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A new isotopic and trace-element standard for the ion microprobe: preliminary thermal ionization mass spectrometry (TIMS) U-Pb and electron-microprobe data

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Abstract: Fragments of a gem zircon megacryst (BR266) were examined using thermal ionization mass spectrometry (TIMS) and electron-microprobe analysis to determine absolute age and elemental composition. The mean $^{206}Pb/^{238}U$ and $^{207}Pb/^{206}Pb$ ages were 559.0 ± 0.3 Ma and 562.2 ± 0.5 Ma, respectively. The mean U, Th, and Hf concentrations were 909 ppm, 201 ppm, and 8220 ppm, respectively, with standard errors of 1–3%. Ion-microprobe isotopic analysis shows that the U-Pb isotopic system at the 10–30 μm scale is homogeneous at about the 1% level. This zircon has been adopted as the principal isotopic and geochemical reference material for zircon studies at the GSC Sensitive High Resolution Ion Microprobe (SHRIMP) laboratory.

Résumé : Des fragments d'un gros cristal de zircon gemme (BR266) ont été analysés par spectrométrie de masse à thermoionisation ainsi qu'à la microsonde électronique afin d'en déterminer l'âge absolu et la composition élémentaire. Les valeurs moyennes de l'âge obtenues à l'aide des rapports $^{206}Pb/^{238}U$ et $^{207}Pb/^{206}Pb$ sont respectivement de 559,0 ± 0,3 Ma et de 562,2 ± 0,5 Ma. Les concentrations moyennes de U, Th et Hf s'élèvent respectivement à 909, 201 et 8 220 ppm et les erreurs-types sont de l'ordre de 1 à 3 %. L'analyse isotopique à la microsonde ionique a révélé que le système isotopique U-Pb est homogène dans une fourchette de 1 % environ à l'échelle de 10 à 30 μm. Au laboratoire de la Commission géologique du Canada où sont menées les analyses à la microsonde ionique à haute résolution et à haut niveau de sensibilité (SHRIMP), on a adopté ce zircon comme principal étalon pour les analyses isotopiques et géochimiques de ce minéral.

INTRODUCTION

The Sensitive High Resolution Ion Microprobe (SHRIMP) has become a vital tool in microscale isotopic, and increasingly, trace-element studies of zircon. Homogeneous and independently characterized reference materials are required in order to convert observed secondary-ion count rates of various trace elements (e.g. Pb, U, and Th) into absolute elemental abundances and ratios. If the accuracy required in determining elemental abundances or ratios is relatively low, for example ±10–20%, then the use of well characterized synthetic silicate glass standards (e.g. NIST SRM 610, 612; Pearce et al., 1997) and the adoption of appropriate analytical protocols may be quite adequate. However, if the accuracy required is ±1–2%, which is the minimum standard for zircon U-Pb dating, a zircon mineral standard is required to minimize matrix effects. Furthermore, it has been found that such accuracy requires closely controlled analytical conditions, including the requirement that the standard be placed within the same sample mount as the unknowns.

Zircon reference materials suitable for SHRIMP U-Pb analysis have been notoriously difficult to find, mainly due to the fact that the interelement isotopic ratios (e.g. $^{206}Pb/^{238}U$) of most zircon samples can be shown to be unacceptably heterogeneous at the scale of the ion beam (5–30 μm). The problem is exacerbated by the requirement for a standard available in sufficient quantities that it is effectively 'disposable,' that is, once placed within the sample mount of the unknown it is seldom removed. Previously, the GSC SHRIMP laboratory used fragments of zircon megacrysts from the 993 Ma Kipawa syenite complex (lab #2430) as its primary U-Pb reference material (Stern, 1997). However, extensive SHRIMP analysis of this zircon and further TIMS analysis have revealed the presence of grain fragments with Pb-loss and others with ages in excess of the nominal value. The Kipawa zircon is also characteristically heterogeneous in trace-element abundances, and thus fails as a trace-element standard. Consequently, continuing efforts have been devoted to finding a better zircon reference material, one that could serve the needs of both U-Pb geochronology and geochemistry. This paper reports on a new zircon standard that appears to be as close to ideal for the purposes of ion-microprobe studies as is likely possible to find in nature.

BR266 (lab #5589) ZIRCON

The BR266 zircon sample (mass ~2.5 g) constitutes approximately one-quarter of a centimetre-sized Sri Lankan gem zircon obtained from A. Kennedy (Curtin University, Perth). The origin of the crystal is unknown, but it was likely collected from an unconsolidated stream deposit. The gem zircons in Sri Lanka are thought to have grown in late-stage pegmatites found in the Highland Group of metamorphic rocks (Munasinghe and Dissanayake, 1981; Kröner et al., 1987).

The zircon had been previously faceted by a gemologist (Fig. 1), and in daylight is light yellow-green and almost perfectly clear. In fragmented form it appears clear and colourless, with no observable internal heterogeneities. It is unknown whether the zircon was heated in an open pit fire, as is common practice amongst gem collectors in Sri Lanka. Nevertheless, as shown below, it has not been annealed.

SAMPLE IMAGING AND FRAGMENTATION

The megacryst was mounted in epoxy to expose the previously cut face, and then imaged with a Cambridge Instruments S360 scanning electron microscope (SEM). No detectable variations in cathodoluminescence or backscattered electron intensity were observed, consistent with trace- and minor-element homogeneity at the sensitivity level

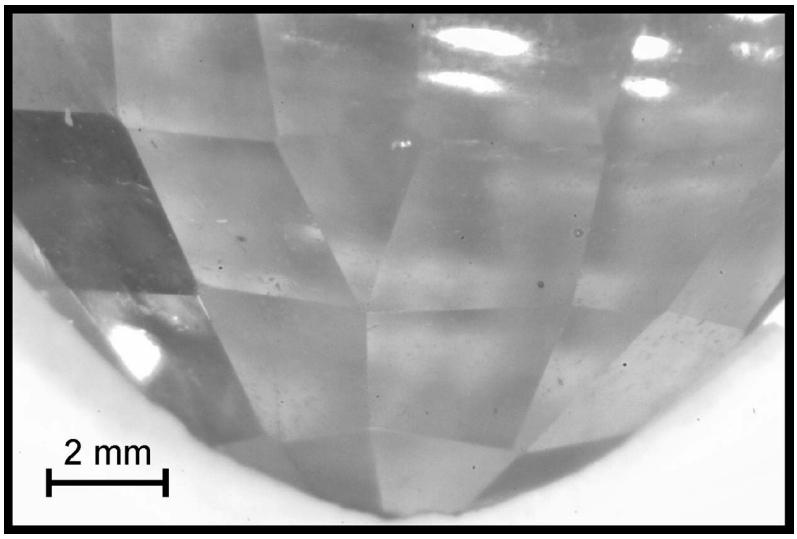

Figure 1. *The gem zircon BR266 in plain light. The zircon specimen was mechanically faceted prior to acquisition.*

of the SEM. The sectioned megacryst was subsequently broken in half, and one of the halves was broken into several millimetre-sized pieces using a tool-steel mortar and pestle. A further subsample was reduced and sieved to <350 μm. This latter zircon fraction was used in subsequent analytical work. SEM imaging of many of these fragments, both at the start of the study and in subsequent routine analytical work, has revealed no intragrain or intergrain variations, again consistent with chemical homogeneity from micrometre to millimetre scales.

POWDER X-RAY DIFFRACTION

A powder X-ray diffraction pattern was obtained on a 300 μm fragment in order to evaluate its crystallinity. Unit-cell parameters obtained were as follows: a = 0.6631 ± 0.0001 (1σ) nm, c = 0.6029 ± 0.0001 nm, unit cell volume = 0.26513 ± 0.00007 nm^3. These data indicate a partially metamict (i.e. not pristine) structure, but still maintaining good crystallinity. The calculated accumulated alpha-radiation dosage, based on age and U and Th concentrations (*see* below), is 0.184 x 10^{16} events/mg, a value that correlates with a 'well crystallized' structure according to Murakami et al. (1991). The unit cell volume is consistent with other Sri Lankan zircons of similar age and uranium concentration (Woodhead et al., 1991). It is concluded that the zircon has not been annealed since it first crystallized, and that it is structurally suitable as a reference material.

TIMS U-Pb DATA

Eight non-abraded fragments with masses of 0.04–0.14 mg were analyzed for U and Pb isotopes by isotope-dilution TIMS according to standard GSC laboratory procedures (Parrish et al., 1987). Data plotting and weighted mean calculations were carried out using the computer program 'Isoplot/EX' version 2.35 (Ludwig, 2000). Analytical data are summarized in Table 1 and displayed on a concordia plot (Fig. 2).

The eight fragments yielded U-Pb isotopic data that are statistically indistinguishable. The weighted mean ages, 95% confidence intervals (2σ), mean square of weighted deviates (MSWD = $\{\Sigma_i^n ((A_i–A) / \sigma_i)^2\}/(n-1)$, where A_i, A, σ_i, and n are the individual ages, mean age, individual absolute 1σ errors, and number of analyses, respectively), and probabilities of fit (P) for the eight fragments are as follows:

$^{207}Pb/^{206}Pb$ age = 562.2 ± 0.5 Ma (MSWD = 0.15, P = 0.994)

$^{206}Pb/^{238}U$ age = 559.0 ± 0.3 Ma (MSWD = 0.86, P = 0.54).

The probability values indicate the likelihood that the MSWD value (which quantifies the observed data scatter relative to the expected scatter) would be exceeded if the data are random and normally distributed measurements of isotopically identical zircon fragments. The high probability values (low MSWD) for both ages indicate that the zircon fragments almost certainly have the same isotopic composition. The fact that the MSWD values for the $^{207}Pb/^{206}Pb$ data are much lower than the statistically expected value of 1 (approximately equivalent to 50% probability for 7 degrees of

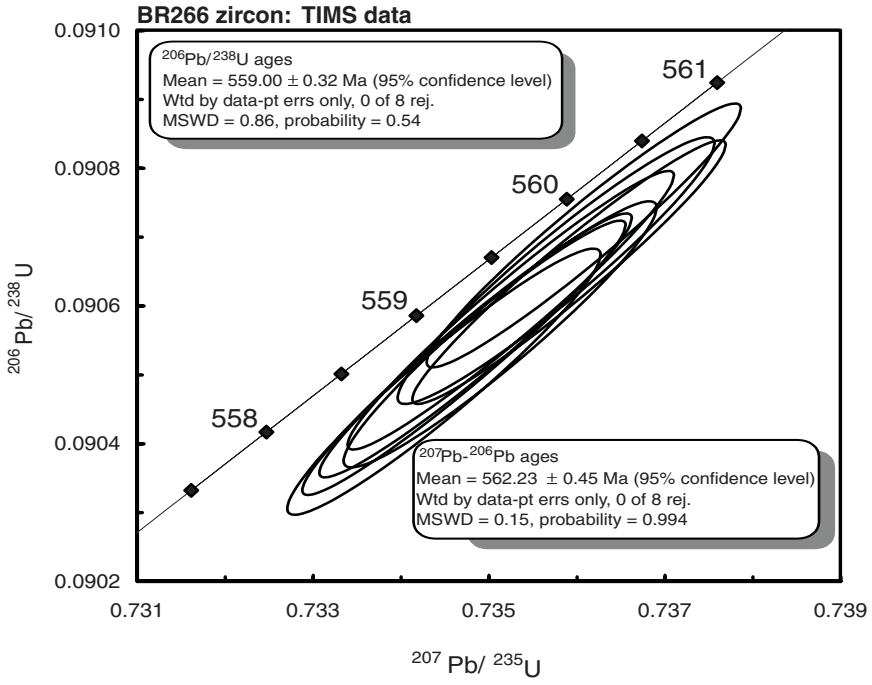

Figure 2.

Isotope-dilution TIMS analytical data for eight relatively large fragments of BR266 zircon. Error ellipses are plotted at 2σ. Weighted mean ages are indicated.

Table 1. TIMS U-Pb analytical data for BR266 ziron.

									Radiogenic ratios ±2σ							
Fraction	Number of grains	Weight (mg)	U (ppm)	Th (ppm)	Th/U (wt.)	Pb (ppm)	Common Pb (pg)	$^{207}Pb/^{204}Pb$	$^{207}Pb/^{235}U$	$\pm^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$\pm^{206}Pb/^{238}U$	Corr. Coeffic.	$^{207}Pb/^{206}Pb$	$\pm^{207}Pb/^{206}Pb$	$^{208}Pb/^{206}Pb$
A	1	0.079	920	204	0.2217	80.8	1.6	15274	0.73480	0.00141	0.09054	0.00015	0.964	0.058864	0.000032	0.069110
B	1	0.120	958	212	0.2215	84.2	3.5	10920	0.73524	0.00150	0.09059	0.00016	0.966	0.058863	0.000033	0.069064
C	1	0.062	871	191	0.2188	76.5	2.5	7181	0.73574	0.00146	0.09065	0.00016	0.952	0.058866	0.000036	0.068227
D	1	0.053	889	197	0.2211	78.2	2.4	6579	0.73605	0.00144	0.09070	0.00016	0.962	0.058858	0.000048	0.068946
E	1	0.090	910	200	0.2193	80.0	2.8	9676	0.73589	0.00144	0.09065	0.00016	0.964	0.058879	0.000032	0.068373
F	1	0.061	896	196	0.2188	78.6	4.4	4154	0.73512	0.00144	0.09056	0.00016	0.951	0.058876	0.000037	0.069199
G	1	0.042	895	199	0.2220	78.5	4.5	2796	0.73448	0.00144	0.09049	0.00016	0.953	0.058870	0.000036	0.069222
H	1	0.139	933	207	0.2220	82.0	6.4	6732	0.73474	0.00151	0.09053	0.00017	0.967	0.058865	0.000032	0.069223
mean			**909**	**201**	**0.2207**	**79.8**					**0.09059**			**0.058868**		

Notes: Th/U calculated from radiogenic $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$; Th abundance calculated from Th/U and U
Common Pb (pg) refers to the total amount of common Pb (picograms) measured in the analysis
Atomic ratios corrected for Pb and U blank, fractionation, and initial common Pb (Stacey and Kramers, 1975)
Uncertainties in ratios reported at 2σ (absolute), calculated by numerical propagation of all known sources of error
%D refers to the percent discordance along a line to zero age

Table 1. (cont.)

	Apparent Ages (Ma) ±2σ						
Fraction	$^{207}Pb/^{235}U$	$\pm^{207}Pb/^{235}U$	$^{206}Pb/^{238}U$	$\pm^{206}Pb/^{238}U$	$^{207}Pb/^{206}Pb$	$\pm^{207}Pb/^{206}Pb$	%D
A	559.4	0.8	558.7	0.9	562.1	1.2	0.60
B	559.6	0.9	559.0	1.0	562.0	1.2	0.54
C	559.9	0.9	559.4	0.9	562.1	1.4	0.50
D	560.1	0.8	559.7	0.9	561.8	1.8	0.39
E	560.0	0.8	559.4	0.9	562.6	1.2	0.58
F	559.6	0.8	558.8	0.9	562.5	1.4	0.66
G	559.2	0.8	558.4	0.9	562.2	1.4	0.69
H	559.3	0.9	558.7	1.0	562.1	1.2	0.62
mean			559.0		562.2		

Table 2. Electron microprobe Si, Zr, and Hf data for BR266 zircon.

Element or ratio	weighted mean	95% confidence level
Si (wt.%)	15.36	0.05
Zr (wt.%)	49.2	0.4
Hf (wt.%)	0.822	0.006
Si/Zr	0.312	0.003
Hf/Zr	0.0167	0.0002

freedom) likely indicates that the analytical errors for $^{207}Pb/^{206}Pb$ have been slightly overestimated. These data indicate that the randomly selected zircon fragments are remarkably homogeneous at the 10^7 μm^3 sampling scale. The fragments are slightly, but apparently uniformly, discordant by 0.57%.

The isotope-dilution U abundances for the eight fragments ranged from 871–958 ppm, with an arithmetic mean of 909 ppm and a standard deviation of 3.0%. The mean total Pb abundance is 79.8 ppm, also with a standard deviation of 3.0%. The Th/U ratios, calculated from the measured $^{208}Pb/^{206}Pb$ and $^{207}Pb/^{206}Pb$, are highly uniform, yielding an arithmetic mean of 0.2207 with a standard deviation of 0.6%. This small amount of scatter in the Th/U values can be accounted for by the individual analytical errors. The calculated mean Th concentration is 201 ppm with a standard deviation of 3.4%. These data indicate a high degree of homogeneity in the abundances of U and Th for the zircon.

ELECTRON-MICROPROBE DATA

Concentrations of Zr, Si, and Hf in approximately 500 μm^3 volumes of BR266 zircon were determined using a Cameca SX50 electron microprobe (GSC Mineralogy Division) with wavelength-dispersive X-ray collection. Analytical conditions included an accelerating voltage of 20 keV and an electron-beam current of 10 nA. Reference materials for standardization were synthetic pure end-member zircon and hafnon crystals acquired from J. Hanchar (George Washington University).

Table 2 presents the weighted mean Zr, Si, and Hf concentrations and 95% confidence intervals for seven separate analytical sessions, each comprising 20 random spot analyses from several individual fragments. No statistically significant differences in element concentrations were found between individual spot analyses or between sessions. The weighted mean Si value of 15.36 ± 0.05 wt % (2σ) is within error of the ideal value for zircon (15.32 wt %), whereas the mean value measured for Zr (49.2 ± 0.4 wt %) is significantly lower than for ideal zircon (49.8%). The mean measured Si/Zr weight ratio is 0.312 ± 0.003, compared with the stoichiometrically ideal value of 0.308. The low Zr and elevated Si/Zr are due to the substitution of Hf and other minor elements in place of Zr. The measured Hf concentration is 0.822 ± 0.006 wt %, yielding a Hf/Zr ratio of 0.0167. As far as is currently known, the only other elements present in significant amounts in BR266 zircon are U, Th (as above), rare-earth elements, and Y (R. Stern, unpub. data, 2001).

SHRIMP ANALYSIS

Randomly selected fragments of BR266 zircon have been analyzed for U, Th, Pb, Hf, and Zr isotopes on numerous grain mounts. The detection limit for these elements is approximately 1–3 ppb, allowing highly precise elemental abundance measurements at scales of 100–1500 μm^3. As the Zr content is uniform, the secondary-ion ratios $^{254}[UO]^+/^{196}[Zr_2O]^+$ and $^{196}[HfO]^+/^{196}[Zr_2O]^+$ correlate directly with U and Hf abundances, respectively. The standard deviations of these secondary-ion ratios for randomly placed spots in any given session were 1–2% of the mean, slightly smaller than those indicated by the isotope-dilution analyses. The reason for this small discrepancy is unknown, but it could be related to the TIMS analytical procedure, particularly the need to achieve better than 1% accuracy in weighing of grain fragments. The standard deviation of mean SHRIMP $^{248}[ThO]^+/^{254}[UO]^+$ (correlating with Th/U) averages 0.6%, in perfect agreement with the standard deviation of Th/U values obtained by isotope-dilution analysis of multiple large fragments. The individual electron microprobe analyses for Hf are too imprecise to allow direct comparison with the SHRIMP Hf abundance data.

SHRIMP evaluation of the degree of homogeneity in $^{206}Pb/^{238}U$ is dependent upon the methods used to model the behaviour of secondary Pb and U isotopes in zircon. Such is not the case for the secondary-isotope ratios previously considered, which are considerably less affected by analytical conditions. Recent studies in the GSC laboratory (R. Stern, unpub. data, 2001) have shown that the correlation of $^{206}Pb^+/^{270}[UO_2]^+$ and $^{254}[UO]^+/^{238}U^+$ secondary-isotope pairs yields improved results compared with previous methods of calibration (Stern, 1997). An example of such a calibration for mount #IP123 is illustrated in Figure 3. Using this method, BR266 zircon was analyzed in 24 separate grain mounts over the course of more than one year.

The standard deviations of $^{206}Pb^+/^{270}[UO_2]^+$ about the linear least-squares calibration curves for the individual mounts ranged from 0.2% to 2.2%, with an average of 1.1%. For most mounts, the observed scatter in the data sets is substantially greater than can be explained by *known* sources of analytical error (i.e. MSWD values are >>1; Fig. 3). The SHRIMP data appear to indicate that BR266 zircon is not as homogeneous at the scale of the ion probe as indicated by the bulk TIMS values. Despite the apparent age heterogeneities observed with the SHRIMP, the range and average standard deviations of $^{206}Pb^+/^{270}[UO_2]^+$ for the mounts are quite acceptable for ion-microprobe studies. Importantly, no areas of gross Pb-loss or unsupported radiogenic Pb have been observed. A concordia plot of the SHRIMP data for mount #IP123 is shown in Figure 4, where the mean of the individual $^{206}Pb/^{238}U$ ages has been forced to correspond with the TIMS value. The MSWD of the $^{206}Pb/^{238}U$ ratios in the concordia plot in Figure 4 (6.6) is lower than that of raw data in Figure 3 (9.7) due to error propagation of the uncertainties related to the slope of the calibration line and the deviation of individual analyses from the centroid.

The mean ^{206}Pb content of 70.8 ppm in BR266 zircon, coupled with its relatively high U content, permits excellent counting statistics for $^{206}Pb^+/^{270}[UO_2]^+$, with an average counting uncertainty of about 1% (2σ) per spot. For $^{207}Pb/^{206}Pb$ and $^{208}Pb/^{206}Pb$, the counting statistics are less favourable due to the lower abundances of ^{207}Pb and ^{208}Pb (4 and 5 ppm, respectively) yielding typical uncertainties of 2–3% per spot, depending, of course, on the counting times. In the case of mount #IP123 considered previously, the weighted mean $^{207}Pb/^{206}Pb$ age is 565 ± 7 Ma (2σ) and the

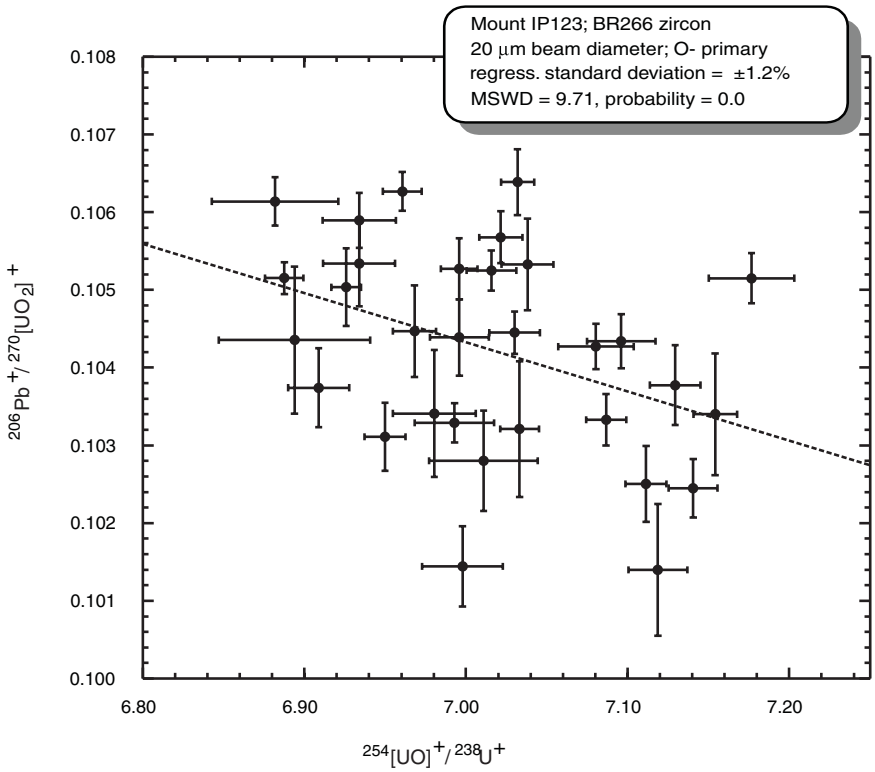

Figure 3. *A plot of $^{254}[UO]^+/^{238}U^+$ vs. $^{206}Pb^+/^{270}[UO_2]^+$ for individual SHRIMP analyses of BR266 zircon from mount IP123 (error bars are 1σ). An O^- primary beam was used to analyze spots approximately 20 μm wide by 1 μm deep. No correction for common Pb was made, but it is insignificant for these data. A linear least-squares fit to the dependent variable $^{206}Pb^+/^{270}[UO_2]^+$ is shown, generating a calibration curve assumed to correspond with the TIMS $^{206}Pb/^{238}U$ age of the zircon.*

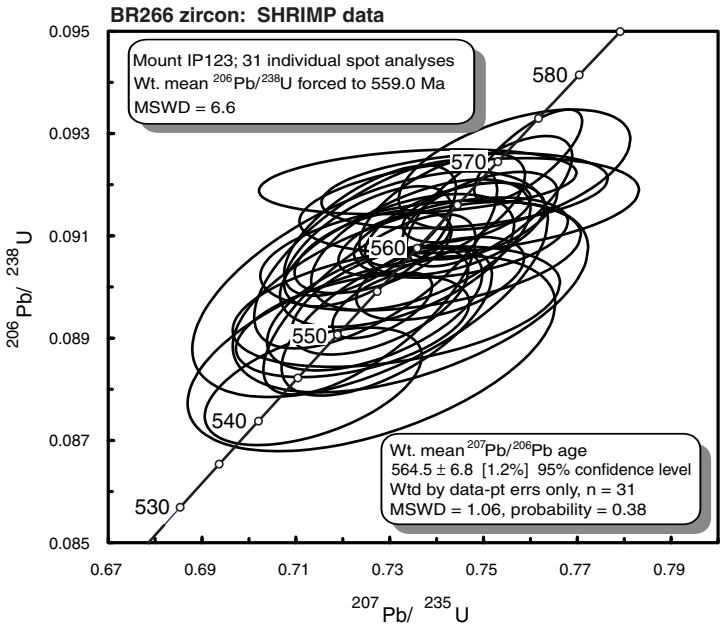

Figure 4.

A concordia plot showing 31 individual SHRIMP analyses of several fragments of BR266 zircon from mount IP123. The raw isotopic data are shown in Figure 3. Lead isotopes were corrected for common Pb using measured ^{204}Pb. The mean $^{206}Pb/^{238}U$ age has been forced to correspond with the TIMS value. The mean measured $^{207}Pb/^{206}Pb$ age is also indicated. Error ellipses plotted at 2σ.

Tukey's (unweighted) mean is 563 ± 7 Ma (2σ), both within error of the TIMS value (562 Ma). The ^{204}Pb in the SHRIMP analyses is always undetectable or extremely low, and in the latter case is attributed to common Pb on the surface of the mounts.

CONCLUSIONS

Isotope dilution and electron-microprobe data for BR266 zircon indicate that U, Th, and Hf concentrations are homogeneous at about the 1–3% level. TIMS U-Pb and Pb-Pb isotopic data on large fragments are also remarkably homogeneous; however, SHRIMP analysis shows the presence of detectable U-Pb age heterogeneities. Further TIMS analysis on smaller fragments may aid in understanding the nature of the small-scale age variations. The zircon is, nevertheless, considered to be highly reliable as a U-Pb isotope reference material, and an improvement over the existing Kipawa zircon standard. Accordingly, BR266 zircon has now been adopted as the primary reference material for zircon U-Pb isotopic and chemical studies at the GSC SHRIMP laboratory.

As BR266 zircon appears not to be perfectly homogeneous in U-Pb isotopes at a small scale, there exists some added analytical uncertainty related to the absolute age assigned to the mean of any given set of SHRIMP $^{206}Pb/^{238}U$ values measured for this zircon. To reduce this uncertainty, a minimum of 10 random SHRIMP analyses on three grain fragments has been adopted as analytical protocol, thus allowing one to confidently assign the mean TIMS $^{206}Pb/^{238}U$ reference age of 559.0 Ma. Nevertheless, an uncertainty in the absolute age remains, and, coupled with uncertainties arising from specific analytical conditions when analyzing unknowns (matrix effects, secondary steering, etc.), it is believed that the population standard deviation (not the standard deviation of the mean) of a set of $^{206}Pb/^{238}U$ ratios for the BR266 zircon is the best estimate of the external error that should be included in an age measurement of an unknown in the same analytical session. Consequently, the fully propagated errors in $^{206}Pb/^{238}U$ from individual spot analyses of unknown zircons are usually no better than ± 2% (2σ).

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