments. Typically, intercalibration experiments exploit the most precisely determined decay constant, $\lambda^{238}\text{U}$, which has an uncertainty of $\pm 0.11\%$ (2σ ; Jaffey et al. 1971). For example, the analyses of closed-system minerals, such as zircon, have been used to improve the accuracy of the other U and Th decay constants relative to $\lambda^{238}\text{U}$: $\lambda^{232}\text{Th}$ (Amelin and Zaitsev 2002), $\lambda^{235}\text{U}$ (Schoene et al. 2006; Mattinson 2010), and $\lambda^{234}\text{U}$ and $\lambda^{230}\text{Th}$ (Ludwig et al. 1992; Cheng et al. 2000). Coeval or relatable mineral pairs have also been used in calibrations of other decay constants, such as $\lambda^{187}\text{Re}$ (Selby et al. 2007), $\lambda^{40}\text{K}$ (Min et al. 2000; Renne et al. 2010), and $\lambda^{176}\text{Lu}$ (Scherer et al. 2001).

Though decay constants determined by intercalibration of different decay schemes provide a means to enhance the relative accuracy of dates, we must recognize that such systems are no longer independent measurements. In practical terms, the accuracy of a system intercalibrated with $\lambda^{238}\text{U}$ is limited by the accuracy of the U–Pb system. The resulting covariance between dates means that systematic uncertainties in the U–Pb system propagate through every other system. These contributions to the uncertainties include the original experiments used to determine the U decay constants (Jaffey et al. 1971), the isotopic composition of uranium (Hiess et al. 2012), and the standard reference materials used in tracer calibration and related experiments (see above).

It is also possible to improve the accuracy of decay constants by comparison with a nonradiometric means of determining geologic time, such as astrochronology, which relies on cyclic climate records preserved in sedimentary rocks as an absolute clock. Intercalibration of radiometric clocks with time estimates from astrochronology has been highly successful (Kuiper et al. 2008), but has also revealed disparities likely created by errors in age models for sedimentary cyclicity (e.g. Westerhold et al. 2012). While researchers continue to explore the best methods to determine accurate and precise decay constants, the current situation is one where different researchers are applying different values to their measurements. This ambiguity can be confusing to the larger geological community, and therefore geochronologists must be particularly careful to state the values of the decay constants and standards used to calculate dates from isotopic ratios, and readers must also look for this information.

FROM DATES TO AGES: GEOLOGIC INTERPRETATION

Transforming a date into an age requires interpreting a date calculated using the age equation to represent a specific geologic process, and this is just as important as the date's numerical accuracy and metrological traceability. Examples of interpretations of mineral dates include assigning crystallization ages in an igneous system, reporting ages of volcanic eruptions based upon dates of minerals from ash beds, associating datable minerals to ages of metamorphic events, using dates of carbonates to determine ages of low-temperature aqueous precipitation, and using dates to calibrate cooling beneath a certain temperature for systems in which diffusion of a daughter product occurs at high temperatures (see Reiners and Ehlers 2005 for the latter example). As the questions we ask become increasingly detailed and sophisticated and as our methods become increasingly precise, the knowledge of how a date is recorded in a mineral, or mineral subdomain, and how that in turn relates to some other geological information (e.g. petrographic context, other isotope and/or geochemical information) becomes crucial.

The application of petrographic and microimaging methods for characterizing the internal structure of minerals has improved our understanding of mineral growth and rock petrogenesis. Analytical methods used for radioisotope ratio measurements tend to capitalize on either high-precision dates using isotope dilution and physical manipulation of mineral fragments (Schmitz and Kuiper 2013 this issue) or high spatial resolution using a focused ion beam or laser, guided by imaging (Nemchin et al. 2013). A frequent point of discussion is the merits of high-spatial-resolution analyses as opposed to dissolution methods, given the complementary strengths of the two methods. Acknowledging that nearly all geologic samples contain some age variation (it can be argued that very few analyzed volumes represent instantaneous crystallization), what is critical is both the temporal and spatial scale of the variation (Fig. 2). In cases where a single crystal records a protracted crystallization history, say an old mineral core surrounded by a much younger overgrowth, analysis of whole minerals can result in dates that represent a mixture of different domains, and microbeam sampling methods are preferred. However, if we wish to measure the timescales of geologic processes that occur more quickly than can be resolved with in situ techniques, employing isotope dilution methods is necessary, and one must attempt to understand the impact of averaging growth histories over a larger volume of material. Several steps can be taken in sample preparation and analysis to help geochronologists determine whether temporal or spatial resolution is more important for a given study, and thus to attain the most accurate dates possible. These are briefly outlined below.

Sample Characterization

Field relationships – Despite the power of geochronology to resolve absolute time, interpreted ages must be consistent with field relationships, for example, crosscutting relationships in igneous bodies or the law of superposition in sedimentary rocks. Rock-sampling strategies in well-mapped areas can discriminate between and refine hypotheses and minimize the number of samples necessary for geochronology.

Petrography – It is essential to use petrographic or mineral-texture data to guide geochronologic sampling. Observations in thin section can help determine the petrogenetic history of datable minerals, for example, by

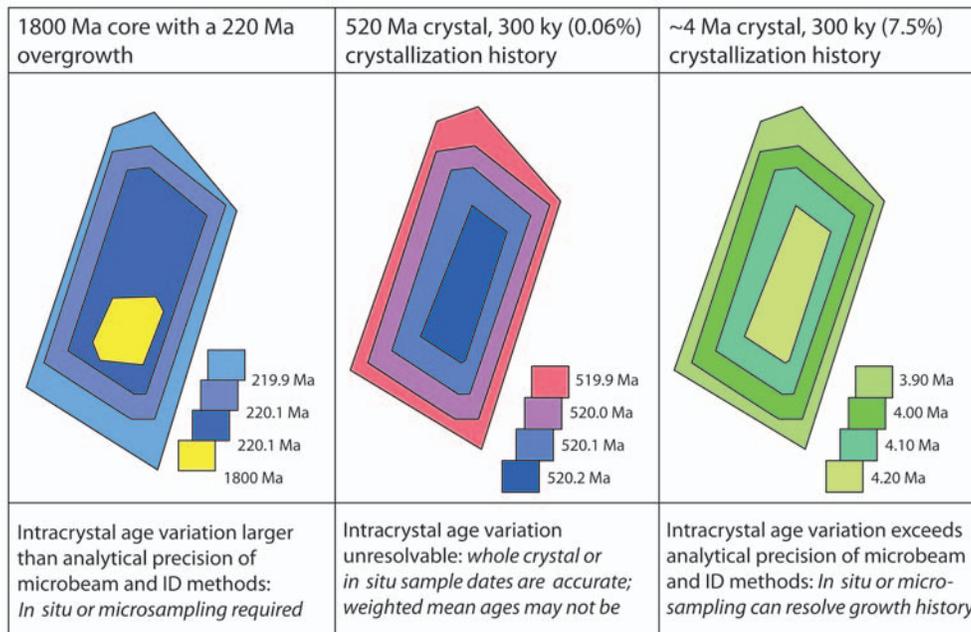


FIGURE 2 Precision versus accuracy in minerals with complex growth histories. This cartoon illustrates how the scale of intracrystal age zonation, combined with the scale of sampling and the analytical precision, impacts the potential accuracy of a date. Mineral zones are color-coded by age, with keys provided; uncertainties are assumed to be >2% for *in situ* microbeam techniques and <0.2% for isotope dilution (ID) techniques. **Left:** A Mesozoic mineral with a Precambrian core. **Center:** A Cambrian grain with 300 ky of crystal

growth. **Right:** An early Pliocene crystal with 300 ky of crystal growth. Note that in all datable minerals with equal parent concentration across a grain, the volume–age relationship is always biased towards the youngest growth domains, but in reality the concentration of the parent nuclide also has to be considered. This figure illustrates that both the spatial resolution of sampling and the temporal precision of the analytical method control whether a single date can be considered accurate.

relating them to metamorphic reactions or equilibrium assemblages. Microbeam methods permit *in situ* analyses of mineral subdomains of interest.

Textural and geochemical characterization – Internal textures of the datable minerals themselves, such as growth zoning, can be observed using optical microscopy or backscattered electron and/or cathodoluminescence imaging, and a scanning electron microscope is usually employed for this. Textural data can also be combined with geochemical and crystallographic data, determined either *in situ* prior to microbeam geochronology or on a portion of the dissolved, dated sample. For example, X-ray diffraction analysis of fossil coral is routinely employed to determine whether secondary/diagenetic calcite is present in a sample, and optical microscopy can be used to assess the presence of secondary aragonite, both of which impact the accuracy of U–Th dates.

Testing for Closed-System Behavior

Some systems offer an internal check for closed-system behavior in that they contain more than one radionuclide, which means that two dates can be obtained from one mineral/rock sample. If the mineral/rock has behaved as a closed system with respect to the parent and daughter nuclides since the start of daughter ingrowth, the dates should be concordant. Examples include ^{238}U – ^{206}Pb and ^{235}U – ^{207}Pb dates on zircon and other uranium-bearing minerals (Schoene 2013), and ^{235}U – ^{231}Pa and ^{234}U – ^{230}Th dates in carbonate (e.g. fossil coral; Edwards et al. 2003). Other possible internal checks include natural isotopic compositions that are predictable in nature when a material forms (e.g. $^{234}\text{U}/^{238}\text{U}_{\text{seawater}}$) but are perturbed during alteration and open-system behavior. Date reproducibility between heating steps also allows for an assessment of open-system behavior in $^{40}\text{Ar}/^{39}\text{Ar}$ analyses (McDougall

and Harrison 1999). Reproducibility among many minerals in the same sample is also a method of verifying closed-system behavior given that the effects of metamorphism, daughter-product loss, and recrystallization tend to be distributed heterogeneously in single samples.

Statistical Models for Combining Multiple Data Points

It is common to apply a statistical model to a set of dates to assess reproducibility and/or to arrive at an interpreted age. The two most common models used are linear regressions (isochrons) and weighted means. Associated with these statistical models are measures of the goodness of fit, such as the mean square of weighted deviates (MSWD), also known as the reduced chi-squared statistic; Wendt and Carl 1991; York et al. 2004) and the related probability of fit. It is important to note that these measures are related to the precision of the single data points used in the statistical model: if the scatter in the single data points can be predicted by their estimated uncertainty, then the MSWD will be near unity; however, if the uncertainties of the same data are much smaller than the intrasample variation, then the MSWD or other measure will highlight the lack of coherence (Fig. 1). It is extremely important that, when statistical models are used to calculate dates or assess closed-system behavior, a goodness of fit is reported, because this helps a reader (and an author) to evaluate the accuracy of the age interpretation (Ludwig 2003b)

SUMMARY AND THE FUTURE

The complexity and abundance of studies in the Earth and meteoritic sciences requiring absolute time constraints have risen in recent years. In general, the reported precision of ages has improved, and the number of studies that integrate multiple dating methods has escalated. With increased

resolving power comes an increased responsibility to use radioisotopic dates and their uncertainties appropriately; this statement applies to both researchers producing and publishing geochronologic data and those who use these ages in their work.

Efforts to hone decay constant and physical constant uncertainties will likely continue, as will experiments to better estimate inter- and intralaboratory agreement. This will help geochronologists to understand and quantify the various sources of random and systematic uncertainties stemming from the laboratory methods, standards, and physical constants used for various decay schemes. More experiments tracing age determinations to standard units and better relating them to one another are crucial for our understanding of absolute uncertainty in geologic time and application to the geologic timescale.

The future of geochronology will see continued increases in precision of age determinations by multiple analytical methods, with respect to both single analyses and statistical treatments of data such as weighted means. Enhanced

age precision must be balanced with complementary efforts to couple geochronology with field, stratigraphic, geochemical, and textural data to ensure that better precision does not come at the expense of accuracy. The rates, durations, and sequence of processes and events determined by isotope geochronology are essential for understanding the physical and chemical underpinnings of mountain-building events, crust formation, paleogeography, volcanic eruptions, paleoclimate, and biotic evolution. Given the increased emphasis in the geosciences on understanding the rich and complex feedbacks among these interrelated Earth systems, a focus on precise and accurate geochronology is of timely importance.

ACKNOWLEDGMENTS

The topics and ideas summarized in this paper are in part a result of ongoing work within the EARTHTIME community and its various inspirations and outgrowths. S. Bowring, M. Cosca, and J. Valley are thanked for their helpful comments on this paper. ■

REFERENCES

- Amelin Y, Zaitsev AN (2002) Precise geochronology of phoscorites and carbonatites: The critical role of U-series disequilibrium in age interpretations. *Geochimica et Cosmochimica Acta* 66: 2399-2419
- Beckinsale RD, Gale NH (1969) A reappraisal of the decay constants and branching ratio of ^{40}K . *Earth and Planetary Science Letters* 6: 289-294
- Cheng H, Edwards RL, Hoff J, Gallup CD, Richards DA, Asmerom Y (2000) The half-lives of uranium-234 and thorium-230. *Chemical Geology* 169: 17-33
- Cutler KB, Edwards RL, Taylor FW, Cheng H, Adkins J, Gallup CD, Cutler PM, Burr GS, Bloom AL (2003) Rapid sea-level fall and deep-ocean temperature change since the last interglacial period. *Earth and Planetary Science Letters* 206: 253-271
- Edwards RL, Gallup CD, Cheng H (2003) Uranium-series dating of marine and lacustrine carbonates. *Reviews in Mineralogy and Geochemistry* 52: 363-405
- Faure G, Mensing TM (2005) *Isotopes Principles and Applications*, Third Edition. John Wiley & Sons, Inc., Hoboken, NJ, 897 pp
- Hiess J, Condon DJ, McLean N, Noble SR (2012) $^{238}\text{U}/^{235}\text{U}$ systematics in terrestrial uranium-bearing minerals. *Science* 335: 1610-1614
- Jaffey AH, Flynn KF, Glendenin LE, Bentley WC, Essling AM (1971) Precision measurement of half-lives and specific activities of ^{235}U and ^{238}U . *Physical Review C* 4: 1889-1906
- Kuiper KF, Deino A, Hilgen FJ, Krijgsman W, Renne PR, Wijbrans JR (2008) Synchronizing rock clocks of Earth history. *Science* 320: 500-504
- Ludwig KR (2003a) Mathematical-statistical treatment of data and errors for $^{230}\text{Th}/\text{U}$ geochronology. *Reviews in Mineralogy & Geochemistry* 52: 631-656
- Ludwig KR (2003b) *Isoplot/Ex Version 3.00: A Geological Toolkit for Microsoft Excel*. Berkeley Geochronology Center Special Publication, 70 pp
- Ludwig KR, Simmons KR, Szabo BJ, Winograd IJ, Landwehr JM, Riggs AC, Hoffman RJ (1992) Mass-spectrometric ^{230}Th - ^{234}U - ^{238}U dating of the Devils Hole calcite vein. *Science* 258: 284-287
- Mattinson JM (2010) Analysis of the relative decay constants of ^{235}U and ^{238}U by multi-step CA-TIMS measurements of closed-system natural zircon samples. *Chemical Geology* 275: 186-198
- McDougall I, Harrison TM (1999) *Geochronology and Thermochronology by the $^{40}\text{Ar}/^{39}\text{Ar}$ Method*, Second Edition. Oxford University Press, New York, NY, 269 pp
- Min KW, Mundil R, Renne PR, Ludwig KR (2000) A test for systematic errors in $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology through comparison with U/Pb analysis of a 1.1-Ga rhyolite. *Geochimica et Cosmochimica Acta* 64: 73-98
- Nemchin AA, Horstwood MSA, Whitehouse MJ (2013) High-spatial-resolution geochronology. *Elements* 9: 31-37
- Potts PJ (2012) Glossary of analytical and metrological terms from the International Vocabulary of Metrology (2008). *Geostandards and Geoanalytical Research* 36: 231-246
- Reiners PW, Ehlers TA (eds) (2005) *Low-Temperature Thermochronology*. *Reviews in Mineralogy & Geochemistry* 58, 622 pp
- Renne PR, Karner DB, Ludwig KR (1998) Absolute ages aren't exactly. *Science* 282: 1840-1841
- Renne PR, Mundil R, Balco G, Min KW, Ludwig KR (2010) Joint determination of ^{40}K decay constants and $^{40}\text{Ar}/^{40}\text{K}$ for the Fish Canyon sanidine standard, and improved accuracy for $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. *Geochimica et Cosmochimica Acta* 74: 5349-5367
- Rotenberg E, Davis DW, Amelin Y, Ghosh S, Bergquist BA (2012) Determination of the decay-constant of ^{87}Rb by laboratory accumulation of ^{87}Sr . *Geochimica et Cosmochimica Acta* 85: 41-57
- Scherer E, Münker C, Mezger K (2001) Calibration of the lutetium-hafnium clock. *Science* 293: 683-687
- Schmitz MD, Kuiper KF (2013) High-precision geochronology. *Elements* 9: 25-30
- Schoene B (2013) U-Th-Pb geochronology. In: Rudnick R (ed), *Treatise on Geochemistry* 3, Elsevier, Oxford, UK, in press
- Schoene B, Crowley JL, Condon DJ, Schmitz MD, Bowring SA (2006) Reassessing the uranium decay constants for geochronology using ID-TIMS U-Pb data. *Geochimica et Cosmochimica Acta* 70: 426-445
- Selby D, Creaser RA, Stein HJ, Markey RJ, Hannah JL (2007) Assessment of the ^{187}Re decay constant by cross calibration of Re-Os molybdenite and U-Pb zircon chronometers in magmatic ore systems. *Geochimica et Cosmochimica Acta* 71: 1999-2013
- Wasserburg GJ, Jacobsen SB, DePaolo DJ, McCulloch MT, Wen T (1981) Precise determination of Sm/Nd ratios, Sm and Nd isotopic abundances in standard solutions. *Geochimica et Cosmochimica Acta* 12: 2311-2323
- Wendt I, Carl C (1991) The statistical distribution of the mean squared weighted deviation. *Chemical Geology* 86: 275-285
- Westerhold T, Röhl U, Laskar J (2012) Time scale controversy: Accurate orbital calibration of the early Paleogene. *Geochemistry, Geophysics and Geosystems* 13: Q06015
- Wiedenbeck M, Allé P, Corfu F, Griffin WL, Meier M, Oberli F, Vonquadt A, Roddick JC, Spiegel W (1995) Three natural zircon standards for U-Th-Pb, Lu-Hf, trace element and REE analyses. *Geostandards Newsletter* 19: 1-23
- York D, Evensen NM, Lopez Martinez M, De Basabe Delgado J (2004) Unified equations for the slope, intercept, and standard errors of the best straight line: *American Journal of Physics* 72: 367-375 ■