

Geological age by instrumental analysis: the 29th Hallimond Lecture

W. COMPSTON

Research School of Earth Sciences, Australian National University, Canberra, ACT 0200, Australia

ABSTRACT

The need in geology for *in situ* U-Pb age determinations of minerals is illustrated by two examples: the internal age dispersion developed within the zircon SL13 shortly after original crystallization, and the occurrence within minerals of old cores and later overgrowths. SL13 contains rare μm -sized patches of unsupported radiogenic Pb and a mainly bimodal distribution of $^{206}\text{Pb}/^{238}\text{U}$ ages otherwise. Both observations are consistent with original crystallization at 580 Ma and Pb loss at 565 Ma. Age precision is controlled by the ions counted for radiogenic Pb, and varies with instrumental sensitivity, age and U contents of the target. Laser-ablation ICPMS has similar spatial resolution and sensitivity to SIMS but consumes more sample because of much greater hole-depth in practice. Like SIMS, the measured Pb^+/U^+ is biased and also changes with depth so comparison with a standard mineral is necessary. Analyses of reference zircons reported here indicate that the reproducibility of Pb/U ages by ICPMS is limited by residual bias, not ion counting errors. For multipurpose ICPMS at least, the Hg background at mass 204 prohibits the measurement of ^{204}Pb for common Pb estimation. A third micro-analytical method, 'CHIME', and future developments in SIMS and ICPMS are discussed briefly.

KEYWORDS: zircon, age determination, SIMS, ICPMS.

Introduction

This paper is the written version of the 1998 Hallimond Lecture which was given at the Winter Meeting of the Mineralogical Society in London on 7th January 1998. It deals mainly with microanalysis of the mineral zircon for U-Pb geochronology by two different methods: secondary ion mass spectrometry, SIMS, and laser-sampling inductively-coupled plasma mass spectrometry, ICPMS, and gives two examples of the need for *in situ* U-Pb age determinations of zircon. The view is put that within-grain age-determination serves geology far better than multi- or even single-grain zircon analyses by mass spectrometric isotope dilution (MSID), despite the higher precision of the latter. It is shown that precision for *every* method is determined mainly by the amount of zircon used, but the larger the amount, the more it averages the likely μm -scale variations in Pb/U that commonly occur within the grain.

Depending on the optimism of individual oracles, the ICPMS technique has been described as complementing, rivalling and even replacing SIMS for the purpose. A first-hand assessment will be given of ICPMS zircon U-Pb data produced in-house by colleagues at the ANU during 1997, and some published misapprehensions of the SIMS method will be corrected.

Elemental discrimination in instrumental analysis

Before proceeding to examples of μm -scale differences in Pb/U within single zircons, two general properties of instrumental analysis need to be indicated. Elemental bias is the first. Instruments never measure the absolute ratios of two elements directly because they detect different elements with different sensitivities. For SIMS as executed by SHRIMP, the measured Pb/U for the standard zircon whose age is known and the zircon whose age is to be found are both

too high by a factor of about three. Even worse, they can be *variably* high during the measurement session over a range of $\times 2$. This problem also afflicts ICPMS, contrary to the initial hopes for uniform ionization of most elements in its plasma-source.

The problem can be corrected for SIMS because the processes that cause discrimination also change the ratio of the collected UO^+ to U^+ , which induces a strong correlation between the measured Pb^+/U^+ (or Pb^+/UO^+) and UO^+/U^+ . As a consequence, the value of Pb^+/UO^+ for the standard at each value for UO^+/U^+ observed in the unknowns can be estimated reliably, which in turn allows the true Pb/U in the unknown to be calculated relative to the known Pb/U in the standard. The correlation between Pb^+/UO^+ and UO^+/U^+ can be linearized by plotting the data as logarithms, as the relationship is best fitted by a power-law (Claoué-Long *et al.*, 1996).

Figure 1 shows comparisons between the standard SL13 and two other reference zircons made alternately during the same analytical session (mount Z2200, 9/6/95). The ratios of the Y-coordinates at the same X gives the $^{206}\text{Pb}/^{238}\text{U}$ ratios between samples and hence their relative $^{206}\text{Pb}/^{238}\text{U}$ ages. After appropriate data-analysis (see below), the SIMS $^{206}\text{Pb}/^{238}\text{U}$ ages agree closely with the Concordia intersection ages made on bulk samples by isotope-dilution.

The reference zircons AS3 and QGNG are fine-grained zircon concentrates, while SL13 is a fragment of a single crystal. Each point on Fig. 1 is one analysis; common ^{206}Pb has been subtracted. The spread in UO^+/U^+ correlates well with the variable discrimination in $^{206}\text{Pb}^+/\text{UO}^+$ and allows the latter to be corrected. The Y-axis scale in Fig. 1 obscures the appreciable slope of the discrimination locus, which was ≥ 0.7 for this particular session (9th June 1995). It also obscures the quality of fit of the data to each line, which is imperfect relative to known analytical errors. As illustrated below in two further examples of $20\ \mu\text{m}$ scale analysis, the imperfect fits are interpreted as due to small-scale but real variation in Pb/U within each sample, rather than to under-estimation of analytical errors. Based on the SL13 standard, most of the spot-ages for AS3 agree at $1095.6 \pm 1.1\ \text{Ma}$ (σ) as compared with the Concordia intersection age of $1099.3 \pm 0.3\ \text{Ma}$ (95% limits, Paces and Miller, 1989), while the remainder are slightly younger consistent with small amounts of Pb-loss. Similarly, half of the QGNG ages agree at $1845.1 \pm 1.8\ \text{Ma}$ (σ) as

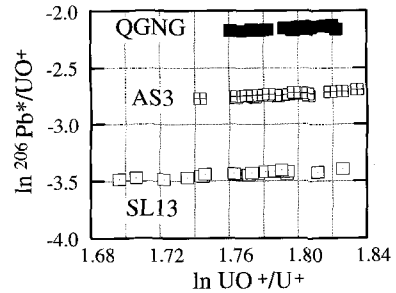


FIG. 1. Primary SIMS data for three reference zircons.

compared with $1849.8 \pm 1.1\ \text{Ma}$ by isotope dilution (2σ limits, C.M. Fanning and G.E. Mortimer, pers. comm.). One QGNG grain (not shown) has reversely discordant ages of $2070 \pm 8\ \text{Ma}$ for $^{206}\text{Pb}/^{238}\text{U}$ and $1898 \pm 3\ \text{Ma}$ for $^{207}\text{Pb}/^{206}\text{Pb}$.

The dependence of precision upon the mass of sample analysed

A second general point that applies to every method, bulk and micrometric, is the fundamental inverse relationship between precision of measurement and the amount of sample consumed, or more exactly, the number of atoms detected. This appears not to be widely known by earth scientists, and certainly it is not often cited in connection with SIMS analysis. The sizes of growth zones within zircons demand that the *in situ* analysis needs to be on an area less than $20\ \mu\text{m}$ wide in order to stay within the same growth zone and preferably not more than a few μm deep. So the analysis must be made using only a few nanograms of zircon, which is a factor of $\times 1000$ smaller than most 'single grain' zircon samples used by MSID. Obviously the amounts of U and Pb consumed by such a microanalysis will be $\times 1000$ smaller also.

A vital question is what are the total numbers of U^+ and Pb^+ ions that can be collected during analysis of such a small mass, because it is these numbers that directly set the minimum precision at which an age can be measured. All electron, ion and photon fluxes are subject to random variations in their rates described by Poisson statistics, for which the standard deviation of N counts received will be \sqrt{N} . Thus, for N_{Pb} of $^{206}\text{Pb}^+$, the coefficient of variation will be $1/\sqrt{N_{\text{Pb}}}$ which

diminishes as N_{Pb} is increased. For N_{Pb}/N_U , which mainly sets the precision of $^{206}Pb/^{238}U$ ages, the coefficient of variation will be

$$\sqrt{(1/N_{Pb} + 1/N_U)}$$

making it clear that $^{206}Pb/^{238}U$ ages for U-rich, old zircons will be much more precise than U-poor, young zircons.

The full calculation of the expected errors in age will include other factors besides ion counting statistics, such as uncertainty in the Pb/U discrimination slope and the subtraction of common Pb, the latter being especially important for young zircons. For counting errors alone, Fig. 2 illustrates the precision of SIMS for the $^{206}Pb/^{238}U$ ages of zircons having different ages and U contents. It is based on the normal sensitivity values for Pb and U found using SHRIMP for the reference zircon SL13, and on the normal SHRIMP analytical procedures (below). As sampled in bulk, MSID analyses show that SL13 contains *c.* 236 ppm of U and 19 ppm of radiogenic ^{206}Pb that accumulated during its lifetime of *c.* 572 Ma. On the scale of 30 μm , SL13 is exceptionally uniform relative to the great majority of other zircons, usually showing a standard deviation in U and Pb concentration of only a few percent, which makes it particularly valuable as a reference zircon.

The SHRIMP analysis per spot typically consumes 2 ng of zircon during a 15 min period, equivalent to an excavation rate of 1.23×10^5 atoms of ^{206}Pb per second for SL13. The flux of $^{206}Pb^+$ ions associated with and generated by this excavation rate is typically 1.5×10^3 counts per second, and typically mass ^{206}Pb is counted for 70 s per analysis. The intrinsic sensitivity for Pb is termed the 'useful yield', defined as the ratio of $^{206}Pb^+$ ions collected to ^{206}Pb atoms sputtered per second. It is just over 1% for the above conditions. The above rules apply to all methods, bulk and microanalytical by SIMS and ICPMS. The reason why bulk MSID is more precise than microanalysis is simply that it uses so much more sample. Similarly, the reason why $^{207}Pb/^{206}Pb$ is not measured precisely for most (but not all) young zircons by SHRIMP is that ^{207}Pb is between $\times 10$ to $\times 20$ less abundant than ^{206}Pb dependent on exactly how young, so that the $^{207}Pb/^{206}Pb$ counting error is always greater than that for $^{206}Pb/^{238}U$. Nevertheless, SHRIMP values of $^{207}Pb/^{206}Pb$ for old and U-rich zircons are commonly better than 0.3% and sometimes better than 0.1%.

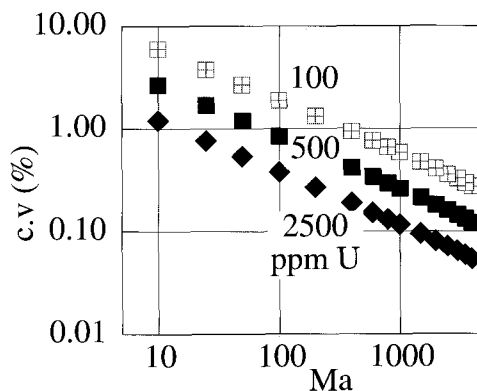


Fig. 2. Counting errors for SIMS $^{206}Pb/^{238}U$ ages as a function of age and U contents.

For old zircons rich in U, the expected error for $^{206}Pb/^{238}U$ ages is commonly $\leq 0.2\%$ (Fig. 2). Young or U poor zircons may have greater errors than shown in Fig. 2 owing to their lower Pb contents and to subtraction of common Pb.

It is not possible to cite a single percentage error for zircon U-Pb age by microanalysis, as the error depends on both the age and U contents of the particular zircon (Fig. 2). Halliday *et al.* (1998a) report that the precision for ICPMS is greater than SIMS mainly because ICPMS consumes much more sample. The SIMS precision could be increased likewise if it was chosen to use higher sputtering rates, wider probe diameters and/or longer analysis times (greater pit depth), but genuine microanalysis excludes such choices. Halliday *et al.* (1998a) also equate the useful yield for Pb by laser-sampling ICPMS with that of SIMS; on the contrary, SIMS is a factor of five greater.

The need for microanalysis: an example of multiple zircon growth

By far the most useful mineral for U-Pb dating is zircon, $ZrSiO_4$, to which the present paper will be restricted. It occurs widely in many types of rock, mainly as an igneous precipitate but also as detrital grains in most sediments and as overgrowths on existing grains in metamorphic and metasomatized rocks. Its lattice structure favours the substitution of U and Th for Zr during mineral growth but it strongly excludes Pb, so that the radioactive U and Th clocks start reliably with

zero daughter-element. It is chemically stable in many environments and it is one of the most robust accessory minerals during sedimentary processes. It has the outstanding property of a very small diffusion coefficient for Pb, U and Th (Lee *et al.*, 1997) which means that the U-Pb age of a zircon, once formed, is extremely slow to be erased during later temperature rises.

The need for microanalysis becomes obvious as soon as imaging methods are applied that depict the growth structure of natural minerals. Figure 3 shows that the well-defined crystal faces and featureless interior from a secondary-electron or reflected light image can disguise the reality of a large inner core and an overlying mantle of later zircon. The growth of the grain is composite in time, rather than the result of a single magmatic precipitation, and its age as a whole-grain age-determination will be an average. It is of course impossible to know the difference in age between the core and younger mantle without measuring both. This image both encapsulates the need for microanalysis and serves to identify the essential target areas.

The Concordia curve is the locus of data for which the two ages calculated from $^{207}\text{Pb}/^{235}\text{U}$ and $^{206}\text{Pb}/^{238}\text{U}$ are equal. The presence of data-points on Concordia to within error means that the

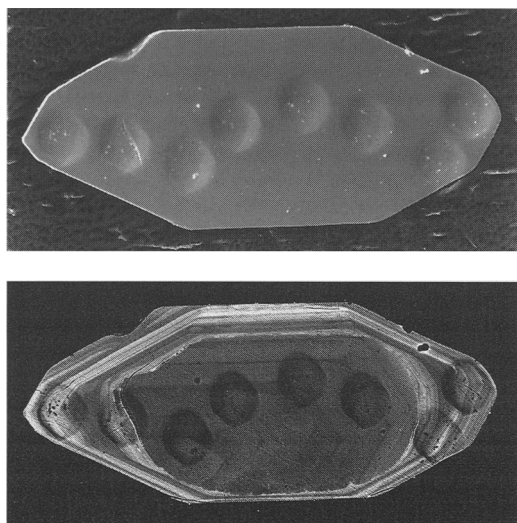


FIG. 3. Secondary-electron (upper) and back-scattered electron images (lower) of the sectioned zircon grain 16, Cowra Granodiorite. Ion probe analysis sites are visible at *c.* 2 μm deep and *c.* 25 μm diameter.

analysed spots have remained chemically closed since crystallization of the particular areas of zircon within the grain. Figure 4 shows that this is plainly the case for some of both the inner core spots and the later zircon overgrowth. We learn from these microanalyses that the original age of the core is close to 1100 Ma, and that the later zircon is very much younger indeed at 400 Ma. The 400 Ma age agrees with the known time of emplacement of the granodiorite, and the 1100 Ma age is a quantitative discovery about the source rocks of the particular granite. Furthermore, there are some areas that straddle the boundary between the core and mantle, and these give composite ages as they should.

The co-existence of the two zircon ages in the single grain emphasizes again the benign nature of the zircon crystal lattice for geochronology: the 1100 Ma is the original age of the core-zircon, because the position of the data on Concordia show that almost none of the radiogenic Pb produced in the original grain since 1100 Ma has been lost. This is despite the temperature rise in the zircon to at least 700°C that must have taken place during formation of the granite magma at 400 Ma.

The importance of this type of information for geology cannot be overstressed. For example, about half of the Palaeozoic granitic plutons in SE Australia, together with their extrusive equivalents, are of the so-called S-type magmas, derived by partial fusion of pre-existing sedimentary rocks (Chappell and White, 1974). The granites and volcanics contain many inherited detrital zircons from the former sediments. In the more mafic types, the only zircon that is precipitated

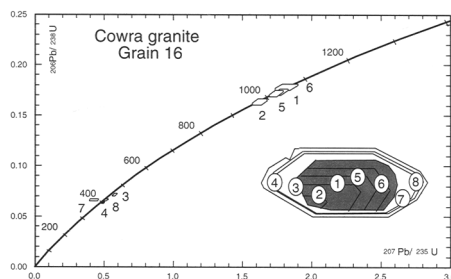


FIG. 4. Wetherill-type Concordia diagram showing the spot-analyses within grain 16, in relation to its zoned core which is truncated and overlain by younger layers of zircon.

from the new Palaeozoic melts is as rims a few μm thick around older grains (Williams, 1992). It is essential therefore to be able to measure the ages of these thin rims.

Submicrometre-scale variation in Pb/U within SL13

Any standard for instrumental analysis ideally should be more uniform in its composition than analytical precision. The most promising zircon standard known to us in 1981, when the SHRIMP ion microprobe was commissioned, was a cm-sized single zircon crystal, SL13. It was uniform in Pb/U on the scale of replicate MSID analyses of mg-sized samples, it had relatively low U concentration which would minimize radiation damage, and its gemlike clarity suggested a lack of chemical zoning. Lee *et al.* (1997) later documented its unaltered crystal structure by X-ray diffraction, and the absence of growth-zoning was confirmed by its featureless cathodoluminescence mapping.

During the initial testing of SHRIMP, any change in the apparent age of SL13 during repeated microanalysis was assumed to be caused by instrument malfunction or operator misuse. The repeatability in age for SL13 seen per analytical session was also assumed to be the best attainable precision for the ages of the unknown zircons. Both of these assumptions have been disproved over the past few years. Within SL13, there are now two types of variation in Pb/U, both

related to post-crystallization mobility of Pb or of its chemical antecedents in the U decay-series.

Patches of unsupported radiogenic Pb

The most obvious type is rare patches of unsupported radiogenic Pb that appear with no visible sign of an inclusion within the crystal and no zonation detected by cathodoluminescence. The effect is illustrated by Fig. 5, a plot of Pb/UO vs. UO/U for the SL13 analyses of a particular session for grain-mount Z1641.

The 'outlier' shows as a much older 'age', very scattered in Pb/U scan-by-scan, averaging '2300 Ma' in this example but with UO/U within the normal range. It is easily recognized, easily excluded from the other analyses as a 'gross outlier', but also easily forgotten when the main analytical purpose is to date the unknown zircons. Nevertheless, its presence gives the picture that radiogenic Pb, or one or more of its radioactive antecedents, were mobilized within SL13 after its original crystallization. The phenomenon has published precedents. Internal variations in Pb/U found by electron microprobe within a single crystal of zircon were assigned to the trapping of radon in radiation-damage sites and its subsequent *in situ* decay to Pb (Suzuki, 1987). Unsupported radiogenic Pb found using MSID during leaching of highly zoned zircons was attributed to Pb diffusion from high to low U sites (Mattinson *et al.*, 1996).

In the SIMS method of microanalysis, a focused beam of energetic primary ions both samples and simultaneously ionizes the target. Because the rate of erosion is low, a long-lasting beam of secondary ions is produced (Fig. 6)

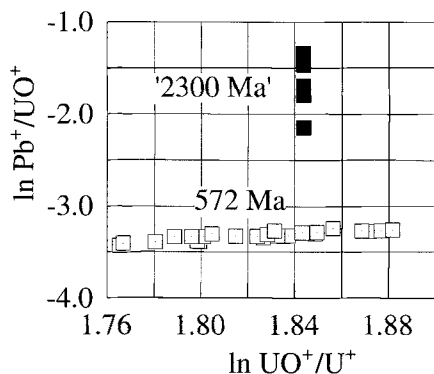


FIG. 5. Z1641 discrimination plot showing the 'outlier' SL13-11.

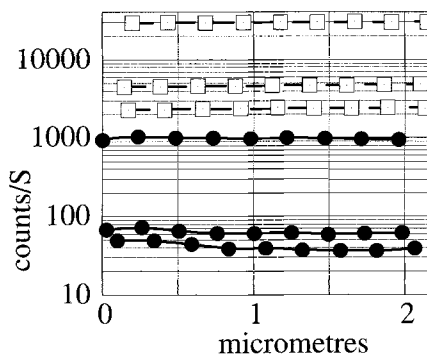


FIG. 6. Within-run secondary ion counting rates from normal SL13 zircon.

whose stability, for a uniform target, is determined mainly by the stability of the primary beam.

In descending order, the open symbols in Fig. 6 are UO^+ , U^+ and ThO^+ and the filled symbols are $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$ and $^{208}\text{Pb}^+$. No $^{204}\text{Pb}^+$ is visible. The analysis time is *c.* 15 min. Figure 7 gives the contrasting raw data for the particular outlier SL13-11 from Z1641 shown in Fig. 5. The UO, U and ThO count-rates are quite stable as the pit deepens but the three Pb count-rates are not: they vary within the analysis, they are well-correlated with each other, and they are distinctly elevated relative to the normal Pb count-rates. The absence of a detectable shift in the U and Th count-rates indicates that the crystal lattice was continuous. In this particular spot and on a μm -scale, the zircon is evidently highly enriched in Pb. The total lack of $^{204}\text{Pb}^+$ shows that the Pb is purely radiogenic. On a scan-by-scan basis, the $^{206}\text{Pb}/^{238}\text{U}$ 'ages' vary widely from 2200 to 4200 Ma, while the $^{207}\text{Pb}/^{207}\text{Pb}$ 'ages' average 974 ± 20 Ma. The richest patch of unsupported Pb yet encountered has even greater $^{206}\text{Pb}/^{238}\text{U}$ 'ages', 5000 Ma to 6750 Ma, and a similar but more stable $^{207}\text{Pb}/^{207}\text{Pb}$ 'age' of 999 ± 5 Ma.

Concordia representation

The above points per scan plus others from two less anomalous analyses are shown in the Tera-Wasserburg Concordia diagram, Fig. 8. The uncertainties shown are standard errors for $^{207}\text{Pb}/^{206}\text{Pb}$ only. Most points lie within error along the tangent to Concordia drawn from the most discordant group, which touches Concordia at 560 Ma. Collectively and between scans for

some spots, the points show a correlation between $^{207}\text{Pb}/^{206}\text{Pb}$ and the total amount of Pb as recorded by $^{238}\text{U}/^{206}\text{Pb}$, which indicates that the total Pb measured is a mixture of radiogenic Pb on Concordia, i.e. 'supported' by the almost uniform U content of SL13, with variable added amounts of unsupported Pb characterized by $^{207}\text{Pb}/^{206}\text{Pb}$ at zero $^{238}\text{U}/^{206}\text{Pb}$ of *c.* 0.073. The scans within the richest and longest-lasting 'outlier' are the most precise and closest to the U/Pb origin, reflecting its relatively huge content of ^{206}Pb . The data from the other more fugitive outliers are much less precise because the observed values for the ratios are more sensitive to the necessary time-interpolations during the scans and being much smaller in count rate, they have higher counting errors.

The U-Pb isotope systematics can be applied to the particular $^{207}\text{Pb}/^{206}\text{Pb}$ value of the unsupported Pb to model the times at which such Pb can be generated internally within SL13. If the unsupported Pb was extracted from its parent U during a very short time interval immediately after crystallization at age T_1 , then T_1 is given by the point at which the tangent drawn from the unsupported Pb point touches Concordia. This is 560 Ma, rather close to the bulk age of 572 Ma but clearly younger. Alternatively, a two-event model may be considered in which the radiogenic Pb that accumulated from the original age for SL13 at T_1 was extracted from the U crystal sites significantly later at T_2 . Families of values for the two ages will be given by the two intersections with Concordia of a family of lines drawn through the unsupported Pb point. For this model, the 560 Ma tangential limit will be exceeded by all T_1

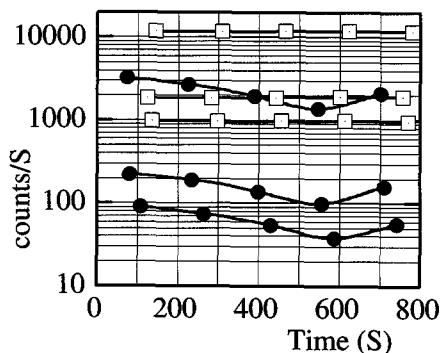


FIG. 7. Within-run secondary ion counting rates for the 'outlier', SL13-11.

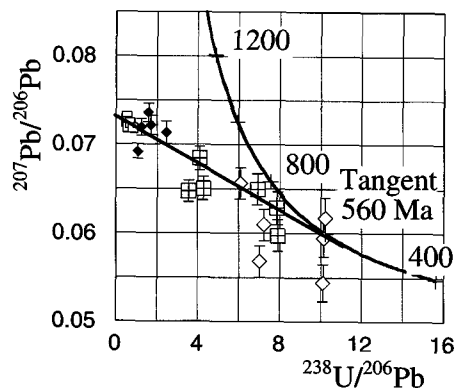


FIG. 8. Concordia diagram showing reversely discordant data for four anomalous spots within zircon SL13.

and will itself exceed all T_2 . For example, if T_1 is 578 Ma, then T_2 will be 540 Ma.

If there was a significant net escape of Pb from the whole SL13 crystal at T_2 , its measured bulk age of 572 Ma will be too young. Regardless of this, the two-event models predict that a range in age will be found within SL13 using microanalysis. Those parts of SL13 that lost all their Pb at T_2 will register the T_2 age, those parts that lost no Pb will register T_1 , and parts having partial loss will be intermediate between T_1 and T_2 . Parts of SL13 that contain mixtures of displaced and supported radiogenic Pb will give ages that exceed T_1 but they will be located to the left hand of the Concordia curve as *reversely discordant* points and recognizable for this reason.

It is clear that very fine depth-resolution, of at least a few tenths of a μm , is necessary during analysis to detect the changing fraction of unsupported Pb during the progressive deepening of the sampling pit.

Internal scatter of ages within SL13

The second type of Pb/U variation is evident from replicate analyses of SL13 made during its use as the standard for routine Pb/U age determinations of unknown zircons, in which analyses of the standard and unknowns are normally alternated within the one analytical session.

On the logarithmic scale, it is obvious that the internal dispersion of the replicate SL13 measurements in Fig. 9 is distinctly greater than that for the LG43 zircons. It is very hard to blame the ion probe or its operator for this effect. The face-value conclusion is that the particular chip of SL13 used here has its own small-scale variability.

Similar variability in SL13 can be seen in all analytical sessions that are conducted at high precision, showing that it is endemic to the crystal rather than present only in particular chips. The variability has been obscured in the past by the use of low sensitivity analyses. The counting-error in Pb/U per spot needs to be 1% or less to detect the variability, otherwise the larger counting errors will mask the internal variation in SL13.

Presentation of replicate measurements

Data-handling and interpretation for U-Pb geochronology using bulk samples deals mainly with how the small number of relatively precise

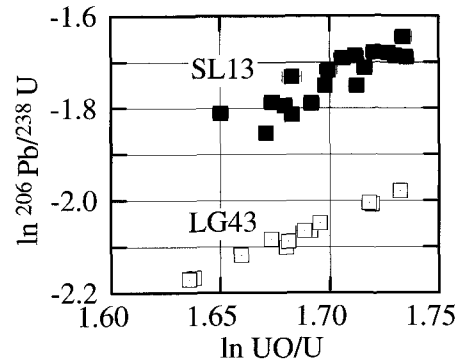


Fig. 9. Excess scatter of SL13 replicates relative to zircons from tonalite LG43, 20/11/93.

$^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages made per rock relate to the Concordia reference curve. In contrast, rapid microanalysis generates large numbers of $^{206}\text{Pb}/^{238}\text{U}$ ages that have larger counting errors because fewer counts are generated from the much smaller sample sizes consumed, and also more variable errors because a wider range in U is usually encountered within and between crystals. In addition, $^{207}\text{Pb}/^{206}\text{Pb}$ data for zircons younger than, say, 800 Ma are usually not precise enough to relate directly to the Concordia curve, owing to its diminishing curvature with decreasing age. Interpretation for microanalytical data therefore starts with different questions: do the many replicate $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages agree to within their variable errors, and if not, can the ages be resolved into one or more groups that might have a geochemical interpretation? The first question is answered by combining the replicates, on a trial basis, to form the weighted mean age

$$T_m = \Sigma\{w_i T_{ij}\} / \Sigma\{w_i\}$$

where w_i is the weight $1/(\sigma_i)^2$ for each age. Then, the Mean Square of Weighted Deviates is formed as

$$\text{MSWD} = \Sigma\{w_i (T_i - T_m)\}^2 / \Sigma\{w_i\}$$

which provides an objective test for internal agreement of the ages. If MSWD tested as a Fisher-variate significantly exceeds unity, it signals that the errors assigned to the individual ages cannot account for the scatter actually observed. Two possibilities now follow: one or more of the measured ages has a greater error than assigned, or one or more is really different in age.

It also signals that the ages cannot be combined validly unless one or more of their errors can be increased to reduce the MSWD. Alternatively, a non-random structure in the age-distribution must be accepted, which would permit the presence of two or more age-populations.

The problem of recognizing a possible structure in the age-distribution when the ages have differing precision can be handled by forming the kerned probability-density plot (Silverman, 1986). Each individual analysis is represented as having its own Gaussian curve that is given unit area but a height and width that reflect its individual precision. Then all the heights over a chosen age interval are summed which gives the probability density for the interval.

The kerned probability-density plot for 208 measurements of zircon $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, expressed as $^{207}\text{Pb}/^{206}\text{Pb}$ ages (Fig. 10), is given here as an example of a well-fitted population of measurements. The ages have unequal standard errors per measurement, ranging from ± 3.5 Ma to ± 33 Ma, with median ± 5.3 Ma, mainly because of the different U contents per spot. The MSWD at 1.2 shows that no excess scatter has been detected, which the plot reflects by displaying a single peak only.

Figure 11a shows a more complex probability plot for $^{206}\text{Pb}/^{238}\text{U}$ ages for SL13 during a single analytical session. It contains just enough data for an adequate statistical sample, and the MSWD at 3.2 signals the presence of more scatter than individual age-precisions can account for. The shape of the diagram is not a single peak but resembles two overlapping peaks, for which the

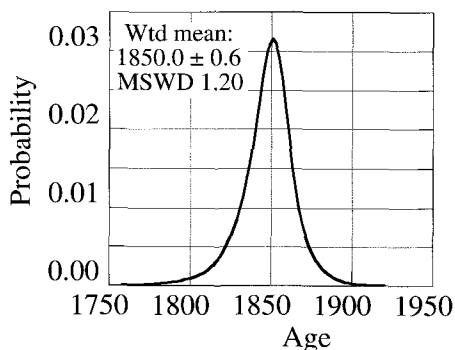


FIG. 10. An example of a unimodal probability density plot: SIMS $^{207}\text{Pb}/^{206}\text{Pb}$ ages for the QNG zircon.

two means can be evaluated from the plot or more objectively, by using mixture-modelling (Sambridge and Compston, 1994).

Counting errors for the Fig. 11a ages range from ± 4 Ma to ± 10 Ma, but the MSWD at 3.2 shows that they cannot account for the observed dispersion. The latter together with the evident bimodal structure of the plot can be attributed to the presence of two age components at the $20\ \mu\text{m}$ sampling scale, rather than one.

Counting errors for the Fig. 11b ages average $\sim 0.5\%$ and the MSWD has increased strongly as a result. The bimodality has been sharpened and remains the principal type of age-variation, although there are now small fractions of older ages detected. The component at *c.* 594 Ma occurs in all high-sensitivity runs and might be a real age. Sporadic ages older than this can be interpreted as caused by admixture with a little of the unsupported radiogenic Pb that formed the gross outliers discussed earlier. Younger age components can also be detected in other sessions,

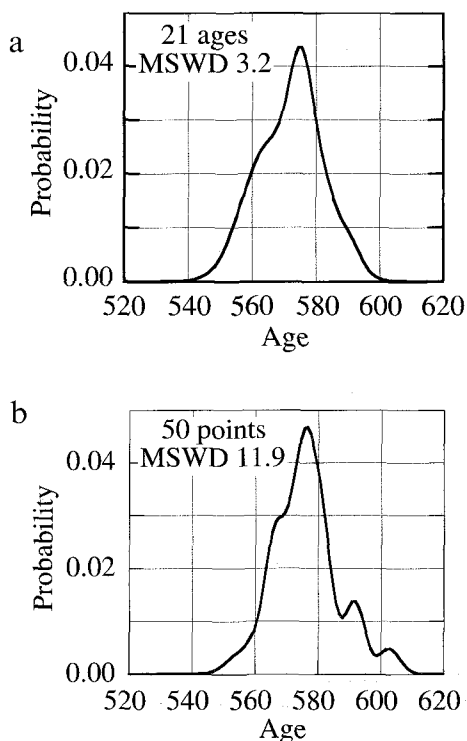


FIG. 11 (a) Probability density plot for 21 $^{206}\text{Pb}/^{238}\text{U}$ ages for SL13 in mount Z2434; (b) the most sensitive $^{206}\text{Pb}/^{238}\text{U}$ ages for SL13.

which might represent a few spots within the crystal that have suffered recent Pb loss.

Geochemical interpretation of variable $^{206}\text{Pb}/^{238}\text{U}$ ages within SL13

For precise analyses of SL13 made during single stable sessions, a bimodal structure for the $^{206}\text{Pb}/^{238}\text{U}$ age distribution is almost always found. When mixture-modelling is applied, the age-ratio of the two peaks is correctly indicated, but the absolute value of either peak is known only relative to the mean age taken for the session. In the past, the same mean age, 572 Ma, was assigned for every session. However, this assignment is now regarded as an approximation only, because there will be fluctuations in the proportions of the younger and older age-populations sampled per session. To avoid this effect, the ages of the two main SL13 age peaks were determined relative to another reference zircon, QGNG, for which most $^{206}\text{Pb}/^{238}\text{U}$ ages defined a main probability-density peak and the remainder gave younger ages consistent with Pb loss. On this basis, the $^{206}\text{Pb}/^{238}\text{U}$ age of the main QGNG peak was equated to its $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1850.0 ± 0.6 Ma, well-defined both by SIMS and MSID. Estimates for the ages of the two main SL13 peaks for a number of sessions agreed within error and their pooled values are 580 ± 1 Ma and 565 ± 1.5 Ma. (These values may change slightly as more calibrated high-sensitivity data are included).

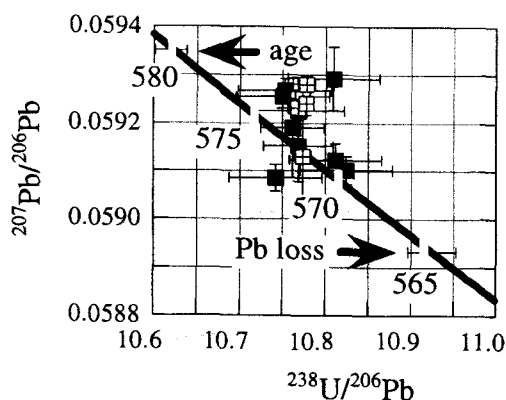


Fig. 12. SL13 Concordia plot for bulk MSID results (filled, RSES; open, van Breemen and Roddick, 1995) and the two main SIMS age groups at c. 580 Ma and 565 Ma.

Figure 12 shows these 'absolute' values for the two SL13 peaks and interprets them from the evidence shown previously for patches of unsupported radiogenic within SL13. It is an expanded part of a Concordia diagram, in which Concordia appears as a straight line over the small range of ages shown.

The original age of SL13 is interpreted as the older 580 Ma peak. There was a metamorphic event some 15 Ma later at 565 Ma, which produced the second main peak. The unsupported radiogenic Pb was produced during this time-interval. At 565 Ma, this internal Pb was redistributed. It was moved out of those parts of the crystal that now give ages around 565 Ma, and at least some of it was concentrated into μm -sized patches to form the unsupported radiogenic Pb described earlier as the 'gross outliers'. The gross outliers are located along the extrapolation of a discordia chord between 565 Ma and 580 Ma, which is their required locus for the model of a single superposed event.

The MSID analyses of SL13 used relatively huge sample-sizes, 30 μg to 3 mg, which appear to average the micro-scale variations found by SIMS beyond detection. However, the bulk $^{206}\text{Pb}/^{238}\text{U}$ ages are located exactly where they should be on this model: between the original age at 580 Ma and the metamorphic event at 565 Ma, and they agree with each other to within error at 572 Ma. The latter value was previously interpreted as signifying the original age but it is viewed here as a composite value that does not signify a crystallization event.

Concluding remarks on SL13 as an age reference

It is not comfortable to contemplate a reference zircon that is less uniform in Pb/U than at least some of the unknown zircons to be dated. Nevertheless, the bimodal age-distribution recorded by the precise *in situ* analyses can now provide two age-calibration lines instead of the one as treated previously. Owing to sampling fluctuations, the two lines are not usually determined in practice with equal precision, so either the older or the younger may be preferred, whichever is the more precise. On this basis, the penalty for continued use of SL13 as a standard is decreased efficiency, not necessarily a loss of accuracy.

Cognitive dissonance is the psychological term that denotes an inability to accept a new picture of

reality because it conflicts with a prior deeply-felt belief. Such a condition has clouded at least the author's understanding of the nature of SL13 over the past 15 years. All conventional procedures involving single and multi-grain samples with MSID are based on the doctrine that selected zircons are perfect or can be made so by prior treatment such as surface-abrasion. It was expected initially and accepted that SL13 would be truly uniform in Pb/U from the evidence both of its crystallinity and of the isotope-dilution results. It was assumed, wrongly, that uniformity on the scale of milligram samples of SL13 meant that SL13 was uniform on a μm scale also. The increased scatter seen in precise SL13 micro-analyses was attributed to instrument or operator malfunctions. The 'gross outliers' seen from time to time were regarded as too rare and too small to bear on the bulk age, and their significance was not considered.

Laser-ablation ICPMS for U-Pb geochronology

A totally different method of micro-sampling is to use a focused laser beam of UV photons to ablate the target into very fine dust particles which can be swept by a stream of Ar into a plasma ion-source. The plasma source itself is very efficient at ionizing. For $\sim 75\%$ of the elements (VG-PlasmaQuad Handbook), all particles leaving the source are nearly completely dissociated into elemental ions, so that molecular interferences are nearly all removed. The use of a low resolution mass analyser is therefore permitted for many specific applications, but with care because isobaric interferences do in fact remain from the remaining 25% of the elements that are not fully dissociated.

Beam production with depth / time

Using ultraviolet lasers, minerals can be sampled as sharply defined pits at upwards of $10\ \mu\text{m}$ diameter, but there is a problem to slow the ablation rate sufficiently so that the pits are not deep. The laser pits in current practice range in depth and diameter upwards from $c. 50\ \mu\text{m}$ and consume $c. 0.5\ \mu\text{g}$ of zircon, comparable with the smallest MSID analyses. This greatly increases the chance of crossing more than one growth zone within single grains, and therefore having to deconvolve the chemistry and age of two or more mineral zones. The material consumed therefore constitutes a bulk- rather than micro-sample.

The typical production of U^+ and Pb^+ ions from two different zircons and the NBS 612 standard glass is shown in Fig. 13, using the VG-PlasmaQuad ICPMS instrument as set up at RSES in Canberra by Dr S. Eggins and others for ablation of solid targets using a pulsed Excimer laser. The mass-resolved ions selected for analysis are sampled in 40 ms periods by a quadrupole mass-analyser. Background counts are measured at each mass and subtracted to obtain the net sample counts.

The laser-ablation patterns for SL13 and NBS represent sampling from targets that have a relatively uniform U and Pb concentration. The decrease with time after the initial maximum is attributed to effects consequent on deepening of the pit (S. Eggins, pers. comm). In contrast, the beam from analysis 34 of the QGNG zircon shows a pronounced decrease in U counts from 12 to 20 s, indicating that the pit has penetrated into a zone having lower U contents.

Background counts for Pb isotopes

The relative sizes of the background count-rates for masses 206, 207 and 208 are consistent with the isotopic composition of common Pb. This strongly suggests the presence of a Pb memory located at one or more unknown places within the system. For the SL13 data shown in Fig. 13, the mass 206 background count-rate was 150 cps, which averaged $c. 0.3\%$ of the ^{206}Pb counts per sampling period. By comparison, the SIMS mass 206 background is normally <0.02 cps. The ICPMS background count-rates probably remain constant per analytical session, while the ^{206}Pb

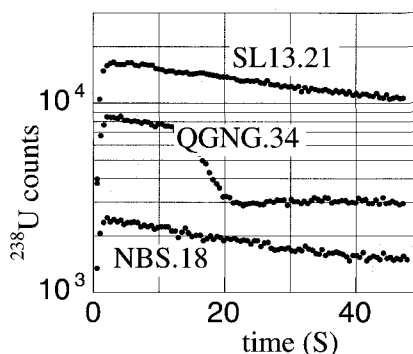


Fig. 13. Yield of $^{238}\text{U}^+$ with time/depth by laser sampling ICPMS (M. Palin and I. Campbell, pers comm. May 1997).

count-rate from the sample will vary inversely as the age and *c.* linearly with U contents. The sample production rate will vary according to the square of the pit-diameter. Thus for 20 μm pits rather than 60 μm , the background fraction at ^{206}Pb from the above rates would increase to $\leq 3\%$. For 20 μm pits and zircon having a similar U content but $\times 10$ younger than SL13, the background would rise to 30%. On the other hand, it would not constitute a problem with older Precambrian zircons of similar U contents.

Variable Pb/U bias and $^{206}\text{Pb}/^{238}\text{U}$ age measurement

The tracking of Pb^+ with U^+ during beam production is distinctly non-linear for the zircons (Fig. 14). The Pb^+/U^+ values for SL13 start at $\sim 35\%$ lower than its MSID value, and although they rise continually, they do not reach the true value at 0.0928. The pattern for QGNG.34 is similar, although it is possible that there is a small increase in Pb^+/U^+ from 15 to 20 S that matches the change in U counts seen in Fig. 13. If real, this would signify that the low U zone is slightly older.

The known $^{206}\text{Pb}/^{238}\text{U}$ in SL13 is *c.* 0.0928 and in QGNG, *c.* 0.3324. The greater scatter about the NBS curve reflects the lower Pb and U and hence greater ion counting noise. The observed Pb^+/U^+ vs. depth for NBS 612 glass differs from that of the zircons. It is relatively flat, but replicate patterns confirm that it also has a slight fall and rise over the duration of the pit. Both of these differences complicate its possible use as a standard for zircon or other minerals.

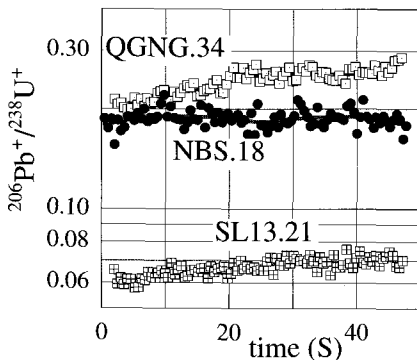


FIG. 14. Variable bias in Pb^+/U^+ for the Fig. 13 data.

Despite the rapid change in ICPMS discrimination with depth, it is still possible to make useful comparisons of Pb/U between a standard and unknown zircons. The discrimination shape for Pb/U as a function of the pit-depth appears to be similar for many zircons, so that the ratio between the measured Pb^+/U^+ for the unknown and for a standard zircon at each point of time can be taken as a correct comparison between their true Pb/U at each depth of the two analysis pits.

Common Pb correction: ^{204}Hg isobar

Common Pb in zircon is most directly measured using the single non-radiogenic isotope, ^{204}Pb , from which the amounts of common ^{206}Pb , ^{207}Pb and ^{208}Pb can be calculated and then subtracted from the total. It is always present on the surfaces of the target zircon owing to contamination during polishing and handling, which can be largely removed during the initial erosion of the sample by the primary beam. It may be present also within the zircon crystal in submicrometre inclusions, if not also in the crystal lattice. Whether the common Pb makes a significant contribution to the total Pb depends on whether the zircon is young or old or has high or low U and Th contents. In any case, an accurate measurement of its amount is at least very desirable. The $^{206}\text{Pb}/^{238}\text{U}$ ages are not very sensitive to the usual amounts of common Pb but $^{207}\text{Pb}/^{206}\text{Pb}$ ages are, because of the lower abundance of radiogenic ^{207}Pb .

Unfortunately, there is a sustained and very large contamination of the PlasmaQuad instrument in Canberra by Hg and certain other volatile elements. ^{204}Hg completely overwhelms the tiny ^{204}Pb count-rate that is associated with zircon analysis, so that its removal by peak-stripping is not possible. The source of contamination has not been found; similar contamination is reported from other ICPMS laboratories. It may be a memory from the analysis of Hg-rich material such as the NBS standard glasses. At present it completely excludes the use of mass 204 for the estimation of common Pb in zircon and other U-rich minerals by the Canberra PlasmaQuad.

There are alternative ways of estimating the proportions of common Pb (Compston *et al.*, 1984) that are valid for young zircons (207-method) or low-Th zircons (208-method), but neither can be applied generally. If $^{207}\text{Pb}/^{206}\text{Pb}$ ages are to be measured independently, then only the 208-method remains and this has been used here for the present ICPMS data.

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

Replicate analyses of the zircons QGNG and AS3 illustrate the capability of the VG PlasmaQuad for radiogenic Pb isotopic ratio measurement. The observed $^{207}\text{Pb}/^{206}\text{Pb}$ for each of these two zircons agreed within counting errors prior to common Pb subtraction (one QGNG analysis excepted). If each analysis is corrected individually using the 208-method, the radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ for the replicates became dispersed beyond expected error, which suggests that the common Pb cannot be measured well enough. Better replication is given by combining the individual common Pb estimates to obtain a single mean value to be applied to all analyses.

For QGNG, all except one of the 15 $^{207}\text{Pb}/^{206}\text{Pb}$ ages agree to within error at 1848 ± 3 Ma (weighted mean), in excellent agreement with TIMS and SIMS at 1850 Ma. The mean precision per analysis is 12 Ma but varies with the individual counting statistics per spot according to its Pb content. The one exception is spot 34 which has a consistently lower age of 1722 ± 26 Ma throughout the pit and is regarded therefore as detecting a younger zircon growth. A small fraction of morphologically different and younger grains is known within the QGNG concentrate from previous MSID analyses (C.M. Fanning & G.E. Mortimer, pers. comm.). For AS3, the radiogenic $^{207}\text{Pb}/^{206}\text{Pb}$ ages from 15 spots agree to within counting statistics after correcting by the mean common Pb content. The weighted mean age was 1117.3 ± 5.8 Ma (σ), marginally greater than the MSID value at 1099 ± 0.3 Ma (95% limits, Paces and Miller, 1989).

There is no detectable bias in ICPMS measurements of zircon $^{207}\text{Pb}/^{206}\text{Pb}$ ratios. However, Pb isotopic ratios measured by ICPMS for NBS 612 contrast with the constancy of the zircon ratios by showing variable isotopic fractionation.

Comparative Pb/U for SL13, AS3 and QGNG by PlasmaQuad ICPMS

The raw data for a cyclic set of PlasmaQuad analyses (May 29, 1997) were kindly made available to the author by Dr M. Palin and Dr I. Campbell on the above trio of zircons. The NBS 612 glass, which may be more uniform in Pb/U than the zircons on a 50 μm -scale, was also analysed to provide independent long term control

for possible drift in elemental discrimination. The data (Fig. 15) were examined to test first whether agreement between analyses can be obtained within each standard to within counting errors, and then whether their relative Pb/U is consistent with that determined by MSID. 'Age' values are shown for NBS 612 glass in Fig. 15 to monitor internal scatter and long-term drift for the zircon ages. Counting errors are negligible for the zircons but not for the glass where they are shown as 1σ error-bars.

If the first two glass analyses are excluded, results for the rest scatter no more than ion counting errors (MSWD 1.5) over the duration of the analytical session. However, if all the glass analyses are used, it is possible that a small long-term decrease in apparent Pb/U with time has taken place. The present results are therefore ambiguous concerning the long-term stability of the laser-power and ICPMS system.

The SL13 analyses, not shown in Fig. 15 to avoid compressing the age-scale, were restricted to a brief part of the session. One age is a low outlier but the internal agreement in Pb/U for the remaining nine still exceeds ion-counting statistics. Internal variation is found by SIMS for this zircon as described earlier in this paper; the standard deviation observed by ICPMS per spot at c. 1% is compatible with such variation. Using mixture-modelling and setting the mean SL13 age at 572 Ma, the SL13 ages by ICPMS can be resolved into a main group at 576 ± 0.8 Ma and another at 560 ± 2.5 Ma, similar to the groups found by SIMS.

Both the AS3 and the QGNG data show large apparent spreads of several percent in Pb/U that are much greater than ion counting precision.

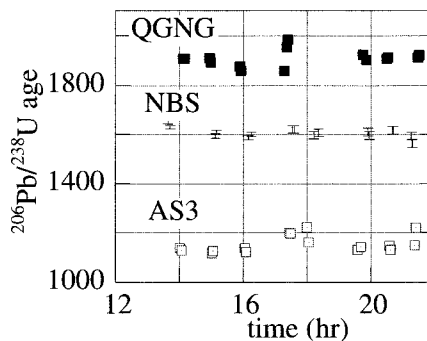


FIG. 15. $^{206}\text{Pb}/^{238}\text{U}$ ages by ICPMS for zircons QGNG and AS3 relative to SL13.

They are also greater than the expected values, relative to 0.0928 assumed for the mean $^{206}\text{Pb}/^{238}\text{U}$ in SL13 (572 Ma). Although real variations in Pb/U within the zircons are always possible, it is unlikely that they would be as frequent as indicated by these results. Variations in Pb/U discrimination that accompany laser sampling caused by subtle matrix or crystallinity differences between the zircons seem a much more likely explanation. Using ICPMS with a multicollector sector mass analyser, Halliday *et al.*, (1998b) also found variability in Pb/U in the NBS standard glasses beyond expected errors, which they also attribute to uncontrolled Pb/U discrimination.

Future ICPMS instruments

The experience and data described above for the PlasmaQuad in Canberra are based on a type of mass-analyser that can be described as outmoded now for the purpose of Pb/U determination. Instead of single-collector quadrupole-type mass analysers, there are now magnetic sector mass analysers equipped with multiple collectors that have a sufficient mass-range to collect the Pb isotopes and ^{238}U simultaneously. The addition of an electrostatic sector to the mass-analyser is a favourable option: it allows operation at higher mass-resolution which diminishes the number of isobaric interferences. The new mass-analyser and detection systems are described further by Halliday *et al.* (1998a,b).

Multicollection has several important advantages. It avoids the need for very rapid peak-switching imposed on single-collectors by the fast rise and fall of laser-ablated material. It also allows the counting of all the U and Pb ions per laser pulse that can be transmitted to the collector, rather than the *c.* 10% duty-cycle limit imposed by peak-switching. Finally, it removes the effects of variations in the collected ion count-rates that are caused by variation in the operation of the plasma-source or the laser. Multiple-collector SIMS also enjoys the same advantages.

However, to achieve *micro-* as distinct from bulk analysis, it is vital that the multicollectors should be multiple *ion-counting* detectors, rather than Faraday cup detectors. This demands that the relative gains of the detectors should remain constant to better than 0.1% per analytical session, which has yet to be documented. Furthermore, it should be realized that multicollection is not the only way of cancelling noise in

the measured ratios due to fluctuations in the plasma source (ICPMS) or the primary beam (SIMS). Variations in the collected secondary ions in SIMS may be nulled by ratioing to concurrent values for the primary beam or a small fraction of the total secondary beam. The latter procedure has been used since the early 1980s, e.g. for precise S isotope ratio measurement (Eldridge *et al.*, 1987).

All the above represent improvements to the mass-analyser part of ICPMS. Also required are improvements in the monitoring and control of elemental discrimination which is central to all Pb/U age determinations, and in the level of Hg and Pb contamination. Until the latter can be eliminated, large sample sizes will continue to be necessary to allow the dating of young and/or low U zircons at reasonable precision.

Halliday *et al.* (1998a,b) do not mention either the Hg contamination or the common Pb background in their review of ICPMS. As the sector instruments that they describe also employ the same plasma source and transfer system, there is no reason to suppose that these problems will be absent. Nor will the improved sensitivity of the latest sector instruments improve the ratio of background to sample.

Comparison of SIMS and laser-sampling ICPMS for Pb/U in zircon

The present advantages and disadvantages for each of these two techniques for Pb/U micro-analysis, as currently perceived by the author from the evidence given above, are summarized in Table 1.

Chemical Isochron Method (CHIME)

The acronym CHIME was coined by Suzuki and Adachi (1991). It represents an improvement of the early chemical method for age-determinations, in which the total Pb found in a bulk sample is allocated between its parental U and Th on the assumptions that each decay-scheme records the same age and the common Pb is negligible in amount compared with the radiogenic. CHIME is carried out using the electron microprobe, with its advantages of greater accuracy in elemental analysis over the early wet-chemical analysis, and with adequate iteration in assigning the total Pb between the three parent isotopes (Bowles, 1990; Montel *et al.*, 1996). By far its greatest advantage is the μm -scale sampling, and μm -scale effects in uraninite (Bowles, 1990) and in

TABLE 1. Advantages and disadvantages of SIMS and ICPMS for U/Pb microanalysis

Advantages	
SIMS	ICPMS
High depth- and spatial-resolution	Short analysis time
Stable sample signal	Small and less expensive
No background or memory effects	
Monitors variable Pb/U discrimination	
Pb/U accuracy <1%	
Disadvantages	
SIMS	ICPMS
Big and expensive	Hg and Pb contamination
Complex if fitted for all applications	Pb/U discrimination not monitored
Slower per analysis	Lower accuracy for Pb/U
Different sensitivities per element	Large samples for young/low U minerals

monazite and zircon have been documented (Suzuki and Adachi, 1991). The latter have recorded edge-related contours in Pb/Th ages within single monazite grains that signify diffusive Pb loss during metamorphism. They have also shown the presence of tightly grouped Pb/Th and Pb/U values in monazites and zircons from both crystalline and sedimentary rocks that can be interpreted only as discrete real ages, and which agree with geological constraints and with the results of independent isotopic methods.

Nevertheless, the CHIME method has the considerable disadvantage that individual Pb isotopes cannot be measured so that U-Pb systematics cannot be determined. It can succeed only when the mineral has truly remained chemically closed, for which the only test available is replication of age within the grain to within errors. In addition, common Pb cannot be separated from radiogenic, which becomes crucial for young, low-U grains. However, the evident success of CHIME in the Mino Terrane (Suzuki *et al.*, 1991) and South Kitakami Terrane of Japan testifies both to chemical closure and to the very small proportions of common Pb in most monazites and zircons.

SHRIMP developments

With respect to the SIMS instrument SHRIMP, precision in Pb/U age better than 1% can be achieved routinely per single analysis for 500 Ma old minerals having U contents >100 ppm from a pit 1 μm deep and 20 μm diameter. For 2500 Ma old minerals, the precision for the $^{207}\text{Pb}/^{206}\text{Pb}$ age can be $\sim \times 10$ higher.

The above figures refer to a single ion-counting collector. A multiple ion-counting collector has been designed, built and assembled but not yet tested. Its principal benefit will be in the improved duty-cycle for U-Pb geochronology, which should improve the above figures by a factor of ~ 3 . Further SHRIMP development includes improving the useful yield, as there is evidence that not all of the usable secondary ions produced from zircon are transmitted to the mass-analyser object-slit.

A major goal is to increase the mass-resolution without loss in transmission, which will improve some existing geological applications and make important new applications feasible. The small isobaric interference at ^{204}Pb observed in some zircons and monazites could be removed by operating at 10,000 R, while isobars at the Sr isotopes could be removed at 15,000 R. To this end, a second model SHRIMP, built at the RSES, uses a reverse-geometry mass-analyser with matching and correcting quadrupole lenses based on the 1990 family of ion optical designs by H. Matsuda. The tuning of this instrument is now underway.

Acknowledgements

I.S. Williams provided the illustrations and data for the Cowra grain 16, and ion-probe staff and students at the Research School of Earth Sciences carried out round-the-clock analyses of SL13 and other reference zircons. L.P. Black, Australian Government Survey Organization, supplied many SL13 and QGNG data from long sessions. I. Campbell and M. Palin provided their raw data

for ICPMS zircon analyses on which my assessment of the technique for zircon geochronology is based. I am most indebted to the above colleagues for their help and associated discussion.

It was some 23 years ago when the decision was taken to build a large ion microprobe at the Research School of Earth Sciences. A very early step was to visit Jim Long at the University of Cambridge to seek his advice, which we have done intermittently ever since and for which we are most grateful.

Finally, I thank the Mineralogical Society for the honour of the Hallimond Lecture and for the pleasure of participating in the Jim Long Symposium.

References

- Bowles, J.F.W. (1990) Age dating of individual grains of uraninite in rocks from electron microprobe analyses. *Chem. Geol.*, **83**, 47–53.
- Chappell, B.W., and White, A.J.R. (1974) Two contrasting granite types. *Pacific Geol.*, **8**, 173–4.
- Compston, W., Williams, I.S. and Meyer, C. (1984) U-Pb geochronology of zircons from lunar breccia 73217 using a sensitive high mass-resolution ion microprobe. *Proc. 14th Lunar Planet. Sci. Conf.: J. Geophys. Res.* **89**, B525–34.
- Claoué-Long, J.C., Compston, W., Roberts, J. and Fanning, C.M. (1996) Two carboniferous ages: a comparison of SHRIMP zircon dating with conventional zircon ages and ⁴⁰Ar/³⁹Ar analysis. *SEPM Special Publication*.
- Eldridge, S., Compston, W., Williams, I.S., Walshe, J.L. and Both, R.A. (1987) In situ microanalysis for ³⁴S/³²S using the ion microprobe SHRIMP. *Int. J. Mass Spectrom. and Ion Processes*, **76**, 65–83.
- Halliday, A.N., Lee, D.-C., Christensen, J.N., Rehkämper, M., Yi, W., Luo, Z., Hall, C.M., Ballentine, C.J., Pettke, T. and Stirling, C. (1998a) Applications of multiple collector ICPMS to cosmochemistry, geochemistry and paleoceanography. *Geochim. Cosmochim. Acta*, **62**, 919–40.
- Halliday, A.N., Christensen, J.N., Lee, D.-C., Rehkämper, M., Hall, C.M., and Luo, X. (1998b) *Multiple Collector ICP-MS. Inorganic Mass Spectrometry: Fundamentals and Applications.* (C.B. Barshick, D.C. Duckworth and D.H. Smith, eds). Marcel Dekker Inc. New York (*in press*).
- Lee, J.K.W., Williams, I.S. and Ellis, D.J. (1997) Pb, U and Th diffusion in natural zircon. *Nature*, **390**, 159–62.
- Mattinson, J.M., Graubard, C.M., Parkinson, D.L. and McClelland, W.C. (1996) *U-Pb Reverse Discordance in Zircons: the role of fine-scale oscillatory zoning and sub-micron transport of Pb. Earth Processes: Reading the Isotopic Code.* Geophysical Monograph **95**, 355–370, American Geophysical Union.
- Montel, J.-M., Foret, S., Veschambre, M. Nicollet, C. and Provost, A. (1996) Electron microprobe dating of monazite. *Chem. Geol.*, **131**, 37–53.
- Paces, J.B. and Miller, J.D. (1989) Precise U-Pb ages of the Duluth Complex and related mafic intrusions. *J. Geophys. Res.*, **98B**, 13997–4013.
- Sambridge, M.S. and Compston, W. (1994) Mixture modelling of zircon ages. *Earth Planet. Sci. Lett.*, **128**, 373–90.
- Silverman, B.W. (1986) *Density estimation for statistics and data analysis.* Chapman & Hall, London, 175 pp.
- Suzuki, K. (1987) Discordant distribution of U and Pb in zircon of Naegi granite: a possible indication of Rn migration through radiation damage. *Geochem. J.*, **21**, 173–82.
- Suzuki K. and Adachi, M. (1991) The South Kitakami terrane, Northeast Japan, revealed by the chemical Th-U-total Pb isochron ages of monazite, zircon and xenotime. *Geochem. J.*, **25**, 357–76.
- Suzuki, K., Adachi, M. and Tanaka, T. (1991) Middle Precambrian provenance of Jurassic sandstone in the Mino Terrane, central Japan: Th-U-total Pb evidence from an electron microprobe monazite study. *Sedim. Geol.*, **75**, 141–7.
- Williams, I.S. (1992) Some observations on the use of zircon U-Pb geochronology in the study of granitic rocks. *Trans. Roy. Soc. Edinburgh*, **83**, 447–58.

[Manuscript received 22 February 1999]