HIGH-PRECISION U-PB ZIRCON GEOCHRONOLOGY AND THE STRATIGRAPHIC RECORD: PROGRESS AND PROMISE

BOWRING, SAMUEL A., SCHOENE, BLAIR, CROWLEY, JAMES L., RAMEZANI, JAHANDAR, AND CONDON, DANIEL J. †
Department of Earth Atmospheric and Planetary Sciences
Massachusetts Institute of Technology
Cambridge, Massachusetts 02139
sbowring@mit.edu

Abstract.—High-precision geochronological techniques have improved in the past decade to the point where volcanic ash beds interstratified with fossil-bearing rocks can be dated to a precision of 0.1% or better. The integration of high-precision U-Pb zircon geochronology with bio/chemo-stratigraphic data brings about new opportunities and challenges toward constructing a fully calibrated time scale for the geologic record, which is necessary for a thorough understanding of the distribution of time and life in Earth history. Successful implementation of geochronology as an integral tool for the paleontologist relies on a basic knowledge of its technical aspects, as well as an ability to properly evaluate and compare geochronologic results from different methods. This paper summarizes the methodology and new improvements in U-Pb zircon geochronology by isotope dilution thermal ionization mass spectrometry, specifically focused on its application to the stratigraphic record.

INTRODUCTION

The stratigraphic record preserves evidence of biological evolution, changes in oceanic and atmospheric chemistry, climate change, sea-level fluctuations, mountain building and erosion, and basin subsidence. However, this record is inherently complex and incomplete, and therefore requires a detailed and precise temporal framework. In the past two decades major advances in geochronology, U-Pb zircon geochronology in particular, have allowed us to evaluate the distribution of time in the rock record and rates of geological processes with unprecedented precision. It is now possible to date volcanic rocks interlayered with fossil bearing strata as young as a few million years with precisions of better than 0.1%. Although high-precision time calibration has been focused on major transitions in Earth history, such as extinctions and radiations, there is considerable promise for a highly calibrated time scale from the Neoproterozoic to Holocene. The combination of improved precision and a dramatic increase in the number of geochronological studies is leading to better constrained age models and time lines for the past 600 million years. There has been a parallel effort within the biostratigraphic community to develop new techniques for sequencing large numbers of stratigraphic events (e.g., Sadler 2004, this volume) and to store and compile the information in community databases. The integration of high-precision geochronology with biostratigraphy, evolutionary biology, and proxy records such as chemostratigraphy and magnetostratigraphy can help answer important questions regarding the tempo and causes of events in Earth history. For example, what are the precise ages and durations of mass extinctions and how long does ecological recovery take? Do evolutionary radiations correlate with changes in chemistry and temperature of ocean-atmosphere system and global climate? Are apparently abrupt isotopic excursions globally synchronous and of the same duration? Although the biostratigraphic record has historically been used to address these questions, we are now in an era when correlation and tempo will be decided by high-precision geochronology and well-constrained

† Present address: NERC Isotope Geoscience Laboratory, Keyworth, Nottinghamshire, NG12 5GG, UK

age models. This means moving beyond simple calibration of the time scale to understanding the detailed distribution of time and life in the rock record and the processes responsible for change.

For many geologists, the published time scale (e.g., Gradstein et al. 2004) is the best resource for the absolute calibration of the biostratigraphic record and one may use it to estimate a numerical age for fossil bearing rocks for at least the past 542 million years. Advancement in geochronological techniques coupled with the compilation of large paleontological and geological databases has resulted in much improved time scales for the Phanerozoic, although a comprehensive absolute time scale for much of the Paleozoic and Mesozoic, including some of the major extinctions, is far from complete. Unfortunately, in an attempt to include all available data, many of these time scales have typically averaged several dates obtained by different techniques and often of highly variable quality. The result, which is propagated throughout the literature, is a time scale that is often poorly calibrated in absolute time. Although the published time scale is an excellent resource, users must be aware of the geochronological, biostratigraphic, and chemostratigraphic data and associated uncertainties that underpin it. This paper attempts to convey to the paleontological community the recent progress and promise of the application of U-Pb geochronology to the stratigraphic record, with the goal of making geochronology an integral tool of the paleontologist. Dramatic changes in geochronological techniques and expectations over the past decade make it difficult for the non-specialist to keep up. While we can now date rocks with remarkable levels of precision, it is crucial that users of geochronological data understand its limitations and sources of uncertainty, as well as geological complexity. In the end, it is hoped that while paleontologists and stratigraphers gain a deeper appreciation for the potential of geochronology, new avenues of research will be pursued. The aim of this contribution is to present an introduction to high-precision U-Pb geochronology and its application to the stratigraphic record, with an emphasis on (1) fundamentals of the technique, (2) recent developments that have led to the current state-of-the-art methods, (3) common complications that require careful data interpretation, and (4) future directions.

VOLCANIC ASH BEDS AND ZIRCON

Volcanic rocks have long been appreciated as important stratigraphic markers, even prior to the advent of high-precision dating, and in many cases the physical volcanology and mineral chemistry of ash beds have been used for regional correlation (e.g., Haynes 1994). The two most common techniques applied to dating ash beds are $^{40}$Ar/$^{39}$Ar in alkali feldspar, biotite, and hornblende (see Renne, this volume) and U-Pb in zircon.

There is no question that ash beds are more abundant in the stratigraphic record than once thought and that stratigraphers and paleontologists are getting better at recognizing them in the field, although there is still much confusion and uncertainty about what constitutes a “good” sample. Experience has shown us that some ash beds are very obvious; such as thick (several meters) white to green clay layers in marine/lacustrine sequences, or welded ash-flow tuffs in terrestrial sequences. In other cases, volcanic ash beds are not distinctive, but present as a thin (down to 1 mm) clay layer on a bedding plane. Diagenetic and exposure history determine their overall appearance, so the guiding criteria should be to keep an eye out for unusual rocks. We estimate that our success rate from sample collection of possible volcanic material to a publishable high-precision age is at best 30%. This low rate is largely due to the fact that we collect many rocks that are not obvious ashes and may contain only a small volcanic component, such as a siltstone. One must sometimes gamble when trying to solve a scientific problem.

The ideal situation is a sequence of volcanic rocks interlayered with fossil-bearing strata in known stratigraphic succession. It is quite possible for volcaniclastic material to be remobilized and re-deposited after original eruption/sedimentation or for volcanic debris to have few to no indigenous zircons or feldspars, but instead to contain many incorporated from older rocks during eruption and deposition. Multiple samples of the same ash bed should be collected and samples from bottom, middle and top of thick layers should be taken if possible. We have documented large differences in zircon size, morphology, proportion of inherited grains, and even age between different parts of
a volcanic “layer”, showing that a single layer could represent an amalgamation of several different eruptions. A first order test of the geochronology is that ash beds yield ages that overlap within analytical uncertainties or correspond to stratigraphic order. However, in many cases only single ash layers are present.

Zircon (ZrSiO₄) is a common accessory mineral in volcanic rocks ranging from lavas to air-fall tuffs and is a nearly ubiquitous component of most clastic sedimentary rocks. The most common volcanic rocks in fossil-bearing sequences are air-fall layers deposited in marine settings that range in thickness from a millimeter or less to many meters. In most of these rocks, the primary volcanic material has been altered, probably soon after deposition, to clay minerals in a process that has little effect on zircon. The refractory and durable nature of zircon over a wide range of geological conditions means that it is likely for zircon to remain a robust indicator of magmatic events even through subsequent metamorphism.

High-precision geochronology of ash beds in a stratigraphic sequence requires a large number of analyses to fully characterize populations of zircon. For ash beds this involves processing enough sample so that a substantial number of the best quality, preferably large zircons can be isolated for analysis. Ash bed sample size can vary from a few grams to kilograms. In our experience, successful heavy mineral separation from clay-rich bentonitic ashes necessitates high-energy ultrasonication during settling of increasingly diluted slurries to minimize loss of zircons through flocculation. Resulting crystalline concentrates are processed by standard heavy liquid and magnetic methods to isolate the highest quality, diamagnetic zircons. U-Pb zircon studies applied to the stratigraphic record are either focused on the dating of detrital material or primary volcanic debris.

In many cases, zircons separated from clastic rocks, including those collected as suspected ash beds, yield useful constraints on depositional age (see Gehrels et al., this volume). The youngest detrital zircons provide a maximum age of deposition as well as provide information on the age of the source terrains providing detritus. In rock sequences for which little is known about the depositional age, such as in the Precambrian or in fossil-poor sequences, this can be a powerful approach. Dating a large number of detrital zircons to characterize an age spectrum for a sedimentary rock is best achieved using microbeam techniques, such as the ion-microprobe and laser-ablation inductively coupled plasma mass spectrometry (LA-ICPMS) that are discussed below. In addition to dating detrital zircons, it is possible to obtain a minimum depositional age by dating diagenetic phases such a pedogenic calcite and/or xenotime overgrowths on pre-existing zircons (see Rasbury and Cole this volume; Rasmussen 2005).

Zircons separated from volcanic ash layers are commonly inferred to date the time of a volcanic eruption and deposition that occurred “instantaneously” in geological time. However, as we will discuss below, this assumption is often problematic due to inheritance or incorporation of slightly older zircons that crystallized in the magma chamber prior to eruption or were derived from older rocks and entrained in the eruption column. For this reason, multiple ash beds in known stratigraphic sequence should be dated.

U-PB ZIRCON GEOCHRONOLOGY

U-Pb geochronology is often regarded as the gold standard of geochronology because unlike all other chronometers it exploits two independent decay schemes, 235U to 207Pb and 238U to 206Pb. Two decay schemes involving the same chemical elements but with different half-lives allow for an internal check on “closed system behavior”, meaning that the parent/daughter ratio in a zircon changes as a function of time only by the process of radioactive decay. Thus, two separate dates for a zircon based on the individual decay schemes may be calculated and compared using the concordia diagram as discussed by Miller (this volume). The advantage of two independent chronometers in the same mineral is that it is possible to detect small amounts of open system behavior such as Pb loss or the inheritance of older material. Knowing the decay constants, the date calculated for 238U→206Pb decay should equal that of 235U→207Pb decay. This is a major factor in our ability to make reliable, high-precision age determinations as we can confirm that the calculated dates record formation of the zircon and not a younger or older date. For most of the Phanerozoic,
the concordia curve has a steep slope and thus Pb loss
can be difficult to detect except at the highest levels
of precision. In this section we review open system
behavior in zircon (Pb loss and inheritance) and ana-
lytical strategies.

Pb loss

The most common form of open system behavior in
zircon is Pb loss, which is likely caused by radiation
damage that accumulates in a grain due to the decay
of U. Experimental measurements of Pb diffusivity in
zircon indicate that Pb loss is not likely dominated by
volume diffusion (Cherniak and Watson 2001; Lee et
al. 1997), but rather related to loss from radiation dam-
aged domains through crystal defects and fractures.
Once the crystal lattice is distorted and damaged, Pb
ions have “short circuit” pathways to diffuse from the
crystal, resulting in grains that have a deficiency of
Pb. This is different from thermally activated volume
diffusion, which is often exploited to understand ther-
mal histories by thermochronologic methods. Histori-
cally, the best way to minimize the effects of Pb loss
has been to choose the clearest, least magnetic, crack-
free grains and submit them to mechanical abrasion
prior to analysis (Krogh 1982a, 1982b). This process
removes the outer rim of the grain, which is often high
in U and thus more likely to have undergone radia-
tion-induced damage. While selection of the best qual-
ity, diamagnetic zircons and the aggressive abrasion
of their outer portions can minimize the effects of Pb
loss, it is a problem that can be difficult to recognize
without a large number of analyses (e.g., Mundil et al.
2001). Furthermore, grains with subtle Pb loss may
influence weighted-mean age calculations; they can
only be recognized and excluded with the highest-pre-
cision analyses.

Inheritance

It is common to find zircons from volcanic rocks that
give dates that are older than the true age of the rock,
though this problem is not always obvious. Older zir-
con can be incorporated into magmatic systems by as-
simulation of the host rock during magma generation
and transport and/or eruption. This is manifested by
old ( xenocrystic) cores of grains that are overgrown
by younger (phenocrystic) magmatic material (result-
ing in a mixed date), or by entirely xenocrystic grains.
It is a common occurrence in airfall ash deposits to
date zircon grains, often identical in appearance to the
indigenous population, that are <1 to >>10 Myr older
than the age of the ash (e.g., Landing et al. 1998). In
some cases, older zircons comprise more than 50% of
the zircons recovered from an ash. When analyzing
zircons from a volcanic rock reworked during deposit-
tion, it should be kept in mind that it is possible for
pre-existing volcanic debris of significantly older age
to be included into the depositional system.

The lifespan of successive stratovolcanoes in large
magmatic arcs can be on the order of <1 to ~10 Myr,
so there is potential for subtle inheritance that reflects
protracted magmatic growth of zircon rather than inher-
ted grains from host-rocks. In this case, distribu-
tions of zircon dates may reflect grains inherited
from slightly older magmas from the same magmatic
system, prolonged growth of single zircons within a
magma chamber, or a combination of the two. Pro-
longed growth in a magma chamber, usually referred
to as “residence time,” occurs on much shorter time
scales (<200,000 years) and has been documented in
many young magmatic systems (Reid et al. 1997; Reid
and Coath 2000; Bindeman et al. 2001; Vazquez and
Reid 2002). For Mesozoic and younger zircons, where
200,000 years can be resolved analytically, this is an
issue that must be considered, especially when trying
to resolve age differences between closely spaced ash-
es or comparing U-Pb zircon and \(^{40}Ar/^{39}Ar\) dates.

Comparison of two mineral-isotopic chronometers
that have contrasting sensitivities to thermal resetting,
like the U-Pb zircon and \(^{40}Ar/^{39}Ar\) sanidine systems,
provides a means of resolving residence time. Spe-
cifically, we can theoretically isolate zircon residence
time by contrasting the differences between U-Pb
zircon ages of several tuffs with the differences be-
tween \(^{40}Ar/^{39}Ar\) feldspar ages of the same tuffs. This
approach cancels out any systematic bias between
the two mineral-isotopic systems. Any dispersion in
these two intervals must then be associated with vary-
ing periods of magmatic residence time for zircon in
the different magma batches. A lack of dispersion in
these intervals would suggest either no residence time
(e.g., any absolute bias in the two chronometers being
attributable to systematic error), or an astonishingly
consistent zircon residence time (with associated pet-
rological and geological consequences). A problem
with this approach is that it requires a large number of high-precision analyses of zircon and feldspar, and thus the problem being attacked should be worthy of this effort.

Calculating an “age” for a given ash layer considering the effects of obvious and subtle inheritance can be difficult, as discussed in detail below. The bottom line is that analyzing a large number of zircons from each sample and restricting analyses to single grains or grain fragments is the best way to detect and overcome this problem. Large uncertainties can mask subtle inheritance, emphasizing the need for high-precision dating. For example, recognizing magma residence in a suite of 200 Ma zircons would require individual analyses that approach 0.1% precision.

Intermediate daughter product disequilibria
While not strictly open system behavior, it has been recognized for more than 30 years that the U-Pb systems of zircons may be affected by disequilibrium partitioning of intermediate daughter nuclides within the U decay chains during crystallization. In most cases the effects have been small enough to be ignored. However, as analytical precision has improved these effects must be considered, especially for Mesozoic and younger rocks. Sufficiently long-lived intermediate daughter products that may significantly perturb equilibrium U-Pb isotopic systematics are $^{230}$Th in the $^{238}$U-$^{206}$Pb decay chain, and $^{231}$Pa in the $^{235}$U-$^{207}$Pb decay chain (Mattinson 1973; Schärer 1984). This problem is important in minerals that preferentially incorporate Th, such as monazite, for which the $^{206}$Pb/$^{238}$U date is older than the crystallization age due to excess $^{206}$Pb. Because of the slightly greater ionic radius of Th relative to U, the intermediate daughter $^{230}$Th is normally preferentially excluded from the octahedral site in zircon, resulting in $^{230}$Th deficiency and anomalously young $^{206}$Pb/$^{238}$U dates that are most dramatic for zircon less than 50 Ma. A rare exception to this deficiency has been noted in carbonatitic zircon (Amelin and Zaitsev 2002). Disequilibrium between minerals and magma may be quantified and $^{230}$Th deficiencies corrected with a standard methodology utilizing $232$Th/$^{230}$U ratios (cf. Schärer 1984). Evaluation of the disequilibrium partitioning is mainly limited by our knowledge of the Th/U of the magma coexisting with the crystal during growth. Assessing this ratio at the time of eruption can be relatively simple for unaltered volcanic rocks through analysis of pumice or glassy lava compositions. In altered bentonites erupted from unknown sources, the corrections are harder to estimate although for most zircon-bearing eruptive systems the range of Th/U is quite limited. For example, Schmitz and Bowring (2001) showed that $^{230}$Th disequilibrium corrected $^{206}$Pb/$^{238}$U dates for zircon from the Fish Canyon Tuff are increased by only $+0.08$ Myr relative to measured $^{206}$Pb/$^{238}$U dates, and that the magnitude of this correction is robust to within 0.02 Myr for large variations in magmatic Th/U. Thus, uncertainties associated with $^{230}$Th disequilibrium do not appear to hamper our ability to resolve time at the $\pm 0.1$ Myr or better level using zircon $^{206}$Pb/$^{238}$U dates.

In the $^{235}$U-$^{207}$Pb decay chain, $^{231}$Pa disequilibrium effects should be of lesser magnitude than those for $^{230}$Th disequilibrium due to the shorter half-life of $^{231}$Pa relative to $^{230}$Th, unless mineral-magma fractionation is significantly greater for Pa than for Th. While a quantitative knowledge of the partitioning of $^{231}$Pa between accessory minerals and melts is lacking, qualitative assessments of Pa partitioning relative to U and Th, based on relative ionic radii, suggest that discrimination against Pa in zircon should be less than that of Th (Mattinson 1973; Barth et al. 1989). The bottom line is that reporting of U-Pb dates corrected for disequilibrium is often inconsistent and one should be aware when comparing dates from different publications.

Analytical Techniques (microbeam vs. ID-TIMS)
There are two main approaches to U-Pb zircon geochronology: microbeam techniques and isotope dilution thermal ionization mass spectrometry (ID-TIMS), with the latter often described as “conventional”. The major difference is that in conventional geochronology, zircon is dissolved and the U and Pb separated from the other elements prior to analysis whereas in microbeam techniques the zircon is analyzed by a laser in a sectioned and polished epoxy mount or thin section. The benefit of the high spatial resolution provided by microbeam techniques is a trade-off, in that analyses are at least an order of magnitude less precise than by ID-TIMS analysis.

U-Pb geochronology by microbeam techniques has
revolutionized geochronology over the past two decades. The two major techniques are Secondary Ion Mass Spectrometry (SIMS), typified by the SHRIMP (Sensitive High Resolution Ion Microprobe), and Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LA-ICPMS). Both of these techniques offer high-spatial resolution analyses using either a focused ion beam to sputter a volume of zircon (SIMS) or a laser that is used to vaporize a volume of zircon (LA-ICPMS).

Importantly, microbeam techniques allow in-situ analysis of very small volumes and thus high-spatial resolution; a typical volume of zircon analyzed by an ion-probe is cylindrical, 20-30 microns in diameter and several microns deep, with somewhat larger volumes for LA-ICPMS (Figure 1). In addition, the analyses can be done relatively rapidly (10’s-100’s of analyses per day for LA-ICPMS), and laboratory contamination can be minimized or eliminated. However, the high spatial resolution comes at a cost in terms of analytical precision. The precision of individual spot analyses using LA-ICPMS and SIMS is lower than ID-TIMS by approximately an order of magnitude (see Ireland and Williams 2003 and Kosler and Sylvester 2003 for recent reviews). This is in part because these are relative dating techniques that depend on alternating the analysis of standard zircons with unknowns. Over the course of a day, the raw measured age of the standard will drift and the same is assumed for the unknowns. Because we know the age of the standard, the unknowns can be normalized. This approach is successful but limits two-sigma precision of individual analyses to about 1-3%, compared to 0.1-0.3% precision by ID-TIMS. LA-ICPMS techniques are constantly being improved (e.g., Kosler and Sylvester 2003) with smaller volumes analyzed, better control of pit shape and size, and implementation of reliable ion counting devices.

In a perfect world, all zircon would be concordant and the large uncertainty associated with microbeam techniques would only be controlled by ion-counting statistics. In this case, one could “beat down” the un-

Figure 1—Relative volumes of zircon and analysis times for analyses by LA-ICPMS, SIMS, and ID-TIMS.
certainties by analyzing many spots in the same zircon or many zircons of exactly the same age and assuming that the uncertainties are normally distributed (i.e. Gaussian) about the age of crystallization. However, in many cases the distribution of dates is not Gaussian (for example, because of scatter due to Pb loss). The low precision of each analysis often precludes the detection of subtle amounts of Pb loss or inheritance described above and the absolute age is controlled to some degree by the variability of the standard analyses. Thus it is possible to have both relatively imprecise and inaccurate results from the microbeam techniques. A comparison of two published studies on zircons from the same ash bed (from the Neoproterozoic Doushantuo Formation of China) in Figure 2 shows that if a weighted mean of many relatively imprecise analyses is calculated, the result can be inaccurate as well as imprecise when compared to ID-TIMS. One interpretation of this dataset is that a number of SIMS analyses were located on domains that had lost a small amount of Pb resulting in a lower mean $^{206}\text{Pb}/^{238}\text{U}$ date when all the analyses are included. The higher precision of the ID-TIMS analyses allows small amounts of Pb loss to be recognized and exclusion of those data points when calculating the final age.

The inability to detect small amounts of Pb loss in small volumes of zircon analyzed by microbeam techniques represents a significant limitation for their application to high-precision geochronology. Thus, it is clear that for the highest precision work, microbeam results cannot be confidently interpreted at better than about 1%. Quoted errors of better than twice the precision on individual analyses are of questionable accuracy (Ireland and Williams 2003). However, in-situ techniques are without question essential tools for characterizing complex zircons from volcanic and metamorphic rocks and for sifting through detrital populations to characterize source areas and in some cases provide robust estimates of the minimum age of a sequence. Ideally, microbeam techniques would be used to rapidly characterize a population of zircons by analyzing a small volume of many zircons, which could then be followed by conventional high-precision geochronology of selected grains.

**NEW DEVELOPMENTS IN ID-TIMS U-PB GEOCHRONOLOGY**

Remarkable improvement over the past decade in our ability to precisely analyze small amounts of U and Pb in zircon has established ID-TIMS as a premier tool for time scale work. This improvement is a result of...
many factors including the development of new techniques that allow very high-precision analyses as well as an increased appreciation of what high-precision geochronology can do for the biostratigraphic record (Tucker et al. 1990, 1995, 1998; Bowring and Erwin 1998; Bowring et al. 1998; Mundil et al. 2001, 2004; Palfy et al. 2003). The MIT geochronology lab has been active in high-precision work since 1991 and our progress mirrors the improvement in the application of the technique in general. During this time period, zircon has been studied in remarkable detail, revealing the importance of chemical and age zoning in single grains and also providing insight into magma chamber processes. The combination of in-situ techniques and improvements in mass spectrometry have led to the recognition that subtle amounts of inheritance and Pb loss occur, and complex magmatic growth histories can be detected, which in turn has driven improvements in analytical blanks and measurement of smaller amounts of sample. These developments have also led to a greater appreciation of the relative importance of all sources of error associated with U-Pb analyses and the sensitivity of a final calculated date to these different sources of error.

The most important developments in ID-TIMS U-Pb geochronology have been: 1) routine imaging or elemental mapping of zircon structures and growth domains; 2) improved grain selection and pretreatment; 3) dramatic lowering of analytical blanks that allows small amounts of Pb to be precisely analyzed; 4) improvement in isotopic measurements coupled with more efficient ionization of Pb and U, such that single grains or grain fragments can be analyzed; and 5) evaluation of the accuracy of the U decay constants.

**Characterizing zircon**

In the past decade it has become clear that pre-analysis characterization of zircons is extremely important and that imaging of zircon using back-scattered electrons (BSE) and cathodoluminescence (CL) provides much insight into their growth history and accumulated radiation damage, which in turn has implication for their viability in precise geochronology (e.g., Connelly 2001). When minerals are bombarded with electrons they exhibit CL, which is related to electron transitions in different elements. This method has been used for decades in sedimentary petrology to, for example, identify multiple generations of carbonate cements. In zircon, the trivalent Rare Earth Elements are thought to dominate CL. U and resulting radiation damage suppresses CL so in high U zircons there is little luminescence. This allows low and high U zones to be distinguished (Figure 3A). BSE imaging, on the other hand, reveals variations in average atomic number of regions within a zircon. The higher the average atomic number, the brighter the region appears on an image. The element that predominantly controls BSE variations in zircon is Hf, although U also plays a role. In many cases CL and BSE images can be obtained using a SEM or an electron microprobe. There are many excellent papers that review imaging techniques and interpretations (see Corfu et al. 2003 for example).

Selection of zircon grains has generally followed the rule that the least magnetic, clearest, most crack- and inclusion-free grains yield the best results. Now it is routine to make polished grain mounts of zircons that allow the detection of small inherited cores, mineral and melt inclusions, and evidence for complex crystallization histories. Figure 3B shows CL images of zircons separated from volcanic rocks with a variety of zoning patterns, including inherited cores. After imaging, it is possible to avoid complicated grains and to microsample selected parts of imaged grains, such as a magmatic overgrowth surrounding a xenocrystic core.

**Pretreatment of grains**

In the past 10-15 years geochronologists have expended much energy attempting to minimize or eliminate internal domains that have experienced open system behavior from zircons prior to analysis. Pb loss has been inferred from large data sets obtained by both conventional and ion-probe analysis (e.g., Compston 2001), indicating the various spatial scales of the phenomenon.

James Mattinson of the University of California Santa Barbara has spent many years developing techniques that attempt to fully remove zircon domains that have experienced Pb loss. His 2005 paper (Mattinson 2005) introduced a new technique called Chemical Abrasion or CA-TIMS. The key innovation is that zircons are first annealed at high temperatures (700–900° C) for 36-60 hours and then undergo partial dissolu-
Figure 3A—CL images (top) and BSE images (bottom) of zircon from the Fish Canyon Tuff.

Figure 3B—CL images of zircon from volcanic ash beds from near the Cretaceous-Tertiary boundary in the Denver Basin. Grains with small rounded inherited cores are shown on the left and those without apparent inherited cores are shown on the right.
tion in hydrofluoric acid. Parts of the zircons that had experienced radiation damage and Pb loss dissolve at a much higher rate than the remaining lower U domains so the result is a low U residue that is more likely to be concordant; by all indications, this occurs without inducing U-Pb fractionation in the residual material. It is crucial to understand that the distribution of high U, radiation-damaged domains can be quite irregular and range from alternating micron scale zones to high U cores or rims. Thus the residue from leaching may indicate extensive “mining out” of the damaged zone. While annealing and leaching times have to be adjusted for different situations, this method has the potential to minimize or eliminate Pb loss as a concern. The method has been adopted by a number of studies with great success (Mundil et al. 2004; Condon et al. 2005; Schoene and Bowring 2006; Schoene et al. 2006; Bowring et al. in press; Furin et al. in press; Lehrmann et al. in press).

Analytical Blanks

The most dramatic development for extracting high-precision ages from zircons has been the ability to make precise measurements of small amounts of Pb. The isotopic composition of Pb in an analysis is composed of two main components: radiogenic Pb (Pb*) produced by the in-situ decay of U with an isotopic composition controlled by age and with no 204Pb and common or unradiogenic Pb (Pb\(_c\)). It is now quite clear that most zircons quantitatively exclude Pb when they crystallize from magma and that all the Pb contained in the zircon crystal lattice is from the decay of U. Exceptions to this are most likely the result of micro inclusions of minerals (apatite, feldspar, sulfides, etc.) that contain Pb. Thus, for high quality zircons all of the Pb\(_c\) in an analysis is introduced during sample processing. Examples of sources of Pb\(_c\) are reagents used to dissolve zircon and chemically separate U and Pb, Teflon capsules used to dissolve zircon, silica gel/phosphoric acid used to enhance ionization in the mass spectrometer, and random air fall during sample processing. Over the years, laboratories have been able to produce very clean reagents using clean Teflon ware and total analytical blanks less than 1 picogram have become common. To calculate a date from the measured Pb isotopic composition, one must first correct for the Pb\(_c\) component. The final propagated age precision is directly proportional to the ratio of Pb* to Pb in the sample. For a very Pb-rich zircon, a blank of 1 or 2 picograms will have little effect on the size of the errors. However, for a small, low U zircon that has 10 picograms of Pb*, the difference between a blank of 1.5 picograms and a blank of 0.3 picograms is dramatic (Figure 4). In many instances of dating volcanic ashes interlayered with fossil bearing rocks, the ashes are distal air-fall tuffs and the zircons very small. Both CA-TIMS and mechanical abrasion further reduces the volume of zircon for analysis by eliminating the highest U (and Pb) domains and thus the precision of most analyses is controlled by the magnitude of the blank. The bottom line is that lowering analytical blanks (now approximately 0.2-0.3 picograms) is necessary for full exploitation of the power of U-Pb zircon geochronology for rocks that range in age from less than 1 Ma to Precambrian. The lowering of analytical blanks permits the dating of zircons once considered too young for ID-TIMS analyses.

Intermediate daughter product corrections become much more significant with “young” zircons and high-precision, as shown in Figure 4 where the effect of correcting the 206Pb/238U date for initial 230Th disequilibrium is displayed. The sensitivity of varying the Th/U ratio of the magma from 4 (crustal average) to 2 varies with age. Using magmatic Th/U values of 4 and 2 increases the 206Pb/238U date of the 252 Ma sample (Figure 4A) by 91 and 78 kyr, respectively, and increases the date of a 7 Ma sample (Figure 4B) by 95 and 81 kyr. For the 252 Ma sample, the magnitude of the correction is small (<0.05%) so the difference between using a magmatic Th/U of 4 or 2 is insignificant. However, for a 7 Ma sample the magnitude of the correction is 1% and the difference from using varying magmatic Th/U values is significant (0.18%).

Analytical Improvements

In the past decade a number of analytical improvements have resulted in higher precision analysis on small amounts of radiogenic Pb. In ID-TIMS, prior to grain dissolution, zircons are spiked with a of tracer solution that contains a known amount of U and Pb isotopes. Within the past 15 years, the use of 205Pb and 232U – which do not occur in nature – as tracer isotopes has allowed for higher-precision determination of the abundance of the unknown isotopes. Adding 202Pb and 235U to the tracer as well has the added benefit of re-
Figure 4—Concordia plot of synthetic U-Pb data showing how errors are affected by the amount of common Pb in the analyses (Pb'), all of which is assigned to procedural blank, and how the 206Pb/238U dates are affected by the correction for initial 230Th disequilibrium. The amount of radiogenic Pb (Pb*) is 10 pg in (A) and 4 pg in (B). Ratios of radiogenic Pb to common Pb (Pb*/Pb') are shown. A procedural blank of 0.3 pg is needed to obtain an error of 0.1% (2σ) on the 206Pb/238U date in (A). The shaded line reflects the 2σ uncertainties of the U decay constants on the concordia curve. Two sets of ellipses are shown for each dataset, those that have been corrected for initial 230Th disequilibrium and those that have not been corrected.

Producing the uncertainty associated with mass-fractionation inside the mass spectrometer. The use of these improved tracer solutions as well as their high-precision calibration removes sources of uncertainties in the resulting date.

After spiking and dissolution, Pb and U are chemically separated from zircon that has been dissolved in hydrofluoric acid (HF) and then combined and loaded on high purity rhenium filaments. Stable ion beams for Pb and U-oxide are obtained by loading the purified metals in a mixture of silica gel and phosphoric acid (Gerstenberger and Haase 1997). Over the years there has been much experimentation with different preparations of this mixture, which has allowed for higher ionization efficiency and very stable ion beams.

For Precambrian zircons or detrital zircons with large amounts of Pb, analyses are often done using Faraday collectors for all isotopes of Pb except 204Pb, which is measured on an ion-counting device. An average Paleozoic zircon has ~20-50 picograms of radiogenic Pb, which should yield an ion beam of approximately 5-20 millivolts (measured across a 10^11 ohm resistor) of 206Pb for several hours. Because 207Pb is 10-20 times less abundant and 204Pb is nearly nonexistent, measurement by ion-counting is necessary. The key to high-precision analyses by ion-counting is a stable ion-beam that can be maintained for hours as opposed to higher intensity maintained for much shorter times. This means that a high-precision U-Pb analysis may take as long as 3-5 hours.

Zircon Standards
Microbeam zircon methods and 40Ar/39Ar require comparison of unknowns with mineral standards. Leading practitioners of these methods search for and characterize homogenous zircons or K-rich minerals that can
be used by multiple laboratories and provide a common calibration. This means that workers must agree on the age of the standards and normalize their data to "accepted values". In most publications, data is reported for the standards and provides an excellent measure of interlaboratory variability. The ID-TIMS community has not traditionally analyzed a large number of standards or routinely reported values, despite some effort (Wiedenbeck et al. 1995). There is a renewed interest in zircon standards that can be distributed to a large number of labs and especially ones that can be analyzed by both microbeam methods and ID-TIMS. One of these standards known as Temora (Black et al. 2003) has been distributed to a large number of labs for analysis. We hope that in the future ID-TIMS labs will adopt the practice prevalent in the Ar community of analyzing standards comparable in age to that of the unknowns and to report standard analyses acquired during the same time interval as the unknowns. We advocate a large number of zircon standards of different age and character so that one may choose an appropriate comparison for the interval being studied.

Accuracy of the U decay constants

Due to the high precision of the U decay constant measurements (0.11 and 0.14% for $^{238}$U and $^{235}$U, respectively (Jaffey et al. 1971), and because of the internal check of their accuracy provided by the dual decay of $^{238}$U to $^{206}$Pb and $^{235}$U to $^{207}$Pb, it has been suggested that other systems can be calibrated against the U-Pb system (Renne et al. 1998; Villeneuve et al. 2000; Begemann et al. 2001). However, there has been a persistent indication that the U decay constants of Jaffey et al. (1971) may be slightly inaccurate (though within the reported errors), based on high-precision U-Pb multigrain zircon data from Phanerozoic samples that plot slightly below the concordia curve (Mattinson 1994a, 1994b, 2000). The increase in both analytical precision and accuracy allows this issue to be explored.

Schoene et al. (2006) tested the accuracy of the decay constants by dating a number of zircons that range in age from ca. 99 Ma to 3.2 Ga. In this study, very high-precision U-Pb datasets from zircon systematically plot below the mean value of concordia, and were interpreted to indicate inaccuracies in one or both of the mean values of the U decay constants. Thus comparing $^{207}$Pb/$^{206}$Pb, $^{207}$Pb/$^{235}$U, and $^{206}$Pb/$^{238}$U dates cannot be done accurately without incorporating decay constant errors (although relative chronology within any one system retains its precision). On the one hand, many suggest that the inaccuracy is most likely in the $^{235}$U decay constant (Mattinson 2000; Begemann et al. 2001; Schoene et al. 2006), in which case it could be empirically recalibrated to the $^{238}$U decay constant in order to achieve concordant data. However, a more ideal approach is to re-measure both decay constants with better precision. In either case, it is important that users of U-Pb data be aware of this issue.

AGES, DATES AND UNDERSTANDING AND REPORTING SOURCES OF UNCERTAINTIES

The words age and date are often used interchangeably and some workers even refer to “age-dates” and “age-dating”. We agree with Faure (1977) that date should be used for the result of solving the decay equation for time (see Miller, this volume) or the weighted mean of many dates, and that age be used for an interpretation of a date such as a crystallization age or eruption age. U-Pb date uncertainties, or errors, are reported in many different ways and it is important to carefully consider what has actually been published when using the data. There are two kinds of errors that must be considered, internal error related to uncertainty in the isotopic measurements and correction for laboratory blank in the absence of systematic or external errors that include tracer calibration and decay constant errors. In the previous section, we discussed ways of reducing the internal errors. Systematic errors become very important when comparing U-Pb results with those obtained from different techniques such as $^{40}$Ar/$^{39}$Ar, or U-Pb data from different laboratories. If one is comparing data from only one technique and from one lab, the decay constant uncertainty and tracer calibration errors can be ignored. We will return to systematic errors below.

In general, U-Pb dates are plotted in concordia space as ellipses, which utilizes a statistical method of plotting data with highly correlated errors. In most cases, uncertainties on the $^{206}$Pb/$^{207}$Pb and $^{207}$Pb/$^{235}$U ratios are positively correlated by their relationship to the $^{207}$Pb/$^{206}$Pb date. In other words, if a positive inac-
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accuracy in one ratio occurs, then a positive inaccuracy in the other ratio is also likely because of measurement uncertainties in the Pb isotopes. Hence, there is a low probability that the true value of the $^{206}\text{Pb}/^{238}\text{U}$ ratio exists near its maximum negative error bounds if the true value of the $^{207}\text{Pb}/^{235}\text{U}$ ratio is near its maximum positive errors bounds. Therefore, U-Pb data with high Pb*/Pb will have the commonly observed diagonal error ellipses. In Phanerozoic zircons, as the Pb*/Pb of an analysis decreases, the precision of the $^{207}\text{Pb}/^{235}\text{U}$ date decreases much more rapidly than that of the $^{206}\text{Pb}/^{238}\text{U}$ because of the disproportionately large contribution of $^{207}\text{Pb}$ from the blank (e.g., the $^{207}\text{Pb}/^{206}\text{Pb}$ of the blank is ~0.75-0.80 and that of the sample is ~0.05-0.10). Graphically, this causes error ellipses to become “horizontal” in concordia space, indicating that the $^{206}\text{Pb}/^{238}\text{U}$ errors and the $^{207}\text{Pb}/^{235}\text{U}$ errors are not highly correlated (i.e., not the result of analytical error). For this reason, high-precision work in the Phanerozoic usually relies on some type of average of the $^{206}\text{Pb}/^{238}\text{U}$ dates of many individual analyses as the best estimate of the crystallization age for a population of zircons. Unfortunately, this approach virtually ignores the power of the dual decay scheme; therefore, reducing laboratory blank and measuring $^{207}\text{Pb}$ as precisely as possible by ion counting methods is important for using the $^{207}\text{Pb}/^{235}\text{U}$ date to evaluate closed system behavior (as shown below).

Whether using a single decay scheme or weighing the equivalence of a set of ellipses, a measure of the “coherence” of a data set is a statistical parameter called the MSWD (mean square of the weighted deviates; York 1967, 1969). A value of approximately 1 indicates that the scatter in the data can be explained by analytical uncertainties alone, values much less than 1 indicates that analytical uncertainties have been overestimated, and values greater than 1 can indicate either that errors have been underestimated or that another source of scatter, often called “geological” scatter, is present. Although this is often misunderstood, sometimes leading to a false sense of security in age interpretations, an MSWD of 1 does not mean there is a single age population. Rather, it means only that if real age variation is present, it cannot be resolved within the precision of the individual analyses. In the past decade, errors associated with ID-TIMS analyses have dropped by almost an order of magnitude, and while this is good, it also exposes complexity at the <0.1% level, resulting in higher values of MSWD. In the end, it is common for the geochronologist to be faced with a population of zircon analyses that do not form a coherent cluster (MSWD=1) and the crucial question is how to “edit” the data to arrive at an age.

Determining an “age” from a population of dates

A key aspect of most geochronological studies is: what question or problem is being addressed and what level of resolution is required to answer that question? This is not always straightforward as some problems become apparent only after the data are acquired! Given the time-intensive and expensive nature of isotopic analyses, it does not make sense to date every rock to a maximum level of precision. On the other hand, some problems, such as the age, duration, and causes of mass extinctions require this. No matter what the problem, most studies yield a population of dates that do not form a coherent cluster and must be “trimmed” or edited to arrive at an “age”. In the case of obvious inheritance or residual Pb loss (dates >> 2 sigma older/younger than a main cluster) or analyses with comparatively large analytical errors (due to either low Pb*/Pb, or poor quality analysis), the analyses can be justifiably excluded from the age calculation. In tightly clustered data sets where Pb loss and inheritance are apparently minimal, the inverse variance weighted mean date of a population of zircons is usually interpreted to represent the eruption/depositional age of an ash bed. Ideally, a relatively large number of zircon dates should be obtained and if all of the dates lie within two standard deviations of a single inverse-variance weighted mean, it may be confidently concluded that there was a single episode of zircon growth. In an ideal situation a geologist would have several ash beds in stratigraphic order and this ordering would provide a constraint on interpreting the results. For example, calculated dates should not violate stratigraphic order although for closely spaced ashes they may be indistinguishable within uncertainties.

More complex data sets with significant dispersion and little stratigraphic control must be rigorously examined in terms of distinguishing the eruption age from the effects of Pb loss and inheritance. It should be stressed that this level of attention is essential for establishing a very high-precision record. In complex
zircon data sets, it is clear that at some point the rejec-
tion of outliers can devolve into a subjective process, and statistically valid means of identifying and reject-
ning outliers and incorporating excess scatter into age
errors remain areas of active research (Ludwig and
Mundil 2002). The method described by Ludwig and
Mundil (2002) has been implemented in the statistical
program Isoplot (Ludwig 1991, 2005), which is used by
most U-Pb labs for calculation and display of isotop-
ic data. As described in the Isoplot notes, the TuffZirc
algorithm attempts to deal with relatively large data
sets (n >10) that may be affected by subtle amounts
of Pb loss or inheritance and overcome the problem
of subjective trimming of data that could yield a bi-
ased age but with an MSWD of around 1. While at-
temting to remove some of the analyt’s subjectivity,
this method does not favor higher precision analyses,
whereas taking weighted means of hand-picked popu-
lations does.

No matter how the data are treated, there is an im-
plcit assumption that there is a population of zircons
that will yield normally distributed errors about a
mean that is the crystallization age. The best way to
test this assumption is by analyzing a large number
of zircons, but a fair question is how many analyses
are enough? The answer in part lies in how the data
are being interpreted – the higher the resolution and
confidence desired, the more data per ash bed that is
required. For time scale work, our experience suggests
that 8 to 20 or more high-quality analyses are often
necessary to arrive at a single ash bed age, depending
upon the complexity of the zircon population.

Figure 5 shows three examples of data distributions
and calculated weighted mean dates of varying com-
plexity. Data from the North Mountain basalt are shown
in Figure 5A (Schoene et al. 2006). These zircons are
high in uranium and thus yield very precise results and
all scatter can be explained by analytical uncertainties.
Figure 5B after Furin et al. (in press) shows a well-
behaved distribution of analyses that form a coherent
cluster with no obvious effects of Pb loss or inheri-
tance. In this case, all of the analyses are included in
the calculation of the weighted mean and the MSWD
indicates that all scatter can be explained by analyti-
cal uncertainties. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date
of 230.91 ± 0.06 is similar to that calculated using the
TuffZirc algorithm of Ludwig and Mundil (2002) of
230.89 ±0.08/-0.04 Ma. Figure 5C from Lehmann
et al. (in press) shows a more complex situation with
a combination of air abraded and CA-TIMS treated
grains. There are clear outliers at both ends indicating
evidence for inheritance and Pb loss (analyses outside
of dashed box). However, deciding which analyses to
use in the calculated age for the rock is more difficult.
Given the success of CA-TIMS in eliminating Pb loss,
there is a temptation to place more weight on those
analyses, yet it should be noted that mechanical abra-
sion can also produce analyses with no evidence for
Pb loss.

In Figure 5C it is clear that for analysis 1 the low
uncertainties allow it to be distinguished from analy-
yses 2 and 3 which are distinctly older than analysis 4.
Analyses 12-14 are excluded from the weighted mean
calculation because they are younger than the precise
analyses 4-6. A slight amount of Pb loss in analyses 12-
14 is not unexpected since there is substantial Pb loss
in analyses 15-16. The weighted mean $^{206}\text{Pb}/^{238}\text{U}$ date
on analyses 4-11 of 247.38 ± 0.10 Ma is slightly older
than (but within error of) the TuffZirc age of 247.31
+0.15 -0.14 Ma. This small difference (ca. 0.03%) is
due to the fact that the analyses with the smallest er-
rors (analyses 4-5) are the oldest and TuffZirc calcu-
lates median dates without considering errors.

Some insight can also be gained from examining the
$^{207}\text{Pb}/^{235}\text{U}$ dates. Despite lower precision due to
smaller amounts of $^{207}\text{Pb}$, it is possible to see a coherent
cluster that is about 0.1% older than the $^{206}\text{Pb}/^{238}\text{U}$ date
in all three examples, which is predicted from consid-
eration of decay constant uncertainties (Schoene et al.
2006) and is consistent with a simple single popula-
tion that has not lost Pb. For the sake of simplicity, we
have used the same analyses to calculate the weighted
mean $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ dates although given
the lower precision of the latter, an additional analysis
(13) could be included in the sample shown in Figure
5C.

In Cenozoic rocks, magmatic residence time can be
an issue and zoned zircons are common. A hypotheti-
cal example based on unpublished data of the authors
is shown in Figure 6. In this situation, there are zir-
cons with obvious rims and cores. Attempts at physi-
cally isolating both populations are imperfect, but in the worst case each component is enhanced in different analyses and in some cases they are completely isolated. In this example, the cores are 35.0 Ma and the overgrowths are 34.8 Ma. Figure 6A shows that all analyses with relatively high blanks yield a statistically significant date assuming that they are normally distributed about the mean. In Figure 6B with slightly lower blanks and higher precision, there is a hint of multiple populations as the MSWD of all analyses is 2.7. Finally, in Figure 6C with low blanks, one could interpret the data as two populations at 34.82 and 35.02 Ma and the MSWD of all analyses has risen to 24. Thus, higher precision (due to lower blanks) allows the exploration of complex data sets and resolution of mixtures. It should be noted that these observations are predicated on the assumption that CA-TIMS is capable of removing all Pb loss. Ideally, CL or BSE imaging and chemical mapping of the zircon would show that distinct core and rim domains exist, and thus the age dispersion is “real” and not due to Pb loss in the youngest analyses.

Looking to the future, establishing geochemical fingerprints for inheritance and magma residence could partially resolve problematic date distributions. Nonetheless, in some cases even the best statistical manipulations or analyses of additional zircons may not adequately resolve problematic date distributions. In these cases, it may be more productive to recollect the ash layer in nearby sections, or date another volcanic layer from the same general stratigraphic interval.

Figure 5—U-Pb dates from (A) a relatively simple population of high U zircon from the North Mountain Basalt (Schoene et al. 2006), (B) a relatively simple population of volcanic zircon (Furin et al. in press) and (C) a relatively complex population of zircon (Lehrmann et al. in press). Bars represent dates from single grains of zircon with errors at 2\(\sigma\). Gray bars extending across the figure represent the weighted mean date of all analyses in (A) and (B) and those within dashed box in (C) with errors at 2\(\sigma\).
ARE THOSE $^{206}\text{Pb}$ YEARS OR $^{40}\text{Ar}/^{39}\text{Ar}$ YEARS? THE IMPORTANCE OF EXTERNAL ERRORS

This is not a joke! For the purposes of constraining the Paleozoic history of life, two major geochronological techniques that offer the highest precision are most commonly applied: U-Pb in high uranium accessory minerals and $^{40}\text{Ar}/^{39}\text{Ar}$ in feldspar, biotite, and hornblende. As with U-Pb, the $^{40}\text{Ar}/^{39}\text{Ar}$ technique has also seen remarkable improvements in the past decade and it is now clear that systematic biases between different labs and different methods often exceed internal analytical precision. For example, it is not possible at present to construct a precise and accurate time scale seamlessly integrating U-Pb and $^{40}\text{Ar}/^{39}\text{Ar}$ geochronology. These issues have led to a community-based organization known as EARTHTIME (www.earth-time.org) whose goal is to eliminate interlaboratory and intertechnique biases, share techniques, standards, and calibrations with a long-term goal of a high-precision calibration of Earth history. The same issues hold for other geochronological techniques, which are successfully being applied to the dating of sedimentary rocks (Rasbury and Cole, this volume). It should be stressed that the effects we are talking about are in the range of 0.1 to 1% and have only recently become important due to the feedback loop between the types of questions we are using geochronological data to evaluate and development of increased analytical precision.

Figure 6—A synthetic data set of $^{206}\text{Pb}/^{238}\text{U}$ dates from a zircon with a 35 Ma core and a 34.8 Ma rim showing the effect of lower blanks and errors on the resolving power of the data. The distribution like (C) could only be obtained if one could recognize cores and rims in CL or BSE images and then microsample them.
Thus, when comparing data sets between techniques or laboratories we must add external errors – such as decay constant uncertainties – to dates before comparison.

One of the most important of these issues is the accuracy and precision of the currently used values and associated errors for the long-lived radionuclide decay constants recommended by Steiger and Jäger (1977). Many studies (Renne et al. 1998; Min et al. 2000, 2001; Renne 2000; Villeneuve et al. 2000; Schmitz and Bowring 2001; Nomade et al. 2004) have noted that $^{40}$Ar/$^{39}$Ar dates are systematically younger than U-Pb dates from rapidly cooled rocks and do not overlap with U-Pb dates if one ignores systematic errors. Much of the bias may be accounted for by inaccuracies in the $^{40}$K decay constant and physical constants, which differ by ~2% from those used in other scientific communities (Renne et al. 1998; Min et al. 2000; Renne 2000). However, U-Pb and $^{40}$Ar/$^{39}$Ar dates do not necessarily form a trend that can be explained by only systematic errors, suggesting that interlaboratory biases or geologic complications are important in many of the published examples. At present, although there may be as much as 1% difference between U-Pb and $^{40}$Ar/$^{39}$Ar dates, there is no simple correction that can be applied to make them equivalent. This is currently the biggest impediment to calibration of the time scale using both $^{40}$Ar/$^{39}$Ar and U-Pb dates. In addition, if either is compared with Re-Os of Lu-Hf dates one must incorporate uncertainty into these decay constants as well. Finally, inaccuracies in the U decay constants (as discussed above) mean that decay constant uncertainties must be included when comparing different U-Pb dates.

Tracer calibration in ID-TIMS analysis is also an important potential source of systematic error. The U/Pb ratio of the tracer is determined by adding it to precisely made gravimetric solutions of U and Pb metals. At present, most labs have an uncertainty in spike calibration of about 0.1%. The EARTHTIME Initiative is working towards the effective elimination of this tracer calibration uncertainty by producing and distributing a mixed $^{206}$Pb-$^{233}$U-$^{235}$U tracer solution that can be made available to labs involved in high-precision time scale geochronology. In addition, through EARTHTIME, common gravimetric solutions are also available so that laboratories’ existing spikes can be re-calibrated. While 0.1% does not seem like much, we are getting to the point where this source of uncertainty will be crucial for constructing a time scale using multiple labs.

When comparing dates obtained for different samples in stratigraphic sequence (i.e., in order to determine rates of inferred climate change, evolutionary rates, or sediment accumulation rates, etc.) it is beneficial to use dates calculated using a single decay scheme and a single tracer solution (in which case decay constant and tracer calibration uncertainties can be ignored). If one is using a combination of chronometers, decay constant uncertainties must be considered for each of the dates being compared. While potentially confusing to the non-geochronologist, the main point of this discussion is that one needs to know the kind of date that is reported before it can be compared with either other U-Pb dates or dates derived from other chronometers. Somewhat paradoxically, this state-of-affairs is a direct result of our ability to make increasingly more precise analyses; as recently as 5 years ago this level of resolution was not possible.

**SUMMARY**

High-precision U-Pb geochronology applied to the stratigraphic record is still in its infancy. Development of the ID-TIMS approach over the past decade means that it is now possible to routinely obtain high-precision (±0.1% and better) ages for volcanic rocks interstratified with sedimentary successions. Perhaps the most significant development over the past decade is the advent of CA-TIMS pretreatment (Mattinson 2005) which often results in the effective elimination of Pb loss from most zircons. Coincident with increased precision has been the increased appreciation of complexity of U-Pb isotopes in zircon and the importance of systematic uncertainties (such as those related to U and $^{40}$K decay constants). While these present challenges for the geochronological community they also allow interpretation of subtle differences in age and new opportunities for the high-resolution calibration of the stratigraphic record.

The next decade will see an explosion of high-pre-
cision geochronological constraints on the rates of geological processes, the ages and durations of mass extinctions, large igneous provinces, chemostratigraphic anomalies, and glaciations. It is crucial that the geological and paleontological communities work with geochronologists to address important issues in Earth history, and for each community to understand the other’s language and approach. The integration of paleontological and climate proxy data with high-precision geochronology offers us an unprecedented opportunity to learn how the planet has operated in the past and will allow informed prediction about the future.

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