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Best of both worlds: combining SHRIMP and CA-TIMS methods in refining geochronological determinations for timescale calibration

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INTRODUCTION

Accurate and precise calibration of the geological timescale is a fundamental aspect of geoscience. The advent of the 'chemical abrasion' technique (e.g., Mattinson, 2005) for zircon preparation prior to thermal ionisation mass spectrometry (CA-TIMS) has significantly improved concordance and coherence of single-zircon analyses across a range of rock types, enhancing the geological accuracy of the interpreted crystallisation ages. This development affords an excellent opportunity to revisit and re-evaluate the accuracy of SHRIMP $^{206}Pb/^{238}U$ dating of natural zircon, and particularly the hypothesis that carefully targeting the 'best' areas of the 'best' grains with the ion beam should yield crystallisation ages closely comparable to those determined via CA-TIMS (cf. Kryza et al., 2012).

This study examines a series of 10 samples, largely assumed to be airfall ash beds, within the coal-rich Middle to Late Permian successions of the Sydney and Bowen basins of eastern Australia. Recent work focussed on understanding mass extinctions and climate change across the critical Late Permian–Early Triassic boundary in eastern Australia has been hampered by the endemic nature of the local faunal assemblages, which has precluded reliable high-resolution biostratigraphic correlations to global stratotypes in China and elsewhere.

METHODS

This study took advantage of the opportunity to test a collaborative approach to zircon $^{206}Pb/^{238}U$ dating, using two commonly-applied analytical methods. Tuff samples were collected from the Sydney and Bowen basins (one from outcrop, nine from drillcore), and were prepared for SHRIMP analysis by conventional heavy-liquid and magnetic separation methods, followed by transmitted- and reflected-light photography and cathodoluminescence imaging of the epoxy mounts prior to analysis. Once SHRIMP analysis was complete, the images and acquired isotopic data were used to guide the removal of individual grains from the mounts, for the purpose of CA-TIMS analysis. The two-stage process aimed to rapidly and effectively identify any SHRIMP-resolvable inherited components, thereby providing better targeting of CA-TIMS analyses.

SHRIMP analyses were performed on the Geoscience Australia SHRIMP IIe, with the 10 samples spread across four different epoxy mounts, each of which contained TEMORA2 (416.8 Ma; Black et al., 2004) as the $^{206}Pb/^{238}U$ reference zircon. Four different analytical sessions yielded 20–50 analyses of each sample. Data were reduced using SQUID 2.50.11.02.03, and common Pb corrections were applied using measured ^{207}Pb. In each session, the TEMORA2 dataset displayed the usual scatter in $^{206}Pb/^{238}U$ beyond analytical uncertainties, and the associated session-specific

external errors (0.50–1.11%; 1σ) and internal errors (0.20–0.47%; 2σ) were added in quadrature to the uncertainties of the individual unknown analyses and the uncertainties of the sample mean $^{206}Pb/^{238}U$ dates, respectively, as is normal SQUID practice. A third source of error, traditionally neglected in SHRIMP data processing but included here, relates to the uncertainty associated with the normalising $^{206}Pb/^{238}U$ reference value of the standard. Black et al. (2004) defined a reference date of 416.8 ± 1.3 Ma (2σ) for the TEMORA2 zircon, which included an uncertainty of 0.13% (1σ) associated with the U/Pb ratio of the University of Toronto tracer used. This additional source of error must be included in SHRIMP mean $^{206}Pb/^{238}U$ dates when comparing them with CA-TIMS dates.

CA-TIMS analyses were performed at the Isotope Geology Laboratory, Boise State University, following Davydov et al. (2010). Individual zircons selected for analysis (8-15 per sample) were annealed at 900°C for 60 hours, and chemically abraded using 120 µL of 29 M HF, heated to 180°C for 12 hours. Each zircon was separated from its leachate and rinsed, before being spiked with the EARTHTIME ^{202}Pb-^{205}Pb-^{233}U-^{235}U (ET2535) isotopic tracer. The U/Pb ratio of the ET2535 tracer has an uncertainty of 0.10% (2σ), which is included (via quadratic addition) in the 2σ uncertainty of the weighted mean $^{206}Pb/^{238}U$ date for each sample.

CA-TIMS VERSUS NATURAL SHRIMP RESULTS

The CA-TIMS and SHRIMP results are presented in Table 1 and Figure 1. Overall agreement is good, with five of the 10 pairs of $^{206}Pb/^{238}U$ dates being equivalent within their 2σ uncertainties, which in all cases are quite small (0.1% for the CA-TIMS dates; 0.4–0.8% for the SHRIMP dates). Two of the natural SHRIMP dates are marginally younger than the corresponding CA-TIMS dates with respect to the calculated uncertainties; the remaining three SHRIMP dates are marginally older (Table 1), but in general, the differences are small. In percentage terms, the largest discrepancy between two $^{206}Pb/^{238}U$ dates from the same sample is 1.0%, which occurs in sample F (Table 1), where the 2σ uncertainties of the CA-TIMS and SHRIMP dates are 0.1% and 0.7% respectively.

Only one of the 10 CA-TIMS datasets (sample G; Table 1) comprises a single population clustered within analytical uncertainties. Each of the other samples contain at least one analysis that yielded a $^{206}Pb/^{238}U$ date only very marginally older than that of the interpreted magmatic population: in seven cases, the age difference between these 'antecryst(s)' and the magmatic population is less than 1 million years, and in the other two, the age difference is less than ~5 million years. Naturally, the much larger individual $^{206}Pb/^{238}U$ uncertainties in the SHRIMP datasets mask such subtle variation, but in three of the 10 SHRIMP datasets, the statistically-coherent mean $^{206}Pb/^{238}U$ date of the interpreted magmatic population is distinguishably older than the corresponding CA-TIMS date, a pattern consistent with the mixing (in varying proportions) of unresolvable 'magmatic' and marginally older 'inherited' zircon components in the SHRIMP data.

A more pressing concern is the two SHRIMP datasets (samples E and F; Table 1) that yielded mean $^{206}Pb/^{238}U$ dates distinguishably *younger* than the corresponding CA-TIMS date. This implies that in some cases, loss of radiogenic Pb from natural magmatic zircon populations cannot be avoided solely by careful selection of targets for the SHRIMP ion beam (see also Kryza et al., 2012). Fortunately, in a comparative sense, measured common ^{206}Pb provides an independent indication of magmatic populations suspected of having experienced post-crystallisation loss of radiogenic Pb. In sample E, for example, the robust mean common ^{206}Pb content of the 24 analyses within the interpreted magmatic population is 0.97 ± 0.30% (Table 1), which is more than triple the mean value of any of the other nine SHRIMP-defined magmatic populations. Sample F has the second highest mean common ^{206}Pb content (0.29 ± 0.10%, Table 1), and although it is not significantly different to that of sample B (0.27 ± 0.06%, Table 1), the CA-TIMS dataset for the latter is dispersed beyond its analytical uncertainties even when 'antecrysts' are ignored: three of the 10 CA-TIMS analyses of sample B are interpreted as having been affected by loss of radiogenic Pb, despite having survived the chemical abrasion process.

Table 1: CA-TIMS and SHRIMP dates (2σ errors), and their probabilities of equivalence. Bold and italics denote SHRIMP dates resolvably younger and older (respectively) than the corresponding CA-TIMS date. Stratigraphic data for samples has been withheld, pending formal publication.

Basin/ Sample	CA-TIMS $^{206}Pb/^{238}U$ (Ma)	Natural SHRIMP $^{206}Pb/^{238}U$ (Ma)	Prob. Equiv.	Natural SHRIMP Common ^{206}Pb (%)
Sydney Basin				
A	248.03 ± 0.26 (7/8)	247.3 ± 2.0 (17/25)	0.47	0.18 ± 0.09
B	253.02 ± 0.25 (6/10)	253.2 ± 1.5 (19/21)	0.84	0.27 ± 0.06
C	*253.11 ± 0.25 (8/9)*	*254.9 ± 1.6 (20/23)*	*0.029*	*0.15 ± 0.05*
D	*255.10 ± 0.25 (6/8)*	*256.7 ± 1.6 (24/25)*	*0.048*	*0.20 ± 0.08*
E	**256.05 ± 0.25 (7/15)**	**253.3 ± 2.0 (24/25)**	**0.007**	**0.97 ± 0.30**
F	**271.45 ± 0.27 (7/8)**	**268.7 ± 1.9 (23/28)**	**0.004**	**0.29 ± 0.10**
Bowen Basin				
G	252.50 ± 0.25 (8/8)	253.5 ± 1.8 (19/20)	0.27	0.06 ± 0.06
H	252.97 ± 0.25 (12/13)	253.7 ± 1.7 (33/36)	0.40	0.05 ± 0.04
I	*252.41 ± 0.25 (8/9)*	*253.9 ± 1.2 (35/36)*	*0.016*	*0.03 ± 0.04*
J	255.88 ± 0.26 (4/10)	256.8 ± 1.1 (41/51)	0.12	0.01 ± 0.03

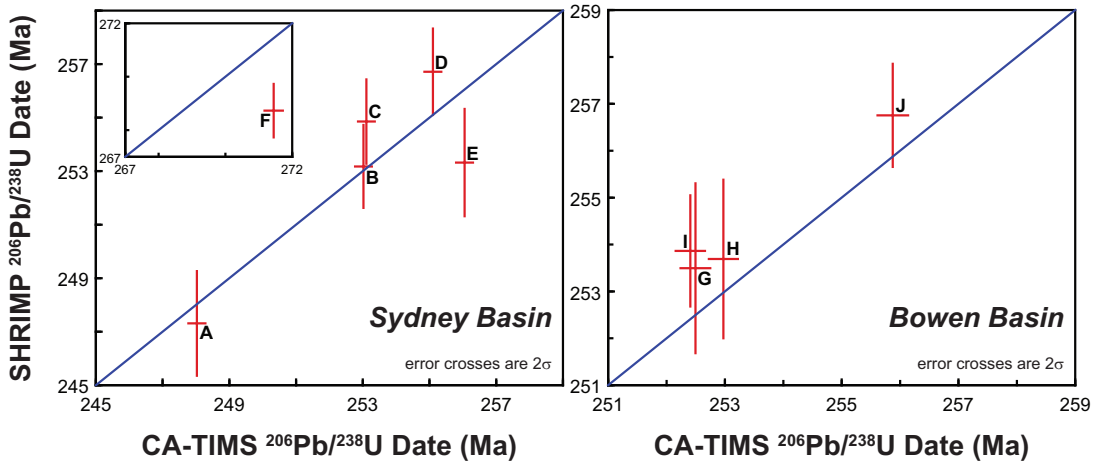

Figure 1: *Comparison of $^{206}Pb/^{238}U$ dates determined via CA-TIMS, and via SHRIMP on natural zircons, with the blue line representing equivalence. Each cross is labelled with a letter keying it to Table 1.*

FACTORS AFFECTING ACCURACY OF SHRIMP $^{206}Pb/^{238}U$ IN NATURAL ZIRCON

This study has shown that mean $^{206}Pb/^{238}U$ dates obtained from natural zircons via SHRIMP *can* be very accurate, and within error of CA-TIMS dates, even when the 2σ error envelopes for the two techniques are of the order of 0.4–0.8% and 0.1% respectively. In this study (cf. Kryza et al., 2012), it is likely that the comparison was aided by the predominantly low-U, low-common ^{206}Pb character of the analysed zircons, which were targeted on the basis of their weak paramagnetism. Most of these crystals contained domains with very good overall crystallinity, and which represented good proxies for the well-ordered zircon that typically survives the chemical abrasion process (Mattinson, 2005).

High-quality SHRIMP $^{206}Pb/^{238}U$ dating of natural zircon probably depends heavily upon isolating 'pristine' zircon in sufficient quantities, which could prove problematic when the quality and/or quantity of the host rock is limited (e.g., in drillcore). It is therefore likely that CA-TIMS and SHRIMP results will diverge whenever it is necessary to analyse less-than-perfect natural zircons with the SHRIMP ion beam. In such scenarios, chemical abrasion of the target zircons may be prudent regardless of the preferred analytical method. However, a traditional strength of SHRIMP is the ability to date individual natural zircons non-destructively, prior to analysis of O and/or Hf

isotopes on the same grains. The effect of chemical abrasion on those isotopic systems in zircon remains largely uninvestigated, and represents an important future avenue of SHRIMP-related study.

REFERENCES

Black, L.P., Kamo, S.L., Allen, C.M., Davis, D.W., Aleinikoff, J.N., Valley, J.W., Mundil, R., Campbell, I.H., Korsch, R.J., Williams, I.S. and Foudoulis, C., 2004. Improved $^{206}Pb/^{238}U$ microprobe geochronology by the monitoring of a trace-element-related matrix effect; SHRIMP, ID-TIMS, ELA-ICP-MS and oxygen isotope documentation for a series of zircon standards. *Chemical Geology* **205**, 115–140.

Davydov, V.I., Crowley, J.L., Schmitz, M.D. and Poletaev, V.I., 2010. High-precision U–Pb zircon age calibration of the global Carboniferous time scale and Milankovitch band cyclicity in the Donets Basin, eastern Ukraine. *Geochemistry Geophysics Geosystems* **11**, Q0AA04, 22p. http://dx.doi.org/10.1029/2009GC002736

Kryza, R., Crowley, Q.G., Larionov, A., Pin, C., Oberc-Dziedzic, T. and Mochnacka, K., 2012. Chemical abrasion applied to SHRIMP zircon geochronology: An example from the Variscan Karkonosze Granite (Sudetes, SW Poland). *Gondwana Research* **21**, 757–767.

Mattinson, J.M., 2005. Zircon U–Pb chemical abrasion ('CA-TIMS') method: Combined annealing and multi-step partial dissolution analysis for improved precision and accuracy of zircon ages. *Chemical Geology* **220**, 47–66.