8 Considerations in Zircon Geochronology by SIMS

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INTRODUCTION

Secondary ion mass spectrometry (SIMS) is a versatile technique for measuring the chemical and isotopic composition of solid materials on a scale of a few microns. A beam of high-energy primary ions is focused onto the polished target surface, sputtering (ablating) atoms and molecules, and in the process ionizing a small fraction. These secondary ions, which reflect the target composition, are analysed by mass spectrometry. The SIMS instrument most common in geoscience is the ion microprobe, which uses a focused primary ion beam in either static or scanning mode to sample target areas usually 10 to 50 µm diameter. Total sampling depth is typically less than 5 µm and the sampled mass only a few nanograms, making the analysis for most samples effectively non-destructive. Coupled with surface imaging techniques such as backscattered electron (BSE) and cathodoluminescence (CL), SIMS enables finely targeted chemical and isotopic analysis of specific domains exposed on a crystal surface.

Zircon is particularly suitable for SIMS U–Th–Pb geochronology. It is a physically and chemically robust mineral that crystallizes under a range of geological conditions, incorporating trace U and Th, but little or no Pb. Zircon grains are commonly composite, having survived and grown during several geological events. This growth record is sometimes visible under an optical microscope, but is best revealed by CL and BSE imaging of polished sectioned grains (Fig. 1). The U–Th–Pb closure temperature of unaltered zircon is very high (>900 °C), and the growth domains commonly can preserve an isotopic record of thermal events spanning tens to thousands of millions of years. This record of provenance, and igneous and metamorphic history, is accessible only to microanalytical techniques such as SIMS.

The first ion microprobe constructed specifically for isotopic analysis of geological materials, the SHRIMP (Sensitive High Resolution Ion MicroProbe), was designed with zircon in mind. Earlier U–Pb dating of lunar minerals using the ARL ion microprobe (Andersen & Hinthorne, 1972) had demonstrated the feasibility of the technique, but also revealed a major limitation—the measured Pb isotopic compositions required large corrections for molecular isobaric interferences. These interferences arose because sputtering produces a complex array of molecular secondary ions, some of which have masses very similar to the Pb isotopes. The problem could be overcome by tuning the ion probe mass analyser to high mass resolution (>3000), but with a grievous loss of signal and precision (Hinton & Long, 1979). The SHRIMP design philosophy was to achieve high mass resolution without loss of sensitivity by using the widest possible object slit, and therefore the largest practicable double focusing mass spectrometer (magnet turning radius 1m). The concept proved extremely effective and was later adopted in the design of other ion probes, the Cameca 1270 and VG Isolab 120.

The application of SHRIMP to zircon geochronology rapidly revealed the rich and complex record of geologic history preserved within individual zircon grains. Although at first received with some skepticism (e.g. Moorbath, 1983), SIMS has now become the benchmark for the dating of polychronic zircon populations. SIMS analysis does not, and probably never will, achieve the precision attainable by isotope dilution thermal ionization mass spectrometry (ID–TIMS) because of
Both zircon crystals appear homogeneous in transmitted light but cathodoluminescence images show the true growth structures: (a) an igneous zircon with simple euhedral oscillatory zoning, and (b) a complex metamorphic zircon with chaotic internal structures. Such images are essential if specific growth domains are to be precisely targeted.

the small volume of material sampled, but it remains unrivaled for its precision and accuracy in U–Th–Pb dating at an intra-crystalline scale (Fig. 2).

In this paper we review the current state of SIMS geochronology and consider its possible future. This work is not intended to be a comprehensive review of all aspects of SIMS geochronology but rather an outline of the procedures involved so as to allow a reference frame for discussion of the current analytical status and potential developments for the future. A more comprehensive discussion of analytical and instrumental parameters can be found in Ireland (1995) and Williams (1998).

SELECTED APPLICATIONS

SIMS-based zircon geochronology has been applied to virtually the whole age range of rocks from Earth and the solar system. SIMS has the particular advantage over other analytical techniques that the tiny sample size required (~2 ng per analysis) makes it possible to analyse very small grains or domains within zoned grains and thereby to deconvolve the products of complex thermal histories. The benefits inherent in SIMS analysis have been exploited in a wide diversity of applications, examples of which are given below. This list is far from exhaustive. Some further examples have been discussed in more detail by Williams (1998).

Oldest zircon in the solar system

The sensitivity and selectivity afforded by ion probe analysis are well illustrated in the dating of 4.56 Ga zircons from the Vaca Muerta and Simmern meteorites (Ireland & Wlotzka 1992). Meteoritic zircon is quite rare, and it normally occurs as small, sometimes interstitial, grains about 10 µm, and occasionally up to 30 µm, diameter. Making analysis even more difficult, the U content of the zircon can be very low (< 1 ppm). Ireland & Wlotzka (1992) analysed three zircon grains <20 µm diameter in thin section, and therefore in a known petrographic context, first for U-Th-Pb to measure their ages, then for rare earth and other trace elements to determine their genesis, still leaving enough sample for subsequent Hf-W isotopic analyses to measure the abundance of extinct $^{182}$Hf (Ireland 1991). Even after all this work, most of the zircon still remains for future study.
Figure 2. Rastered ion images of $^{206}$Pb, $^{208}$Pb, UO and ThO distributions in a zircon from the Paleozoic Cowra granodiorite showing the broad correlation between U and uranogenic Pb, Th and thorogenic Pb, and lack of correlation between Th and U. Core of the zircon as seen in BSE image is Paleoproterozoic and rim is 410 Ma. The core shows an extreme range of discordance but in detail, the $^{206}$Pb is seen to be graded along the length of the core rather than varying as a function of the U zoning. Note that the core is barely visible in the transmitted light image.

Development of fractionated lunar crust.

Large numbers of zircon grains were recovered from the sawdust produced by the processing of rocks returned from the Moon. Although these could be dated relatively easily by ID-TIMS, the great majority of the rocks were breccias, so the measured ages had no petrographic context. After exhaustive searches of lunar breccia thin sections, however, numerous single zircons, and rare zircon clusters, were found. Many were isolated grains, but in rare cases the zircon was clearly part of a lithic fragment, the mineralogy of which indicated the composition of the source rock. Dating lunar zircon was one of the earliest applications of the SHRIMP (Compston et al. 1984) and provided much of the impetus to achieve the highest possible accuracy in the measurement of Pb/U. A subsequent more comprehensive study of lunar zircon in lithic fragments made it possible to trace
the extended history of the evolution of the lunar crust (Myer et al. 1996). It demonstrated that the earliest zircon-bearing rocks (~4.37 Ga) were the most mafic, but that they were soon followed (at ~4.32 Ga) by highly evolved rocks (granophyres). Production of both rock types continued for more than 300 million years, ceasing abruptly at ~3.9 Ga, the proposed time of the terminal lunar cataclysm. As in the case of the meteoritic zircon, the SIMS analyses consumed so little material that these rare, invaluable samples remain intact for future study.

**The oldest-known terrestrial rocks**

SIMS is not only useful for studying complexity, but also for measuring accurate ages in spite of it. The Acasta gneiss complex from the Northwest Territories, Canada, contains the oldest-known terrestrial rocks, and the only rocks presently available from the Priscoan eon (Stern & Bleeker, 1998; Bowring & Williams, 1999). The gneiss has had an extremely complex history, including at least four major thermal events, each involving the production of partial melts. The rocks therefore contain multiple generations of zircon, commonly co-existing within individual grains. Making the age measurements even more difficult, most of the zircon crystals are extensively altered and or recrystallised. Using relict euhedral oscillatory zoning as a guide, Bowring and Williams (1999) analysed remnants of original igneous zircon. Even though such zircon had a single primary age, the patterns of discordance were complex because different domains had responded in different ways to the later thermal events. Instead of defining a quasi-linear discordance array, as is common in the zircon from most high-grade rocks, the data were widely dispersed towards a range of lower concordia intercepts. Only from their consistent convergence towards the same upper intercept, and a few concordant analyses at that intercept, was it possible to infer that the zircon first crystallised at 4.03 Ga.

**Detrital-zircon age spectra**

The high speed of ion-probe analysis opened up a range of new applications in which the dating of large numbers of grains was more important than achieving high precision on individual measurements. A dramatic early success was the discovery of rare >4.1 Ga zircon grains in early Archean sediments from Western Australia (Froude et al., 1983), the first direct evidence for evolved terrestrial crust prior to 4.0 Ga and the first samples of crust known to have survived the massive meteorite bombardment of Earth at 3.9 Ga, the time of the terminal lunar cataclysm. An intensive search is currently under way to identify enough pre-4.0 Ga zircon to be used for a range of further geochemical studies of the composition of the Priscoan crust. Surveying the requisite many thousands of detrital zircons can only be done by ion probe because other techniques for measuring the radiogenic Pb isotopic composition, including laser ICP-MS, are too destructive. Use of multiple collection has reduced the time per reconnaissance analysis to about 20 seconds (Mojzsis et al., 2002). The more common use of ion probes in the study of sediments and sedimentary rocks is to define the complete detrital zircon (or monazite, rutile etc.) age spectra. The relative abundances of grains of different ages are a fingerprint from which it is possible to infer the provenance of a sediment and to make very reliable correlations with other sedimentary units. Changes in that fingerprint through time can be a very sensitive record of changes in erosion patterns and the continental scale tectonics that have caused those changes. Noteable examples are the studies by Ireland et al. (1998) and Goodge et al. (2002) of the early Paleozoic sediment sequences in eastern Australia which record the tectonic development of the Pacific margin of Gondwana. These signatures also pervade the southern Australian beach sands with little influence from the adjacent craton (Sircombe 1999). The detrital zircon in desert dune sands has provided important new insights into more recent sediment transport patterns in Australia, identifying water, not wind, as the principal transport mechanism (Pell et al. 1997). Wind played a major role, however, in the formation of Bauxite deposits in Western Australia, the zircon in the bauxite showing the contribution to the ore from the underlying basement rocks to be relatively minor (Brimhall et al, 1992).
Analysis of thin rims and near-surface concentration gradients (depth profiles)

A major application of SIMS instruments, particularly in the semiconductor industry, is for the measurement of near-surface concentration profiles. The finest depth resolution (less than a nanometre) is achieved when the primary beam is rastered over the sample surface and the measurements are made only at the centre of the rastered area. This eliminates edge effects and guarantees a very uniform penetration rate. Depth profiling of small geological samples is usually done with a static primary beam, however, relying on the relatively uniform beam density produced by Kohler illumination to achieve uniform penetration. An early application of the technique was the dating of very thin Miocene metamorphic overgrowths on Precambrian zircons from Himalayan paragneisses (Zeitler et al. 1989). The zircon was prepared for the experiment with minimal polishing, but nevertheless even the 2 µm deep analysis pit in some cases penetrated through the overgrowth and into the core. Within the resolution of the method, no evidence was found for diffusion of core Pb into the overgrowth during the granulite grade metamorphic event. Measuring the rates of Pb, U and Th diffusion in natural zircon has proved extremely difficult, not least because the rates are so slow and zircon with even moderate U and Th contents is prone to radiation damage. Using ion probe depth profiling, Lee et al. (1997) were able to measure all three rates directly by analysing the concentration gradients produced when low-U, gem quality zircon was heat treated at temperatures of up to 1100 °C for up to three months. Even for the highest temperatures and longest times, the depths of Th and U diffusion were less than 20 nm. The closure temperature for Pb diffusion, measured on only 19 ppm $^{206}$Pb, was calculated to be $\geq 940$ °C, consistent with the value later measured by Cherniak & Watson (2000) using Rutherford Backscattering Spectrometry.

The youngest zircons

The blanks for SIMS U-Pb geochronology are intrinsically very low, depending only on how well the mount is cleaned after polishing and the Pb content of the Au coat. They are reduced even further if the primary beam is used to ion etch the surface of the target prior to analysis. It is therefore possible to measure radiogenic Pb contents down to a few ppb and thereby to measure the Pb/U age of zircon as young as a few hundred thousand years. At this age, the principal limitation on precision is counting statistics, not uncertainty in the Pb/U calibration. Those statistics can be improved by longer counting times and targeting zircon grains or zones that are U-rich. Care must be taken, however, not to take the latter to excess as SIMS determinations of Pb/U become increasingly biased with increasing U once U levels exceed about 3000 ppm (Williams & Hergt 2000). Even lower ages can be measured using $^{234}$U-$^{230}$Th disequilibria (Reid et al. 1997; Bacon et al. 2000). In some cases, isochrons can be constructed for individual zircons (Lowenstern et al. 2000).

Timescale

Nothing tests the limits of a dating technique more than measurements of absolute age to calibrate the geological time scale. Not only does this require the greatest precision and accuracy, but there is a very large pre-existing data set with which any new measurements must be reconciled. Discrepancies quickly become evident and reasons for them, either geological or analytical, have to be found. The low precision of SIMS geochronology limits its usefulness for time scale calibration, particularly when the question arises of which, if any, of the analyses are concordant. There is also concern about the possibility of analytical bias at about the 1% level, particularly since the standard used for much of the SIMS time scale work has been shown to be heterogeneous (Compston, 1999). The uncertainty in SIMS measurements of $^{207}$Pb/$^{206}$Pb on Phanerozoic zircon is such that the concordance of individual analyses cannot be tested. SIMS does have the advantage, however, that independently of standardisation, quite subtle differences in age between the grains in ostensibly homogeneous zircon populations can be detected as excess scatter in the Pb/U measurements. Such differences were missed in much of the early TIMS work on multigrain samples of volcanic zircon
populations, but having been pointed out (eg. Compston & Williams 1992), are now also being found by TIMS single grain analyses (eg Mundil et al. 2001). Compston (1999, 2000a; b) continues to be a strong advocate for the application of SIMS to time scale work, but the highest precision will always be achieved when analysing larger samples by TIMS. Ideally the two techniques should be employed in tandem, SIMS for testing large numbers of grains for age uniformity, and TIMS for precise, accurate analyses of a chosen few. Only if the results of both techniques are internally consistent can the measured age be considered reliable. That leaves only the question of geological significance, which given the long residence time of zircon in magmatic systems and the propensity of volcanism to resample the products of previous eruptions, does not necessarily have a simple answer.

INSTRUMENTAL AND ANALYTICAL APPROACHES

To prepare zircon for SIMS analysis, it is mounted in epoxy with reference zircon of known age, polished to expose the centres of the grains, documented by a range of imaging techniques (reflected and transmitted light microscopy, CL, BSE), and gold coated to prevent charging during sputtering. The primary ion beam is usually focused to 10–30 µm diameter. Narrower beams are possible, but for a given primary beam density, secondary ion yield falls in proportion to spot area. If, for example, the spot diameter is halved, analysis time must be increased by a factor of four to maintain precision. To some extent loss of secondary ion yield can be compensated by increasing the primary beam density, but this is ultimately limited by increasing inter-element fractionation. As a general rule, up to a beam diameter of ~40 µm, the best data are obtained using moderate primary beam densities and the largest diameter permitted by the scale of the growth domains to be analysed.

The main isobaric interferences potentially affecting the analysis of Pb in zircon are molecules of Zr, Hf, Si, rare earth element (REE), O and H (Fig. 3). Complex molecules, such as Zr₂O, are readily separated at a resolution of ~1200. To resolve HfSi requires ~3750, REE and Hf dioxides require ~5100 and Pb hydrides about 30000. Given a practical upper limit of ~1 m for the turning radius of the mass analyser magnet, both the SHRIMP and Cameca 1270 have been designed for a mass resolving power of ~10000, which translates to a routine high transmission operating resolution of ~5000, sufficient to resolve all interferences except hydrides, which are minimized by the use of cryogenic pumping. In other respects, however, the two instruments differ, the Cameca 1270

Figure 3. Mass spectrum of $^{206}$Pb showing separation of isobaric interferences in zircon. Mass resolution is 6,000 R (10 % peak height), a standard operating condition for high mass resolution SIMS instruments. Ineffective separation of these interferences caused inaccuracies in data from lower resolution ion probes.
being a derivative of the secondary ion microscope designed by Castaing & Slodzian (1962), and the SHRIMP a derivative of the ion probe mass analyser of Liebl (1967). The main difference is in the secondary ion focusing—whereas the Cameca 1270 is designed primarily to provide ion images of the target, the SHRIMP transforms the secondary ions to a line image which accurately matches the acceptance of the mass analyser in dimension and divergence but does not transfer a direct image of the target. The two instruments have been compared in detail by Ireland (1995), so will be discussed only briefly here.

**SHRIMP**

SHRIMP I was built in the late 1970s based on one of a series of theoretical ion optic designs devised by Matsuda (1974) to correct for image aberrations up to second order in double-focusing mass spectrometers. SHRIMP II, an improved version of the instrument built in the late 1980s and now also produced commercially by Australian Scientific Instruments, is similar in basic concept and operation.

Oxygen is the preferred primary ion beam for U–Pb analysis. It is highly electronegative, thereby chemically enhancing secondary ion production, and it is an easy gas to handle, causing much less damage to ion optical components than other electronegative gases such as Cl and F. The oxygen ions are produced in a cold-cathode duoplasmatron then passed through a Wein mass filter to select the required primary ion species, O$_2^-$ in most cases. The primary column is held at +10 kV relative to ground, and the duoplasmatron at approximately -10 kV relative to the column, namely close to real-ground potential. Sharp focus and uniform primary beam density at the target surface are achieved using Kohler illumination, in which the image of an intermediate aperture, not the primary ion source, is projected onto the target. A Schwarzschild optic system provides a high quality reflected or transmitted light image of the sample surface.

Secondary ions are extracted at -10 kV relative to the sample, which is biased about 750 V above column potential to minimize secondary ion fractionation. The ions are focused onto the object slit of the secondary mass analyser by a quadrupole lens triplet adjusted to match the emittance at the slit to the acceptance of the analyser. In doing so they are sampled by a beam monitor, the signal from which can be used to normalize out secondary beam noise. The forward geometry mass analyser consists of three main elements, an 85° electrostatic sector, a static quadrupole and a 72.5° magnetic sector. The purpose of the electrostatic sector is to cancel the energy component of the momentum dispersion in the magnet, essential because of the large energy spread (~150 V) in the secondary ions, producing pure mass dispersion at the collector slit. For zircon analysis the ions are normally counted by a single electron multiplier. Analysis combining multiple collection of the Pb isotopes with single collection of the Zr, U and Th species is also possible.

**Cameca 1270**

The Cameca 1270 is a high resolution derivative of the successful Cameca ims 3f–6f product line. These instruments were developed as ion microscopes and as such the main secondary lens system is stigmatic, designed to project ion images of the target or slits onto a channel plate detector at the exit to the mass spectrometer. The source of negative primary ions again is a duoplasmatron, the required primary ion species being selected using a sector magnet. Typically Cameca ion probes use atomic $^{16}$O rather than molecular $O_2^-$ for zircon analysis, the higher flux of $^{16}$O more than compensating for the lower secondary ion yield per primary ion. The electrical configuration is similar to that of SHRIMP, although the primary ion energies are commonly higher, up to 20 kV. The secondary ion beam is focused onto the object slit of the mass spectrometer by cylindrical einzel lenses. Apertures can be used to constrain the beam such that only ions from the centre of the analysed area pass into the mass spectrometer. Unlike SHRIMP, an energy window is commonly used to restrict the range of secondary ion energies transferred to the main analyser magnet in order to optimize mass resolution. An alternative astigmatic secondary lens system provides enhanced
transmission for secondary ion analysis. Zircon is normally analysed using a single electron multiplier, but multiple collection of the Pb isotopes also is an option.

**Operational Comparison**

Although in general terms the operation of the two instruments for zircon U–Pb isotopic analysis is quite similar, there are some significant differences in detail.

The main difference apparent to operators of the two instruments is the sole use of photon imaging (reflected light) to select targets on the SHRIMP and the additional availability of ion imaging on the Cameca 1270, both for spot verification and for tuning. The Schwarzchild optics on SHRIMP allow high-magnification images to be viewed continuously and the quality of the normal reflected light imaging on SHRIMP is sufficient to permit precise targeting guided by reflected light and CL photomicrographs of the grain mount. Reflected-light images are available on the Cameca but the lighting is oblique and at lower magnification, and accurate spot positioning is more difficult. Spot placement can be confirmed by ion imaging although zircon grains are generally of sufficient size that within grain placement is not difficult. For heterogeneous zircons, ion imaging on the Cameca 1270 allows targeting based on the sample composition, as well as the potential to mask out of unwanted areas within the analysed spot.

The availability or not of secondary ion imaging also governs the way the ion optics of the two instruments are tuned. On the Cameca 1270, an ion image of the primary beam on the target is used to tune the primary beam for size, shape, sharpness and uniformity, an ion image of the source slit is used to maximize secondary ion transmission, and an ion image of the collector slit is used to maximize mass resolution. On the SHRIMP, the shape and sharpness of the primary beam is tuned using the reflected light image of the target, the transmission is maximized using a secondary beam monitor between the electrostatic analyser and magnet, and the resolution is maximized using scans of the secondary beam across the collector slit.

Raising the partial pressure of oxygen in the vicinity of the target has been found to increase the secondary ion yield of the Cameca 1270 by a factor of 2 to 3 (Schuhmacher et al. 1993; Quidelleur et al. 1997). For SHRIMP, the Pb⁺ ion yield increases by only about 20% under the same O-flooding conditions. The Cameca 1270 is therefore operated with an oxygen bleed to the source chamber, whereas the SHRIMP is not. Under these conditions, both instruments have a similar sensitivity for Pb, about 25 cps per ppm Pb per nA of primary beam. Primary beam fluxes for both instruments typically are limited to ~10 nA to minimize charging and depth effects on interelement discrimination, making the normal maximum sensitivity for zircon analysis about 200 cps/ppm. Analytical precisions are therefore similar. Stronger primary beams can be used to increase the sensitivity and precision for common-Pb analyses.

For both instruments, good initial tuning and consistency in retuning between analyses are of paramount importance in achieving the stable analytical conditions required for accurate, precise measurement of U–Pb ratios.

**ZIRCON ANALYSIS**

The procedures for SIMS U-Th-Pb isotopic analysis and instrumental factors to be taken into account have been discussed in detail by Ireland (1995) and Williams (1998). The single collector analysis cycle for zircon U-Th-Pb typically consists of a Zr molecular species (e.g. Zr₂O), the Pb isotopes ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb, two of the U and U oxide species (U, UO, and/or UO₂) and a Th species, normally ThO. Measurement of the Zr molecule serves two main purposes, as a major element reference for the calculation of Pb, U, and Th concentrations, and as a mass reference for location of the ²⁰⁴Pb peak. The four Pb isotopes are used to calculate both the size of the common Pb correction and the radiogenic Pb isotopic composition. At least two U species must be measured in order to calculate the true target Pb/U, because the basis for the Pb/U calibration is an empirical observation that the secondary ion ratio Pb⁺/U⁺ changes in sympathy with the ratios of the U oxide
ions. The Th species is measured for the calculation of Pb/Th age, to provide a measure of Th/U (sometimes a chemical diagnostic of the conditions under which zircon crystallized), and in special cases to allow calculation of the expected radiogenic $^{208}\text{Pb}/^{206}\text{Pb}$ for common Pb corrections.

**Pb isotopes**

The Pb isotope composition of zircon is generally taken as measured. Several attempts have been made to estimate the mass dependent mass fractionation of the Pb isotopes but the low Pb concentrations in zircon and the difficulty of resolving any PbH isobars ($M/\Delta M = 33000$; Fig. 4) make an accurate measurement of fractionation very difficult. Currently it is considered unlikely that the fractionation exceeds about 0.2%/amu, that measured on common Pb from feldspar. The good agreement between SHRIMP and conventional ID-TIMS Pb isotope analyses of a number of zircon samples has been used to suggest that the mass fractionation is minimal (as is the hydride component) and therefore that no correction need be applied (Compston et al. 1986). Hydrides and fractionation have opposite effects, however, raising and lowering the $^{207}\text{Pb}/^{206}\text{Pb}$ respectively. The apparent lack of Pb fractionation might in part be due to mutual cancellation of the two contributions.

The mass resolution required for the isotopic analysis of Pb in zircon, >5000, is determined mainly by the need to resolve the Pb isotopes from HfO$_2^+$ and HfSi$^+$ isobaric interferences. $^{204}\text{Pb}$ is also theoretically subject to interferences from complex REE hydroxides, Hg$^+$ and WO$^+$, although in practice these effects are usually extremely small. Such an interference might account, however, for rare cases where excess 204 counts are detected that cannot be explained in other ways (e.g. wrong corrections for background or scattered ions). Isobaric interferences are also present in the vicinity of the U$^+$, UO$^+$ and UO$_2^+$ peaks, but they are small and easily resolved ($M/\Delta M < 15000$).

![Figure 4](image.png)

**Figure 4.** Mass spectrum of mass 207 from a uraninite grain showing presence of PbH$^+$ adjacent to $^{207}\text{Pb}^+$. The spectrum was obtained on SHRIMP RG at ANU operating with a mass resolution of ca. 30,000 R (10% peak height). The Pb hydride appears on the high mass side of $^{206}\text{Pb}^+$ at a mass separation of 6.3 mamu (equivalent to 32,500 R). The hydride appears only partially resolved because of the relative peak heights. The shape of the Pb hydride is estimated from the $^{207}\text{Pb}$ peak and the $^{207}\text{Pb}$ tail is estimated from the shape of the $^{206}\text{Pb}$ peak.
Correction for common Pb

Although most zircon incorporates vanishingly small amounts of Pb at the time of crystallization, the presence of common Pb in zircon analyses cannot be ignored if an accurate age is to be calculated. This is particularly so for analyses of zircon poor in radiogenic Pb, for example low-U or young zircon. Common Pb in a zircon analysis can originate from several sources: sub-microscopic mineral inclusions, Pb added to the zircon during or after alteration, Pb physically trapped in microfractures, laboratory Pb from polishing compounds, aerosols, and coating materials. Each is of a different composition, and the measured common Pb will be a mixture. In practice, low levels of common Pb are assumed to be laboratory-derived, and higher levels to be a mixture of laboratory Pb and rock Pb. Only in very rare cases, such as lunar zircons in which the common Pb is unusually radiogenic, is the measured age very sensitive to the choice of common Pb composition.

Common or initial Pb content can be estimated in several different ways. The most direct method is by measuring $^{204}$Pb, the only Pb isotope unique to common Pb. Knowing the initial Pb isotopic composition, the other Pb isotopes can be subtracted from the analysis. If $f$ is defined as the fraction of total $^{206}$Pb in an analysis that is initial $^{206}$Pb, i.e.

$$f = \frac{^{206}Pb_{init}}{^{206}Pb_{tot}}$$

then $f$ can be calculated from the measured $^{204}$Pb/$^{206}$Pb as,

$$f = \frac{(^{204}Pb/^{206}Pb)_{tot}}{(^{204}Pb/^{206}Pb)_{init}}$$

The isotopic composition of initial rock Pb can be measured on cogenetic common Pb-rich minerals such as feldspar, or estimated from common Pb growth curves, knowing the approximate age of the zircon. The composition of laboratory-derived Pb, in continental Australia at least, is that of late Proterozoic massive Pb sulfide ore. If a cogenetic suite of zircons has a wide range of common Pb contents, the composition of the common Pb can be estimated with reasonable reliability by plotting a set of Pb isotope and U/Pb mixing lines and extrapolating to zero U.

Although $^{204}$Pb provides the most direct measure of common Pb, the low relative abundance of $^{204}$Pb makes the correction imprecise, particularly for analyses of young or low-U zircons with low $^{207}$Pb/$^{204}$Pb. A more precise estimate of common Pb can sometimes be made from $^{208}$Pb/$^{206}$Pb and the measured Th/U, $f$ being calculated as:

$$f = \frac{(^{208}Pb/^{206}Pb)_{tot} - (^{208}Pb/^{206}Pb)_{rad}}{(^{208}Pb/^{206}Pb)_{init} - (^{208}Pb/^{206}Pb)_{rad}}$$

To calculate the expected radiogenic $^{208}$Pb/$^{206}$Pb from Th/U relies on the assumptions that neither Th/U nor radiogenic $^{208}$Pb/$^{206}$Pb has changed throughout the zircon’s history, except by radioactive decay, and that the zircon’s age is known. The last is not critical, as the factor relating radiogenic $^{208}$Pb/$^{206}$Pb to Th/U ranges only from 0.25 to 0.32 over the full range of geological time. This method of correction normally works very well for zircon with low Th/U (<0.1), but becomes less precise for Th-rich zircon (Th/U > 1) as radiogenic $^{208}$Pb/$^{206}$Pb approaches the $^{208}$Pb/$^{206}$Pb of common Pb. It is also prone to error, because altered zircon tends to lose $^{208}$Pb more readily than $^{206}$Pb, resulting in an underestimate of the common Pb content. A variant of this procedure devised by Andersen (2002) takes better account of Pb loss, but requires the additional assumption that the time of the loss is known.

If it is assumed that the zircon analyses are concordant, a very precise correction for common
Pb can be made using the measured \(^{207}\text{Pb}/^{206}\text{Pb}\). The correction is iterative, a calculation of \(f\) from

\[
 f = \left( \frac{^{207}\text{Pb}/^{206}\text{Pb}}{^{207}\text{Pb}/^{206}\text{Pb}} \right)_{\text{tot}} - \left( \frac{^{207}\text{Pb}/^{206}\text{Pb}}{^{207}\text{Pb}/^{206}\text{Pb}} \right)_{\text{rad}}
\]

giving a corrected \(^{206}\text{Pb}/^{238}\text{U}\) age, from which a revised \(f\) and age is derived. The method is applicable only to zircon so young (Phanerozoic) that the discordance of individual analyses cannot be detected within the limits of analytical uncertainty. It produces a suite of radiogenic \(^{206}\text{Pb}/^{238}\text{U}\) estimates that can be assessed for equivalence free of correlated errors propagated from the common Pb corrections. Any discordance and/or inheritance is evident as excess scatter in the corrected \(^{206}\text{Pb}/^{238}\text{U}\) values.

**U/Pb calibration**

Determination of accurate interelement ratios such as Pb/U and Pb/Th is more difficult by SIMS than by isotope dilution. Using isotope dilution, Pb, U and Th concentrations are measured directly with high precision and accuracy, and interelement ratios are calculated from them. Measurement of these concentrations by SIMS is indirect, involving estimation of abundances from secondary ion ratios between trace and major element species (e.g. \(^{206}\text{Pb}^+/^{196}(\text{ZrO})^+\)) relative to a reference material of known trace element content. This procedure is subject to inaccuracies of several percent or more, so interelement isotope ratios are best determined directly from the secondary ion ratios of those isotopes. A complication is that different elements have different secondary ionization efficiencies and different propensities to form multiple oxides, so not only do the measured secondary ion ratios differ substantially from the isotope ratios in the target, but those ion ratios also change during a SIMS analysis, even if the target is chemically homogeneous. The calibration procedures used to correct for these effects, and their accuracy, are one of the most contentious issues in SIMS U–Pb geochronology.

The Local Thermodynamic Equilibrium (LTE) Model of Andersen & Hinthorne (1973) has been one of the most successful in calculating target compositions from secondary ion yields. The model is based on the premise that a plasma in thermodynamic equilibrium is present at the sputter site, and predicts the secondary ion yields of atoms and oxide molecules based on the electron density and “temperature” of that plasma. Although such a plasma is unlikely to exist, because the sputtering process is so fast that the energy injected by each primary ion is dissipated before the next arrives (Williams 1979), the model is capable of providing elemental concentration estimates, usually accurate within a factor of two, for a wide range of target materials. While this accuracy is insufficient for U–Pb geochronology, a prediction from the LTE model that the secondary ion ratios \(^{206}\text{Pb}^+//^{238}\text{U}^+\) and \(^{206}\text{UO}^+//^{238}\text{U}^+\) will co-vary for a target of constant Pb/U (Hinthorne et al. 1979) has become the basis for subsequent SIMS U–Pb calibration procedures (Fig. 5).

Hinthorne et al. (1979) first calculated zircon Pb/U based on an exponential relationship between \(^{206}\text{Pb}^+//^{238}\text{U}^+\) and \(^{206}\text{UO}^+//^{238}\text{U}^+\). When calculating Pb/U in lunar zircon, Compston et al. (1984) assumed the correlation to be linear, but subsequent more extensive data sets indicated that a quadratic relationship was more appropriate (Williams & Claesson, 1987). This was later simplified to a power law (Claoué-Long et al. 1995) with an exponent of 2.0, although debate continues over whether the exponent can be regarded as a constant or a variable (e.g. Claoué-Long et al. 1995; Black et al. submitted). The question applies particularly to small or clustered data sets for which the form of the calibration curve is poorly defined. In reality the answer is of little consequence unless there is a wide dispersion in UO/U, which in itself is a warning that there was unusually large variation in target bulk composition and/or sputtering conditions during a run. Normal practice is to assume an exponent of 2 unless there is a compelling reason for a particular data set to do otherwise. Based on this assumption, and given a homogeneous reference zircon, Pb/U isotope ratios can be measured in zircon samples with an accuracy of about 1%. Multiple analyses are necessary to
Figure 5. The \( \text{Pb}^+ / \text{U}^+ \) vs \( \text{UO}^+ / \text{U}^+ \) has been the cornerstone of SIMS Pb/U calibration. Pb/U covaries with UO/U for different analyses allowing a calibration curve for a specific age to be determined. Data for unknowns, with their own measured Pb/U and UO/U can then be referenced to this curve and an age determined. Data for 17 analyses of 1099 Ma FC1 are shown. In this case the age of the unknown A would be given by 

\[
\text{Age}_A = 1099 \frac{(\text{Pb}/\text{U})_A}{(\text{Pb}/\text{U})_B}
\]

where \( (\text{Pb}/\text{U})_B \) represents the Pb/U of the 1099 Ma standard at the UO/U of the unknown A. Errors are 1σ (relative standard deviation).

Zircon calibrations also have been developed based on other combinations of U⁺ and U oxide molecular-ion species. In examining the energy distributions of Pb⁺, U, and U oxide ions, Schumacher et al. (1993) noted the closer similarity of Pb⁺ to the molecular U oxide species, with the \( \text{UO}_2^+ \) and Pb⁺ in particular having very similar distributions. Schumacher et al. (1993) therefore noted the potential for better calibration based on the \( \text{Pb}^+ / \text{UO}^+ \) and \( \text{Pb}^+ / \text{UO}_2^+ \) species. Whitehouse et al. (1997) have used the \( \text{UO}_2^+ / \text{U}^+ \) as the discriminant. Stern (2000) has evaluated the \( \text{Pb}^+ / \text{UO}_2^+ \) system and found it to be substantially less affected by sputtering conditions, that is, \( \text{Pb}^+ / \text{UO}_2^+ \) is fairly constant during the course of an analytical session. These observations suggest that secondary ion energy is an important parameter in calibrating U/Pb ratios. However, the basis of the calibration and the species used to monitor the fractionation are not as important as the robustness of the calibrated ratios they produce. The reproducibility of ratios from known materials (standards) should be the sole discriminator between the available procedures. Stern and Amelin (in press) indicate that residual artifacts limit SIMS U/Pb data to ca. 1 % independent of the calibration procedure.

A calibration procedure must be used to calculate Pb/Th and Th/U from \( \text{Pb}^+ / \text{Th}^+ \) and \( \text{Th}^+ / \text{U}^+ \) respectively. Because of the difficulty of obtaining reference materials with known and constant Th/U, the latter is normally calculated as a correction factor to \( \text{ThO}^+ / \text{UO}^+ \) based on the difference between the measured and expected slope of the \( ^{208}\text{Pb} / ^{206}\text{Pb} - ^{232}\text{Th} / ^{238}\text{U} \) isochron. For zircon, the correction factor correlates weakly with measured UO⁺/U⁺.

Concentrations of Pb, U, and Th are not used for any geochronological calculations but are obtained for information regarding zircon chemistry and possible petrogenetic relationships. The U concentration is calibrated from the measured \( \text{Zr}_2\text{O}^+ / \text{U}^+ \) and the U concentration in a standard. The Pb and Th concentrations are then derived from the calibrated Pb/U and Th/U ratios respectively. The concentration standard and the Pb/U standard need not be based on the same reference material.
OTHER MINERALS

This discussion is concerned primarily with zircon, but the same analytical approach, with some modifications, is applicable to a range of other U-bearing minerals that can be used for U–Pb geochronology.

Monazite

Monazite is a light REE phosphate common in sediments, metasediments, and peraluminous igneous rocks. Th substitution for the light REE can reach several weight percent, so the Pb/Th age of monazite can be measured with greater analytical precision than the Pb/U age (e.g. Harrison et al. 1995, Ireland and Gibson 1998). The Pb/Th age also is likely to be the more accurate because of uncertainties in the amount of $^{206}$Pb produced by the decay of initial $^{230}$Th. The mass spectrum of monazite in the vicinity of the Pb isotopes contains unresolvable complex molecular isobaric interferences. This is particularly apparent at $^{204}$Pb, which if used as a measure of common Pb leads to major over-corrections. The interference under $^{204}$Pb, identified as $(^{232}\text{Th}^{144}\text{Nd}^{16}\text{O}_2)^{++}$ (Ireland et al. 1999), can be monitored at mass 143.5 $(^{232}\text{Th}^{143}\text{Nd}^{16}\text{O}_2)^{++}$ and the $^{204}$Pb corrected by peak-stripping. Alternatively, moderate levels of energy filtering will remove the interference from the mass spectrum. Monazite U/Pb and Th/Pb calibrations have utilized a variety of element/element oxide ratios (UO/U, UO/UO$_2$ etc and similarly for Th and its oxides). The extent to which each of these is sensitive to changes in the monazite composition, for example to the substitution of huttonite (ThSiO$_4$), the high-temperature monoclinic polymorph of thorite, for CePO$_4$, has yet to be explored in detail. The variable Th and Ce concentrations due to this substitution compromise the use of Ce as an internal concentration reference (cf Zr in zircon).

Xenotime

Xenotime is a HREE phosphate with a high degree of substitution of other elements, including U and Th. It has a low common Pb content and can retain radiogenic Pb better than zircon of similar U content, but it is much less common than zircon and monazite, occurring in highly fractionated granites and in association with monazite in high-grade metamorphic rocks (Pyle et al. 2001), so has been little used for geochronology. Xenotime is isostructural with zircon, and can occur as a component in zircon in solid solution. It also forms a solid solution with monazite, the miscibility gap between the two providing a sensitive geothermobarometer (Gratz and Heinrich 1997). SIMS U–Pb analysis of diagenetic xenotime nucleated on detrital zircon provides one of the few direct ways to date the deposition of Precambrian sediments (McNaughton et al. 1999). Calibration of SIMS determinations of xenotime Pb/U using element/element-oxide ratios has proved problematic because of variable matrix effects, but greater success has been reported with a calibration based on UO$^+$/YPO$^+$ (Stern & Rainbird 2001). Interferences from $(\text{ThNdO}_2)^{++}$ isobars, are likely to be present at low levels but have not been reported, even at $^{204}$Pb.

Apatite (+whitlockite)

The Ca phosphates contain only low levels of U and relatively high initial Pb, and also have relatively low U–Pb closure temperatures, so have not been widely used for geochronology. They were, however, amongst the group of minerals first analysed by SIMS to date lunar rocks by Pb–Pb (Andersen & Hinthorne 1972; 1973). More recent work on apatite has included measurement of Pb/U using calibrations based on UO/U (Sano et al. 1999). Because of the high initial Pb contents, however, apatite ages are better calculated using the U/Pb–Pb/Pb isochron approach than from the conventional concordia diagram. For apatite with high OH contents, it is also necessary to monitor and correct for PbH. The potential of apatite dating in the study of thermal histories has yet to be realised. It also is one of the few available techniques for the direct U–Pb dating of biological materials (e.g. Sano and Terada 1999).
Titanite

Titanite (sphene) is one of the few minerals suitable for U–Pb dating that has a well-understood paragenesis in metamorphic rocks (Aléinikoff et al. 2002; Castelli and Rubatto 2002). It also occurs in some metaluminous igneous rocks. Calibration procedures are similar to those for zircon, and work well with either \(\text{UO}_2/\text{UO}\) or \(\text{UO}/\text{U}\) as the reference parameter. Although there is some variability in titanite chemistry (especially Fe substitution) no matrix effects on the calibration have yet been reported. There are no obvious interferences on the Pb isotopes. Most titanite contains less U and more common Pb than zircon, so common Pb corrections can be very large, compromising the precision of the Pb/U age. Accuracy also can be compromised unless the isotopic composition of the common Pb is well known. Best practice is to analyse a range of titanite grains from a single sample, defining a mixing line on a Tera-Wasserburg diagram from which both the radiogenic \(^{238}\text{U}/^{206}\text{Pb}\) and initial \(^{207}\text{Pb}/^{206}\text{Pb}\) can be inferred. This procedure only works if the titanite radiogenic U–Pb system is concordant.

Baddeleyite

Baddeleyite (ZrO\(_2\)) is the principal Zr trace mineral in igneous rocks that are silica undersaturated or marginally saturated. Even in suitable lithologies it usually occurs in very low abundance and the mineral separation process is difficult, usually involving digesting the host rock in HF. Nevertheless, baddeleyite remains the most widely used mineral for ID–TIMS U–Pb dating of mafic dikes (LeCheminant & Heaman 1989). Early SHRIMP work on baddeleyite used a logarithmic \(\text{UO}_2/\text{UO}\)-based calibration, but this was later replaced by a power law \(\text{UO}/\text{U}\) calibration with an exponent close to 2. This calibration is compromised, however, by being sensitive to the orientation of each baddeleyite grain relative to the direction of the incoming primary ion beam (Wingate & Compston 2000), a sensitivity sought, but never found, in zircon. No simple solution has been found, so the precision and accuracy of baddeleyite U–Pb ages remains limited to several percent. Pb–Pb ages are unaffected, however, so SIMS baddeleyite dating has been applied most widely to rocks of Precambrian age.

Rutile

Rutile (TiO\(_2\)) occurs as an accessory mineral in mafic igneous and high grade metamorphic rocks and, because of its chemical and physical stability, is a common component in sedimentary rocks. It has not been used widely for SHRIMP geochronology, however, because of its relatively low U and high initial Pb contents. It also has a relatively low Pb–U closure temperature, \(~400\) °C (Mezger et al. 1989). Pb/U calibrations based on both \(\text{UO}/\text{U}\) and \(\text{UO}_2/\text{UO}\) have proved equally effective for rutile (Sircombe, 1997; Clark et al. 2000). Th contents are commonly extremely low, meaning that all \(^{208}\text{Pb}\) measured can be attributed to common Pb, giving a much more accurate common Pb correction than can be obtained using \(^{204}\text{Pb}\). To improve precision, rutile is commonly analysed with very large primary beams of O.

Perovskite

Perovskite (CaTiO\(_3\)) occurs as a trace mineral in some peridotites, norites, nephelinites and kimberlites. It is also a minor constituent of the refractory inclusions in some meteorites. The propensity of perovskite to contain fine grained inclusions of other minerals makes it difficult to date well by ID–TIMS, so for work on kimberlites in particular, SIMS is often the technique of choice. The preferred calibration curve for perovskite is a quadratic equation based on \(\text{UO}_2/\text{UO}\) (Ireland et al. 1990).

Allanite

Allanite is an epidote group mineral with high levels of REE and quite variable chemistry that occurs in metaluminous and alkaline igneous rocks, metasediments, some pegmatites and skarns. A ThO\(_2\) content of about 1% makes it amenable to Pb–Th dating. The Pb/Th calibration for allanite is
very matrix sensitive, however, and calibration relative to \( \text{ThO}_2^+ / \text{Th}^+ \) alone, as is sometimes used for monazite, can lead to large systematic errors. Accuracy is greatly improved by introducing a calibration parameter that reflects the allanite Fe content \( (\text{FeO}^+ / \text{SiO}_2^+) \), thereby defining a calibration plane (Catlos et al. 2000). In this way, allanite Pb/Th ages can be measured to ±10%, quite useful for young allanites, although having only restricted application for samples that are older than late Mesozoic.

**DATA ANALYSIS**

Unlike ID–TIMS, SIMS data acquisition and reduction procedures must be designed with the expectation that the measured isotopic ratios are changing with time in different ways. The changes can be large (several percent), caused not only by small-scale heterogeneity in the composition of the target, but also by a falling contribution from surface contaminants and by sputtering-related changes in the secondary ion emissions of the various elements and oxides. It is common, for example, that during an analysis the \( \text{Pb}^+ \) signals fall, the \( \text{U}^+ \) and \( \text{Zr}_2\text{O}_4^+ \) rise, and the \( \text{ThO}_2^+ \) and \( \text{UO}_2^+ \) remain relatively constant. Some of these changes are correlated and accommodated by the Pb/U calibration procedures, but the problems remain of how to make an unbiased measurement of the ratios and in particular, how to estimate the analytical uncertainties.

Most TIMS instruments measure isotope ratios in pairs or in a cycle of several isotopes repeated many times over. The latter is more appropriate if the isotopic composition is changing, but has the drawback that the repeat measurements of each isotope are separated by relatively long periods of time, necessitating corrections for time-dependent changes in signal strength. This correction normally takes the form of a linear interpolation of the denominator isotope count rate to the times at which each other isotope was measured. More sophisticated approaches include interpolation by fitting a polynomial or cubic spline curve to the denominator measurements, or the double interpolation of both numerator and denominator counts (Dodson 1978). The end product is always the same, multiple estimates of each isotope ratio that are averaged to obtain a best estimate of each and their associated precisions.

This procedure is largely unsuitable for SIMS geochronology where the objective is rapid analysis of a composite secondary ion beam of changing composition. There is time for only a few cycles through the isotopes of interest, and simply averaging the changing ratios yields inflates analytical uncertainties. A preferred solution developed for SHRIMP (in the PRAWN data reduction program) is to fit lines to the time-variant count rates for each isotope, and from these to obtain a best estimate of the count rates at the mid time of the analysis, the uncertainties in the estimates being a simple function of the counting statistics and quality of the fit (Mendenhall & Sincich 1995). If the fit is poor, the data set can be tested for outliers. One value for each isotope ratio is calculated from the mid-time estimates, and the uncertainties are determined by error propagation. The uncertainties are lowest when the changes in ion yields are systematic and correlated, such as result from the sputtering process, but become higher in targets where the scale of compositional heterogeneity is small compared to the depth of sampling (~2 µm).

Changes in target composition during analysis in most cases result in non-linear changes in count rate with time, but the changes nevertheless will be systematic. Changes in common Pb content will cause correlated changes in the count rates for all four Pb isotopes. If there is no Pb loss, changes in U content will be tracked by changes in \( ^{206}\text{Pb} \) and \( ^{207}\text{Pb} \), and changes in Th content will be tracked by changes in \( ^{208}\text{Pb} \). Such data are best reduced by treating each scan through the isotopes as a separate analysis. A cubic spline (as used in PRAWN) or other functional curve can be fitted to the isotope measurements, isotope ratios are calculated for each scan, each set of ratios is corrected for interelement fractionation and common Pb, then all values are combined to yield mean isotope ratios independent of the fluctuations in parent element abundance. This is also the basis for the program SQUID (Ludwig 2001), an Excel program for processing SHRIMP U–Th–Pb geochronology data in conjunction with the widely used IsoPlot (Ludwig 1999).
Analytical uncertainties

Accurate determination of the target isotopic composition is of prime importance, but it is also important to make an accurate estimate of the analytical uncertainties. Knowing the uncertainties makes it possible to discriminate between more and less reliable measurements, to assess a set of measurements for evidence of significant variations in target composition, and to ensure that measurements are correctly weighted in the calculation of their mean. Underestimation of uncertainties leads to the identification of age differences that in fact are not significant, and the unjustified rejection of measurements as outliers. Overestimation leads to real age differences and outliers being overlooked. Both can result in the final age determination being inaccurate. The desire to measure with an accuracy limited only by counting statistics is the driving force behind the progressive refinement of SIMS analytical procedures.

$^{207}\text{Pb}/^{206}\text{Pb}$ ratio

Because $^{238}\text{U}$ and $^{235}\text{U}$ decay at different rates, producing $^{206}\text{Pb}$ and $^{207}\text{Pb}$ respectively, the isotope ratio $^{207}\text{Pb}/^{206}\text{Pb}$ provides a measure of age that is independent of Pb/U, and therefore of the uncertainties associated with Pb/U calibrations. Given the relatively low precision of SIMS analyses, however, age measurements using $^{207}\text{Pb}/^{206}\text{Pb}$ are usually feasible only for Precambrian zircons. There are several reasons. Because $^{235}\text{U}$ ($T_{1/2} = 704 \text{ Ma}$) now comprises less than 1% of natural U, relatively little $^{207}\text{Pb}$ has been produced in the Phanerozoic. Not only are most Phanerozoic zircon radiogenic $^{207}\text{Pb}$ contents low (<2.5 ppm) and therefore difficult to measure with high precision, but also the change in radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ for zircon between 500 and 0 Ma old is small (0.057–0.046). The measurements are very sensitive to the common Pb correction and error magnifications are high, for example a 1% error in measuring radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ in a 100 Ma old grain results in a 23% error in the calculated age. The situation becomes much more favorable as the zircon becomes older. An average 3.0 Ga zircon, for example, will contain ~65 ppm of $^{207}\text{Pb}$, have a $^{207}\text{Pb}/^{206}\text{Pb}$ of 0.22, and a 1% error in measuring that $^{207}\text{Pb}/^{206}\text{Pb}$ will result in only a 0.5% error in the age.

To some extent the precision of $^{207}\text{Pb}/^{206}\text{Pb}$ measurements can be improved by increasing the count time on $^{207}\text{Pb}$, but there are practical limits. For count times over about 1 minute the cycle time becomes too long and there is an increased risk of partial signal loss due to instrumental drift. The optimal allocation of time to $^{207}\text{Pb}$ and $^{206}\text{Pb}$, or in fact to any isotope ratio, is to set the ratio of the count times to the inverse of the square root of the count rates. If $^{207}\text{Pb}/^{206}\text{Pb} = 0.06$, for example, $^{207}\text{Pb}$ is best counted for four times as long as $^{206}\text{Pb}$. Even if this is done, counting errors remain so large that SIMS cannot measure radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ on average composition Phanerozoic zircon well enough to detect the discordance due to Pb loss. This is only possible by checking for excess dispersion in the radiogenic $^{206}\text{Pb}/^{238}\text{U}$.

U–Pb ratio

The detection of discordance and inheritance within ostensibly cognetic zircon populations has become a contentious issue in the interpretation of zircon ages measured by SIMS, particularly those measured on volcanic rocks to calibrate the Phanerozoic time scale (Tucker & McKerrow 1995; Mundil et al. 2001). Much of the argument hinges on questions of precision and accuracy. ID–TIMS analyses are demonstrably more precise than SIMS analyses, but are they also more accurate? In part the question reduces to one of whether the imprecision of SIMS analyses masks dispersion in radiogenic $^{206}\text{Pb}/^{238}\text{U}$. The answer depends upon the correct assessment of uncertainties in the $^{206}\text{Pb}/^{238}\text{U}$ measurements.

As discussed above, SIMS determinations of Pb/U are based on calibrations against reference minerals that are assumed to have uniform radiogenic $^{206}\text{Pb}/^{238}\text{U}$. If this assumption is valid, then any apparent variation in $^{206}\text{Pb}/^{238}\text{U}$ measured on the reference material is due either to a failure of the calibration procedure or underestimation of the analytical uncertainties. Early SIMS analysts at the ANU assumed the former, adding to every sample analysis a component of uncertainty calcu-
lated from the scatter in the analyses of the reference material. As a consequence, little dispersion in radiogenic $^{206}\text{Pb}/^{238}\text{U}$ was detected in most samples, but the mean ages were relatively imprecise. As calibration procedures improved, it became evident that the principal zircon reference standard, SL13, was in fact heterogeneous; many zircon samples were found to have more reproducible radiogenic $^{206}\text{Pb}/^{238}\text{U}$ than SL13. Thus any error propagation based on reproducibility of the standard was flawed and dispersion in $^{206}\text{Pb}/^{238}\text{U}$ was assessed on counting statistics alone. The precision of the age measurements therefore improved (except for very young samples, where the counting errors far outweighed the calibration errors) and Pb loss and inheritance were detected more often. However, attributing deviations to inheritance and Pb loss has consequences in geological interpretation. Furthermore, the accuracy of the measurement remained in doubt because the composition of the standard remained poorly defined. The problem could only be solved by locating reference material in which radiogenic $^{206}\text{Pb}/^{238}\text{U}$ was more uniform.

**Standards**

Reference material for SIMS U–Pb geochronology ideally should be, on a sub-micron scale, uniform in Pb, U and Th content, uniform in radiogenic $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$, free of initial Pb, isotopically concordant, sufficiently rich in radiogenic Pb that the Pb isotope ratios can be measured precisely, but not so old or U and Th rich that there has been a significant accumulation of radiation damage. No known natural zircon fulfills these requirements perfectly, but some are good enough to be a viable standard. Synthetic standards have been considered, but at present are not favored. Glasses are not suitable because it is not yet possible to correct for the differences in secondary ion emission between glass and different crystalline matrices with the 1% accuracy required (Stern & Amelin, in press). The standard for zircon would need to be synthetic zircon, and for monazite, synthetic monazite etc. Zircon with a suitable Pb/U (~0.1) has not yet been synthesized that matches the quality of the best natural zircon, namely is uniform in Pb/U to better than 1% on a sub-micron scale.

The first standards used for SHRIMP analysis were Neoproterozoic zircon megacrysts from stream gravels in Sri Lanka. Some of these relatively large grains (≥1 g) are quite uniform in trace element content (most importantly U), with no obvious growth zoning. Following a series of γ-counting experiments two grains were selected for ID–TIMS characterization, SL3 (U = 3540 ppm) and SL13 (U = 238 ppm). SL3 was used as a standard first because of its higher, and therefore more easily measured, radiogenic Pb content. However analytical inconsistencies began to emerge, with samples of known age yielding Pb/U ratios about 4% lower than expected. The problem was twofold. Transmission electron microscope examination of SL3 showed that it was badly radiation damaged, being about 60% structureless zirconium oxide and silica glass (McLaren et al. 1994). Analysis of this mixture with an unfiltered primary ion beam consisting of approximately equal amounts of O⁻ and O₂⁻ was introducing matrix effects for which the calibration procedure was not compensating. SL3 was therefore superseded by SL13.

TIMS analyses of 19 fragments of SL13 by five analysts from three laboratories showed it to be very uniform in U and Pb/U on a microgram scale. As it was used as a SIMS standard and analytical procedures improved, however, significant heterogeneity in Pb/U became evident. The heterogeneity was on two scales, ∼5% range in Pb/U on a scale of microns, possibly reflecting the presence of zircon of two different ages, and sub-micron regions with radiogenic Pb contents up to an order of magnitude greater than that attributable to in situ U and Th decay (Compston 1999). The latter have yet to be satisfactorily explained. Both effects precluded the use of SL13 as anything other than a U concentration standard, and as soon as alternatives became available most analysts abandoned it. The SIMS zircon standard used at Curtin University, CZ3, is also a Sri Lankan megacryst. It has a higher U content than SL13 (500 ppm) but no similar heterogeneity in Pb/U has been reported.

Reservations remain about the suitability of megacrysts as reference materials. Apart from the
fact that the supply of individual crystals is limited, these crystals have geological attributes that are of potential analytical consequence. The megacrysts appear to be metamorphic as suggested by geological association as well as lack of trace element zoning and low Th/U. Possibly, the megacrysts were extant prior to metamorphism, as indicated by old initial Hf isotopes (Kinny et al. 1991). These grains are different in trace element content from the igneous zircon that most commonly is dated. They also sputter somewhat differently, under some circumstances giving different secondary ion yields and UO\(^+\)/U\(^+\) from igneous zircon. In part this might be due to the way the zircon grains are mounted, igneous zircon normally being oriented with the c-axis parallel to the mount surface, chips of standard being oriented at random. Although the differences might be of no consequence, in the quest to optimize Pb/U to higher levels, such potential matrix effects need to be considered.

Identifying zircon suitable for use as an international SIMS isotope standard has proved difficult. Harvard University zircon sample 91500, distributed through Geostandards (Weidenbeck et al. 1995), is the best currently available for a variety of elemental abundances and isotopic compositions. It has been analysed for U–Pb isotopes by several ID–TIMS laboratories, and also for trace elements and Hf and O isotopes. Being a megacryst, however, its supply is limited. Further, as a SIMS geochronology standard it is too low in U (81 ppm) and radiogenic Pb (15 ppm) for use in monitoring \(^{207}\text{Pb} / ^{206}\text{Pb} \) fractionation. The low radiogenic Pb also makes it difficult to measure Pb/U with high precision, and there is evidence that suggests 91500 is not uniform in Pb/U at the 1% level.

SIMS laboratories still mostly rely on in-house standards for each of the minerals they are dating. SHRIMP analysts at ANU have tried a succession of potential zircon standards, retaining SL13 as a concentration reference but searching for zircon more uniform in Pb/U for interelement calibrations. First choice was AS3, zircon from a 1.1 Ga anorthositic syenite from the Duluth Complex, Minnesota, from which Paces & Miller (1993) obtained consistently concordant ID–TIMS analyses. AS3 also proved quite uniform in Pb/U when analysed by SIMS, however, good quality zircon was scarce (Schmitz et al. in press), with most grains being skeletal, finely fractured and stained by iron oxides. Attempts to collect better material from the original sample site were unsuccessful, so a site at Forest Centre, 250 km NW of Duluth (FC1: Paces and Miller, 1993), was chosen from which abundant good quality zircon was obtained. FC1 is now widely used as a Pb/U standard in the ANU lab, and also in the National Institute of Polar Research laboratory in Tokyo.

Geoscience Australia (formerly AGSO, and before that the BMR) initially referenced their SHRIMP analyses to sample QGNG, zircon from a 1.85 Ga gabbro from the Cape Donnington Suite, South Australia. This zircon has the advantage that it contains sufficient \(^{207}\text{Pb} \) for \(^{207}\text{Pb} / ^{206}\text{Pb} \) fractionation to be monitored, but both ID–TIMS and SIMS analyses have shown it to be heterogeneous in Pb/U. Further, cross calibration against other zircon of known age showed that even the most concordant of the QGNG SIMS analyses must be about 0.6% discordant. Although this could be accommodated in calibration calculations, it reduced QGNG’s value as a Pb/U standard. The standard now used by Geoscience Australia and ANU analysts working particularly on Phanerozoic zircon is Temora, zircon collected from the 417 Ma Middledale quartz diorite. More than two dozen ID–TIMS analyses show this zircon to be extremely uniform in Pb/U on a microgram scale, and similar uniformity on a nanogram scale has been demonstrated by SIMS (Black et al., submitted). A weakness of the Temora standard is that radiogenic Pb is generally low (<20 ppm), limiting the precision of the SIMS Pb/U measurements, and too low to monitor the fractionation of \(^{207}\text{Pb} / ^{206}\text{Pb} \). Temora has been widely distributed and is available from Geoscience Australia on request.

Use of several zircon standards creates the problem of relating analyses based on one standard to analyses based on another. To address this, Black and others (submitted) undertook a major inter-standard comparison, including SL13, QGNG, AS3, two Temora samples (Temora 1 and 2), and R33, a proposed standard from the Braintree complex, Vermont. The study showed, with the notable exception of SL13, that when the best quality material was selected and analytical conditions
were stable, most Pb/U measurements on each standard were equal within counting statistics error. There were small but consistent discrepancies in the calibrated mean ages, however. Relative to Temora, QGNG and AS3 yielded a lower Pb/U than expected from their ID–TIMS ages, and SL13 yielded a higher Pb/U. Relative to ages measured against Temora, therefore, ages referenced to SL13 would be low and those referenced to QGNG or AS3 high. The differences are of the order 1%. The reasons for these differences have yet to be determined, but must be resolved if SIMS Pb/U calibrations are to achieve better than ~1% accuracy.

Stern & Amelin (in press) have also assessed error propagation in SIMS U-Pb analysis based on measurements of a suitable natural zircon (z6266) and NIST SRM 610 glass. Their findings are similar to those described above in that reproducibility of U-Pb analysis exceeds that expected from the measurement errors with an unaccounted error of ca. ± 1 % (1σ) error per analysis.

Data assessment

The literature now contains a large amount of SIMS geochronology data that are available for comparison and assessment. Comparisons can be made between, for example, different sessions from one laboratory, different analysts from one laboratory, different SIMS laboratories, and SIMS and other techniques. Such comparisons invariably lead to attempts at reconciliation even when results differ within the cited levels of uncertainty. While the scrutiny of comparison is a necessary part of the scientific process, the caveats inherent in the data analysis must be appreciated before sound conclusions can be reached.

A basic premise of comparison is that all data are equal. They are not. There is no canonical data reduction procedure common to all SIMS labs, and even if there were it would not necessarily help. SIMS data are measurements of isotope ratios, but the scientific questions addressed even by different analysts of the same sample may be quite different and hence the sampling strategy and statistical treatment quite different as well. Even when two practitioners ask the same question, most commonly, “how old is that rock?”, the ways of getting to that endpoint may be quite different.

Propagation of errors is of particular importance both in assessing the data within an analytical session and in arriving at a final answer. SIMS analyses are not absolute determinations, but measurements relative to a standard of independently known age. The statistics governing this procedure are reasonably straightforward but as is often the case with scientific analysis, the distinction between random and systematic errors must be addressed at several levels of, and propagated through, the calculations. Unfortunately the approach of many analysts is to minimize uncertainties rather than to produce a statistically robust data set.

The statistics governing the estimation and combination of measurement errors are critical in assessing geological data. In the case of SIMS U–Pb analysis, there are two virtually independent sets of measurements, each of which needs to be pooled—estimates of $^{207}$Pb/$^{206}$Pb, and estimates of $^{206}$Pb/$^{238}$U (or the ages calculated from them). Pooling $^{207}$Pb/$^{206}$Pb data is straightforward; a weighted mean is calculated, the weighting of each estimate being inversely proportional to its variance. The weighted mean has an associated statistical parameter, the reduced $\chi^2$ or mean square of weighted deviates (MSWD), by which scatter beyond that expected from the analytical uncertainties can be detected and possible outliers identified. The uncertainty in most SIMS $^{207}$Pb/$^{206}$Pb data is dominated by counting errors in the measurement and common Pb correction, and the age resolution is poor compared to TIMS analyses over most of geological time.

It is in combining $^{206}$Pb/$^{238}$U data that there is the greatest variation in statistical approach. From the time of the earliest SHRIMP analyses, it was noted that measurements of Pb/U in ostensibly cogenetic zircon populations commonly were more dispersed than could be accounted for by measurement errors alone. Either the samples were heterogeneous or there was a source of analytical error that was not being taken into account. In addition, there was an error in measuring the $^{206}$Pb/$^{238}$U of the zircon standard that must somehow be propagated into error in measuring the $^{206}$Pb/$^{238}$U of the unknowns. The question was how best to do it.
No matter how errors are assessed, the $^{206}\text{Pb}/^{238}\text{U}$ age of a sample cannot be known better than the relative error in measuring $^{206}\text{Pb}/^{238}\text{U}$ in the calibration standard. In statistical terms, the coefficient of variation of the standards should be summed in quadrature with that of the sample. This is no different from the summing of errors when forming a ratio. The error in measuring the standards is treated as a systematic analytical error and represents a minimum error for the calibration.

When assessing replicate analyses of standards and samples, however, it is common to find more scatter than expected from counting error alone. It then becomes a question of determining the relative contributions of analytical and geological affects. One approach is to assert that the standard is isotopically homogeneous and that all the error observed is analytical. The reproducibility of the standard thereby represents the external reproducibility of all analyses. The relative standard deviation of the $^{206}\text{Pb}/^{238}\text{U}$ measurements of the standards is therefore added in quadrature to the uncertainty for each $^{206}\text{Pb}/^{238}\text{U}$ measurement of the sample. If the number of standard and sample analyses is the same, this has the same effect on the uncertainty in the final age measurement as summing the standard error of the standards in quadrature with the standard error of the unknowns. If many more samples than standards are analysed, however, then the error in the mean age may be underestimated because the calibration error should have been treated as being systematic, rather than random.

Summing the error in this way takes no account of possible heterogeneity in the standard and risks obscuring heterogeneity in the sample. This became evident in early analyses relative to SL13 where the standard deviation of the samples commonly was smaller than that of the standards. Inflating individual analytical uncertainties masks the statistical distribution of the sample data, making it more difficult to detect true variation due to isotopic disturbance, inheritance, or mixed populations of slightly different age (Fig. 6). The procedure reduces the MSWD, however, allowing more analyses to be combined before scatter is detected, adding credibility to the end result.

On the other hand, reliance on counting errors alone at this stage of the calculation can result in some analyses receiving undue weight. Analyses of high-U zircons, for example, commonly have very small counting errors due to the high count rates, but because of radiation damage are often subject to (low-temperature?) Pb loss. Such analyses rarely reproduce within analytical error yet dominate the weighted mean and inflate the MSWD. Knowing this, is it appropriate that they receive more weight than less precise analyses of lower-U zircon that are more likely to represent the undisturbed isotopic composition?

One possible solution is to use a minimum error for each analysis that equates to the long-term average standard deviation of U–Pb analyses of well-behaved samples, whether they be standards or unknowns. Such an error component is essentially a calibration error and will be a function of the specific technique used for analysis. Our long-term experience at ANU is that the minimum calibration error is typically 0.5 %. Using this minimum error for each analysis still requires that the final error in the Pb/U calibration be summed in quadrature with the final error in measuring the unknown.

Comparison of different analytical sessions

Assessment of systematic error between analytical sessions, particularly if different standards are used, is the most difficult error assessment of all. SIMS access is so restricted and costly that rarely is a sample run more than once. Exceptions are the cross-calibrations between standards, and analyses of some Paleozoic samples where very fine time resolution is required (e.g. Black et al. submitted). Usually the mean Pb/U ages for different sessions on the same sample agree within the assigned uncertainties, but sometimes apparently well-calibrated measurements differ by up to 2%, far more than can be explained by any random error.

Comparisons are even more difficult when assessing analyses against different standards, because systematic biases in the analyses and assumed compositions of those standards must be taken into account. There is much difference of opinion, however, over what those biases might be, especially given the different approaches to data reduction. Early comparisons of analyses against SL3...
Figure 6. The choice of statistical treatment affects the assessment of possible outliers as well as potentially biasing data when outliers are dominantly on one side of the mean. This data set consisting of twenty $^{206}\text{Pb}/^{238}\text{U}$-age analyses of AS3 illustrates the effects of choosing three different error treatments. Outliers are rejected in two groups (A,B). Group A is two points of very low age suggesting Pb loss. Group B is two points that are closer to the mean, one high and one low. It is difficult to assess whether data like these are due to analytical effects or geological, but in this case the high point is almost certainly analytical because of no documented inheritance in AS3. (a) Errors shown are internal measurement errors alone; a high initial MSWD indicates excess scatter. After rejecting outliers A and B, the scatter remains excessive suggesting there is an additional error component. (b) Errors are augmented by 0.5% (summed in quadrature). After rejection of outliers A, the MSWD is still marginally excessive but the outliers B are only marginally deviant from the mean. (c) Errors are augmented by 1%. The MSWD of all points is excessive but after rejecting outliers A, the MSWD is consistent with a single population. In SIMS zircon geochronology, the variance of the standard is commonly added to the unknowns which can mask outliers. If minimum errors are used, excess scatter can be used to misidentify marginally deviant points as due to geological effects (Pb loss, inheritance).
and SL13 showed a systematic bias between the two of about 4% that required the age of SL3 to be assigned as 570 Ma, not 552 Ma as measured by ID–TIMS. This was eventually identified as a matrix effect exacerbated by high-U, radiation damage, and the use of a mixed species primary ion beam. Possible biases between other standards are more subtle. Analyses of several Paleozoic time scale samples by SIMS and ID–TIMS showed the SIMS ages referenced to SL13 to be consistently ≤1% less than the TIMS ages, the difference attributed to inheritance by the SIMS analysts and to calibration error by the TIMS analysts (Tucker & McKerrow 1995). Subsequent single grain ID–TIMS analyses and SIMS comparisons of standards suggest that both are probably correct at some level. The question remains, however, whether simple correction factors can be applied in comparing data referenced to different standards. The comprehensive comparisons of standards by Black et al. (submitted) provide a huge data set on which to make a more educated decision. They show that although the sense of difference between the standards is consistent, the magnitude of the differences varies from session to session, such that any correction factors applied are only approximations. Furthermore, it should be noted that a correction factor must necessarily have an uncertainty associated with it and it is likely that the propagation of that uncertainty will further reduce age resolution such that the correction factor would be irrelevant in terms of the augmented errors.

The question of accuracy remains because for the best standards there is no compelling reason to prefer one over another, yet they yield slightly different calibrations. The possibility of systematic biases between standards remains an extremely important matter to be resolved and will impose a fundamental limitation on the accuracy of analyses by current methods if it is not. Nevertheless, the use of at least two known standards in the course of analysis would offer an assessment of reliability for any given analytical session. One of the standards can be reported as an unknown allowing an independent criterion for assessing the veracity of the unknown sample. This of course requires an added time commitment but when accuracy is paramount such a method may be worthwhile.

The bottom line is, if the result is critical, take all necessary means to replicate the analyses and justify the error conditions. If seeking maximum resolution of the age difference between two or three samples, run them on the same mount at the same time against the same standards so that the differences are measured independently of the absolute Pb/U calibration. \(^{206}\text{Pb}/^{238}\text{U}\) is measured most accurately when the standard is measured as frequently as the sample. Measure two or more standards in the session. Ultimately, check the result by running a duplicate session.

**FUTURE DEVELOPMENTS**

It is now twenty years since the first publications of SHRIMP U–Pb data (Compston et al. 1982; Froude et al. 1983; Williams et al. 1983). Although over that time there has been a growing appreciation of the measurement technique and especially the uncertainties involved, there has been no fundamental change in the method. This is a testament to the original choice of approach to the analysis of zircon and other minerals, and to the utility of SIMS geochronology in solving often complex geological problems. However it also reflects analytical conservatism. It is widely recognised that ID–TIMS provides much higher precision than SIMS, although for complex zircon the accuracy of the answer can be difficult to assess without reference to microanalyses of individual components. A concerted effort is now required if the accuracy of SIMS is to be improved.

Replicate SIMS analyses of well-characterized reference materials suggest that with present Pb/U calibration techniques, the accuracy of SIMS determinations of \(^{206}\text{Pb}/^{238}\text{U}\) and \(^{208}\text{Pb}/^{232}\text{Th}\) appears limited to about 1%. For samples less than 100 Ma old this equates to an uncertainty of less than 1 m.y., an acceptable age resolution, but for early Paleozoic samples the same uncertainty amounts to as much as 5 m.y., of little value for defining the numerical time scale or dating rapid faunal changes. The principal limitation on accuracy is not counting error, which for average composition zircon becomes significant at the 1% level only for ages less than about 15 Ma, but the Pb/U calibration procedure. Theoretically, with perfect standards and calibration, with existing SIMS instruments it should be possible to analyse the \(^{206}\text{Pb}/^{238}\text{U}\) of an average 400 Ma zircon with a
precision, reproducibility and accuracy of about 0.4% (95% confidence limits). Pooling 16 such analyses potentially could define the age with an accuracy of about 0.1%, comparable to the precision achieved by ID–TIMS.

Improvement will come only with improved calibration procedures. There are clearly some factors affecting relative secondary ion emissions that are not accounted for by present calibration methods. First, it is observed that analyses of apparently homogeneous standard zircons sometimes scatter about the UO/U- or UO$_2$/UO-referenced calibration lines, or Pb/UO$_2$, more than predicted from counting errors, that scatter in the standards is commonly accompanied by similar scatter in the sample analyses, and that the amount of scatter varies from session to session (See also Stern & Amelin, in press). Secondly, there are the small but consistent differences between the ages expected and measured in the interstandard comparisons. It is known that for other minerals (e.g. xenotime and baddeleyite) there are matrix effects not accommodated by simple uranium oxide-based calibrations, so the same is possibly true of zircon. Black et al. (submitted) suggest that one factor needing to be taken into account is the zircon REE content. Substitution of YPO$_4$ for ZrSiO$_4$ might also be important. Wingate & Compston (2000) suggest that for baddeleyite, the composition of the secondary ion beam is affected by the orientation of the crystal relative to the incoming primary ions.

When zircon Pb/U calibration procedures were first being developed for SHRIMP, several different element/element-oxide combinations of Zr and U were explored as possible reference parameters. Pb/U–UO/U was chosen because it showed the best correlation, even though Pb/UO varied over a much smaller range. To improve calibrations further, it will be necessary either to change the procedure entirely, or to introduce another reference parameter that correlates with the deviation of analyses from perfect Pb/U–UO/U correlation. One possibility, but as yet untried procedure, is calibration against a reference plane defined by U/UO, UO$_2$/UO and a ratio of Pb against one of these three species. The logic is that there are virtually no Pb oxides in the secondary ion spectrum, so the ratio of Pb$^+$ to a U ion species will change primarily as a function of the U-oxide speciation. A disadvantage of this procedure is that it takes no direct account of changes in the bulk zircon composition. If the calibration scatter is matrix sensitive, it would perhaps be more beneficial to include P, Y, Hf, and REE species, as proxies for total trace element substitution, which is reasonable for most zircon crystals, as calibration parameters. The calibration correction based on U concentration proposed by Williams & Hergt (2000) is a crude way of doing this. There is another indication that introducing an extra parameter can help—before SHRIMP II at ANU, was correctly tuned, scatter of several percent about the Pb/U–UO/U line was found to be closely correlated with the Zr$_3$O$_4^+$ count rate.

Even if an improved calibration procedure is found, the accuracy of calibrations will still ultimately be limited by the sub-micron scale heterogeneity of Pb/U in the reference material. It has been argued that in any natural zircon of heterogeneous U content, small scale Pb/U heterogeneity is inevitable because of the micro-redistribution of Pb due to $\alpha$-recoil. Also, even though the volume diffusion rate of Pb in zircon is extremely slow below about 1000 °C (Cherniak & Watson, this volume), grain boundary diffusion of Pb along micro or macro defects in the crystal structure, particularly under hydrous conditions, occurs at much lower temperatures.

An alternative to a natural zircon would be an artificial standard. Synthetic zircon of suitable composition and uniformity is unlikely to become available in the near future. First, it is extremely difficult to synthesize zircon doped with trace elements of isotopic interest, that are homogeneous to within 1% due to zoning that is inherent to synthetic zircon grown under laboratory conditions (Hanchar et al 2001). Second, due to the sluggish volume diffusivities of those elements in zircon (Cherniak & Watson, this volume), it is not practical to attempt to homogenize doped synthetic zircon crystals in the laboratory, due to temperature and time constraints (e.g., months to years, and temperatures as high as 1600 °C would be required). It might be possible to produce a glass with sufficiently uniform levels of Zr, U, Th, and Pb to be measured by SIMS at high precision. Such a
material would not necessarily be the primary calibration standard for age determinations, but rather
could serve as a monitor of those instrumental conditions that cause fluctuations in the secondary
ion ratios. Instrumental factors contributing to scatter could thereby be quantified independently and
used to refine the analyses of both zircon standards and unknowns.

Collectors equipped with multiple ion counters, now available on the Cameca 1270 and
SHRIMP II ion probes, offer scope for substantial improvement in the precision of the Pb isotope
measurements, which is limited by counting statistics, but not in the measurements of Pb/U. The
improvement comes at a price, however. The tiny electron multipliers required in constructing
multiple collectors, even for high-dispersion instruments such as SHRIMP II, change their gain as a
function of total ions counted much more rapidly than do the physically larger multipliers used for
single collection. These changes must be closely monitored if analyses are to be accurate, incurring
a substantial additional overhead in gain calibrations or the measurement of isotope standards. The
gain drift is also a function of count rate, restricting multiple collectors to the analysis of minerals
with relatively low-U and Th concentrations. Until electron multiplier technology improves,
multiple collectors are likely to be used more for the analysis of rare, valuable, heterogeneous or
very low-level samples than for routine geochronology.

The main strength of SIMS analysis is its spatial selectivity. For most applications, the
internal variations in target composition that are the objective of the analysis are very much larger
than the precision and accuracy of individual measurements. It is principally in resolving small age
differences in the early Phanerozoic, as is required in defining the geologic time scale, that the
limitations of SIMS geochronology become apparent. Even then, however, it was SIMS work that
first picked up the subtle range in the ages of zircons in tuffs (Compston 2000) that subsequently
has been confirmed by high precision ID-TIMS (Mundil et al. 2001). As with many new isotopic
techniques, SIMS has not proved to be the universal panacea that some early proponents claimed.
Nor has it made ID-TIMS redundant. The ultimate resolution of the most demanding
demands the combined approach of mineral characterization by imaging techniques such as BSE and CL, testing by SIMS for age homogeneity and single-grain sample selection, and analysis by ID-TIMS for maximum precision
and accuracy. For work on complex, polychronic zircons, however, SIMS remains the technique of
choice. The thrill of instant gratification as the ion probe turns out a new age measurement every
few minutes is one few geochronologists can now resist.

ACKNOWLEDGMENTS

We are grateful to our colleagues, particularly at the Research School of Earth Sciences, for
sharing unpublished data and their experiences in the analysis of zircon. Comments by J Hanchar, J
Wooden and R Stern are greatly appreciated.

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