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The application of SHRIMP to Phanerozoic geochronology; a critical appraisal of four zircon standards

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Abstract

Derivation of Phanerozoic zircon $^{206}Pb/^{238}U$ ages by SHRIMP depends on calibration against an independently dated standard. The qualities of four different zircon standards (SL13, QGNG, AS3 and TEMORA 1) are assessed herein. Not all of these behave consistently on SHRIMP with respect to their ages as determined by IDTIMS. SL13, the most commonly used standard over the past decade and a half, is the most heterogeneous in Pb/U. In addition, when SL13 is used as the calibration standard, the varied ages resulting from that heterogeneity are generally younger than ages derived from the other three standards. AS3-calibrated ages are the oldest of the group. Only QGNG and TEMORA 1, when calibrated relative to each other, yield ages on SHRIMP that are consistent with their IDTIMS ages. Of these two, TEMORA 1 has the distinct advantage of producing consistent IDTIMS ages at high precision. Because of these factors and its availability, we recommend its use in geological studies where precise and accurate Pb/U zircon ages are imperative. Approximate conversion factors have been derived to improve quantitative inter-comparison between SHRIMP ages that have been calibrated against the different standards. These refinements significantly advance the role that SHRIMP can play in the numerical calibration of the Phanerozoic timescale.

Keywords: Zircon; U–Pb, geochronology; Ion probe; SHRIMP method; Phanerozoic; Time scales

1. Introduction

The ^{238}U–^{206}Pb radioactive decay scheme is almost exclusively employed for SHRIMP zircon dating of comparatively young rocks (younger than about 1000 Ma), because the relatively small amount of ^{207}Pb accumulated during that time does not permit precise $^{207}Pb/^{206}Pb$ dating. Utilisation of the $^{238}U/^{206}Pb$ method, however, is complicated by the fact that metallic ions of those isotopes are produced in a very different proportion to their atomic counterparts within the zircon. Correction for this effect involves the joint analysis of zircon of known age ("the standard"), quantifying the ionisation bias obtained for that

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standard, and then applying that correction factor to the unknowns. The variable discrimination is described by Claoué-Long et al. (1995) as following the relationship $Pb^+/U^+ = a(UO^+/U^+)^b$, where b was suggested to have a value of 2.0. Traditionally, this procedure has been accomplished by comparing $\ln(^{206}Pb^+/^{238}U^+)$ vs. $\ln(^{238}U^{16}O^+/^{238}U^+)$ for both the standards and the unknowns (Claoué-Long et al., 1995). Zircons of equivalent age appear as a linear trend (Fig. 1), with older suites plotting on a trend of similar slope (given by the exponent, b) higher on the diagram. Vertical offset provides a direct measure of age difference, which is essentially independent of the slope assigned to the alignments, providing they have a similar range in UO/U.

Recently, Ludwig (2002) has developed an alternative method of data processing (SQUID), in which the relevant parameter that is used for the correction of Pb/U fractionation is $(^{206}Pb^+/^{238}U^+)/(^{238}U^{16}O^+/^{238}U^+)^b$. This is calculated using the analyses of the zircon standard from the data acquired during each of the analytical scans (five for every individual analysis of this study). The assumption that Pb/U fractionation for the standards is the same as that for the unknown zircons is common to both data processing methods.

Because it is critical to the derivation of Pb/U ages, a standard needs to meet several strict requirements. It must have been dated accurately and precisely by an independent method. The zircon should have constant Pb/U from the sub-micron to the intergranular scale, which normally requires it to represent a single generation of growth that did not experience later isotopic disturbance. A standard should ideally be sufficiently abundant to be used indefinitely.

About a dozen different samples have been tested as zircon standards at the Research School of Earth Sciences (RSES), Australian National University—Geoscience Australia (GA, formerly AGSO) laboratory over the past two decades. Some of these have subsequently become in-house standards. This article compares the characteristics of four of the most recently used standards, each of which is of quite different age. Three of these standards (SL13, AS3 and QGNG) have been in use for some years, whereas the fourth (TEMORA 1) is a recent initiative.

Because of the volume of the experimental data, only the most important details of their interpretation are reported here. Details of the more than 1000 individual SHRIMP analyses are available on request from the senior author.

2. Origin of the different standards

SL13, unlike the other three standards, consists of fragments derived from a single megacryst of gem-quality zircon. The nature of its original host rock is speculative, with both igneous (pegmatite) and meta-

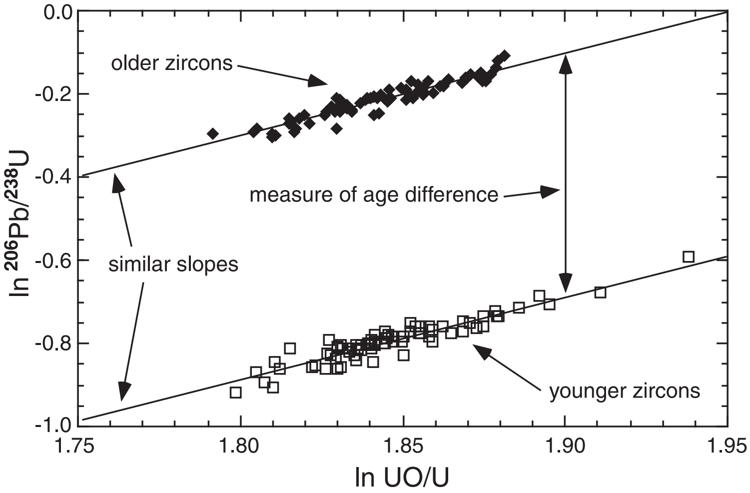


Fig. 1. $^{238}U^{16}O^+/^{238}U^+ - ^{206}Pb^+/^{238}U^+$ diagram to illustrate the principle of SHRIMP Phanerozoic zircon dating (see text). It depicts a calibration slope of two, and two zircon suites separated in age by 750 million years.

morphic (marble and paragneiss) hosts having been proposed (Kinny et al., 1991). One advantage of SL13 over the other standards is its relatively constant U and Th content (~ 240 ppm ± 20%), which allows elemental concentrations of concurrently analysed zircons to be estimated with moderate accuracy.

QGNG zircons are derived from an outcrop of coarse-grained Palaeoproterozoic quartz gabbronorite gneiss from the Donington Suite, in the Precambrian Gawler Craton of South Australia (Mortimer et al., 1988).

AS3 zircons come from the anorthositic series of mafic rocks in the composite Mesoproterozoic Duluth Complex of northeastern Minnesota (Paces and Miller, 1993).

TEMORA 1 zircons are derived from the Middledale Gabbroic Diorite (Wormald, 1993; Warren et al., 1995), a high level stock in the Palaeozoic Lachlan Orogen of eastern Australia.

3. IDTIMS documentation

3.1. SL13

Claoué-Long et al. (1995) list 19 individual IDTIMS analyses for SL13. These results were obtained at RSES in the early 1980s (nine analyses) and in the early 1990s (three analyses), and at the Geological Survey of Canada (Roddick and van Breemen, 1994) in the early 1990s (seven analyses). Despite the diverse sources of the data, the measured ^{206}Pb/^{238}U values of these 19 megacryst fragments are remarkably consistent, and yield a weighted mean age of 572.1 ± 0.4 Ma (2σ). Claoué-Long et al. (1995) report that, except for some of the earliest analyses, ^{207}Pb/^{206}Pb is also constant, a point exemplified by all seven precise analyses of Roddick and van Breemen (1994). The latter authors also demonstrated that their combined data, with a weighted mean ^{207}Pb/^{206}Pb age of 576.3 ± 0.8 Ma (2σ), are on average ~ 0.7% discordant. Based on the results of Mortensen et al. (1992), they attributed that discordance (an undesirable characteristic for a standard) to an excess of ^{207}Pb, possibly due to the extraneous incorporation into the zircon crystal of ^{231}Pa, an intermediate decay product of the ^{235}U decay series. However, if the U decay-constant uncertainties reported by Mattinson (1987) are taken into account, the probability of concordance (0.16) is not diminishingly low.

3.2. AS3

The U–Th–Pb characteristics of this zircon were well documented by Paces and Miller (1993) as part of a regional study of the Duluth Complex. Two members each from the anorthositic and the troctolitic series yield precise, indistinguishable ages of 1099 Ma. All six analyses of AS3 (from the Duluth area) produced consistently concordant data, with weighted mean ^{206}Pb/^{238}U and ^{207}Pb/^{206}Pb ages, and 95% precision limits of 1099.0 ± 0.7 and 1099.1 ± 0.5 Ma, respectively.

3.3. QGNG

Initial IDTIMS documentation of this standard was by G.E. Mortimer and C.M. Fanning. Although the data are still to be published, their concordia intercept age of 1849.8 ± 1.1 Ma (2σ) has been formally reported by Daly et al. (1998). None of the 10 analyses are concordant, but two of the three single-grain analyses approach concordance (Mortimer, personal communication, 1999). A subsequent study by Dougherty-Page and Bartlett (1999) using the evaporation technique (Kober, 1987) produced an indistinguishable age of 1850.0 ± 1.2 Ma (2σ). Four zircon grains were analysed for a total of 41 heating steps. There is the possibility of some subjectivity in their selection of the 19 heating-steps from which the age was calculated because there is no totally unambiguous definition of either the young or old end of the chosen age plateau. It should also be emphasised that as this technique does not allow an estimate of concordance, resultant data reflect only ^{207}Pb/^{206}Pb ages, which may represent merely an older limit for ^{206}Pb/^{238}U ages.

Because of these limitations, further IDTIMS dating of QGNG was initiated (Table 1), at both the Berkeley Geochronology Center (BGC) and at the Royal Ontario Museum (ROM). Slightly different pre-dissolution procedures were employed at the two laboratories, with the objective of obtaining as concordant data as possible. The ROM procedure was to abrade each fraction in air (Krogh, 1982) in order to remove any exterior surfaces that might have lost Pb.

Table 1
U–Pb isotopic data for single zircon crystals of QGNG obtained by IDTIMS

Analysis		Comment	Abraded leached	Weight (mg)	U (ppm)	Th/U	PbCom (pg)	207/204	206/238	2σ	207/235	2σ	207/206	2σ	ρ	206/238 age (Ma)	2σ	207/235 age (Ma)	2σ	207/206 age (Ma)	2σ
	ROM																				
1	sk13p52	1 whole grain, colourless	A	0.023	459	0.53	0.9	28,586	0.3319	0.0011	5.178	0.018	0.11315	0.00009	0.97	1847.5	5.2	1848.9	3.0	1850.6	1.5
2	sk13p53	1 whole grain, colourless	A	0.007	366	0.75	1.3	4720	0.3301	0.0008	5.151	0.012	0.11317	0.00015	0.84	1839.0	3.7	1844.6	2.1	1850.9	2.4
3	sk13p54	1/2 grain, colourless	A	0.006	289	1.02	1.0	4155	0.3307	0.0007	5.161	0.013	0.11319	0.00010	0.93	1841.6	3.5	1846.1	2.2	1851.2	1.7
4	sk13p55	1 fragment, colourless	A	0.006	261	1.05	1.0	3829	0.3304	0.0009	5.158	0.016	0.11322	0.00012	0.94	1840.5	4.6	1845.8	2.6	1851.8	1.9
5	sk13p63	1 whole grain, colourless	A	0.008	697	0.68	0.9	14,500	0.3323	0.0009	5.186	0.015	0.11319	0.00012	0.92	1849.4	4.2	1850.3	2.4	1851.3	2.0
6	sk13p73	grain amount #4 NO CHEM	A	0.002	399	1.00	0.4	4438	0.3306	0.0009	5.159	0.015	0.11319	0.00012	0.93	1841.1	4.2	1845.8	2.4	1851.2	1.9
7	sk13p74	grain amount #268 NO CHEM	A	0.001	627	0.66	0.4	3963	0.3316	0.0011	5.173	0.018	0.11316	0.00012	0.95	1846.0	5.1	1848.3	2.9	1850.8	1.9
8	sk13p75	grain amount #276	A	0.015	405	0.72	0.6	24,136	0.3311	0.0010	5.167	0.016	0.11317	0.00012	0.94	1843.9	4.7	1847.2	2.7	1850.9	2.0
9	sk13p62	1 whole grain, pale brown	A	0.020	1151	0.38	3.0	18,022	0.3268	0.0010	5.086	0.016	0.11287	0.00009	0.97	1822.8	4.7	1833.7	2.7	1846.2	1.5
	BGC																				
1	QGNGZ01		A/L	0.0057	162	1.08	1.7	1201	0.3081	0.0016	4.806	0.026	0.11311	0.00014	0.97	1731.5	9.1	1785.9	9.8	1850.0	2.3
2	QGNGZ02		A/L	0.0057	35	0.83	3.9	122	0.2910	0.0009	4.502	0.028	0.11219	0.00060	0.54	1646.5	4.9	1731.2	11.0	1835.3	9.7
3	QGNGZ03		A/L	0.0042	49	1.02	0.6	784	0.3227	0.0014	5.028	0.026	0.11299	0.00028	0.88	1803.1	8.1	1824.0	9.5	1848.1	4.5
4	QGNGZ04		L	0.0032	166	0.94	1.9	659	0.3172	0.0025	4.927	0.040	0.11265	0.00019	0.98	1776.3	14.1	1806.9	14.7	1842.5	3.0
5	QGNGZ05		L	0.0035	157	0.99	1.8	606	0.2750	0.0008	4.227	0.014	0.11148	0.00016	0.91	1566.2	4.7	1679.3	5.7	1823.6	2.6
6	QGNGZ06		L	0.0048	74	0.89	1.8	427	0.2896	0.0006	4.471	0.012	0.11198	0.00018	0.81	1639.6	3.1	1725.7	4.6	1831.8	2.9
7	QGNG07		L	0.0071	90	1.04	2.0	692	0.3030	0.0020	4.693	0.032	0.11233	0.00022	0.96	1706.2	11.0	1766.0	12.0	1837.5	3.6
8	QGNGZ08		A	0.0009	231	1.02	5.5	105	0.3306	0.0020	5.177	0.041	0.11355	0.00058	0.77	1841.5	10.9	1848.8	14.8	1857.0	9.2
9	QGNGZ09		A	0.0008	202	0.95	1.4	294	0.3270	0.0009	5.113	0.017	0.11341	0.00021	0.84	1823.8	4.7	1838.3	6.1	1854.8	3.3
10	QGNGZ10-1		A	0.0005	172	0.99	2.0	117	0.3261	0.0022	5.082	0.043	0.11302	0.00055	0.82	1819.6	12.0	1833.1	15.4	1848.6	8.8
11	QGNGZ10-2		A	0.0017	141	0.87	8.7	69	0.2776	0.0034	4.225	0.064	0.11037	0.00095	0.82	1579.3	19.1	1678.8	25.4	1805.6	15.7
12	QGNGZ11		A	0.0005	315	1.01	2.8	148	0.3315	0.0017	5.187	0.032	0.11347	0.00040	0.83	1845.9	9.2	1850.5	11.9	1855.7	6.3
13	QGNGZ15		A	0.0021	232	0.99	1.6	725	0.3295	0.0032	5.150	0.050	0.11336	0.00014	0.99	1835.9	17.6	1844.4	17.9	1854.0	2.3

Th/U is calculated from the ^{208}Pb/^{206}Pb ratio and the ^{207}Pb/^{206}Pb age.

PbCom is total common Pb, and assumes all has laboratory blank isotopic composition.

% Disc is percent discordance assuming zero-age Pb loss.

The resultant data (Fig. 2) form a group of eight analyses and a lone, more discordant, analysis. The latter represents a grain that was more highly coloured (pale brown) and had higher U (by 450 ppm) and higher common Pb (by a factor of three) than any of the other ROM analyses. These characteristics of the brown grain are typical of discordant zircon, and are not representative of the QGNG zircon (selected on the basis of stronger cathodoluminescence, which equates with relatively low U) that is preferentially targeted for SHRIMP analysis. The isotopic composition of the latter zircon should be more typical of the other eight, comparably low-U, ROM analyses (and the three most concordant BGC analyses—see below). The eight near-concordant ROM analyses have mutually indistinguishable $^{207}Pb/^{206}Pb$ (MSWD = 0.6, probability of fit = 0.76), with a weighted mean age of 1851.6 ± 0.6 Ma (2σ). They represent five whole grains, and three that had been polished down to about half of their section in a resin mount.

In contrast to $^{207}Pb/^{206}Pb$, there is a significant spread ($\chi^2 = 3.0$) in $^{206}Pb/^{238}U$ for the eight grouped ROM analyses, and it is also clear that although some are within error of concordia, the group as a whole is discordant if only measurement uncertainties are considered. The weighted mean $^{206}Pb/^{238}U$ age for these data is 1842.0 ± 3.1 Ma (95%, taking the excess scatter into account), equivalent to an average 0.5% loss of Pb from the zircon in geologically recent times if only measurement uncertainties are considered. However, if the decay-constant uncertainties reported by Mattinson (1987), together with uncertainties associated with the calibration of the ROM spike (± 0.26%, 2σ), are taken into account, the probability of concordance (0.12), although low, cannot be totally excluded.

All zircons analysed at the BGC were selected from the same resin mount that provided zircon for three of the ROM analyses. However, in this instance, some of the individual grains were abraded prior to dissolution, others were leached in HF, and the remainder were treated by both processes (Table 1). The three most concordant BGC analyses yield a weighted mean $^{206}Pb/^{238}U$ age of 1842.9 ± 6.5 Ma (MSWD = 0.6,

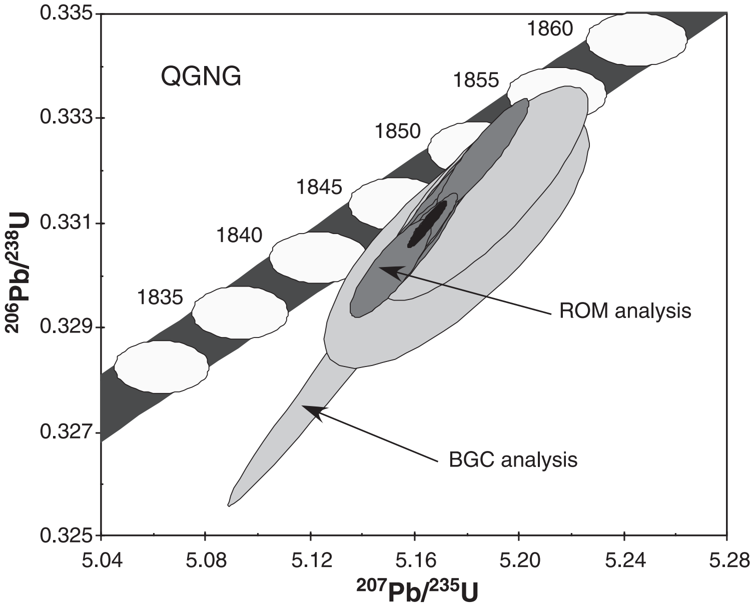


Fig. 2. $^{207}Pb/^{235}U$–$^{206}Pb/^{238}U$ concordia diagram showing the newly acquired near-concordant IDTIMS analyses of QGNG (from Table 1) with ± 2σ error ellipses. The concordia itself is depicted as a band that incorporates the uncertainty of the U decay constants. The three BGC analyses are shown in pale grey, whereas the eight ROM analyses are a darker shade of grey; the black ellipse at their centre represents the weighted average of the ROM results. The BGC and ROM data are slightly displaced from each other.

probability of fit = 0.57) that is indistinguishable (probability of equivalence = 0.80) from the corresponding ROM age of 1842.0 ± 3.1 Ma. The remaining 10 BGC analyses are considerably more discordant (Fig. 3). The three near concordant BGC analyses also have mutually indistinguishable ^{207}Pb/^{206}Pb (1854.4 ± 2.1 Ma, MSWD = 0.3, probability of equivalence = 0.75). However, the 0.15% difference between the mean ^{207}Pb/^{206}Pb ages from the two laboratories is outside the quoted errors (probability of equivalence = 0.010). An offset of this order is puzzling, but possibly relates to common Pb correction, because there is a significant difference between the common Pb levels in the analyses from the two laboratories. The results from the ROM are used as the reference, not only because they involve more near-concordant analyses, but also because new standards that will be inter-compared in a forthcoming publication (Black et al., in preparation) have only been analysed at the ROM. Consistent use of results from a single laboratory should minimize the possibility of instrumental and analytical protocol biases being factors in the detailed inter-comparison of standards.

The features described above (notably a distinct possibility of non-concordance, and a significant spread in ^{206}Pb/^{238}U) are not desirable characteristics for a zircon standard. Nevertheless, providing the ± 0.4% spread in ^{206}Pb/^{238}U exhibited by the 11 near-concordant IDTIMS analyses is also reasonably representative of heterogeneity on the much smaller volumes sampled by SHRIMP, this would not be detectable at the reduced precision offered by SHRIMP analysis. This might explain the consistency of QGNG-calibrated ^{206}Pb/^{238}U SHRIMP ages that is documented below.

The possibility of discordance of the near-concordant QGNG IDTIMS analyses (when they are considered as a group) poses another question—which of the ages should be used as the reference for ^{206}Pb/^{238}U dating? Clearly, it should be the age of the material being analysed by SHRIMP, but what does this actually represent? Valid use of the ^{207}Pb/^{206}Pb IDTIMS age would require that SHRIMP analyses be made on parts of the zircon that have not lost radiogenic Pb. Conversely, using the ^{206}Pb/^{238}U IDTIMS age as the reference is

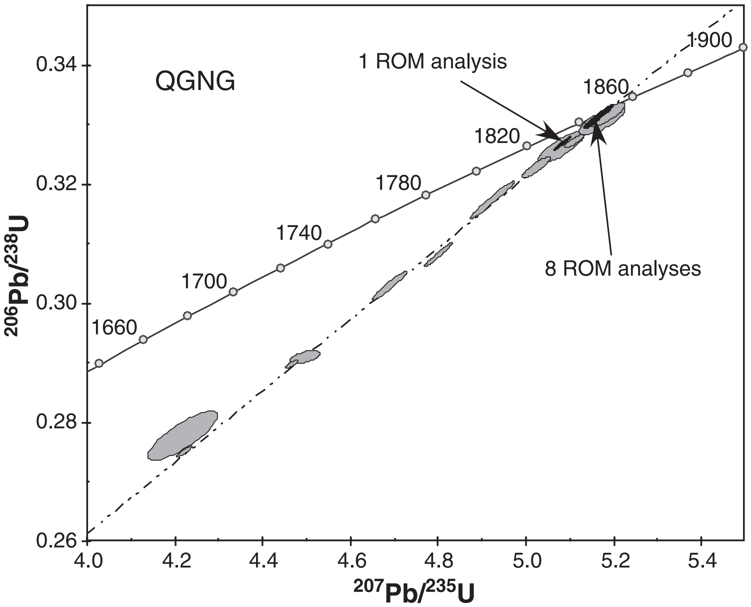


Fig. 3. ^{207}Pb/^{235}U – ^{206}Pb/^{238}U concordia diagram showing all of the BGC (pale grey) and ROM (dark) IDTIMS data for QGNG. The most discordant analyses are presumed to represent grains from which regions of high Pb loss were not completely removed prior to analysis. Detail of the near-concordant analyses is provided in Fig. 2.

consistent with all or most of the zircon having lost about 0.5% of its radiogenic Pb. IDTIMS analyses of three other zircon standards (Black et al., 2003, in preparation) indicate that the abrasion technique in use at the ROM combined with careful picking can completely remove isotopically disturbed zircon. However, significant dispersion within the eight near-concordant analyses indicates that this was not achieved with QGNG. The easiest way to reconcile those observations is to conclude that isotopically pristine zircon is (at best) rare in QGNG, the least disturbed regions having, on average, lost about 0.5% of their Pb. Cathodoluminescence images, which are used to select the sites of SHRIMP analyses, commonly show that QGNG grains have poorly luminescent exteriors. These areas are high in U, most probably represent the main sites of Pb loss, and are avoided during SHRIMP dating. It is probable that the non-complete removal of these high-U rims is responsible for the strongly discordant BGC analyses. Calibrating QGNG against other precisely dated standards such as TEMORA 1 (this study, see below; Black et al., 2003) produces ^{206}Pb/^{238}U ages that agree with TIMS values when the QGNG ^{206}Pb/^{238}U age is used, but are beyond error when the ^{207}Pb/^{206}Pb age is used. Thus, it seems probable that the volumetrically dominant interiors of QGNG grains have lost about 0.5% of their radiogenic Pb, and it is most appropriate to use the ^{206}Pb/^{238}U age of 1842.0 ± 3.1 Ma as the reference value for SHRIMP dating.

3.4. TEMORA 1

The IDTIMS age of this standard has been established by 21 analyses of single grains, single fragments, or many fragments from analyses made at the Royal Ontario Museum (Black et al., 2003). The analyses show no significant scatter (MSWD = 1.14 for ^{206}Pb/^{238}U), and are within error of concordia when the uncertainties in the decay constants for ^{238}U and ^{235}U as reported by Mattinson (1987) are taken into account. Its ^{206}Pb/^{238}U IDTIMS age has been determined to be 416.75 ± 0.24 Ma (95% confidence limits), based on measurement errors alone. Black et al. (2003) recommend that to accommodate the spike-calibration uncertainty of 0.26% (2σ), a value of 416.8 ± 1.1 Ma should be used for U–Pb inter-comparison between laboratories using different Pb/U spikes.

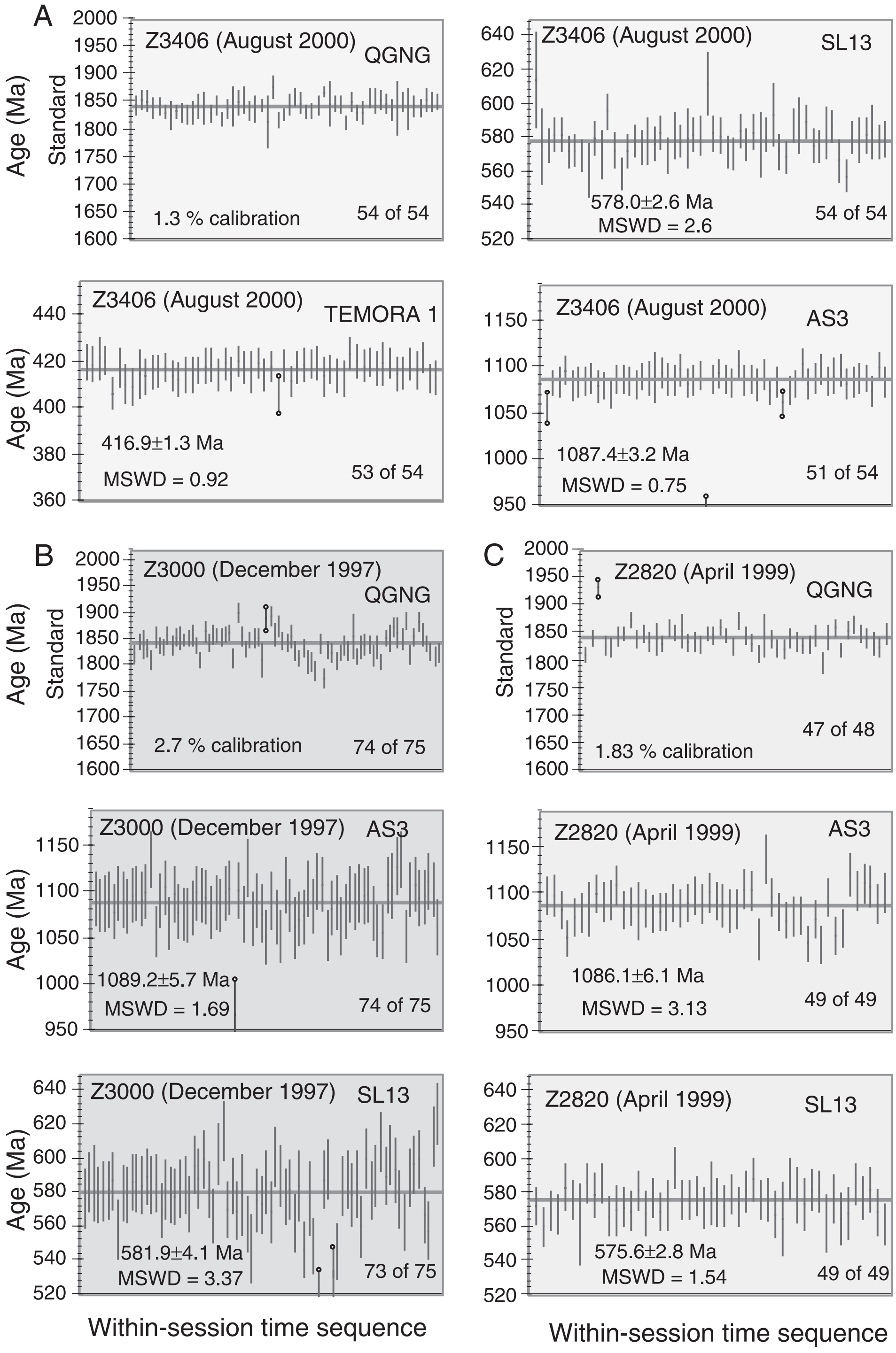
4. SHRIMP analytical procedures

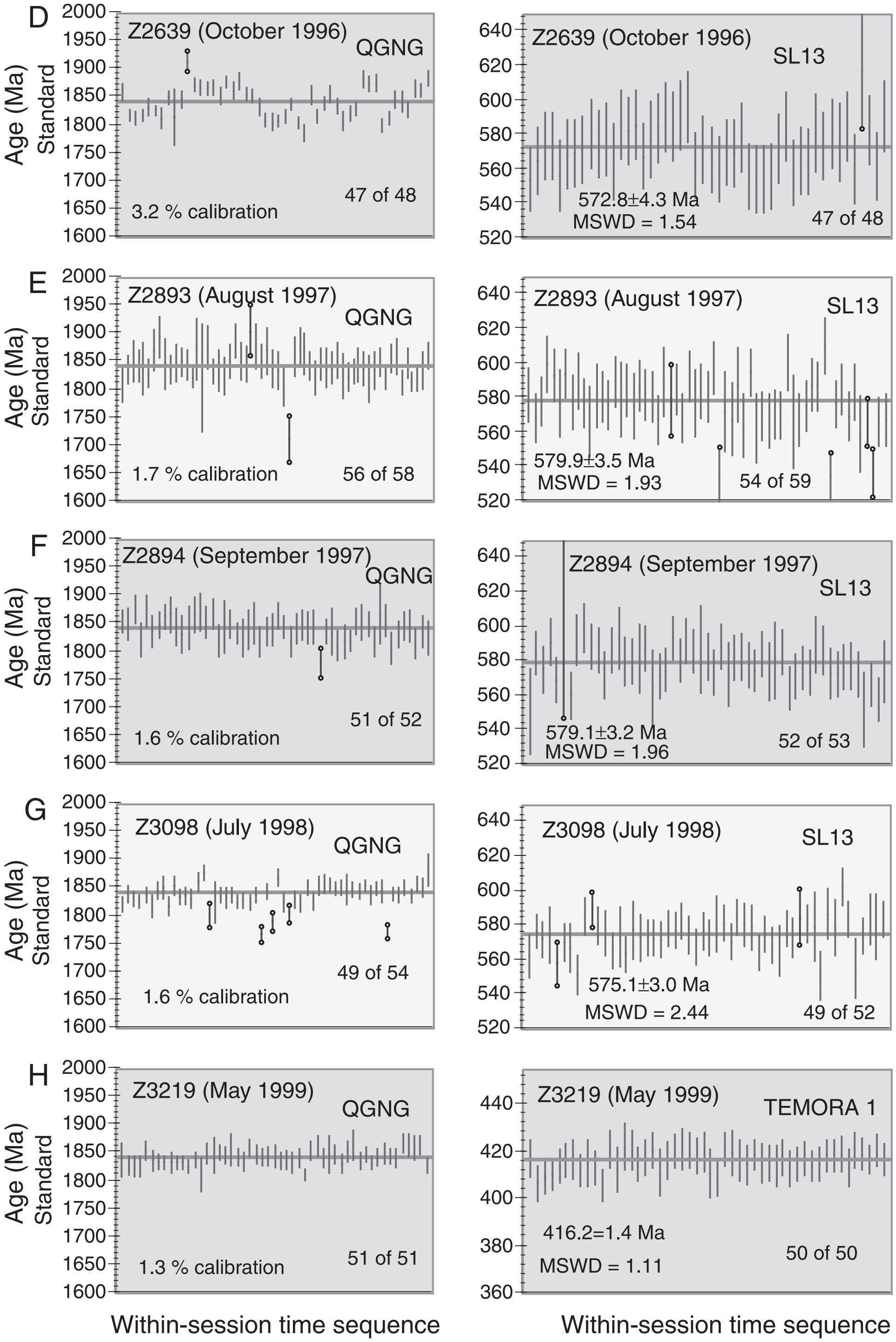
Analytical procedures are largely based on those reported by Compston et al. (1984), Claoué-Long et al. (1995), Williams et al. (1996) and Williams (1998). Data were mostly acquired from five cycles between the isotopic species—Zr_2O, ^{204}Pb, background, ^{206}Pb, ^{207}Pb, ^{208}Pb, U, ThO and UO. ^{204}Pb-corrected data are reported throughout this article. The SQUID software of Ludwig (2002) has been used as the primary data processing platform. Although not explicitly reported here, the data have been processed also with the PRAWN-LEAD program of T.R. Ireland to confirm that there are no significant differences in the ages produced by the two techniques. Unless otherwise specified, all reported errors define 2σ confidence limits.

In all but three of the experiments, the canonical value of 2.0 (Claoué-Long et al., 1995) has been used as the exponent in the equation used to correct for variable fractionation of Pb/U. The three exceptions (1.81 for Z3406, August 2000; 2.28 for Z2893, August 1997; 2.70 for Z2894, September 1997) have values that are clearly different from 2.0. Assignment of different values for the exponent has the potential to generate different ages, but only when there is a significant offset in the average and/or range of ln UO/U values between the different zircon suites under comparison. Selection of a different exponent can also alter which analyses appear as outliers, and might therefore be culled. However, in none of the following examples does the choice of assigned slope produce significantly different ages.

5. SHRIMP inter-comparisons

Ideally, the relative ^{206}Pb/^{238}U age differences determined by IDTIMS for the different zircon standards should directly correlate with their age differences as measured on SHRIMP. Due to the crucial role of the standard this relationship needs to be tested, and not just assumed. Consequently, a series of experiments, conducted on SHRIMP II, was designed to examine


A
Z3406 (August 2000) QGNG
Age (Ma) Standard
2000 1950 1900 1850 1800 1750 1700 1650 1600
1.3 % calibration
54 of 54
Z3406 (August 2000) SL13
640 620 600 580 560 540 520
578.0±2.6 Ma
MSWD = 2.6
54 of 54
Z3406 (August 2000) TEMORA 1
Age (Ma)
440 420 400 380 360
416.9±1.3 Ma
MSWD = 0.92
53 of 54
Z3406 (August 2000) AS3
1150 1100 1050 1000 950
1087.4±3.2 Ma
MSWD = 0.75
51 of 54
B
Z3000 (December 1997) QGNG
Age (Ma) Standard
2.7 % calibration
74 of 75
C
Z2820 (April 1999) QGNG
Standard
1.83 % calibration
47 of 48
Z3000 (December 1997) AS3
Age (Ma)
1089.2±5.7 Ma
MSWD = 1.69
74 of 75
Z2820 (April 1999) AS3
1086.1±6.1 Ma
MSWD = 3.13
49 of 49
Z3000 (December 1997) SL13
Age (Ma)
581.9±4.1 Ma
MSWD = 3.37
73 of 75
Z2820 (April 1999) SL13
575.6±2.8 Ma
MSWD = 1.54
49 of 49
Within-session time sequence
Within-session time sequence


D
Age (Ma) Standard
Z2639 (October 1996)
QGNG
3.2 % calibration
47 of 48
Z2639 (October 1996)
SL13
572.8±4.3 Ma
MSWD = 1.54
47 of 48
E
Z2893 (August 1997)
QGNG
1.7 % calibration
56 of 58
Z2893 (August 1997)
SL13
579.9±3.5 Ma
MSWD = 1.93
54 of 59
F
Z2894 (September 1997)
QGNG
1.6 % calibration
51 of 52
Z2894 (September 1997)
SL13
579.1±3.2 Ma
MSWD = 1.96
52 of 53
G
Z3098 (July 1998)
QGNG
1.6 % calibration
49 of 54
Z3098 (July 1998)
SL13
575.1±3.0 Ma
MSWD = 2.44
49 of 52
H
Z3219 (May 1999)
QGNG
1.3 % calibration
51 of 51
Z3219 (May 1999)
TEMORA 1
416.2=1.4 Ma
MSWD = 1.11
50 of 50
1600 1650 1700 1750 1800 1850 1900 1950 2000
520 540 560 580 600 620 640
360 380 400 420 440
Within-session time sequence
Within-session time sequence

this issue in depth. The centrepiece of the study is a high-quality SHRIMP session (summarised in Fig. 4A) carried out to inter-compare the Pb/U characteristics of all four standards. Supplementary information is supplied from seven other experiments that included some but not all of those standards (Fig. 4B–H). It is not possible to report even the majority of the scores of comparative studies that have been made (particularly between QGNG and SL13) over the past 7 years, but the most relevant of these are included. Also discussed are certain aspects of a poor quality session that provides valuable information on SHRIMP performance.

As reported above, one of the jointly analysed zircon suites must be selected as the reference standard in order to establish numerical ages for the others. Despite the uncertainty of its concordance, that role has been given to QGNG in this study because it is the only standard included in all of the experiments, and because it behaves in a predictable fashion on SHRIMP (see below). The strength of the design of the experiments is that each allows relative age differences to be determined for each of the analytical sessions, irrespective of the chosen calibration standard. Continuous analytical sessions lasting for several days were routinely used in this study in order to furnish large data sets (Fig. 4) acquired under relatively constant instrumental conditions, unencumbered by systematic errors associated with the setting up of a series of sessions.

Table 2
SHRIMP ^{207}Pb/^{206}Pb data for Proterozoic standards AS3 and QGNG

Session	AS3	QGNG
Z3406	1096.0 ± 4.4 (54 of 54)	1848.8 ± 2.7 Ma (54 of 54)
Z3000	1102.2 ± 2.5 Ma (75 of 75)	1853.1 ± 1.7 Ma (75 of 75)
Z2820	1093.2 ± 3.2 Ma (49 of 49)	1851.4 ± 1.7 Ma (49 of 49)
Z2820*	1099.2 ± 3.2 Ma (42 of 42)	1850.8 ± 1.9 Ma (42 of 42)
Z2983		1851.0 ± 3.1 Ma (57 of 58)
Z2984		1849.3 ± 3.6 Ma (52 of 52)
Z2639		1852.4 ± 1.6 Ma (46 of 48)
Z3219		1851.9 ± 2.3 Ma (48 of 51)
Z3098		1852.0 ± 2.4 Ma (51 of 54)
Weighted mean	1098.5 ± 6.6 Ma (MSWD = 7.1) prob. of equivalence = 0.000	1851.6 ± 1.0 Ma (MSWD = 1.4) prob. of equivalence = 0.19
IDTIMS ^{207}Pb/^{206}Pb	1099.1 ± 0.5 Ma	1851.6 ± 0.6 Ma

Note that uncertainties for the individual sessions represent two standard errors of the mean, whereas those reported for the grand totals are 95% confidence limits (in order to account for the excess scatter between the AS3 session ages). Numbers in parentheses below the ages indicate the number of analyses that have been combined to produce the reported age. None of those data combinations is significantly scattered at the 95% level of confidence.

* Denotes an analytical session that was not included in the assessment of ^{206}Pb/^{238}U analyses because it was complicated by a distinct calibration shift.

6. Comparison of the different analytical sessions

6.1. ^{207}Pb/^{206}Pb

QGNG, which was included in all experiments, yields a grand mean ^{207}Pb/^{206}Pb age of 1851.6 ± 1.0 Ma (Table 2) from nine large datasets (Fig. 5). This age is indistinguishable from the ^{207}Pb/^{206}Pb age of 1851.6 ± 0.6 Ma (2σ) provided by the eight near-concordant ROM IDTIMS analyses, and there is no significant scatter (at the 95% confidence level) in the pooled SHRIMP data (MSWD = 1.4, probability of equivalence = 0.18). As listed in Table 2, four of the

Fig. 4. Calibrated ages for the individual analyses during each of the eight SHRIMP analytical sessions (the time sequence within each session is from left to right). QGNG has been used as the calibration standard in all cases. The errors shown for the analyses in the other zircon suites have been augmented to take account of the uncertainty of the QGNG calibration. The latter is represented by the calculated 2σ spot-to-spot error of Ludwig (2002). Analyses that have been excluded from the mean age calculations are terminated by small circles. Most of the analyses that are shown as extending to the boundary of a box, extend beyond its confines. All depicted errors represent $\pm 2\sigma$. The numbers in the bottom right of each box indicate how many of the individual analyses have been retained for the calculation of the mean age. The information included in this diagram forms the basis for the data summaries depicted in Fig. 6. (A) Z 3406 (August 2000). (B) Z3000 (December 1997). (C) Z2820 (April 1999). (D) Z2639 (October 1996). (E) Z2893 (August 1997). (F) Z2894 (September 1997). (G) Z3098 (July 1998). (H) Z3219 (May 1999).

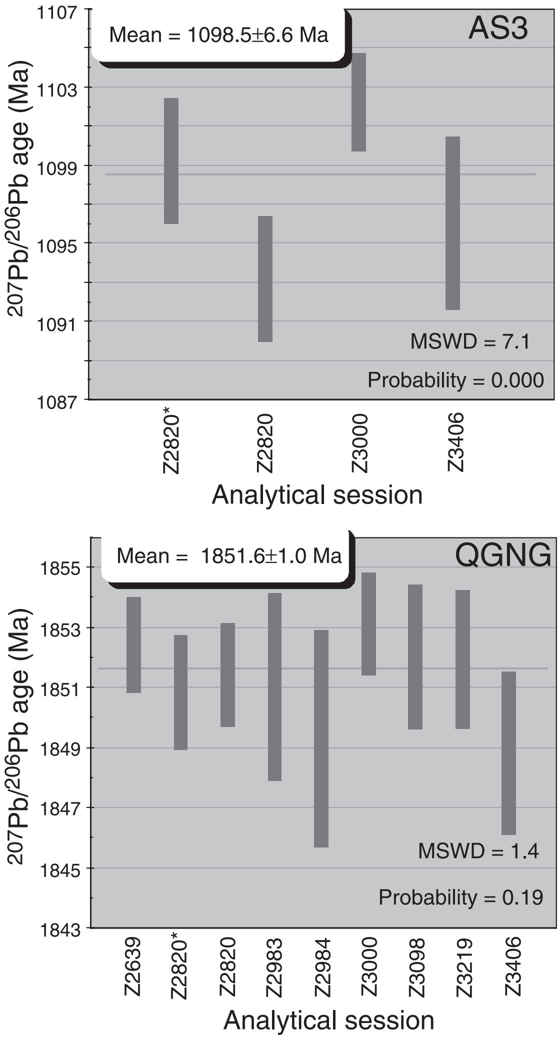


Fig. 5. Weighted mean $^{207}Pb/^{206}Pb$ ages for AS3 and QGNG for each of the sessions in which they were included. The QGNG results are not significantly dispersed at the 95% confidence level, but the AS3 results are dispersed.

nine sessions contain a small number of analyses that are significantly dispersed from the mean, but this is a very small effect, only involving nine $^{207}Pb/^{206}Pb$ ages out of 483.

All four sessions in which AS3 was included (Fig. 5) yield a grand mean $^{207}Pb/^{206}Pb$ age of 1098.5 ± 6.6 Ma (95%) for that standard (Table 2). Although this is indistinguishable from the corresponding IDTIMS age of 1099.1 ± 0.5 Ma (2σ), there is significant scatter in the data (MSWD = 7.1, probability of equivalence = 0.000), even though the concurrent, and inherently more discerning, QGNG analyses were well behaved. Even the exclusion of session Z2820, with its younger than normal $^{207}Pb/^{206}Pb$ ages, does not produce an acceptable MSWD (3.3, probability of equivalence = 0.037) for the AS3 analyses.

In summary, the SHRIMP and IDTIMS $^{207}Pb/^{206}Pb$ ages are in close agreement for both QGNG and AS3, indicating that SHRIMP does not produce any significant net fractionation of those isotopes. Not only is QGNG the theoretically most sensitive means of monitoring mass fractionation of this ratio (because of its enhanced Pb levels), but the data presented above suggest that its $^{207}Pb/^{206}Pb$ is more homogeneous than that of AS3 on SHRIMP analytical volumes.

6.2. $^{206}Pb/^{238}U$

The experiments described above reveal a wealth of information (Table 3, Figs. 4 and 6) about the $^{206}Pb/^{238}U$ characteristics of the different standards, not all of which is mutually consistent. Discussion of these results begins with the TEMORA 1–QGNG comparisons because, although only two in number, they are the product of two high quality analytical sessions, each of which encompassed at least 50 analyses of each of those standards.

6.2.1. TEMORA 1

The Z3406 session (August 2000) generates a QGNG-calibrated age of 416.9 ± 1.3 Ma from 53 of 54 analyses of TEMORA 1 with no rejects from QGNG. For Z3219, the corresponding age is 416.2 ± 1.4 Ma, without any rejection of QGNG or TEMORA 1 analyses (Fig. 4). The combined data are well within error of each other (MSWD = 0.54; probability of equivalence = 0.46), and the weighted mean age of 416.6 ± 1.0 Ma is indistinguishable from the average IDTIMS $^{206}Pb/^{238}U$ age of 416.75 ± 0.24 (416.8 ± 1.1 Ma if spike-calibration uncertainties are included). This agreement between SHRIMP and IDTIMS provides confidence not only in both of those standards, but also in the SHRIMP technique itself. It is recognised, however, that the possible non-concordance of the QGNG IDTIMS data is less than ideal, which has provided the incentive to move to TEMORA as the preferred standard. Nevertheless,

Table 3
Comparative SHRIMP ^{206}Pb/^{238}U data for the four zircon standards (calibrated against a QGNG age of 1842 Ma)

Session	Primary standard	AS3 Age (Ma)	TEMORA 1 Age (Ma)	SL13 Age (Ma)
Z3406	QGNG (54 of 54) (0.8%)	1087.4 ± 3.2 (51 of 54) (0.7%)	416.9 ± 1.3 (53 of 54) (0.8%)	578.0 ± 2.6 (54 of 54) (1.8%)
Z3000	QGNG (74 of 75) (1.4%)	1089.2 ± 5.7 (74 of 75) (1.9%)		581.9 ± 4.1 (73 of 75) (2.8%)
Z2820	QGNG (47 of 48) (1.0%)	1086.1 ± 6.1 (49 of 49) (1.8%)		575.6 ± 2.8 (49 of 49) (1.4%)
Z2893	QGNG (56 of 58) (1.2%)			579.9 ± 3.5 (54 of 59) (2.0%)
Z2894	QGNG (51 of 52) (1.1%)			579.1 ± 3.2 (52 of 53) (1.9%)
Z2639	QGNG (47 of 48) (1.6%)			572.8 ± 4.3 (47 of 48) (2.1%)
Z3219	QGNG (51 of 51) (1.0%)		416.2 ± 1.4 (50 of 50) (1.0%)	
Z3098	QGNG (49 of 54) (0.9%)			575.1 ± 3.0 (49 of 52) (1.7%)
Weighted mean		1087.5 ± 2.5 (MSWD = 0.28)	416.6 ± 1.0 (MSWD = 0.54)	577.4 ± 1.2 (MSWD = 2.8)
IDTIMS		1099.0 ± 0.7	416.75 ± 0.24	572.1 ± 0.4

Note that the age uncertainties in this table represent two standard errors of the mean. Numbers in parentheses directly below the ages indicate how many of the total analyses have been combined to produce the reported age. Percentage values in parentheses below the ages represent the coefficient of variation (one standard deviation expressed as a percentage) of the ^{206}Pb/^{238}U dataset from which the reported ages were derived: lower values define better quality data.

previous consistency between QGNG results (e.g. Black et al., 1997) is taken to signify that, with careful siting of the ion beam, it is reasonably easy to avoid areas of that standard that have experienced significant degrees of Pb loss. If the total spread of ^{206}Pb/^{238}U (0.65%) documented by the near-concordant IDTIMS analyses is also representative of heterogeneity at the scale of SHRIMP dating, this would not be discernible by the less precise (but nevertheless, accurate) SHRIMP method.

6.2.2. AS3

AS3 was measured during three of the sessions. These results are within error of each other (MSWD = 0.28, probability of equivalence = 0.75), and yield a weighted mean age of 1087.5 ± 2.5 Ma (Table 3, Fig. 6). Once again, very little culling has been imposed on the data, with only 2 of 177 QGNG analyses and 4 of 178 AS3 analyses being excluded (Table 3). Although the QGNG-calibrated ^{206}Pb/^{238}U ages for AS3 form a tight group, its weighted mean SHRIMP age is significantly younger (by close to 1.0%) than its IDTIMS age of 1099.0 ± 0.7 Ma at considerably more than the 99.9% confidence level.

One possible reason for this discrepancy is that the analysed AS3 grains might have lost a significant proportion of their radiogenic Pb. If correct, this would imply that the quality of the whole (abraded) grains used for IDTIMS analysis is superior to the zircon domains analysed by SHRIMP. In common with QGNG, the consistency of the SHRIMP–AS3 data would be interpreted to reflect a relatively small range of discordance that is hidden by the comparative imprecision of this technique. However, if Pb loss from AS3 does indeed provide the explanation for the offset between the SHRIMP and IDTIMS data, it is puzzling that the SHRIMP data do not define a range of ages that extends close to the AS3 IDTIMS age.

The latter relationship is more consistent with a matrix effect, as is discussed below for SL13. Any such matrix effect is unlikely to result from accumulated radiation damage, which should be most pronounced in the considerably older QGNG zircon (1850 Ma as opposed to 1099 Ma) but, as shown above, the youngest (TEMORA 1) and the oldest (QGNG) of the standards have completely compatible Pb/U characteristics.

6.2.3. SL13

SL13, which was included in seven of the sessions, behaves differently from TEMORA 1, AS3, and QGNG. SL13 gave the most scattered data during all but one of the sessions (Table 3, Fig. 7), the exception being AS3 in Z2820. Based on this observation, it is not surprising that SL13 also shows the most variation between sessions. Whereas it was demonstrated above that both the QGNG-calibrated AS3 and TEMORA 1 session-to-session data are consistent, the SL13 ^{206}Pb/^{238}U ages vary between sessions (Table 3—

MSWD = 2.8, probability of equivalence = 0.010). This apparently documents real variation within this standard on the scale of SHRIMP analysis, even when a relatively large number of analyses (averaging more than 50 per session) have been made.

A second difference with SL13 is that its grand average QGNG-calibrated ^{206}Pb/^{238}U SHRIMP age (derived from 378 of 390 analyses) of 577.4 ± 1.2 Ma (2σ) is 0.9% older than its IDTIMS age (572.1 ± 0.4 Ma). This difference is significant at greater than the 99.9% confidence level. In contrast, TEMORA 1 yielded the same age by both methods, while AS3 produced a difference, but in the opposite sense. If SL13 with its IDTIMS age of 572.1 Ma had been chosen as the reference standard, AS3, TEMORA 1 and QGNG would all yield ages that are significantly younger than their IDTIMS values.

A serious difficulty of interpreting SL13 SHRIMP data is trying to manage its dispersion in ^{206}Pb/^{238}U. Clearly, the spread of ages obtained both within and between sessions, and the weighted mean ages that are produced, are critically dependent on the nature of the culling process. It might be argued that the process that has been followed in this article is not unique, and that other rejection alternatives are possible. Such an argument has some merit, although the rejection criteria that have been applied in this article are considered reasonable. In any case, the data illuminate a severe weakness in the application of SL13 as a standard. No respectable standard should produce results that are dependent on a significant degree of data culling (or manipulation) for their consistency.

Compston (1999, 2001) has attempted to circumvent the problem with SL13 by means of statistical modelling (Sambridge and Compston, 1994). However, the application of his method has relied on there being no source of instrument-related error (other than that arising from counting statistics), but this is not supported by the available evidence. The high-quality

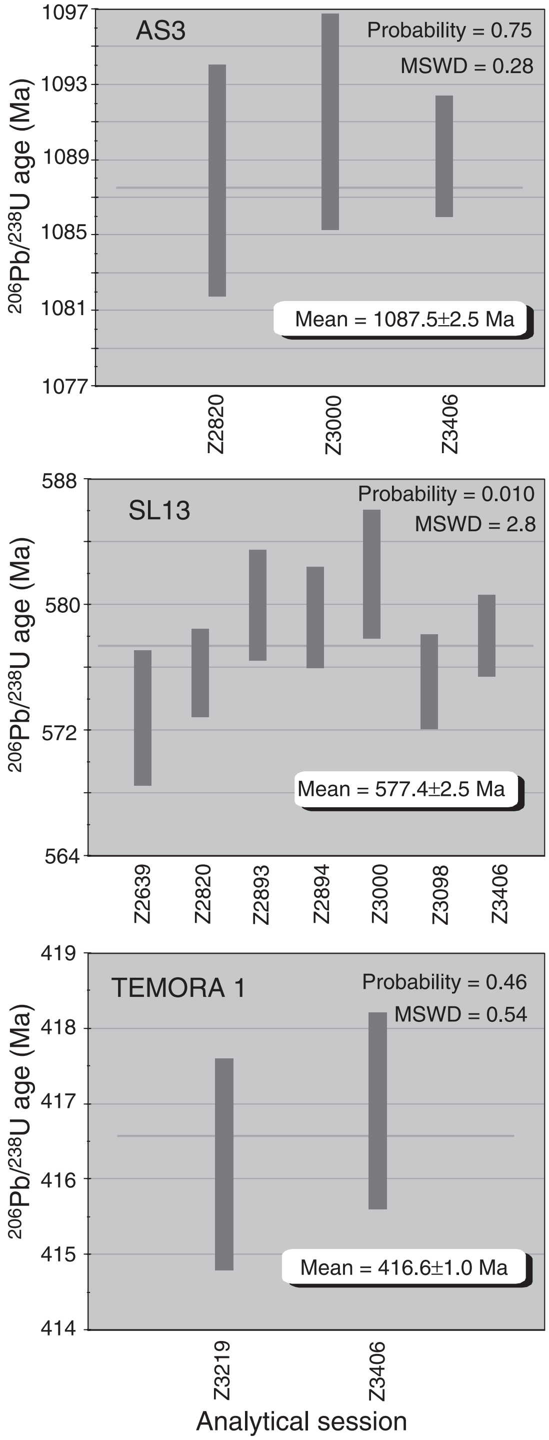


Fig. 6. Weighted mean ^{206}Pb/^{238}U ages for AS3, SL13 and TEMORA 1, as referenced to a QGNG age of 1842.0 Ma. The TEMORA 1 and AS3 results both form tight isotopic groupings, but the SL13 data do not, which mirrors their respective within-session behaviour (Fig. 4). When referenced to QGNG, only TEMORA 1 yields an age that is consistent with its IDTIMS value (see text).

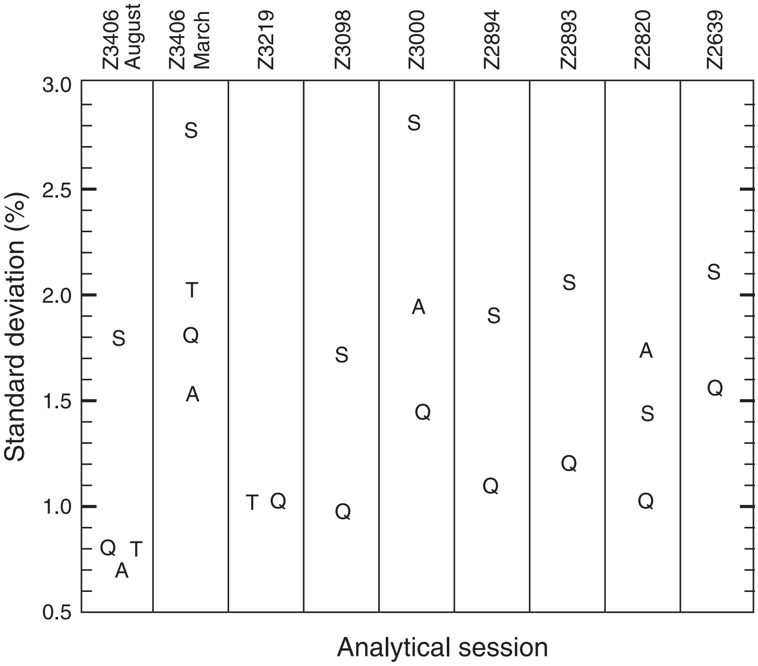


Fig. 7. Standard deviations (expressed as a percentage) obtained for the $^{206}Pb/^{238}U$ of the different standards for each of the analytical sessions, illustrating the varied performance of SHRIMP (A = AS3, Q = QGNG, S = SL13, T = TEMORA 1).

August 2000 session on Z3406 reported above was a second attempt to obtain reasonable data on this mount. Analyses in March 2000 yielded considerably inferior data (Fig. 7) apparently resulting from inconsistencies in SHRIMP performance. Reasonably comparable count rates for those two sessions (an average of 3355 and 4634 cps for ^{206}Pb in QGNG for the March and August sessions, respectively) ensure fairly constant errors from counting statistics. Also, analysis of the same four zircon suites minimises any potential contribution of differential errors from geological factors. The only remaining feasible source of the additional imprecision in the March session is SHRIMP itself.

The same conclusion can be drawn from the relative behaviour of the different standards in the analytical sessions summarised above. Fig. 7 shows that SL13 generally yields the least precise results for any given session. In contrast, within-session precisions of AS3, QGNG and TEMORA 1 (and especially the latter two) are mostly quite similar to each other. There is thus a reasonable correlation between the relative precisions of the standards in any one session, but these precisions can vary markedly between sessions. It is highly unlikely that the major contributor to this effect is sample heterogeneity, because each of the standards would need to have misbehaved to similar extents during any particular session. Moreover, the effect is striking in two different sessions (including many analyses of the very same grains) on the same ion-probe mount (Z3406). These observations demonstrate, contrary to the assertions of Compston (1996, 1999), that the variations are not due only to counting statistics and sample heterogeneity, and thus Gaussian unmixing methods cannot be reliably used to resolve internal age structure. Acknowledgment of a source of instrument bias does not call into question the SHRIMP itself or its performance. It merely means that due compensation must be made for this effect during data processing in order to generate meaningful $^{206}Pb/^{238}U$ ages.

Based on the IDTIMS and SHRIMP data reported above, TEMORA 1- and QGNG-calibrated ages are compatible with each other. This is true for QGNG, provided the mean $^{206}Pb/^{238}U$ age of 1842.0 Ma based on the relatively tight grouping of ~ 0.5% discordant data is used, not the $^{207}Pb/^{206}Pb$ age, even should this be based on a matrix effect that is unique to QGNG. Previously reported QGNG-based ages that have not been referenced to the $^{206}Pb/^{238}U$ age (e.g. Black et al., 1997) will need to be adjusted by the appropriate amount (≃0.4%). In contrast, an approximate factor of − 1% is needed for the conversion of AS3-derived ages to those based on TEMORA 1 (or QGNG). Although SL13-calibrated ages are on average about 1% low, they are variably offset, making it difficult to derive any reliable conversion factor to relate them to ages calibrated against the other standards.

7. Anomalous results from SL13

Although it might be possible to explain the discrepancy between SHRIMP and IDTIMS results for TEMORA 1-QGNG versus AS3 in terms of a small degree of Pb loss, the SL13 SHRIMP results are displaced in the opposite sense, ruling out that explanation. The other obvious difference between SL13 and the other standards is its less homogeneous Pb/U.

In all but one instance (Z2820, when AS3 behaved more poorly), SL13 analyses are significantly more scattered in Pb/U than any of the other concurrently analysed standards (as shown by the coefficients of variation in Table 3). This characteristic is considered by Compston (1996, 1999) to reflect real variation of Pb/U in SL13. At first glance, this conclusion might appear to be at variance with the previously reported homogeneity for SL13 as established by IDTIMS. Each of those TIMS analyses, however, consumed about 10,000 times as much zircon as each SHRIMP analysis, and therefore these results have little if any bearing on homogeneity on the scale of SHRIMP dating.

Compston (1996) concluded that the heterogeneity in SL13 is primarily the product of a bimodality of ages, and has proposed that it is best treated by identifying the dominant (older) component, and assigning it an age of 579.2 ± 1.3 Ma. As stated above, his identification of the two components, using the mixture modelling of Sambridge and Compston (1994) is based on the assumption that none of the uncertainty of the individual SHRIMP analyses is instrument related. The markedly contrasting performances of SHRIMP during the two Z3406 sessions, however, demonstrate that such an assumption is not realistic. An underestimation (or non-estimation) of instrument-generated errors will lead to erroneous ages for the postulated age components, and will also tend to overestimate the number of identified components.

Hoskin and Black (2000) have recently studied a type of zircon that they believe to form from solid-state metamorphic recrystallisation of pre-existing zircon. That zircon has comparably low Th/U and a similar lack of internal structure (as shown by cathodoluminescence) as SL13, raising the possibility that SL13 might be of similar origin. A critical feature of the Hoskin and Black (2000) zircon is that some areas that no longer retain any CL evidence of their original oscillatory zoning have not been completely reset in terms of their age. These recrystallised areas yield a range of ages, the youngest of which were interpreted as dating recrystallisation, and others as documenting incomplete isotopic resetting by that event. If the analogy with SL13 is correct, its isotopic variability may be best interpreted as having no regular structure, rather than being of predominantly bimodal form.

The heterogeneity reported above should only generate an increased dispersion of SL13 data, and not be responsible for the observed offset in Pb/U from the other standards. The latter is possibly a consequence of idiosyncratic behaviour during SHRIMP analysis. Perhaps the most fundamental assumption associated with U–Pb zircon SHRIMP dating is that the enrichment in Pb^+/U^+ over Pb/U in the target zircon that occurs during the sputtering process is the same for standards and unknowns. The discrepancy observed in this study for SL13 is consistent with it having slightly different ionisation characteristics than the other three standards. If this is correct, it implies that there is a critical difference in the crystal lattice of SL13 compared with those of AS3, TEMORA and QGNG. Indeed, there is evidence to suggest that SL13 zircon is chemically different from the other three. For example, Kinny et al. (1991) contend, primarily on the basis of Hf isotopic evidence, that the alluvial zircon megacrysts from Sri Lankan highland gravels, of which SL13 is a representative, probably grew during metamorphism of older Precambrian rocks.

This conclusion is consistent with the very low Th/U (averaging 0.09) for SL13. Very low Th/U ratios also characterise the pegmatitic zircons that Mortensen et al. (1992) deduced had been affected by excess ^{231}Pa. In contrast, TEMORA 1, AS3 and QGNG have typical average igneous zircon values of 0.51, 0.66 and 0.87, respectively. The latter three also display euhedral, oscillatory igneous zonation. In contrast, the lack of evidence of zoning in SL13 is quite unlike that of similarly aged igneous zircons with comparably low U contents, but similar to the metamorphically recrystallised zircon described by Hoskin and Black (2000).

Preliminary electron microprobe data, derived from 20 analyses each of QGNG, SL13, and AS3, indicate that SL13 contains dramatically lower Y (below detection limits) than either AS3 (2300 ± 500 ppm) or QGNG (1600 ± 400 ppm). As the REEs within zircon are dominantly of the Y group (Deer et al., 1982), this indicates unusually low HREE concentrations. Hinton and Upton (1991) have shown for one unrelated zircon megacryst that REE substitution is not coupled with PO^{4-} or other anions. They also argue that it is unlikely to be balanced by the presence of 5^{+} cations, because no major substitution other than Hf, REEs, Th and U occurs in that megacryst. Their conclusion that the substitution of REE^{3+} for Zr^{4+} (note that Hf is tetravalent) should produce a charge vacancy might provide an explanation for the apparently different behaviour of SL13 during SHRIMP analysis. Perhaps a charge effect of that type (or a compensating lattice defect, such as a deficiency of O) would have a significant effect on the relative ionisation of U with respect to Pb during the SHRIMP sputtering process. If this deduction is correct, SL13 might prove to be a suitable standard for dating zircon of comparable chemical composition (such as metamorphic zircon). However, in most instances the SHRIMP ^{206}Pb/^{238}U dating of Phanerozoic zircon is directed at igneous zircon, for which the QGNG, TEMORA and AS3 igneous zircons might be more appropriate standards.

8. Implications for chronostratigraphic correlation

The conclusions of this study have significant implications for the assignment of numerical ages to the geological timescale. Indeed, they provide a possible explanation for some reported anomalies between SHRIMP and TIMS data. For example, Tucker and McKerrow (1995) point out that SHRIMP U–Pb zircon ages reported by Compston and Williams (1992) for the Early Palaeozoic are about 1–2% younger than TIMS dates for the same samples. Tucker and McKerrow (1995) inferred that there is a problem either with SHRIMP itself or with the manner in which the resulting data are processed. The current study, however, indicates that the problem probably lies with the standard that was used (SL13), and not with the instrument. This conclusion is consistent with that of Roddick and Bevier (1995), who reported that the SL13 zircon standard is biased by about 1% (in the same sense) relative to most other zircon samples.

In a similar vein, Draper and Fielding (1997) debate apparently contradictory SHRIMP ages derived by Roberts et al. (1996) for the Late Palaeozoic of Australia. They state that "the discrepancies between dates and the overlapping of dates between formations that were clearly separated in time, indicate either a problem with the technique or with the interpretation of the results", and conclude "that the SHRIMP method is suspect for Late Permian rocks of the Bowen Basin". Once again, the conflicting results are explicable in terms of the heterogeneity of SL13, and its tendency to variably underestimate ages, and do not reflect adversely on SHRIMP itself.

The consistent behaviour, though not necessarily that which would have originally been foreseen, of the other standards, and their enhanced homogeneity compared with that of SL13, validates the use of SHRIMP for Pb/U zircon dating. The less predictable nature of SL13-derived ages, however, necessitates a review of any such ages that have been used to define the Phanerozoic timescale. It might not be possible to interpret any such ages with conviction.

9. Conclusions

1. Four zircon standards have been compared in a series of SHRIMP experiments. Only two of the four show consistent inter-relationships with respect to their IDTIMS ages.

2. The $^{206}Pb/^{238}U$ ages of the TEMORA 1 and QGNG standards are compatible with each other. The slight discordance (~ 0.5%) of QGNG, however, and the small but distinct range of Pb/U in its highest-quality grains (± 0.3%, as determined by IDTIMS) lessens its appeal as a primary Pb/U standard. Nevertheless, it is possible to directly inter-compare ages obtained with these two standards, providing the IDTIMS $^{206}Pb/^{238}U$ age of 1842.0 Ma rather than any of the reported $^{207}Pb/^{206}Pb$ ages are used for QGNG.
3. SHRIMP data for AS3 are incompatible with all of the other standards, even though the IDTIMS age of this zircon is definitively concordant. This discrepancy might signify that the majority of zircon recovered from the host anorthosite experienced a slight degree of Pb loss, unlike the six grains that were selected for IDTIMS analysis. Alternatively, a distinct offset of AS3 ages from their expected value, rather than a spread of ages, is more suggestive of a matrix-dependent effect. Whatever the explanation, consistency within the inter-comparisons indicates that AS3-based ages can be reliably compared with those derived from TEMORA 1 (and QGNG), providing a conversion factor of about − 1% is applied.
4. SL13-calibrated ages are on average about 1.0% younger than those based on the TEMORA (or QGNG) standard. However, it is unrealistic to uniformly apply such a conversion factor because of demonstrable Pb/U heterogeneity within SL13. It is therefore not possible to assess the significance of ages obtained from this standard with the same confidence with which it can be done for the other three. A current bimodal model for the nature of the Pb/U heterogeneity would not appear to provide a realistic solution to this problem.
5. Within the limitations listed above, it is possible to compare ages derived from the different zircon standards. On balance, however, consistency (as determined by IDTIMS), predictable behaviour on SHRIMP, and availability, indicate that TEMORA 1 is superior to the other zircon standards described above. It also has the advantage of being comparable in age (Phanerozoic) to zircons that are critically dependent on $^{206}Pb/^{238}U$ dating.
6. SHRIMP has provided a valuable means for chronological quantification of the Phanerozoic timescale. It is now possible to more realistically reassess the significance of some of those ages.

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