

1 **Precision and Accuracy in Geochronology**

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8 **Abstract/Summary**

9 There is an increasing demand for geochronology in Earth and solar system science, and this
10 demand is not only for more, but for higher precision, more accurate, and more easily
11 interpreted temporal constraints. Because modern research often requires multiple dating
12 methods, scrupulous inter- and intra-method calibration in absolute time is required.
13 However, improved precision has highlighted systematic analytical biases and uncovered
14 geologic complexity that affects mineral dates. At the same time, both enhanced spatial
15 resolution through microbeam geochronology and creative uses of disparate datasets to
16 inform age interpretations have helped explain complexities in age data. Quantifying random
17 and systematic sources of instrumental and geological uncertainty is vital, and requires
18 transparency in methodology, data reduction, and reporting. Community efforts toward inter-
19 and intra-calibration of chronometers will continue to help achieve the highest possible
20 resolving power for integrative geochronology.

21

22 *The uncertainty of a date is as important as the date itself.* (Ludwig, 2003a)

23

24 **1. The importance of precision and accuracy**

25 Few if any scientific disciplines publish numerical data that are accepted by non-experts and
26 propagated through the literature as extensively as ages determined by geochronology.
27 Radioisotopic dates are used to constrain the age of a wide variety of rocks and mineral types,
28 from 4.4 billion year old zircons to volcanic eruptions and corals only a few tens to hundreds
29 of years old. Driven by increasingly intricate geological questions and a more complete
30 geologic time scale, more precise and accurate time constraints are required through
31 integrating multiple analyses from different laboratories using different decay schemes. Of
32 paramount importance, therefore, is that reported dates are of adequate precision and
33 accuracy to answer the question asked. But how do we distinguish precision from accuracy
34 in geochronology, and how do we use these terms quantitatively? In this article we attempt
35 to outline “where radioisotopic dates come from”-their foundation in metrology, mass
36 spectrometry, chemistry, and physics, and show how measurement and geologic uncertainty
37 propagate into age interpretations.

38 Radioisotopic methods capitalize on radioactive decay of parent to daughter nuclides. Though
39 the sources of uncertainty and the calculation of dates vary for each dating method, we
40 highlight below some key generic themes common to many dating methods. Terminology is
41 important and often the terms precision, accuracy, and uncertainty are used loosely in the
42 geological literature even though strict definitions are used in the metrology and analytical
43 chemistry communities (e.g., Potts, 2012). Definitions for precision, accuracy and
44 uncertainty are given in the Glossary of Useful Terms (Page XX) and Fig. 1 illustrates their
45 common usage in geochronology. Precision is one component of uncertainty, where higher
46 precision measurements are more repeatable and reproducible. Accuracy, another component
47 of uncertainty, expresses how close a measurement comes to the true value (Fig. 1).

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

56 Differentiating between random and systematic uncertainties is important, so that one can
57 confidently answer the question “are these two dates really different from one another?” For
58 example, to quantify the time difference between two samples dated by one method, say U-
59 Pb, we can ignore decay constant uncertainties that would bias both ages in the same
60 predictable manner. If however, we wanted to compare two dates, one Rb-Sr and one
61 $^{40}\text{Ar}/^{39}\text{Ar}$, we must incorporate the decay constant uncertainties of both systems so as to not
62 mistake inter-chronometer bias for a real age difference (see Text Box).

63 Field observations can be used to establish relative time constraints for geologic events
64 through stratigraphic analysis or using cross-cutting relationships. Geochronology, however,
65 provides what are often referred to as “absolute” time constraints. Absolute dates are ones
66 that can be traced to standard units (e.g. kilogram, Becquerel) through a series of
67 metrological experiments (traceability). This allows quantification of systematic uncertainties
68 and permits comparison of radioisotopic dates to chronologies based upon independent
69 temporal proxies. For example, U-Th dates that are calibrated against metrologically
70 traceable standards and the U and Th decay constants (see below) can be meaningfully
71 compared to independently derived models of solar insolation as a means to assess potential
72 cause and effect between drivers of ice sheet volume change and sea-level (e.g., Cutler et al.,
73 2003).

74 Many geochronologists distinguish the terms date and age. A date is a number calculated
75 using measured isotopic ratios and the decay equation, and a date becomes an age when
76 geologic significance is attached to that number. Correctly reporting a date as an age thus
77 depends on accurate interpretation of radioisotopic data, which is not easy given the
78 complicated nature of geologic processes. Over the past several decades, analyses employing
79 new technology with increasing spatial resolution have revealed intra-mineral isotopic
80 variability important for interpreting mineral dates. Recognition of millimeter- to
81 micrometer-scale isotopic variation has inspired microsampling (e.g. microdrilling) and in-
82 situ ‘microbeam’ techniques (primarily SIMS and LA-ICP-MS; Nemchin et al., this volume).
83 These methods offer the potential for more informed sampling and coupling with
84 geochemical and textural data and thus contribute to more accurate age interpretations.
85 During this same period of time, precision in some lower-spatial resolution techniques (i.e.,
86 those that require manual manipulation and/or dissolution) has improved from several percent
87 to less than a permil on single dates (e.g. ± 3 Myr to ± 100 kyr for a 100 Ma sample). As a
88 result, systematic biases now often dominate uncertainty in comparisons between dating
89 methods and between laboratories. Improving values of physical constants, such as decay
90 constants, and verification of measured unknowns by analysis of reference materials, has
91 become increasingly important.

92 Comparing and integrating dates from different dating methods thus requires incorporation of
93 geochemical and isotopic data with stratigraphic and field data. In other words,
94 understanding complex geologic systems requires relating each date to a process, which
95 results in an exciting interplay between scientists from nearly all realms of geosciences.

96

97 **2. Determining parent/daughter isotope ratios (mass spectrometry)**

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

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

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

106 In brief, determining accurate D/P ratios using isotope ratio mass spectrometry is
107 complicated for several reasons, including: (1) differential ionization of isotopes from
108 different elements (i.e., U and Pb, Re and Os); (2) fractionation of the D/P ratio during ion
109 exchange chemistry (employed to purify an element prior to mass-spectrometry); (3) mass
110 dependent fractionation of different isotopes during mass spectrometry; (4) correction for
111 non-radiogenic D , namely that the measured sample may contain not only the daughter
112 isotope derived from the decay of the parent, but also D that is within the material when it
113 formed and/or introduced during sample processing in the laboratory; and (5) traceability of
114 age standards employed by some methods (e.g., $^{40}\text{Ar}/^{39}\text{Ar}$). Each of these factors can
115 contribute to inaccurate dates, depending on the nature of the material being analyzed, the
116 type of mass spectrometer, and radioisotopic method being used.

117 Tracing D/P back to first principles measurements can be done accurately provided
118 systematic and random uncertainties are carefully accounted for. In order to effectively
119 eliminate fractionation of D/P during chemical purification of a sample and/or isotope ratio
120 mass spectrometry, a method termed isotope dilution is employed. This involves adding to
121 the sample synthetic or highly enriched tracer isotopes (T_D and T_P) of the D and P elements,
122 with precisely determined T_D/T_P (e.g., ^{205}Pb and ^{233}U tracers added to a sample targeted for
123 U-Pb dating) prior to any procedures that could result in D/P fractionation. As the sample is
124 processed and D/P fractionates in the laboratory, T_D/T_P also fractionates in exactly the same
125 way. Therefore knowledge of T_D/T_P allows determination of D/P , even if the isotope ratio
126 measurements of D and P are carried out using different methods and/or at different times. A
127 critical link in the traceability chain is the calibration of these tracers, and this is done in a
128 similar manner, this time treating T_D and T_P as unknowns and mixing them with a
129 gravimetric reference solution (Cheng et al., 2000; Wasserburg et al., 1981). These solutions
130 are made by dissolving large amounts of precisely and accurately weighed high-purity
131 reference material (typically salts or metals) of the D and P elements such that their elemental
132 ratio is known relative to the kilogram.

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

140

141 **3. From isotope ratios to time (decay constants)**

142 The absolute accuracy of radioisotopic geochronometers universally depends on the decay

143 constant of the parent isotope in the age equation. Some systems rely on decay constants for
144 multiple isotopes; others rely on branched decays, where a single parent isotope has multiple
145 daughter isotopes. Other physical constants are important in some decay schemes, in
146 particular natural isotopic ratios. For example, U-Pb dating often relies, in part, on assuming
147 a natural and constant $^{238}\text{U}/^{235}\text{U}$ ratio, while the $^{40}\text{Ar}/^{39}\text{Ar}$ system relies on the atmospheric
148 $^{40}\text{Ar}/^{36}\text{Ar}$ ratio to differentiate radiogenic ^{40}Ar from atmospheric ^{40}Ar , as well as the natural
149 $^{40}\text{K}/^{39}\text{K}$ ratio.

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

159 An alternative approach is inter-calibration, where the accuracy of one system can be
160 exported to another system by selecting minerals or rocks that 1) are amenable to high-
161 precision geochronology using multiple methods and 2) are relatable to a set of processes that
162 occurred at the same time, for example crystallization of two minerals immediately prior to a
163 volcanic eruption or rapid crystallization and cooling beneath Earth's surface. The result is
164 that one can compare dates from different techniques (e.g., U-Pb zircon and $^{40}\text{Ar}/^{39}\text{Ar}$
165 sanidine) with uncertainties that are smaller than the decay constant experiments. Typically,
166 intercalibration experiments exploit the most precisely determined decay constant $\lambda^{238}\text{U}$, with
167 an uncertainty of $\pm 0.11\%$ (2σ ; Jaffey et al., 1971). For example, the analyses of closed
168 system minerals, such as zircon, have been used to improve the accuracy of the other U and
169 Th decay constants: $\lambda^{238}\text{U}/\lambda^{235}\text{U}$, (Mattinson, 2010; Amelin and Zaitsev, 2002) and $\lambda^{238}\text{U}/$
170 $\lambda^{234}\text{U}$ and $\lambda^{238}\text{U}/\lambda^{230}\text{Th}$ (Cheng et al., 2000; Ludwig et al., 1992). Coeval or relatable
171 mineral pairs have also been used in calibrations of other decay constants, such as $\lambda^{187}\text{Re}$
172 (Selby et al., 2007), ^{40}K (Min et al., 2000; Renne et al., 2010), and ^{176}Lu (Scherer et al.,
173 2001).

174 Though decay constants determined by intercalibration of different decay schemes provide a
175 means to enhance the relative accuracy of dates, we must recognize that such systems are no
176 longer independent measurements. In practical terms, the accuracy of a system inter-
177 calibrated with $\lambda^{238}\text{U}$ is limited by the accuracy of the U-Pb system. The resulting covariance
178 between dates means that systematic uncertainties in the U-Pb system propagate through
179 every other system. These contributions include the original experiments used to determine
180 the U decay constants (Jaffey et al., 1971), the isotopic composition of uranium (Hiess et al.,
181 2012), and also the standard reference materials used in tracer calibration and related
182 experiments (see above).

183 It is also possible to improve the accuracy of decay constants by comparison with a non-
184 radiometric means of determining geologic time, such as astrochronology, which relies on

185 cyclic climate records preserved in sedimentary rocks as an absolute clock. Intercalibration of
186 radiometric clocks with time estimates from astrochronology have been highly successful
187 (Kuiper et al., 2008), but have also revealed disparities likely created by errors in age models
188 for sedimentary cyclicity (e.g., Westerhold et al., 2012). While researchers continue to
189 explore the best methods to determine accurate and precise decay constants, the current
190 situation is one where different researchers are applying different values to their
191 measurements. This ambiguity can be confusing to the larger geological community, and
192 therefore geochronologists must be particularly careful to state the values of the decay
193 constants and standards used to calculate dates from isotopic ratios, and readers must also
194 look for this information.

195

196 **4. From dates to ages (geologic interpretation)**

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

210 Application of petrographic and micro-imaging methods for characterizing the internal
211 structure of minerals has improved our understanding of mineral growth and rock
212 petrogenesis. Analytical methods used for radioisotope ratio measurements tend to capitalize
213 on either high-precision dates using isotope dilution and physical manipulation of mineral
214 fragments (Schmitz and Kuiper, this volume), or high spatial resolution using a focused ion
215 beam or laser, guided by imaging (Nemchin et al., this volume). A frequent point of
216 discussion is the merits of high-spatial resolution analyses as opposed to dissolution methods,
217 given the complimentary strengths of each method. Acknowledging that nearly all geologic
218 samples contain some age variation (it can be argued that very few analyzed volumes
219 represent instantaneous crystallization), what is critical is both the temporal and spatial scale
220 of the variation (Fig. 2). In cases where a single crystal records a protracted crystallization
221 history, say an old mineral core surrounded by a much younger overgrowth, analysis of
222 whole minerals can result in dates that represent a mixture of different domains, and micro-
223 beam/sampling methods are preferred. However, studies that wish to measure the timescales
224 of geologic processes that occur more quickly than can be resolved with *in situ* techniques,
225 employing isotope dilution methods is necessary and one must attempt to understand the
226 impact of averaging growth histories over a larger volume of material. There are several

227 steps that can be taken in sample preparation and analysis that help geochronologists
228 determine whether temporal or spatial resolution is more important for a given study, and
229 thus to attain the most accurate dates possible. These are briefly outlined below.

230

231 **Sample characterization**

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

237 *Petrography* - It is essential to use petrographic or mineral texture data to guide
238 geochronologic sampling. Observations in thin section can help determine the petrogenetic
239 history of datable minerals, for example by relating them to metamorphic reactions or
240 equilibrium assemblages. Microbeam methods permit *in situ* analyses of mineral sub-
241 domains of interest.

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

251

252 **Testing for closed-system behavior**

253 Some systems offer an internal check for closed-system behavior in that they contain more
254 than one radionuclide, which means that two dates can be obtained from one mineral/rock
255 sample. If the mineral/rock has behaved as a closed system with respect to the parent and
256 daughter nuclides since the start of daughter in-growth, the dates should be concordant.
257 Examples include ^{238}U - ^{206}Pb and ^{235}U - ^{207}Pb dates in zircon and other uranium bearing
258 minerals (Schoene, in press), and ^{235}U - ^{231}Pa and ^{234}U - ^{230}Th dates in carbonate (e.g., fossil
259 coral; Edwards et al., 2003). Other internal checks can include natural isotopic compositions
260 that are predictable in nature when a material forms (e.g., $^{234}\text{U}/^{238}\text{U}_{\text{seawater}}$) but are perturbed
261 during alteration and open-system behavior. Date reproducibility between heating steps also
262 allows for an assessment of open-system behavior in $^{40}\text{Ar}/^{39}\text{Ar}$ analyses (McDougall and
263 Harrison, 1999). Reproducibility between many minerals in the same sample is also a
264 method of verifying closed-system behavior given metamorphism, daughter-product loss, and
265 recrystallization tends to be distributed heterogeneously in single samples.

266

267 **Statistical models for combining multiple data points**

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

281 **5. Summary and the future**

282 The complexity and abundance of studies in the Earth and meteoritic sciences requiring
283 absolute time constraints has increased in recent years. In general, the reported precision on
284 ages has improved, and the number of studies that integrate multiple dating methods has
285 increased. With increased resolving power comes an increased responsibility that
286 radioisotopic dates and their uncertainties are used appropriately; this statement applies to
287 both researchers producing and publishing geochronologic data and to others who use these
288 ages in their own work.

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

296 The future of geochronology will see continued accuracy in precision of age determinations,
297 both on single analyses and on statistical treatments of data such as weighted means.

298 Integration of geochronologic data with geochemical, textural, and stratigraphic proxies will
299 aid such age interpretations. Greater confidence is to be gained through the reproduction of
300 results with different sample sets, and generation of higher fidelity datasets can help inform
301 geologic uncertainty.

302

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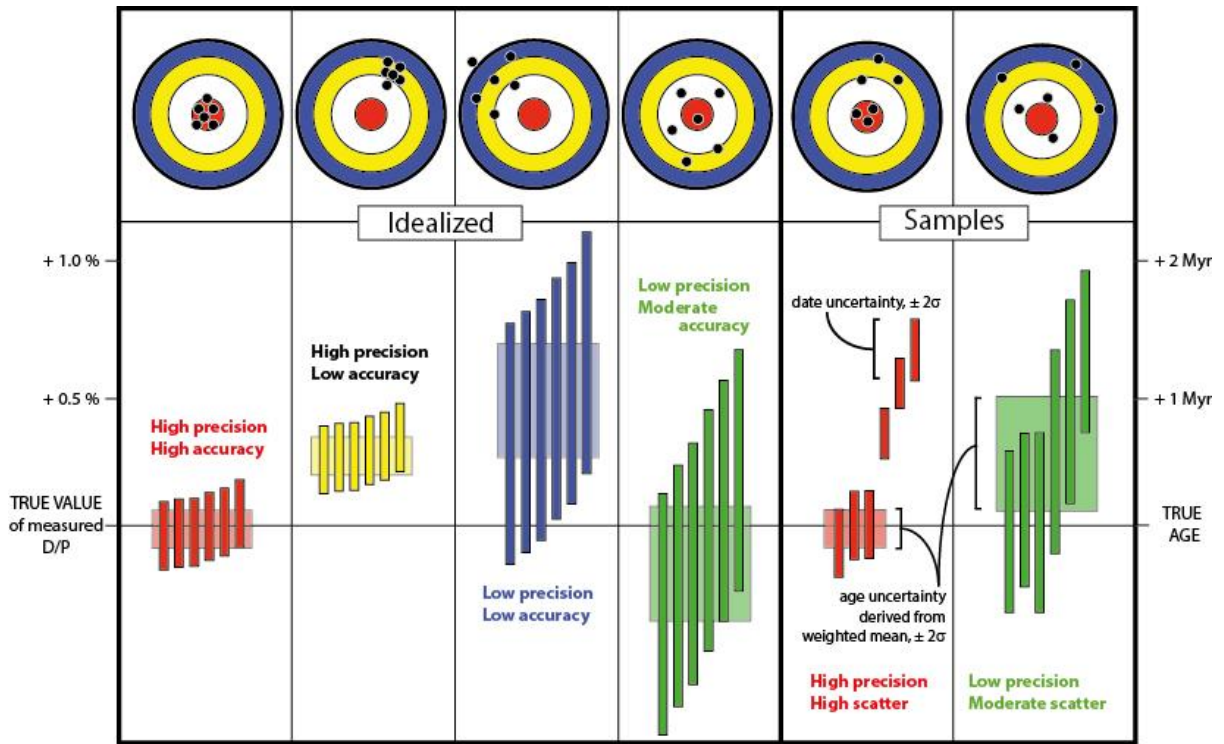
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383

384 **Figure 1.** Schematic plot illustrating variably accurate and precise data sets. The top panel is
 385 a series of bulls eye targets typical of those used to illustrate precision and accuracy, and
 386 below are plots more typical of those used in geochronology studies, which plots ratios or
 387 dates versus analysis number. Colored rectangles represent single analyses where the height
 388 of the bar reflects the 2-sigma uncertainties for that analysis. Y-axis on the left is in % of the
 389 true parent to daughter ratio (D/P), and on the right is in millions of years.

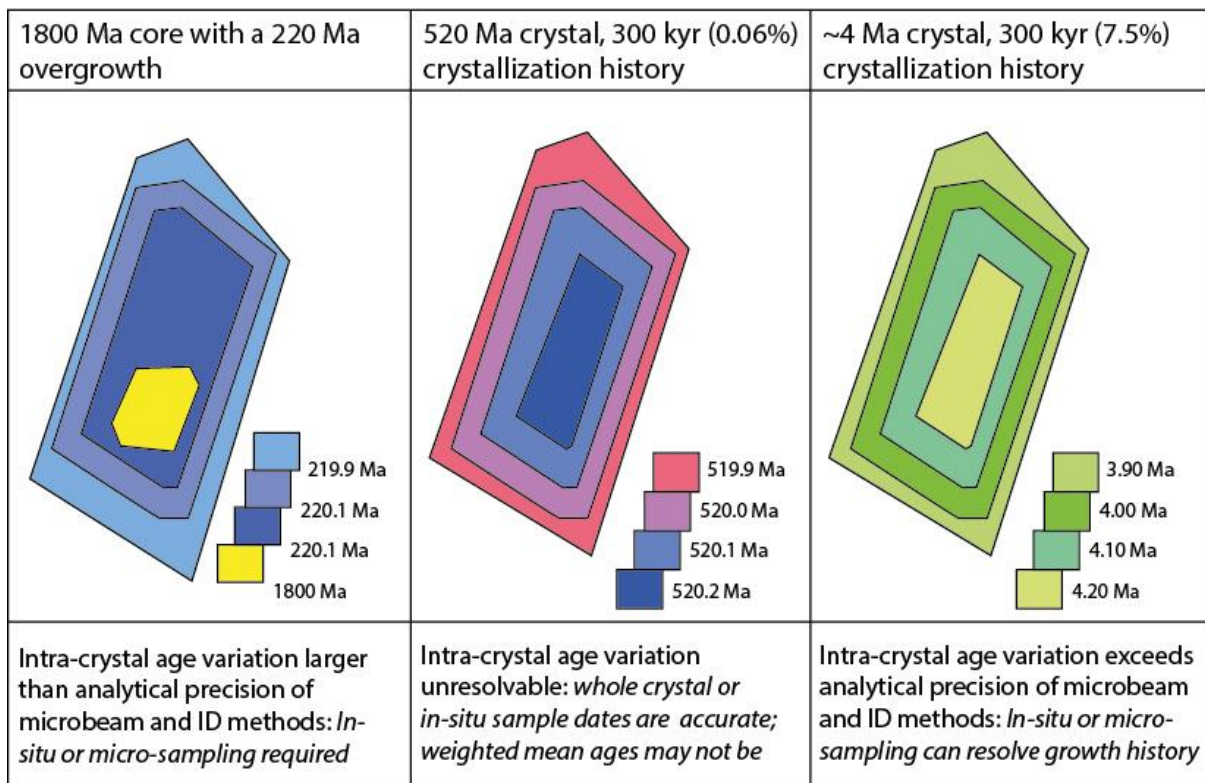
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392 **Figure 2.** Cartoon illustrating how the scale of intra-crystal age zonation, combined with the
 393 scale of sampling and the analytical precision, impact the potential accuracy of a date.
 394 Mineral zones are color-coded by age with key provided; assumed >2% uncertainties for *in*
 395 *situ* microbeam techniques and <0.2% precision for ID techniques. **(left)** A Mesozoic aged
 396 mineral with a Precambrian core; **(middle)** A Cambrian grain with 300 kyr of crystal growth,
 397 and **(right)** an early Pliocene crystal with 300 kyr of crystal growth. Note that in this
 398 example the volume-age relationship will be biased towards the youngest growth phases, and
 399 in real minerals the concentration of the parent nuclide also has to be considered. This figure
 400 illustrates that both the spatial resolution of sampling and the temporal precision of the
 401 analytical method control whether a single date can be considered accurate.

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405 **Text Box: What is an *Error Bar*?**

406 An error bar, or confidence interval, illustrates a range of possible values for a measured
407 parameter, like a date. It is a visualization of the uncertainty of the measured parameter, and
408 should always be presented along with an estimate of the probability that the parameter falls
409 within the bounds given. (a) Most high-precision geochronologic data is normally
410 distributed, as shown here in blue, and the confidence level of the error bar corresponds to the
411 area under the curve between its bounds. For instance, the true value of the date has about a
412 68% chance of lying within a one-dimensional $\pm 1\sigma$ error bar, depicted as a black line below,
413 and about a 95% chance of lying within a $\pm 2\sigma$ error bar, depicted as a red bar. While error
414 bars are a simple, succinct way of depicting data, the reader should imagine the shape of the
415 distribution they imply. Thus, there is a higher probability that the true value lies near the
416 center of the error bar than the outside, and importantly there is a finite probability that the
417 true value lies outside the error bar. This is expected about 32% of the time for a correctly
418 estimated $\pm 1\sigma$ error bar and about 5% of the time for a $\pm 2\sigma$ error bar, and does not imply that
419 the measurement is “wrong.” (b) Both random (analytical) and systematic uncertainties may
420 be displayed in the same error bar: In the two analyses depicted, the smaller black bar
421 represents the analytical uncertainty for each analysis, while the larger white bar
422 encompasses the combined random and systematic uncertainties. In the case where the two
423 analyses are from the same dating method (i.e. Lu-Hf, Re-Os, U-Pb, etc.) and the systematic
424 contribution is from decay constants only, the white portion of the error bar needn’t be
425 considered: There is a high probability that these two dates are different. The situation
426 changes, however, if the two analyses are from different isotopic systems. In this case,
427 although the analyses agree poorly within analytical uncertainties (black), they agree well
428 when the systematic uncertainties associated with their different decay constants are
429 considered: The dates must be considered indistinguishable (see Renne et al, 1998).

