6th International SHRIMP Workshop

Program and Abstracts

Edited by: N. Kositcin and S. Bodorkos
Program by: E. Chisholm, N. Kositcin and K.N. Sircombe
6th International SHRIMP Workshop – Program and Abstracts

GEOSCIENCE AUSTRALIA
RECORD 2012/52

Edited by
N. Kositcin and S. Bodorkos

Program by
E. Chisholm, N. Kositcin and K.N. Sircombe
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Welcome to the 6\textsuperscript{th} International SHRIMP Workshop, 2012

The Geoscience Australia Geochronology Laboratory welcomes you to discuss, debate and celebrate all matters SHRIMP at the 6\textsuperscript{th} International SHRIMP Workshop, 1–4 August 2012, in the heart of the World Heritage listed Lamington National Park near Brisbane, Australia. This workshop immediately precedes the 34\textsuperscript{th} International Geological Congress in Brisbane starting on the 5\textsuperscript{th} of August, 2012.

This workshop provides us with the valuable opportunity to present SHRIMP-related research activities, successes, difficulties and enhancements at a number of laboratories around the world, and also to discuss future directions for SHRIMP applications and technical developments.

We trust that you will all enjoy your attendance at this workshop and gain from it new ideas for future applications and technology of the SHRIMP instrumentation.

\textit{Figure 1: SHRIMP IIe, Geoscience Australia Geochronology Laboratory, Canberra, Australia.}
# Program

## SCHEDULE AT A GLANCE

<table>
<thead>
<tr>
<th>Date</th>
<th>Activities</th>
</tr>
</thead>
</table>
| **31 July 2012**<br>Tuesday | Delegates Arrive in Brisbane  
17:30 Icebreaker – Decks Seafood and Steak Restaurant |
| **1 August 2012**<br>Wednesday | 10:00 Depart ibis Hotel for O’Reilly’s Rainforest Retreat  
12:00 Lunch at The Outpost Café, Canungra  
14:00 Arrive/Check-in at O’Reilly’s Rainforest Retreat  
15:30 Welcome & Inter-Laboratory Calibration Forum  
17:00 Keynote Speaker – Lance Black | Pre-dinner drinks  
19:00 Dinner |
| **2 August 2012**<br>Thursday | 07:30 Breakfast  
08:30 Scientific & Technical Session 1 | Morning Tea  
10:40 Scientific & Technical Session 2  
12:10 Lunch  
12:50 Outdoor Activities  
14:10 Scientific & Technical Session 3  
14:40 Scientific & Technical Sessions 4 & 5 | Afternoon Tea  
18:00 Keynote Speaker – Dan Condon  
19:00 Conference Dinner |
| **3 August 2012**<br>Friday | 07:30 Breakfast  
08:30 Scientific & Technical Session 6 | Morning Tea  
10:40 Scientific & Technical Session 7 | Data Reduction Forum  
12:10 Lunch  
12:50 Outdoor Activities  
14:10 Scientific & Technical Session 8 | Afternoon Tea  
15:40 Scientific & Technical Session 9  
16:20 Technical Discussions | Free time  
17:30 Pre-dinner Drinks | Dinner  
20:00 Evening Activities | 7th International SHRIMP Workshop |
| **4 August 2012**<br>Saturday | 07:30 Breakfast  
09:30 Depart O’Reilly’s Rainforest Retreat  
12:00 Lunch at David Fleay Wildlife Reserve  
17:00 Arrive Brisbane Airport  
18:00 Arrive Brisbane City |
Key to Program and Map

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Reference</th>
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<tbody>
<tr>
<td></td>
<td>Airport</td>
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<tr>
<td></td>
<td>Bus Transport to and from O’Reilly’s Rainforest Retreat</td>
</tr>
<tr>
<td></td>
<td>Check in and check-out at Reception, ibis Hotel and O’Reilly’s Rainforest Retreat.</td>
</tr>
<tr>
<td></td>
<td>The key symbol indicates the discussion for the 2014 SHRIMP Workshop held in the Toolona Conference Room adjacent to the Main Building. The Toolona Conference Room can be accessed using the main path between the Main Building and the Mountain View Rooms.</td>
</tr>
<tr>
<td></td>
<td>Meals served in the Main Building Dining Room, O’Reilly’s Rainforest Retreat – see map for location. For delegates that require transport between the Main Building and the Lost World Conference Centre, this will be made available by O’Reilly’s – see the schedule of transfer times and locations below.</td>
</tr>
<tr>
<td></td>
<td>Meals held in the Lost World Conference Centre – Morning and Afternoon Tea, Lunch and buffet dinner on the 1st August.</td>
</tr>
<tr>
<td></td>
<td>Indicates sessions held in the Lost World Conference Centre, O’Reilly’s Rainforest Retreat. Lost World Conference Centre is down the hill beneath the Villas. Transport is available for delegates – see schedule of transfer times and locations below.</td>
</tr>
<tr>
<td></td>
<td>Drinks at the Bar, upstairs from reception in the Main Building. This is not included in your registration costs – pay as you go.</td>
</tr>
<tr>
<td></td>
<td>Leisure time. Activities are provided by O’Reilly’s at your own cost and your own risk. These activities are not covered by your Workshop registration.</td>
</tr>
<tr>
<td></td>
<td>Mini-bus transfer from Lost World Conference Centre to Main Building</td>
</tr>
</tbody>
</table>

Transfers between O’Reilly’s venues

| Meeting place for minibus transfer from Lost World Conference Centre to Main Building |
| Meeting place for mini-bus transfer from Main Building to the Lost World Conference Centre |

BREAKFAST TRANSFERS:

7:30 am: Minibus departs Lost World Conference Centre for breakfast in Main Building
8:20 am: Minibus departs Main Building for Workshop in Lost World Conference Centre
# Program

## SCHEDULE DETAILS TUESDAY 31ST JULY – WEDNESDAY 1ST AUGUST

### 31 July 2012
**Tuesday**

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>16:50</td>
<td>Walking group departs ibis Hotel foyer for Icebreaker venue, walk will be via Ferry Terminal for those catching the Ferry</td>
</tr>
<tr>
<td>17:30</td>
<td>Icebreaker – Drinks and Canapés sponsored by ASI at: Decks Seafood and Steak Restaurant 26a Waterway Avenue, Southbank Parklands, Brisbane (Decks are able to accommodate delegates for dinner at delegates own cost. Other dining options are also available nearby)</td>
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### 1 August 2012
**Wednesday**

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>10:00</td>
<td>Depart for O’Reilly’s Rainforest Retreat from: ibis Hotel: 27-35 Turbot Street, Brisbane QLD 4000 Transfers to and from O’Reilly’s are with The Mountain Coach Company Late arrivals will not be transported to O’Reilly’s unless prior arrangements have been made</td>
</tr>
<tr>
<td>12:00</td>
<td>Lunch at Canungra’s Outpost Café</td>
</tr>
<tr>
<td>14:00</td>
<td>Arrive at O’Reilly’s Rainforest Retreat Check-in at Reception, Main Building</td>
</tr>
<tr>
<td>15:30</td>
<td>Welcome – Keith Sircombe, Geoscience Australia Inter-Laboratory Calibration Forum and Afternoon Tea Convenors: Bill Davis, Geological Survey of Canada Keith Sircombe, Geoscience Australia</td>
</tr>
<tr>
<td>17:00</td>
<td>Keynote Speaker Abstract Volume: Lance Black, Geoscience Australia ..... Page 15</td>
</tr>
<tr>
<td>17:40</td>
<td>Speaker Ed Roberts, Australian Scientific Instruments</td>
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<tr>
<td>18:00</td>
<td>Drinks on the Terrace Sponsored by Australian Scientific Instruments</td>
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<tr>
<td>19:00</td>
<td>Dinner</td>
</tr>
<tr>
<td>20:00</td>
<td>Leisure Time – Activities at delegates own cost</td>
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</tbody>
</table>
# Program

## SCHEDULE DETAILS THURSDAY 2\textsuperscript{ND} AUGUST

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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</table>
| 07:30 – 08:30 | Breakfast  
Dining Room, Main Building  
Minibus departs from the Lost World Conference Centre at 07:30 |
| 08:40 – 10:00 | Scientific and Technical Session 1: Applications  
Session Chair: Keith Sircombe  
Abstract Volume: |
| 8:40 | Neal McNaughton, Curtin University  
The Closepet Granite: a transcrustal magma chamber?  
Page 88 |
| 9:00 | Miguel Angelo Stipp Basei, Institute of Geosciences, Brazil  
U–Pb zircon ages and Hf isotopes from zircon megacrysts:  
Alto Paranaíba (Minas Gerais) and Juína (Mato Grosso) kimberlitic provinces, Brazil  
Page 13 |
| 9:20 | Nickolay Rodionov, VSEGEI  
Paleozoic activation of the Salmi rapakivi batholith (Baltic Shield) revealed by SIMS SHRIMP zircon dating  
Page 96 |
| 9:40 | Geoff Fraser, Geoscience Australia  
Zircon from iron-ore, Middleback Ranges, South Australia:  
isotope resetting and the age of supergene fluid-alteration?  
Page 54 |
| 10:00 – 10:40 | Morning Tea  
Official Photograph  
Poster Session: Applications |

### Poster Session: Applications

1. **Monika Kusiak**, Geochronology of granitoids from the Eastern Dharwar Craton, India
2. **Shinae Lee**, SHRIMP U–Pb mineral ages of Mesozoic granitoid plutons in the central Okcheon belt, Korea
3. **Namhoon Kim**, SHRIMP zircon geochronology of Late Cretaceous to Oligocene granitoid plutons in the eastern part of the Gyeongsang Basin, Korea
4. **Sergey Presnyakov**, An experience of Pleistocene-Pliocene zircon and perovskite dating: application to paleoarchaeology
5. **Kei Sato**, U–Pb SHRIMP IIe dating of zircon from Santa Catarina Quartzite – Luiz Alves Craton, South American Platform
6. **Tomokazu Hokada**, SHRIMP contributions to the geology of the Sor Rondane Mountains in Antarctica: the crossing of Late Neoproterozoic / Cambrian collision zones in Gondwana
<table>
<thead>
<tr>
<th>Time</th>
<th>Session/Activity</th>
<th>Abstract Volume</th>
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<tbody>
<tr>
<td>10:40</td>
<td><strong>Scientific and Technical Session 2: Applications</strong></td>
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<td><strong>Session Chair: Pete Kinny</strong></td>
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<tr>
<td>10:40</td>
<td>Chris Lewis, Geoscience Australia  .........................................................</td>
<td>Page 86</td>
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<tr>
<td></td>
<td><em>Insights into provenance pathways on the North West Shelf, Australia</em></td>
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<tr>
<td>11:10</td>
<td>Neal McNaughton, Curtin University  .......................................................</td>
<td>Page 90</td>
</tr>
<tr>
<td></td>
<td><em>Cratonic Source Codes</em></td>
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<tr>
<td>11:30</td>
<td>Simon Bodorkos, Geoscience Australia  ....................................................</td>
<td>Page 16</td>
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<tr>
<td></td>
<td><em>Accuracy of SHRIMP 206Pb/238U dating of natural zircon relative to CA-TIMS, with application to the Early Devonian timescale</em></td>
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<td>11:50</td>
<td>Andrew Cross, Geoscience Australia  .......................................................</td>
<td>Page 35</td>
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<tr>
<td></td>
<td><em>SHRIMP U–Pb isotopic and EPMA chemical U–Th–Pb dating of uraninite: some preliminary comparisons and pitfalls</em></td>
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<tr>
<td>12:10</td>
<td>Lunch On the Terrace</td>
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<tr>
<td>12:50</td>
<td>Leisure/Recreation Time – activities available through O’Reilly’s at delegates own cost (e.g., Birds of Prey Flight Show 13:00 – 13:40)</td>
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<tr>
<td>13:00</td>
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<td>Return to the Lost World Conference Centre by 2.10 pm</td>
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<td>14:10</td>
<td><strong>Scientific and Technical Session 3</strong></td>
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<td><strong>Lightning Impact Presentations: Applications</strong></td>
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<td><strong>Session Chair: Natalie Kositcin</strong></td>
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<tr>
<td>14:10</td>
<td>Daniel Dunkley, Curtin University  ..........................................................</td>
<td>Page 48</td>
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<tr>
<td></td>
<td><em>Multiple ages in prolonged orogenesis – an example from ‘Pan-African’ East Antarctica</em></td>
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<td>14:15</td>
<td>Chris Carson, Geoscience Australia  ........................................................</td>
<td>Page 27</td>
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<tr>
<td></td>
<td><em>Geoscience Australia’s SHRIMP program in the Australian Antarctic Territory</em></td>
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<tr>
<td>14:20</td>
<td>Ian Fletcher, Curtin University  .............................................................</td>
<td>Page 52</td>
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<tr>
<td></td>
<td><em>What is the source of Hadean zircons?</em></td>
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<td>14:25</td>
<td>Ian Fletcher, Curtin University  .............................................................</td>
<td>Page 53</td>
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<td></td>
<td><em>In situ dating of zircon in micro-tuffs supports a Proterozoic ‘snowball Earth’</em></td>
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<td>14:30</td>
<td>Keith Sircombe, Geoscience Australia  .....................................................</td>
<td>Page 104</td>
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<td></td>
<td><em>Experiments visualising detrital zircon age data with bumps and barcodes</em></td>
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<tr>
<td>Time</td>
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<td>14:40 – 15:20</td>
<td>Scientific and Technical Session 4: Methods</td>
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<td>14:40 David DiBugnara, Geoscience Australia</td>
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<tr>
<td></td>
<td>Mount making: from sample preparation to</td>
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<td>analysis</td>
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<td></td>
<td>Daniel Dunkley, Curtin University</td>
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<tr>
<td></td>
<td>Working towards paperless geochronology:</td>
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<td>integrating imaging, analysis and databases</td>
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<td>into an automated workflow</td>
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<td>15:20 – 15:40</td>
<td>Afternoon Tea</td>
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<td>15:40 – 16:40</td>
<td>Scientific and Technical Session 5:</td>
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<td></td>
<td>Developments</td>
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<td></td>
<td>15:40 Kenji Horie, NIPR</td>
<td>Page 64</td>
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<td></td>
<td>New calibration method for Hf in zircon:</td>
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<td>simultaneous analysis of Hf content with</td>
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<td>U–Pb dating</td>
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<td>16:00 Charles Magee, ASI</td>
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<td>Pb sensitivity dependence on primary ion</td>
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<td>impact energy</td>
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<td></td>
<td>16:20 Hiroshi Kaiden, NIPR</td>
<td>Page 105</td>
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<tr>
<td></td>
<td>Development of motorized O2 feed valve</td>
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<td>control system II</td>
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<td>16:40 – 18:00</td>
<td>Discussion time</td>
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<td>18:00 – 19:00</td>
<td>Keynote Speaker</td>
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<td></td>
<td>Lost World Conference Centre</td>
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<tr>
<td></td>
<td>Dan Condon, British Geological Survey</td>
<td>Page 32</td>
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<tr>
<td></td>
<td>$^{238}$U/$^{235}$U variation and the U–Pb</td>
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<td></td>
<td>chronometer</td>
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<td>19:00 – 23:00</td>
<td>Conference Dinner, served in the Dining</td>
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<td>Room, Main Building</td>
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<td>Mini-bus transfer will be available from the</td>
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<td>Lost World Conference Centre to the Main</td>
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<td></td>
<td>Building at 19:00</td>
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Program

SCHEDULE DETAILS FRIDAY 3RD AUGUST

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<thead>
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<th>Time</th>
<th>Event</th>
<th>Location</th>
</tr>
</thead>
<tbody>
<tr>
<td>07:30 – 08:30</td>
<td>Breakfast</td>
<td>Dining Room, Main Building</td>
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<tr>
<td></td>
<td>Minibus departs from the Lost World Conference Centre at 07:30</td>
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<tr>
<td>08:40 – 10:00</td>
<td>Scientific and Technical Session 6: Developments</td>
<td>Lost World Conference Centre</td>
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<tr>
<td>8:40</td>
<td>Ian Williams, ANU</td>
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<tr>
<td></td>
<td>Concerning conodonts</td>
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<tr>
<td>9:00</td>
<td>Hiroshi Hidaka, Hiroshima University</td>
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<tr>
<td></td>
<td>In situ Sm isotopic analysis of neutron-irradiated materials</td>
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<tr>
<td>9:20</td>
<td>Mami Takehara, Kyushu University</td>
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<tr>
<td></td>
<td>Application of zircon REE patterns</td>
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<tr>
<td>9:40</td>
<td>William Davis, Geological Survey of Canada</td>
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<td></td>
<td>Adventures in uraninite geochronology</td>
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</tr>
<tr>
<td>10:00 – 10:40</td>
<td>Morning Tea</td>
<td>Lost World Conference Centre</td>
</tr>
</tbody>
</table>

Poster Session: Methods and Techniques

7. Simon Bodorkos, Best of both worlds: combining SHRIMP and CA-TIMS methods in refining geochronological determinations for timescale calibration

8. Jeongmin Kim, Late Permian to Early Triassic arc magmatism and Middle-Late Triassic thermal overprint in southeastern Korea: SHRIMP U–Pb zircon geochronology and Nd isotope geochemistry

9. Chang-sik Cheong, Mixing effects in SHRIMP zircon U–Pb dating: an example from a quartzfeldspathic dyke in the Yeongdeok pluton, SE Korea

10. Jorge Vazques, SHRIMP-RG $^{238}\text{U} - ^{230}\text{Th}$ dating of Late Pleistocene allanite

11. Hongyan Geng, SHRIMP remote control and MC-ICP-MS at the University of Hong Kong

12. Carlos E. Ganade de Araujo, Arc reworking during collision: combined Lu–Hf LA-ICP-MS and U–Pb SHRIMP results from the Tamboril-Santa Quitéria complex, NE Brazil
### Scientific and Technical Session 7: Data Processing Forum

**Session Chair:** Andrew Cross

- **10:40**  
  **Keith Sircombe**, Geoscience Australia  
  *SQUID in the Clouds – what is next for SHRIMP data processing?*  
  Page 101

- **10:50**  
  **Hiroshi Kaiden**, NIPR  
  *SQUID-2 compatibility problem for non-English speaking countries*  
  Page 66

- **10:55** Discussion until lunch

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### Scientific and Technical Session 8: References

**Session Chair:** Daniel Condon

- **14:10**  
  **Ian Fletcher**, Curtin University  
  *The Moacyr monazite standard: identity and compositional complications*  
  Page 49

- **14:30**  
  **Bob Pidgeon**, Curtin University  
  *Radiation damage in the TEMORA zircon standard*  
  Page 91

- **14:50**  
  **Allan Kennedy**, Curtin University  
  *SHRIMP apatite analysis and data reduction*  
  Page 68

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**12:10 – 12:50** Lunch On the Terrace

**12:50 – 14:10** Leisure/Recreation Time – activities available through O’Reilly’s at delegates own cost (e.g., Birds of Prey Flight Show 13:00 – 13:40)

Return to the **Lost World Conference Centre by 2.10 pm**

**15:20 – 15:40** Afternoon Tea
### Scientific and Technical Session 9: Lightning Impact Presentations | Technical Discussions

**Session Chair:** Ian Williams

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<thead>
<tr>
<th>Time</th>
<th>Speaker</th>
<th>Institution</th>
<th>Abstract</th>
<th>Page</th>
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<tbody>
<tr>
<td>15:40</td>
<td>Emma-Kate Chisholm</td>
<td>Geoscience Australia</td>
<td><em>The distribution of TEMORA2: from one small paddock to the world</em></td>
<td>30</td>
</tr>
<tr>
<td>15:45</td>
<td>Andrew Cross</td>
<td>Geoscience Australia</td>
<td><em>Rock crushing, radiation protection and regulations</em></td>
<td>37</td>
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<tr>
<td>15:50</td>
<td>Keewook Yi</td>
<td>KBSI</td>
<td><em>Recent technical development of triple oxygen isotopic analysis using SHRIMP-11e/MC</em></td>
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<tr>
<td>15:55</td>
<td>Monika Kusiak</td>
<td>Curtin University</td>
<td><em>Pb isotopes in zircon by ion imaging</em></td>
<td>83</td>
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<td>16:00</td>
<td>David DiBugnara</td>
<td>Geoscience Australia</td>
<td><em>Automated SEM location of monazite in polished thin section</em></td>
<td>44</td>
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<td>16:05</td>
<td>Patrick Burke</td>
<td>Geoscience Australia</td>
<td><em>Improving duoplasmatron reliability</em></td>
<td>25</td>
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<td>16:10</td>
<td>Patrick Burke</td>
<td>Geoscience Australia</td>
<td><em>SHRIMP preventive maintenance program</em></td>
<td>26</td>
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<tr>
<td>16:20</td>
<td></td>
<td><strong>Technical Discussions</strong></td>
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### Evening program

<table>
<thead>
<tr>
<th>Time</th>
<th>Activity</th>
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<tbody>
<tr>
<td>17:30</td>
<td><strong>4WD bus departure from the Lost World Conference Centre for dinner at “The Slaughterhouse”</strong></td>
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<tr>
<td>17:45</td>
<td><strong>Official Close of Conference</strong> – Keith Sircombe, Geoscience Australia</td>
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<tr>
<td></td>
<td>Campfire Drinks followed by Dinner</td>
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<tr>
<td>20:00</td>
<td><strong>7th International SHRIMP Workshop 2014 Discussion</strong></td>
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<td></td>
<td>Toolona Conference Room, <strong>Main Building</strong></td>
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<tr>
<td></td>
<td><strong>4WD bus will transfer participating delegates from dinner to the Toolona Conference Room</strong></td>
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<tr>
<td>20:00</td>
<td>Leisure/Recreation Time – activities available through O’Reilly’s at delegates own cost.</td>
</tr>
</tbody>
</table>
### Program

**SCHEDULE DETAILS SATURDAY 4\(^{\text{TH}}\) AUGUST**

<table>
<thead>
<tr>
<th>Time</th>
<th>Event</th>
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</table>
| 07:30 – 08:30 | **Breakfast**  
Dining Room, Main Building  
*Minibus for breakfast departs from the Lost World Conference Centre at 07:30, and returns at 08:30.*  
*A minibus for checkout will depart from the Lost World Conference Centre at 08:45 for Reception for delegates in Villa accommodation who require assistance with luggage to reception* |
| 09:00 | **Check-out**  
Reception, Main Building  
*Please ensure you have your luggage with you as the bus will be departing from the Main Building Bus area.*  
*For delegates staying in Villa accommodation, mini-bus transfers will depart the Lost World Conference Centre for the Main Building at 08:45* |
| 09:30 | **Depart** O’Reilly’s Rainforest Retreat  
Main Building Bus Area |
| 12:00 – 14:30 | **Lunch** at the David Fleay Wildlife Reserve  
Burleigh Heads |
| 14:30 | **Bus departs Wildlife Reserve for Brisbane**  
via Burleigh Heads |
| 17:00 | **Bus arrives at Brisbane Airport for delegates departing Brisbane in the evening** |
| 18:00 | **Bus returns to Brisbane City for delegates staying in Brisbane** |
| 19:00 | Recreation time for interested delegates: Australian Football game at Gabba Stadium, Brisbane |

**5 August 2012**  
**Sunday**  
**34\(^{\text{TH}}\) International Geological Congress commences, Brisbane**
U–Pb zircon ages and Hf isotopes from zircon megacrysts: Alto Paranaíba (Minas Gerais) and Juína (Mato Grosso) kimberlitic provinces, Brazil

M.A.S. Basei¹, D. Svisero¹, K. Sato¹, W. Iwanuch², C.C.G. Tassinari¹ and W.M. Sproesser¹

¹Instituto de Geociências, USP, SP, BRAZIL
²Faculdade de Geologia, UERJ, RJ, BRAZIL

INTRODUCTION
The wide geographical distribution of diamond field occurrences in the Brazilian territory is itself evidence of the existence of several kimberlite provinces, among which we stress the Alto Paranaíba (Minas Gerais State) and Juína (Mato Grosso State) provinces. The Alto Paranaíba Province comprises hundreds of intrusive Cretaceous bodies within allochthonous metasedimentary cover of the southwestern border of the São Francisco Craton. The Juína Province is composed of many kimberlite intrusions in sandstones that cover the metamorphic basement of the southwestern Amazonas Craton. Here we present new U–Pb (SHRIMP) zircon ages and Hf isotopes (LA-ICP-MS) from zircon megacrysts of the Alto Paranaíba and Juína provinces.

U–Pb ANALYTICAL PROCEDURE
All analyses were performed at the Centro de Pesquisas Geocronológicas of Institute of Geosciences, University of São Paulo, Brazil. The zircons were extracted from saprolite derived from kimberlite intrusions, and hand-picked under a binocular stereomicroscope. The crystals were mostly rounded, yellow-pink to translucent and rarely transparent, averaging between 0.6 and 1.5 cm in diameter. Prior to analysis, these crystals were washed several times with MilliQ water and 6N HNO₃ for removal of common lead adhered to the crystal surface. Cathodoluminescence imaging showed that most of the crystals are oscillatory zoned and do not contain any inherited cores.

Obtaining reliable ages from these Cretaceous, low-U (10–30 ppm) zircons posed an analytical challenge. The procedures and analytical conditions routinely used in the SHRIMP analyses were modified to the following configuration: Primary Beam: Kohler aperture = 120 µm, spot size = 30 µm, and O₂ beam density around 6–4 ηA; Secondary Beam: Source Slit = 80 µm; Mass Resolutions for ¹⁹⁶(Zr₂O), ²⁰⁶Pb, ²⁰⁷Pb, ²⁰⁸Pb, ²³⁸U, ²⁴⁸(ThO) and ²⁵⁴(UO) greater than 5000 (1%) with residuals less than 0.025 without high energy slit, low energy slit = 1 mm, and collector slit = 100 µm. Data acquisition involved a 2-minute raster with 2 minutes of burning time and a spot size of 120 µm; Primary autotune (Src Steering Y and Z) was enabled, as was secondary autotune (QT1Y and Z). The ²⁵⁴(UO) peak was used as the autorun selector, and peak autocentring was performed using 50% peak height. Data were acquired using 7 cycles through the run table, and all raw count rates have been corrected for a collection system dead time of 25ηs (also see Table 1). The standards used were SL13 for U concentration calibration (238 ppm), and TEMORA (417 Ma) for ²⁰⁶Pb/²³⁸U isotopic normalization.

RESULTS
SHRIMP ages of zircons from both provinces confirm the Cretaceous ages previously obtained by K–Ar, Ar–Ar and U–Pb TIMS methods. In the Alto Paranaíba Province there is an age distribution that may reflect three distinct emplacement pulses for the kimberlitic intrusions (92.4 ± 1.5 Ma, 88.2
± 2.1 Ma and 82.4 ± 2.1 Ma). Age data from the Juína Province revealed a single population with a mean average of 92.8 ± 2.9 Ma.

Table 1: Conditions of U–Pb zircon analysis.

<table>
<thead>
<tr>
<th></th>
<th>$^{206}$Pb</th>
<th>$^{204}$Pb</th>
<th>$^{207}$Pb</th>
<th>$^{206}$Pb</th>
<th>$^{208}$Pb</th>
<th>$^{238}$U</th>
<th>$^{254}$ThO</th>
<th>$^{254}$UO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delay (s)</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Counting Time (s)</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>40</td>
<td>2</td>
<td>10</td>
<td>5</td>
</tr>
<tr>
<td>Auto Center</td>
<td>On</td>
<td>Off</td>
<td>Off</td>
<td>Off</td>
<td>Off</td>
<td>On</td>
<td>Off</td>
<td>On</td>
</tr>
</tbody>
</table>

Time = seconds, $^{204}$Pb = background, Mass Auto Center: enabled = On, disabled = Off

Previous Hf studies have shown that the signatures of Alto Paranaíba Province kimberlitic-type rocks are distinct from those that characterize the Juína Province. The $\varepsilon$Hf(t) values are predominantly negative for the Alto Paranaíba Province (-25.4 to -1.6) with occasional values reaching up to +2. However, in the Juína Province, the $\varepsilon$Hf(t) values are strongly positive (+6.4 to +16.5), with the exception of the Acuri intrusion, which exhibits moderately negative values (-4.7 to -2.7).

CONCLUSIONS

The U–Pb SHRIMP data do not conclusively establish an age difference between the Juína Province and the Alto Paranaíba Province, with the oldest age of 92 Ma occurring in both provinces. Moreover, the new U–Pb SHRIMP data support the suggestion that the kimberlitic magmatism in the Alto Paranaíba Province was recurrent, with the most recent event extending up to about 82 Ma. The available Hf data suggest a significant difference between the two provinces, with $\varepsilon$Hf(t) values being predominantly positive in the Juína Province, and negative in the Alto Paranaíba Province.

In addition, considering that whole-rock Sm–Nd isochron age of 850 Ma obtained in kimberlites from the Alto Paranaíba Province is similar to the zircon U–Pb ages of most of the juvenile granites that characterize the initial phases of the Goiás magmatic arc, it is possible to suggest that an important mantle melting associated with Neoproterozoic subduction occurred at this time that led to the generation of the arc. This frozen lithospheric mantle coupled to the base of the São Francisco Craton would be the source of the Cretaceous kimberlites of the Alto Paranaíba Province. In contrast, the predominant positive $\varepsilon$Hf signature of the kimberlites from the Amazonas Craton (Juina Province) suggests a more primitive and much deeper asthenospheric source.
An ageing geochronologist's perspective on the role of Geoscience Australia in the development of SHRIMP dating

L.P. Black*

Geoscience Australia, GPO Box 378, Canberra, ACT 2601 AUSTRALIA
*retired

Geoscience Australia’s (GA) SHRIMP dating capability has developed from a close association with the ANU Research School of Earth Sciences (RSES) over almost half a century. Most of that time has been spent in a shared facility at the RSES. This association began with Rb–Sr and K–Ar dating. Conventional ID-TIMS U–Pb zircon dating, commenced in the mid 1970s, was complemented by SHRIMP dating in the early 1980s and eventually replaced by it.

Although GA had only a minor input in the development of SHRIMP I, the undoubted value of this instrument for geological dating led to GA investing in a one third share of the development costs for SHRIMP II. This instrument, located at the RSES, then became the workhorse for GA geochronology for well over a decade. The main problem was that demand was so high that a one-third share of a single SHRIMP became insufficient to meet all of GA’s needs. Consequently, an order was placed with Australian Scientific Instruments (ASI) to construct another SHRIMP II, to be housed at GA, where it was commissioned in April 2008.

It is a testament to the extraordinary nature of SHRIMP that it has remained at the forefront of geochronology for more than three decades. GA has contributed significantly to the procedural innovations that have been made to enhance the performance of the instrument. These include the instigation of prolonged analytical sessions that incorporate more than one zircon suite in order to maximise the amount of data obtained during a single calibration. Another important role has been the assessment of various zircon reference standards. This process has led to the identification and documentation of the TEMORA zircon standard, which is now being used in GA and in more than 100 other laboratories throughout the world. TEMORA is not only an excellent U–Pb standard, but has more recently been shown to also be a quality reference for hafnium and oxygen isotopic studies.
Accuracy of SHRIMP $^{206}\text{Pb}/^{238}\text{U}$ dating of natural zircon relative to CA-TIMS, with application to the Early Devonian timescale

S. Bodorkos¹, D.J. Pogson², R.M. Friedman³ and E.I. Chisholm¹

¹Geochronology Laboratory, Minerals and Natural Hazards Division, Geoscience Australia, GPO Box 378, Canberra ACT 2601, AUSTRALIA
²88 Talleen Road, Nelson Bay, NSW 2315, AUSTRALIA
³Pacific Centre for Isotopic and Geochemical Research, Department of Earth and Ocean Sciences, University of British Columbia, 6339 Stores Road, Vancouver BC V6T-1Z4, CANADA

simon.bodorkos@ga.gov.au

INTRODUCTION

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 $^{206}\text{Pb}/^{238}\text{U}$ 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 five felsic volcanic rocks from the Eastern Subprovince of the Lachlan Orogen (New South Wales, Australia), which is notable for earliest Devonian (Lochkovian–Pragian) felsic volcanism with good biostratigraphic control. The global paucity of felsic volcanism in this interval confers timescale significance on precise and accurate isotopic ages constraining the eruption events.

EARLY DEVONIAN FELSIC VOLCANISM IN THE EASTERN LACHLAN OROGEN

Biostratigraphic constraints

The five samples (Figure 1) are from the Bulls Camp Volcanics, the Turondale Formation, and three samples (lower, middle and upper) from the Merrions Formation, which stratigraphically overlies the Turondale Formation. The Bulls Camp Volcanics and Turondale Formation are biostratigraphically constrained to the early and middle parts of the Lochkovian respectively, based on terminal Pridolian (and, in places, earliest Devonian) graptolites in the conformably underlying shales, and the presence of delta to pesavis zone conodonts in the conformably underlying shales, and the presence of delta to pesavis zone conodonts in the uppermost Turondale Formation and overlying sedimentary rocks (Pogson and Watkins, 1998). Deposition of the Merrions Formation probably commenced in the early Pragian, and the unit is conformably overlain by sedimentary rocks containing the Pragian index tentaculitid Nowakia acuaria, and conodonts referable to the Pragian kindlei and pireneae zones (Packham et al., 2001), so a middle Pragian age is indicated for the Merrions Formation.

Previous U–Pb SHRIMP zircon analyses

All five samples were analysed via SHRIMP in the late 1990s (Jagodzinski and Black, 1999), by which time it had become apparent that mean $^{206}\text{Pb}/^{238}\text{U}$ dates calibrated using SL13 (572 Ma) were often younger by 1% or more, relative to the same data calibrated using QGNG (1850 Ma). Jagodzinski and Black (1999) therefore normalised all of their SL13-calibrated ages to QGNG indirectly, using an intermediary ‘internal standard’ from the Merrions Formation (not part of this study), for which independent SL13-calibrated and QGNG-calibrated ages were obtained. This manipulation improved the accuracy of their interpreted mean $^{206}\text{Pb}/^{238}\text{U}$ dates, but inevitably degraded their precision, due to the need to add (in quadrature) the uncertainty in the age of the
‘internal standard’ to all the other sources of error (Jagodzinski and Black, 1999). The final age uncertainties were about 1.5% ($2\sigma$), and would ordinarily be unacceptable as constraints on the Paleozoic timescale. So the fact that two of these QGNG-calibrated ages (413.4 ± 6.6 Ma for the Turondale Formation, and 409.9 ± 6.6 Ma for the lower Merrions Formation) were utilised in the Geological Time Scale 2004, as constraints on the latest Lochkovian and latest Pragian respectively, highlights the global stratigraphic significance of these earliest Devonian volcanic units, and underlines the importance of improving the isotopic constraints on the eruption ages.

**METHODS**

Zircons for this study were sourced from the remainder of the least paramagnetic mineral separates originally prepared for Jagodzinski and Black (1999). For CA-TIMS, handpicked zircons were analysed at the Pacific Centre for Isotopic and Geochemical Research, University of British Columbia (UBC), following Scoates and Friedman (2008). Zircons selected for analysis (5–6 per sample) were annealed at 850°C for 48 hours, and chemically abraded using 500 µL of ultrapure 50% HF and 50 µL of $^{14}$NHNO$_3$, heated to 200°C for 16 hours. Each zircon was separated from its leachate and rinsed, before being spiked with the UBC $^{205}$Pb-$^{233}$U-$^{235}$U isotopic tracer. The associated with the U/Pb ratio of the tracer has an uncertainty of 0.10% ($2\sigma$), which is included (via quadratic addition) in the $2\sigma$ uncertainty of the weighted mean $^{206}$Pb/$^{238}$U date for each sample.

For SHRIMP, new zircon aliquots (~300 grains per sample) were co-mounted with two bracketing rows of TEMORA2 (416.8 Ma), in an attempt to quantify across-mount variation in measured $^{206}$Pb/$^{238}$U. A single 112-hour session on the Geoscience Australia SHRIMP Ile acquired 32 analyses of each of the five samples, interspersed with 72 analyses of TEMORA2, which constituted a single dataset for calibration purposes. Data were reduced using SQUID 2.50.11.02.03, and common Pb corrections were applied using measured $^{204}$Pb. The TEMORA2 dataset displayed the usual scatter in $^{206}$Pb/$^{238}$U beyond analytical uncertainties (MSWD = 3.2), and the associated external error (1.00%; $1\sigma$) and internal error (0.30%; $2\sigma$) 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 ($2\sigma$) for the TEMORA2 zircon, which included an uncertainty of 0.13% ($1\sigma$) 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 compared with CA-TIMS dates.
CA-TIMS VERSUS NATURAL SHRIMP RESULTS

The new CA-TIMS and SHRIMP results are presented in Table 1 and Figure 2. Overall agreement is excellent, with every pair of $^{206}$Pb/$^{238}$U dates equivalent within their 2σ uncertainties, which in all cases are quite small (0.12–0.23% for the CA-TIMS dates; 0.59–0.67% for the SHRIMP dates). Two CA-TIMS analyses from the Bulls Camp Volcanics were affected by Pb loss that was not discerned during SHRIMP analysis of the natural zircons. This probably reflects incomplete chemical abrasion of some of the natural crystals, which are paramagnetic, inclusion-rich, and slightly elevated in U relative to the other samples analysed.

Dispersion beyond analytical uncertainty is evident in all three CA-TIMS datasets from the Merrions Formation, and is attributed in each instance to the presence of marginally older (‘Turondale-aged’) inheritance. The much larger individual $^{206}$Pb/$^{238}$U uncertainties in the SHRIMP datasets naturally mask such subtle variation, but in each case the dominant, statistically-coherent mean SHRIMP date is marginally older than (although well within error of) the CA-TIMS date, a pattern consistent with the mixing (in varying proportions) of unresolvable ‘magmatic’ and marginally older ‘inherited’ zircon components in the SHRIMP datasets.

Table 1: Comparison of CA-TIMS and natural SHRIMP dates (both with 2σ errors). Parenthetical values reflect the number of analyses included in the mean, out of the total number collected.

<table>
<thead>
<tr>
<th>Sample</th>
<th>CA-TIMS $^{206}$Pb/$^{238}$U (Ma)</th>
<th>SHRIMP $^{206}$Pb/$^{238}$U (Ma)</th>
<th>SHRIMP U (ppm)</th>
<th>SHRIMP Common $^{206}$Pb (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulls Camp Volcs</td>
<td>417.7 ± 0.5 (3/5)</td>
<td>417.9 ± 2.5 (33/33)</td>
<td>344 ± 35</td>
<td>0.25 ± 0.06</td>
</tr>
<tr>
<td>Turondale Fm</td>
<td>415.6 ± 0.5 (6/6)</td>
<td>416.0 ± 2.7 (32/32)</td>
<td>187 ± 15</td>
<td>0.37 ± 0.09</td>
</tr>
<tr>
<td>Lower Merrions Fm</td>
<td>411.7 ± 0.9 (4/6)</td>
<td>413.0 ± 2.7 (30/32)</td>
<td>147 ± 22</td>
<td>0.73 ± 0.16</td>
</tr>
<tr>
<td>Middle Merrions Fm</td>
<td>413.8 ± 0.8 (4/5)</td>
<td>414.2 ± 2.5 (32/32)</td>
<td>166 ± 18</td>
<td>3.08 ± 0.44</td>
</tr>
<tr>
<td>Upper Merrions Fm</td>
<td>412.7 ± 1.0 (3/5)</td>
<td>413.3 ± 2.6 (32/32)</td>
<td>178 ± 17</td>
<td>0.48 ± 0.11</td>
</tr>
</tbody>
</table>

Figure 2: Comparison of natural $^{206}$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 the probability of equivalence of the two dates. The heavy horizontal and vertical lines represent three different positions for the Lochkovian (top right)-Pragian (bottom left) boundary: GTS 2012 = Gradstein et al. (in press); K 2006–P 2009 = Kaufmann (2006) and Pogson (2009); This study = approximate position based on the data presented herein, and the biostratigraphic evidence for a Pragian age for the Merrions Formation.
Implications for the Early Devonian timescale

In terms of the Early Devonian timescale, the combined biostratigraphic and isotopic data presented here suggest that the Lochkovian–Pragian Stage boundary lies near ~414 Ma, marginally older than the value proposed by Kaufmann (2006) and Pogson (2009), and significantly older than that in the Geologic Time Scale 2012 (Figure 1). Our data support Lochkovian and Pragian Stages of similar total duration (~5 million years), and the implied 'slowing' of conodont evolution (implied by the presence of only three conodont zones in the Pragian, as opposed to four in the Lochkovian; Figure 1) is consistent with the longer-term pattern established in the Early Devonian, where individual conodont zones in the Emsian are inferred to span up to ~5 million years, and possibly longer.

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

This study has shown that under good analytical conditions, mean $^{206}\text{Pb} / ^{238}\text{U}$ dates obtained from natural zircons via SHRIMP can be very accurate, and well within error of CA-TIMS zircon dates, even when the 2σ error envelopes for the two techniques are of the order of 0.6% and 0.2% respectively. In this study (cf. Kryza et al., 2012), it is likely that the comparison was aided by the low-U, low-common $^{206}\text{Pb}$ character of the analysed zircons, which were targeted on the basis of their weak paramagnetism. These crystals contained abundant domains with very good overall crystallinity, which clearly represented good proxies for the well-ordered zircon that typically survives the chemical abrasion process (Mattinson, 2005).

High-quality SHRIMP $^{206}\text{Pb} / ^{238}\text{U}$ dating of natural zircon probably depends heavily upon isolating such pristine zircon in sufficient quantities, and one important but often overlooked consideration in such comparisons is the quality and quantity of the host rock material sampled. All five samples in this study were zircon-rich rocks collected in considerable bulk (20–30 kg) from good-quality outcrop, and the abundant zircon yields permitted the luxury of pursuing target zircons in the ‘best’ ~0.01% of the population, which is biased strongly against grains with low density or strong paramagnetism. Such options will rarely be available for samples with low zircon yields and/or restricted rock volumes (e.g., diamond drillcore), and it is likely that CA-TIMS and SHRIMP results will diverge as a consequence of the necessity of analysing less-than-perfect natural zircons with the ion beam. In such scenarios, chemical abrasion of the recovered zircons may be prudent regardless of the preferred analytical method, although the extent to which chemical abrasion could compromise the post-SHRIMP measurement of HF and O isotopes remains largely uninvestigated.

REFERENCES


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

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\section*{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 \( ^{206}\text{Pb}/^{238}\text{U} \) 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.

\section*{METHODS}
This study took advantage of the opportunity to test a collaborative approach to zircon \( ^{206}\text{Pb}/^{238}\text{U} \) 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 \( ^{206}\text{Pb}/^{238}\text{U} \) 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 \( ^{207}\text{Pb} \). In each session, the TEMORA2 dataset displayed the usual scatter in \( ^{206}\text{Pb}/^{238}\text{U} \) 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
\(^{206}\text{Pb}/^{238}\text{U}\) 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 \(^{206}\text{Pb}/^{238}\text{U}\) 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 \(^{206}\text{Pb}/^{238}\text{U}\) 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 \(^{202}\text{Pb},^{205}\text{Pb},^{233}\text{U},^{235}\text{U}\) (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 \(^{206}\text{Pb}/^{238}\text{U}\) 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 \(^{206}\text{Pb}/^{238}\text{U}\) 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 \(^{206}\text{Pb}/^{238}\text{U}\) 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
\(^{206}\text{Pb}/^{238}\text{U}\) 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 \(^{206}\text{Pb}/^{238}\text{U}\) uncertainties in the SHRIMP datasets mask such subtle variation,
but in three of the 10 SHRIMP datasets, the statistically-coherent mean \(^{206}\text{Pb}/^{238}\text{U}\) 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
\(^{206}\text{Pb}/^{238}\text{U}\) 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 \(^{206}\text{Pb}\) 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 \(^{206}\text{Pb}\) 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 \(^{206}\text{Pb}\) 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.

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

Figure 1: Comparison of 206Pb/238U 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 206Pb/238U IN NATURAL ZIRCON

This study has shown that mean 206Pb/238U 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 206Pb 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 206Pb/238U 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


Improving duoplasmatron reliability

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Unstable and unreliable duoplasmatron performance is a primary cause of poor quality data and SHRIMP instrument downtime. At Geoscience Australia, we have implemented a regime to improve duoplasmatron reliability and stability, which has contributed to increased utilisation efficiency and minimised instrumental data effects.

Standardised methods of duoplasmatron cleaning, preparation, maintenance and component replacement have been developed and duoplasmatron running parameters have been optimised. Modifications to duoplasmatron components have been made where necessary. Outcomes include longer periods of analytical ‘uptime’ between service intervals, improved beam quality and stability, longer Kohler aperture life, and minimised instrumental effects.
SHRIMP preventive maintenance program

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Unexpected equipment failures can be a major cause of SHRIMP instrument downtime. At Geoscience Australia we have implemented a preventive maintenance program (PMP) to major serviceable components to improve instrument reliability.

A PMP both requires and allows planning of downtime periods and the predictability of a PMP means downtime can be minimised. Several maintenance issues may be amalgamated into one maintenance period, which may then be scheduled in and around analytical sessions. This minimises inconvenience to both SHRIMP users and laboratory staff.
Geoscience Australia’s SHRIMP program in the Australian Antarctic Territory

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Geoscience Australia has recently recommenced development of special-edition 1:25000 scale Antarctic onshore geological map products within the Australian Antarctic Territory (AAT). In order to maximise the utility of these map products, an accompanying SHRIMP geochronology program (and whole rock Sm–Nd analysis) has been also implemented thereby ‘value-adding’ important geological information to these strategically important map products. The acquisition of baseline geochronological data from these often poorly understood regions is invaluable to the wider geoscience community in order to foster intrinsic understanding of the geological evolution of the Antarctic. Furthermore, quality onshore map products of the AAT are utilised by the Australian Government to support a range of activities, including environmental management and protection, thus fulfilling commitments to the Antarctic Treaty System.

Geoscience Australia (and its predecessors, BMR and AGSO) has had a long and vibrant history of regional geological mapping in the AAT, and during the 1980–90s, was supported by the pioneering isotopic investigations of BMR-AGSO-GA geochronologist Dr L.P. Black. It is hoped that this reinvigorated geochronological agenda will re-establish Geoscience Australia’s Antarctic geochronology program within the Antarctic Geoscience community to levels not seen since the glory days of Antarctic geochronology driven by Dr Black.
Mixing effects in SHRIMP zircon U–Pb dating: an example from a quartzofeldspathic dyke in the Yeongdeok pluton, SE Korea

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A swarm of quartzofeldspathic dykes intruded the Permian–Triassic Yeongdeok pluton and xenoliths therein in southeastern Korea. Zircons from the dyke intruding a diorite xenolith yield Sensitive High Resolution Ion Microprobe (SHRIMP) 206Pb/238U dates ranging from Middle Permian (c. 260 Ma) in the crystal cores to Late Cretaceous (c. 82 Ma) in the outermost rims, with a negative correlation between U contents and ages (Figures 1A, 1B).

The U contents of the rims (3300–17000 ppm) are much higher than those of the cores (160–6700 ppm). The negative trend between U contents and ages (Figure 1B) indicates an initial mixing relationship between the older, low-U component and the younger, high-U component. The older end-member is easily identified as zircons from the diorite, in light of their coeval ages and comparable U contents with the zircon cores. These inherited zircons were overgrown in the crystal-melt system when the dyke intruded the diorite. Therefore the other end-member could be represented by the youngest (82 Ma) data point in zircon rims having the U concentration of c. 12000 ppm. The exact timing of dyke intrusion and mixing in the zircon is, however, difficult to determine because high-U zircons (U >2500 ppm) are likely to experience radiogenic Pb loss, and tend to yield overestimated Pb/U ratios (Williams and Hergt, 2000). As we have no independent age control, mixing in the zircon grains is assumed to have occurred at 82 Ma for the model calculation.

In Figure 1C, the initial (at 82 Ma) mixing relation is shown between the end-member ‘A’, the older (261 Ma) and medium-U (238U = 2100 ppm on average) zircon crystals inherited from the diorite, and the end-member ‘B’, the younger (82 Ma) and high-U (238U = 12000 ppm) zircon rims grown during intrusion of the dyke. It is not likely that U and Pb have always been incorporated into the end-member ‘B’ with the same proportion principally because the melt composition should have changed. Three mixing lines are shown in Figure 1C between the end-member ‘A’ and the end-member ‘B’ having different 238U/206Pb ratios of 79, 185 and 1503 (their present-day common Pb fractions are calculated to be 0.5, 0.3 and 0.05, respectively). In this mixing model, the 207Pb/206Pb ratio of common Pb was assumed to be 0.841 after Stacey and Kramers (1975) and the common Pb fraction in the end-member ‘A’ to be 1%. It is likely that the U content in the end-member ‘B’ has changed during the growth of zircon rims. The U contents of the end-members, however, do not affect the mixing vectors in Figure 1C. In Figure 1D, the present positions of the mixing lines in Figure 1C are shown on a Tera-Wasserburg plot with measured uncorrected data. Common Pb-uncorrected data points mostly plot in the field encompassed by mixing lines of which common Pb fractions are 0.05 and 0.5. Some points plotting beyond this field might have had the lower (<79) or higher (>1503) 238U/206Pb ratios in the end-member ‘B’ during mixing. Alternatively, recent remobilization of U or Pb might shift their horizontal positions on the plot. The common Pb fractions estimated from the measured 204Pb counts are generally in agreement with those calculated from our mixing model.
This model satisfactorily explains the variations in SHRIMP U–Pb isotope data of zircons from the dyke. The mixing proportions of the end-member ‘A’ in the zircons are broadly estimated to be higher than 60%, although they are dependent on the model U contents of the end-members. Most U–Pb isotope data of zircon in this case have no geochronological significance except for the end-member compositions, requiring caution in interpreting each result.

**Figure 1**: (A) A Tera-Wasserburg plot for 204Pb-corrected zircon data from the dyke; (B) Plot of U concentrations vs. 207Pb-corrected 206Pb/238U dates with error bars (1σ) for analysed spots of zircons from the dyke; (C) Initial (T = 82 Ma) mixing lines between the end-member ‘A’ and the end-member ‘B’ having different U/Pb ratios (238U/206Pb = 79, 185 and 1503) are shown on a 207Pb/206Pb vs. 238U/206Pb plot. Circles along the lines indicate mixing proportions of the end-member ‘A’ (f_A) in 10% increments when present 238U concentrations are 2100 ppm and 12000 ppm for the end-member ‘A’ and ‘B’, respectively; (D) Evolved present mixing lines (206Pb/206Pb_total in the end-member ‘B’ = 0.5, 0.3 and 0.05) are shown on a Tera-Wasserburg plot with data points uncorrected for common Pb. Error ellipses are at 1σ level.

**REFERENCES**


The distribution of TEMORA2: from one small paddock to the world

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TEMORA2

The TEMORA2 zircon crystallised within the Early Devonian Middledale Gabbroic Diorite (MGD), a small high-level stock in the Eastern Lachlan Orogen near Temora, New South Wales, Australia (Figure 1). The zircon reference material is sourced from rocks on the northern margin of the stock (Black et al., 2004). ID-TIMS analysis of the zircons gives a best estimate age for TEMORA2 of 416.78 ± 0.33 Ma (Black et al., 2004).

DISTRIBUTION OF TEMORA2

Geoscience Australia (GA) is the custodian of the TEMORA2 zircon reference and the material is distributed around the world both as zircon separate and whole rock. The material is currently used in 113 laboratories in 26 countries, with material sent regularly to assist laboratories establishing their internal references.

GA does not charge for the distribution of TEMORA2. GA will supply a 0.02 g (20 mg) aliquot of grains separated to handpicking stage to assist laboratories establishing their own in-house reference material. GA does not have the facilities to provide separated zircon material for ongoing use in...
laboratories as the primary reference. Laboratories interested in using TEMORA2 as an ongoing reference material are offered 10 kg of whole rock for their own separation procedures, provided under a Memorandum of Understanding (MOU).

The MOU establishes the supply of ‘raw’ TEMORA2 rock from GA to the requesting institution/laboratory. The MOU formally establishes several caveats that GA has placed on the supply of the material, in particular, preventing reselling of the material for commercial benefit, and to emphasise the spirit of collegiality in which GA and the landowners wish to see the material used.

THE PROJECT
Further study is being undertaken by Honours student Kieran Iles from Melbourne University, supervised by Janet Hergt. The broad aim of the project is to improve our understanding of the local geological history of the MGD, with a specific focus on determining what processes have taken place during and post emplacement, cooling and crystallisation.

In detail, the project will establish a whole rock grainsize and geochemical profile across the MGD, determine if there is any variation across the pluton using SHRIMP $^{206}\text{Pb}/^{238}\text{U}$ zircon dating, examine apparent $\delta^{18}$O variation in parts of the pluton, and assess the Lu–Hf isotopic composition of the zircons within the regional geological framework. Additionally, the project will assess the spatially associated Windover and Woodlands granites to further understand the local geological history.

REFERENCE
**238U/235U** variation and the U–Pb chronometer

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The present-day \(^{238}\text{U}/^{235}\text{U}\) ratio has fundamental implications for U–Pb geochronology. A value of 137.88 has previously been considered invariant and used without uncertainty to calculate terrestrial mineral ages, to calibrate mixed U–Pb tracers, and to correct for instrumental bias. Recent studies (Stirling et al., 2007; Weyer et al., 2008) of uranium from a range of geological materials, mainly low-temperature precipitates, have demonstrated per mil level variations in \(^{238}\text{U}/^{235}\text{U}\) that are largely attributed to reduction-oxidation reactions. Therefore, the natural materials we utilise for U–Pb geochronology require detailed investigation of their \(^{238}\text{U}/^{235}\text{U}\) composition. Such studies aim to: 1) assess natural variability, 2) be accurate and traceable to SI-units, and 3) provide a basis for realistic uncertainties of \(^{238}\text{U}/^{235}\text{U}\) for use in U–Pb geochronology.

\(^{238}\text{U}/^{235}\text{U}\) ratios have been determined for a suite of commonly used natural (CRM 112a, SRM 950a, and HU-1) and synthetic (IRMM 184 and CRM U500) uranium reference materials (Condon et al., 2010) using the gravimetrically calibrated IRMM 3636 \(^{233}\text{U}/^{236}\text{U}\) double spike to accurately correct for mass fractionation (Richter et al., 2008). Total uncertainty on the \(^{238}\text{U}/^{235}\text{U}\) determinations is estimated to be <0.02% (2\(\sigma\)). The \(^{238}\text{U}/^{235}\text{U}\) values for these reference materials are different from the widely used ‘consensus’ value (137.88), with each standard having lower \(^{238}\text{U}/^{235}\text{U}\) values by up to 0.08%. The \(^{238}\text{U}/^{235}\text{U}\) ratio determined for CRM U500 and IRMM 184 are within error of their certified values; however, the total uncertainty for CRM U500 is substantially reduced (from 0.1% to 0.02%). These new \(^{238}\text{U}/^{235}\text{U}\) values will thus provide greater accuracy and reduced uncertainty for a wide variety of isotopic determinations.

In addition to the isotopic composition of uranium reference materials, U–Pb geochronology is reliant upon knowledge of the \(^{238}\text{U}/^{235}\text{U}\) value for the mineral being analysed. We have made high-precision \(^{238}\text{U}/^{235}\text{U}\) measurement determinations for a suite of uranium-bearing minerals from 58 samples representing a diverse range of lithologies (Hiess et al., 2012, Figure 1). This data set exhibits a range in \(^{238}\text{U}/^{235}\text{U}\) values of >5 per mil, with no clear relation to any petrogenetic, secular, or regional trends. Variation between co-magmatic minerals suggests that \(^{238}\text{U}/^{235}\text{U}\) fractionation processes operate at magmatic temperatures. A mean \(^{238}\text{U}/^{235}\text{U}\) value of 137.818 ± 0.045/0.050 (2\(\sigma\)) in zircon samples reflects the average uranium isotopic composition and variability of terrestrial zircon and we propose that this value be used for U–Pb geochronology of zircon. The latter uncertainty (±0.050) includes the systematic uncertainty contribution of the IRMM 3636 tracer.

In order to assess the impact of this value on U–Pb dates compared to those calculated using the consensus value \((^{238}\text{U}/^{235}\text{U} = 137.88)\), we have modelled the age difference and uncertainty as a function of sample age. For \(^{207}\text{Pb}/^{206}\text{Pb}\) dates the new average zircon \(^{238}\text{U}/^{235}\text{U}\) value results in dates that are younger compared to those calculated using \(^{238}\text{U}/^{235}\text{U} = 137.88\) by between 1.1 and 0.65 Myr (Figure 2). The uncertainty in the new \(^{238}\text{U}/^{235}\text{U}\) value, which is dominated by the observed variation, limits the precision of \(^{207}\text{Pb}/^{206}\text{Pb}\) dates that lack a co-determined \(^{238}\text{U}/^{235}\text{U}\) value to between ±0.8 and ±0.45 Myr. For the U–Pb dates the impact is reduced and dependent upon the measurement protocol employed, however, for ages less than one billion years, the age difference between \(^{206}\text{Pb}/^{238}\text{U}\) dates calculated using \(^{238}\text{U}/^{235}\text{U} = 137.88\) and \(^{238}\text{U}/^{235}\text{U} = 137.818 ± 0.045\) is <10 kyr, insignificant for even the most high-precision isotope dilution data.
In addition to routine U–Pb geochronology, accurate $^{238}\text{U}/^{235}\text{U}$ values for uranium-bearing minerals and reference materials are essential for high-accuracy U–Pb dating that is metrologically traceable, providing the accurate foundations of the U–Pb system. The analyses of closed system zircon for the determination of $\lambda_{238}\text{U}/\lambda_{235}\text{U}$ (e.g., Mattinson, 2000; 2010) is an exemplar of accurate U–Pb geochronology, and we explore how these new data impact such experiments.

![Figure 1: Plot of $^{238}\text{U}/^{235}\text{U}$ determinations on zircon and other U-bearing minerals. All data from Hiess et al. (2012).](image1)

![Figure 2: Plot showing the absolute difference in $^{207}\text{Pb}^{206}\text{Pb}$ dates when calculated with the newly defined value of 137.818 ± 0.045 (younger) as opposed to the consensus $^{238}\text{U}/^{235}\text{U}$ value of 137.88 (older). Gray bands represent the 2σ uncertainty from the variability in zircon $^{238}\text{U}/^{235}\text{U}$.](image2)
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SHRIMP U–Pb isotopic and EPMA chemical U–Th–Pb dating of uraninite: some preliminary comparisons and pitfalls

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The U–Pb geochronology of uraninite (UO₂) can be complicated by a number of factors including a wide range in chemical composition, the seemingly ubiquitous presence of inclusions, as well as post-crystallisation alteration and Pb-loss. Microanalytical geochronological methods such as SHRIMP U–Pb isotopic or Electron Probe Microanalysis (EPMA) chemical U–Th–Pb dating have previously been used to date uraninite. The advantage of these techniques is their ability to target the most uniform regions of the grains for analysis. Our preliminary results can be used to demonstrate the relative merits of these two techniques.

Experiments used a Cameca SX100 electron microprobe and SHRIMP RG located at the Australian National University, Canberra (analytical details and explanation of the chemical U–Th–Pb technique is given in Cross et al., 2011 and references therein). Prior to SHRIMP RG analysis, elemental EPMA analyses were undertaken at each uraninite sample spot in order to help detect possible chemically-induced matrix effects. Uraninite standards used were U6897 (~1058 to ~1043 Ma; pers. comm. W. Davis, Geological Survey of Canada) and M6302 (1027.8 ± 1.1 Ma, pers. comm. Don Chipley, Queens University, Canada).

The SHRIMP RG 207Pb/206Pb and EPMA chemical U–Th–Pb results for the two uraninite standards both gave ages within error of their reference values. Additionally, the two methods are in close agreement for a uraninite sample from the Rössing South uranium prospect, Namibia, with ages of 496 ± 4 Ma (chemical U–Th–Pb) and 512 ±15/-12 Ma (SHRIMP 207Pb/206Pb), which are similar to the inferred age of this deposit (Cross et al., 2011). These three uraninites also have very low 204Pb/206Pb ratios of <2 x 10⁻⁵. For a fourth uraninite sample however, the results from the two methods differ markedly. Whereas the chemical U–Th–Pb results are remarkably consistent (MSWD = 0.3), the SHRIMP isotopic results demonstrate that it has very high proportions of common Pb, leaving the chemical age with little credibility.

These results, as well as those reported by Stern et al. (2002), demonstrate the ability of the SHRIMP to accurately measure 207Pb/206Pb and 204Pb/206Pb ratios in uraninite. Our preliminary investigations however, also indicate that the SHRIMP 206Pb/238U calibration for uraninite is complicated by both chemically-induced and crystal orientation-related matrix effects, potentially placing a limitation on this method. In contrast, the assumptions inherent to chemical U–Th–Pb dating must be borne in mind when using this technique — namely that common Pb is negligible and that no post-crystallisation alteration of the U–Th–Pb system has occurred. To some extent, these assumptions can be assessed. For uraninite analysis, Kempe (2003) and Alexandre and Kyser (2005) have linked an increase in Ca content to a decrease in chemical age and evidence for alteration. The uraninite measured in this study with very high common Pb concentrations also has a high Ca content of ~6 wt%, providing the warning to its likely alteration and high common Pb.
The $^{206}\text{Pb}^{238}\text{U}$ matrix effects associated with SHRIMP U–Pb uraninite analysis presently limit this method to rocks older than the mid Paleozoic, where $^{207}\text{Pb}^{206}\text{Pb}$ ratios can be used. EPMA chemical U–Th–Pb dating of uraninite, although limited in not being able to directly detect common Pb or isotopic disturbance, is in some circumstances capable of providing relatively inexpensive, good, reconnaissance-level radiometric age determinations useful for the geochronology of uranium systems.

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Rock crushing, radiation protection and regulations

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Geochemical and geochronological studies of earth materials are an essential component of many geological investigations. Some earth materials contain elevated U and Th concentrations. During crushing and pulverising, radioactive airborne mineral dust can be released and inhaled. For geochemistry laboratories that are not appropriately licensed to process radioactive Naturally Occurring Radioactive Materials (NORM), understanding (1) the regulations that classify radioactive materials and (2) how best to comply with the regulations presents a challenge.

There is a low level of awareness and understanding among non-radiation protection professionals of the regulatory framework for radiation protection. In particular, the threshold question of what is and is not a radioactive material. This is further complicated by a lack of consistency in classifications between the Commonwealth and the States. These issues need to be addressed.

The following paragraph contains a synthesis of our interpretations of the Australian Radiation Protection and Nuclear Safety Agency (ARPANSA) regulations for the classification of radioactive materials.

The relevant ARPANSA regulations and exemption levels are contained in Schedule 2, Part 1 of the Australian Radiation Protection and Nuclear Safety Regulations 1999. The exemption levels are based upon the activity concentration and total activity of the material. For radioactive materials, U and Th are the elements of concern. For a rock sample to be considered radioactive by the Act it must have an activity of over 1000 Becquerels (Bq) and an activity concentration of over 1 Bq/g. These limits are applied to $^{238}$U and $^{232}$Th whereby it is assumed that all progeny are in secular equilibrium. The specific activity of each element (a function of its half-life and atomic mass) can be used to convert Bq/g to concentration (typically ppm). The exemption levels for U and Th convert to 80 ppm and 250 ppm respectively. However, for most rocks, U and Th usually occur together so calculation of the activity concentration must include the effect of both elements and be equal to or less than 1 Bq/g.

The vast majority of rocks contain U and Th concentrations well below the exemption levels. Establishing an appropriate screening tool for those that are not, without prior sample preparation, has led Geoscience Australia to investigate two alternative methodologies: a Hand-Held Portable XRF and a Hand-Held gamma ray spectrometer. Our preliminary results show that although the samples so far studied vary in crystal size and internal apparent heterogeneity, both methods are able to provide reasonable, albeit reconnaissance-level quantitative compositional estimates useful for the classification of radioactive rocks and therefore compliance with ARPANSA regulations.
Adventures in uraninite geochronology

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BACKGROUND
Uraninite was amongst the first minerals utilized for quantitative geochronology over 100 years ago (Boltwood, 1907). In principle, uraninite offers the possibility of very precise ages at the highest spatial resolution. However, uraninite dating by ion microprobe is complicated by a number of significant challenges including: 1) the identification of high quality homogeneous mineral standards (Stern et al., 2002), 2) calibration (Stern et al., 2002; Fayek et al., 2002), and in most applications 3) secondary alteration (e.g., Alexandre and Kyser, 2005). Collectively these conspire to limit the routine and effective application of uraninite dating by ion probe, particularly for Phanerozoic samples, where accurate Pb/U ratios are essential. Standards currently in use at the GSC lab show some disturbance in both Pb/Pb and U–Pb ages (Stern et al., 2002). However, achieving accurate results in unknown samples is well beyond the uncertainties related to inhomogeneous standard material. Matrix effects may be important (Stern et al., 2002; Fayek et al., 2002), but a systematic evaluation of these effects remains to be completed. Uraninite is very susceptible to secondary alteration at all scales and may exhibit variable concentrations of many trace elements (REE, Ca, Fe, Si, P). Often, changes in matrix composition are accompanied by disturbance of the U–Pb system (e.g., Alexandre and Kyser, 2005) so that separating matrix effects from Pb-loss is very challenging.

CASE STUDIES
Recent case studies carried out at the SHRIMP lab in Ottawa have focussed on uraninite associated with different styles of uranium mineralization. In most cases, the uraninite has been affected to varying degrees by post-crystallization alteration resulting in disturbed U–Pb systematics. Accurate and reliable ages have proven difficult to obtain. Working within petrographic context to identify and target uraninite crystals that are enclosed within other minerals and therefore shielded from later fluid interaction has proven successful. This approach is similar to the targeting of monazite or xenotime minerals enclosed in early metamorphic porphyroblasts to date prograde metamorphic reactions. In a study of pegmatites from the Paleoproterozoic Great Bear Magmatic zone, Northwest Territories, Canada, uraninite occurs as inclusions in tourmaline and is thus shielded from later fluids. Ion probe analyses yield accurate Paleoproterozoic ages in agreement with Re–Os and Ar–Ar chronometers (Ootes et al., 2010).

Unfortunately this approach is not widely applicable to other uranium deposit types, such as unconformity-related deposits, as uraninite commonly occurs within the rock matrix. Uraninite ages in unconformity-type deposits are often younger than the original formation age and provide minimum estimates of ore formation. Other minerals, including phosphates, such as apatite and xenotime, may form synchronously with the primary uranium mineralization, and provide an alternative approach to the direct dating of uraninite in these systems. Apatite in these settings may have elevated U and low initial common Pb and relatively precise ages can be determined. In the Thelon Basin, Nunavut, apatite yields ages of 1.67–1.68 Ga (Davis et al., 2011), significantly older than the oldest uraninite age reported in the basin.

In some cases the recrystallization of uraninite results in the formation of secondary Pb-rich minerals that can be used to help constrain the timing of uraninite alteration and secondary redistribution of uranium. Micro-galena crystals, on the order of 5–20 μm in size, are a common product of uraninite
alteration. The Kitts deposit in Labrador shows a wide range of discordant ages for uraninite and secondary uranium minerals from ~1.8 Ga to 0.4 Ga. The oldest Pb/Pb age provides a minimum age on primary mineralization. Discordance combined with uncertainties in accurately measuring the Pb/U ratio limits the ability to quantitatively determine upper and lower intercept ages. In situ analyses of the micro-galena crystals yield radiogenic compositions with $\frac{206}{204}$Pb/$\frac{204}{204}$Pb ranging from 5500–7300 with low $\frac{208}{204}$Pb/$\frac{204}{204}$Pb ratios. These compositions indicate Pb derived from a very high U and low Th source consistent with the composition of the uraninite in the deposit. The composition of the Pb in the galena can be modelled to indicate the time interval between formation of the primary uraninite and the secondary galena. Such an approach indicates that a significant alteration occurred at ~450 Ma, presumably due to the far-field effects of orogenic processes within the Appalachian orogen to the southeast.

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I would like to acknowledge contributions of colleagues N. Rayner and T. Pestaj and collaborators who provided samples discussed in this abstract: Luke Ootes (Northwest Territories Geoscience Office); Greg Sparkes (Newfoundland and Labrador Geological Survey); Charlie Jefferson, Sunil Gandhi and Rob Rainbird (Geological Survey of Canada).

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Arc reworking during collision: combined Lu–Hf LA-ICP-MS and U–Pb SHRIMP results from the Tamboril-Santa Quitéria Complex, NE Brazil

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INTRODUCTION

Final configuration of the Borborema Province in northeastern Brazil has been attributed to collisional and post-collisional tectonics at ca. 640–600 Ma due to convergence of the West African-Amazonian and São Francisco-Congo cratons, including the participation of the Saharan metacraton. Within this time interval, high-grade metamorphism (including high-pressure rocks >17 kbar; Santos et al., 2009) and extensive migmatization took place in the northern portion of the province, particularly in the Ceará Central Domain.

Although the timing of arc-building processes (Andean-type margin) in the Borborema Province is usually attributed to the 650–600 Ma time interval (Pan African-Brasiliano Orogeny), new evidence suggests that arc assemblages could have developed as early as 850 Ma (de Araújo et al., in press). In this context, the onset of the collision (Himalayan-type orogen) is still roughly constrained by the age of eclogitic metamorphism at ca. 650 Ma (Amaral et al., 2010), which would indicate that all granitoids post-650 Ma are collisional to post-collisional.

The Tamboril-Santa Quitéria Complex in northeastern Brazil records an intricate association of magmatic rocks with combined crustal and mantle sources, ranging from ca. 640 Ma to 610 Ma (Fetter et al., 2003; de Araújo et al., 2012). Numerous Neoproterozoic intermediate granodioritic to tonalitic gneisses occur along the eastern border of this complex. These orthogneisses have arc-type geochemical characteristics and were migmatized during the late Neoproterozoic. Earlier geochronological studies of these rocks provided a protolith crystallization age of ca. 800 Ma. In one of the mapped units from this complex, diatexites with abundant schollen of intermediate gneissic rocks were recognised. Field evidence of partial melting of these schollen shows the involvement of the produced melt as one of the sources of the diatexites.

In this abstract we present U–Pb SHRIMP zircon results combined with in situ Lu–Hf zircon isotopic data from one orthogneiss in order to determine the timing of protolith crystallization and its migmatization. The data provides geochronological evidence for the timing of crustal reworking of arc-derived granitoids during continent-continent collision and the characterization of melts generated in collisional settings.

U–Pb SHRIMP AND Lu–Hf LA-ICP-MS RESULTS

Sample preparation, U–Pb SHRIMP and Lu–Hf LA-ICP-MS analyses were carried out in the Geochronological Research Centre at São Paulo University, Brazil.

Sample DKE-221 is a hornblende-biotite stromatic metatexite of tonalitic composition that outcrops along the eastern border of the Tamboril-Santa Quitéria Complex (Figure 1A). Zircons were extracted either from the paleossome or the protolith, avoiding contamination with the neossome. Zircons from this sample are euhedral with well-developed oscillatory zoning (Figure 1B). Some
zircons have low-U thin metamorphic rims too small for SHRIMP analysis. A mean age of 831 ± 7.3 Ma (n = 10) is interpreted as the crystallization age of the protolith (Figure 1C). The Epsilon Hf(t) yielded mostly positive values (+8 to +20), indicating contribution of juvenile material.

Sample DKE-273 is a schollen diatexite with schollen composed of biotite patchy-metatexite of granodioritic composition (sample A in Figure 1A) embedded in diatexitic matrix of granitic composition (sample B in Figure 1A) with abundant syn-tectonic flow structures defined by biotite schlierens. Two clusters of crystallization ages were obtained from zircons in the schollen. The older, with a weighted mean age of 889 ± 9.1 Ma is considered the protolith age, and was obtained from both zircons with older cores and from zircons with prominent oscillatory zoning but lacking overgrowths. The younger cluster with a mean age of 618 ± 5.6 Ma is interpreted as the age of anatexis and was obtained from magmatic overgrowths (melt-precipitated) around older cores (Figure 1B, C). The Epsilon Hf(t) from the older cluster is mainly positive with subordinate negative values (-2 to +7).

Sample DKE-273B, representative of the diatexite matrix, also displays the same bimodal cluster, although a predominance of younger ages (anatexis) is apparent. The younger cluster at 618 ± 4.1 Ma, obtained from newly formed zircons or from melt-precipitated overgrowths around older magmatic cores, is virtually identical to the ages obtained from the melt-precipitated overgrowths

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**Figure 1:** (A) Field aspects of the dated samples (arrows indicate the rocks sampled). (B) CL images of the investigated zircons. (C) U–Pb SHRIMP data of orthogneiss and diatexite from the eastern border of the Tamboril-Santa Quitéria Complex, NE Brazil.
found in the zircons from the schollen (Figure 1B, C). In this sample, ages from older cores scatter and do not define a precise age in the Concordia diagram, either due to Pb-loss during the partial melting event or due to high contents of common Pb in these zircons. However, a poorly defined mean age (n = 2) of 876 ± 5.6 Ma overlaps within error of the age of the schollen (sample DKE-273A). The Epsilon Hf(t) for the younger melt-precipitated zircons from sample DKE-273B are mainly negative with subordinate positive values (-9 to +4).

DISCUSSION AND INITIAL CONCLUSIONS
Throughout the development of orogenic systems, accretionary orogens are inevitably overprinted by collisional orogens. In the Ceará Central Domain of the Northern Borborema Province, the discovery of relics of eclogitic rocks (Santos et al., 2009) with P-peak ages(?) older than the main magmatic phases of the Tamboril-Santa Quitéria Complex (640–610 Ma; Fetter et al., 2003; Amaral et al., 2010), has led some authors to discuss the collisional nature of this migmatitic-granitic complex (e.g., de Araujo et al., 2012). Evidence for pre-collisional magmatism within this domain is indirectly demonstrated by abundant Tonian and Cryogenian detrital zircons in the supracrustal rocks (de Araujo et al., in press). Geological correlations with northwest Africa and central Brazil, combined with detrital zircon provenance studies, suggest that the Neoproterozoic paleogeography of the Borborema Province is consistent with a long-lived active margin. Ongoing geochemical studies in these juvenile ca. 830–890 Ma orthogneisses suggest an arc-derived component, perhaps indicating that these pre-collisional rocks were formed in an Andean-type arc setting. The ca. 620 Ma age for anatexis of the ca. 830–890 Ma orthogneisses is in agreement with metamorphic overgrowths dated in detrital zircon from supracrustal rocks adjacent to the Tamboril-Santa Quitéria Complex (de Araujo et al., in press), and they constrain the timing of high-T metamorphism and crustal reworking within this particular domain. Thus, the data presented here indicates that part of the Tamboril Santa-Quitéria Complex was derived from the partial melting of previous arc-related intermediate magmatism during continental collision, with combined involvement of basement and minor participation of supracrustal rocks. Although Ediacaran mantle-derived magmas do exist within the Tamboril Santa Quitéria Complex, Hf isotopic data from the melt-precipitated zircons found in the schollen diatexite indicates that previous Nd TDM ages around 900–800 Ma for some granitoids of the complex would in fact reflect partial melting of older juvenile Neoproterozoic rocks instead of mantle involvement.

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Mount making: from sample preparation to analysis

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At the heart of every analysis is good sample preparation and mount production. Poor quality mounts and sample management can have a direct impact on analysis and certainty of published data. Poor mounts can result in adverse analytical and machine effects whilst potential contamination gives rise to uncertainties within data sets.

There are many factors that contribute to quality mounts and sample integrity. This discussion will emphasize the issues concerning sample contamination, both from internal or external sources, and will highlight effective cross contamination management techniques. Separation methods and sample processing efficiencies will also be examined.

Further to this, the many factors surrounding the production of mounts will be discussed. This will include preparation of mineral grains, issues with epoxy, polishing methods and final image preparation. With the many aspects of mount preparation, it is vital to get each step right in order to yield a high quality product.
Automated SEM location of monazite in polished thin section

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The SHRIMP U–Pb isotopic analysis of often tiny hydrothermal or diagenetic xenotime and monazite crystals can provide geochronological information not attainable by any other means. Locating suitable grains for analysis by manual SEM investigation of polished thin sections however, can be a time consuming and painstaking process. Geoscience Australia has recently purchased Particle Analysis, a software package developed by JEOL Ltd. for forensic investigation of gunshot residue. This application has been successfully applied to the search for tiny monazite grains.

The Particle Analysis software initially locates potential monazite targets by their relative backscattered electron ‘brightness’ and identification is then either confirmed or rejected by EDX analysis. The program can be set to exclude grains <10 µm in diameter ensuring that only targets capable of analysis by SHRIMP are located. Our initial trials with this software are very positive and indicate that it reduces the time taken to locate suitable monazite targets by about 80 to 90%.
Working towards paperless geochronology: integrating imaging, analysis and databases into an automated workflow

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INTRODUCTION

The development of an automated, paperless workflow for the SHRIMP II, incorporating sample data management and processing instructions, mount imaging, autoanalysis, data logging, plotting and graphics generation, has the potential for improving the efficiency of data acquisition, reducing on-machine time for analysts, easing laborious tasks in data processing and illustration and, perhaps most importantly, enabling digital compilation of results and graphics for archiving and dissemination. This abstract summarises works in progress at Geoscience Australia (GA) in developing such systems, describing technological components, processes and outputs of analytical workflow.

Components (as configured at GA)

- **DATABASE**: Laboratory Information Management System (LIMS; Sullivan, 2012)
- **SEM**: JEOL JSM-6490LV with Smile Station, Analysis Station and Particle Analyser (JEOL)
- **Optical Microscope**: Leica DM6000M microscope with automated image stitching capabilities
- **SHRIMP II**: Sample Auto Analysis (SAA; Australian Scientific Instruments) with Stage Map Drive function
- **SHRIMP-linked PC**: Microsoft Access with LIMS, Hydesoft’s DPlot ([www.dplot.com](http://www.dplot.com)), and Adobe Acrobat
- **Graphics processing-capable PC**: Adobe Acrobat, Photoshop and Illustrator CS5 or higher with user-defined macro sets
- **ARCHIVE**: Geochronology data management and online delivery system

Processes

A. **Mount preparation**: samples are selected and input into LIMS, along with field site information, associated data such as geochemistry, processing instructions and target minerals for separation. LIMS is also used to plan mounts and track stages of sample processing and mount preparation (Figure 1A).

B. **Pre-analysis**: accurate, high-resolution maps of sample mounts are produced from stitching reflected light, transmitted light (Leica), cathodoluminescence and/or backscattered electron (JEOL SEM) images. If matched, whole mount maps can be used to pre-select and output tables of points of interest using GPix (ASI) or ImageJ ([rsbweb.nih.gov/ij](http://rsbweb.nih.gov/ij)) for loading into Stage Map Drive on the SHRIMP (Figure 1B).

C. **Analysis**: sessions are programmed and run using SAA. Results are extracted periodically from *.prn files by LIMS and displayed in MS Access (Figure 1C).
D. **Plotting:** any parameter in LIMS (e.g., spot label, age, Th/U) can be extracted and plotted by DPlot as line charts or maps with stage y-z coordinates. Map plot coordinate transformations are obtained from Stage Map Drive calibrations or directly from a mount image so that it can be placed as a background and saved as *.pdf, retaining resolution of the raster image and spot labels as vector graphics (Figure 2D).

E. **Post-analysis:** mounts are re-imaged under reflected light (Leica), matched to mount maps using autoalign in Photoshop, and processed in Photoshop to generate vector paths from outlines of analysis pits. Vector paths are converted to predefined ellipse objects in Illustrator and used as an overlay on whole mount map images with spot labels from *.pdf files made using DPlot. This provides a near publication-ready graphic with accurate spot placement and editable vector components (Figure 2E).

F. **Archiving and delivery:** along with raw data and processed results, made available through the geochronology data delivery and management system (Figure 2F, [www.ga.gov.au/geochron-sapub-web/geochronology/shrimp/search.htm](http://www.ga.gov.au/geochron-sapub-web/geochronology/shrimp/search.htm)), digitised graphical records also can be made available.
**Figure 2:** D. Spots and labels plotted from LIMS by DPlot, with reflected light map as background. E. Stages of image generation with exact spot placement through macros. F. Delivery webpage.

**Outputs**
- Raw and auto-processed data, spot images and *.xml print records from SHRIMP.
- User-processed results and reporting.
- Labelled mount maps in *.pdf, optionally with accurate spot placement, near-ready for publication and digital archiving.

**REFERENCE**
Multiple ages in prolonged orogenesis – an example from ‘Pan-African’ East Antarctica

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In large, hot orogens produced by the collisions of multiple continental terranes to form supercontinents, the links between assembly of tectonic plates and the timing of metamorphic mineral growth are obscured by the extended duration of elevated geotherms and the pervasiveness and complexity of multistage deformation. In the western Lützow-Holm Complex of East Antarctica, granulite to UHT-grade metamorphism and high-strain deformation obscures crustal elements and stages of orogenesis, which can only be revealed through multiphase geochronology. The sequence of orogenic events ranges from magmatism at ca. 630 Ma, through high-grade metamorphism and decompression from 600 Ma to 510 Ma, and slow cooling down to Ar–Ar closure temperatures in K-feldspar at ca. 420 Ma. Zircon and monazite genesis in granulites is controlled by events and host rock types. For example, zircon production in metasediments of the small UHT zone of the complex peaks at ca. 540 Ma, as it does elsewhere to the north, but also occurs at ca. 590 Ma, similar to lower grade gneisses to the south. Monazite in the same samples grows mostly at ca. 590 Ma, as it does to the south, but not to the north, where it forms at ca. 540 Ma. These differences reflect the metamorphic reactions that produce zircon and monazite, and help extract the stages of thermotectonism in the complicated history of this key component of the East-West Gondwana assembly.
The Moacyr monazite standard: identity and compositional complications

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INTRODUCTION

The Moacyr monazite, from the Bananeira 1 pegmatite in the Itambé Province, northeast Brazil (Silva et al., 1996), is a well-established reference material for SEM-based analyses (Seydoux-Guillaume et al., 2004 and references therein). It has characteristics that would also render it useful for a SIMS reference, particularly its U and Th contents (~1000 ppm and ~6%, respectively) and the fact that abundant material is available from the original sampling site. However, there are only limited TIMS reference data available, and some of the data ascribed to Moacyr appear to come from a mis-identified sample. New data have been obtained which clarify the question of identity of several samples now in use for SIMS. They also show complexity in the data for various samples from Bananeira but also illustrate that the complexity does not preclude using these samples as calibration standards.

PUBLISHED DATA

The first published TIMS data that were attributed to Moacyr (‘Moacir’) came from Seydoux-Guillaume et al. (2002). These are so markedly different from subsequent data that we choose to disregard them for this discussion. Gasquet et al. (2010) have since published a substantial data set that provides the main reference for sample identification.

NEW DATA

A sample (GSC z8570), identified as Moacyr, was provided by Mike Williams, University of Massachusetts. TIMS data acquired at the Geological Survey of Canada from this sample show strong similarities to the Gasquet et al. (2010) data but have much higher Th/U, almost double that of the original sample.

The GSC have also analysed two additional crystals from Bananeira 1, one being predominantly red (GSC z8153), the other predominantly yellow (GSC z8154). Both of these have similar Th contents to the Gasquet sample but much higher U: ~2000 ppm for z8153 and ~2800 ppm for z8154. All three of these samples differ from the Gasquet sample in both 207Pb/206Pb (Figure 1) and 206Pb/238U (Figure 2), in ways that can be attributed mainly to excess 206Pb arising from initial 230Th/238U disequilibrium.

MIS-IDENTIFIED SAMPLES

Some years ago, two SHRIMP groups in Perth acquired monazite samples from different collaborators in France which were, in both cases, described as being electron probe standards, from Madagascar. These were presumed to be from the Manangoutry Pass locality of Paquette et al. (1994) and labelled ‘MAD-1’ (Kinny, 1997) and ‘French’ (Fletcher et al., 2010). TIMS data for French and partial data for MAD-1, as well as subsequent SHRIMP comparisons, showed the two to be indistinguishable. However, data plotted by Paquette et al. (2007) for Manangoutry Pass monazite are quite inconsistent with the data for MAD-1/French. In contrast, MAD-1 and French are
indistinguishable from the Gasquet et al. (2010) data for Moacyr. Although there is no documentary trace between MAD-1/French and Moacyr, we consider them to be from the same original crystal.

**DATA TRENDS**
When all the TIMS data from samples from Bananiera 1 are compiled (e.g., Figures 1 and 2) they display strong trends, but there substantial discrepancies and the trends are not readily explained. Although variation in \(^{207}\text{Pb}/^{206}\text{Pb}\) can be attributed to having variable Th/U fractionation from a melt, the trend in Figure 1 does not conform to a simple model fractionation locus, which would be almost linear over this range of \(^{207}\text{Pb}/^{206}\text{Pb}\). The trend in \([^{206}\text{Pb}/^{238}\text{U}]\) (Figure 2), although within precision of being linear for the data from a single laboratory, does not extrapolate to the crystallization age determined from \(^{207}\text{Pb}/^{235}\text{U}\) and \(^{208}\text{Pb}/^{232}\text{Th}\). This implies either extreme curvature of the trend line as it approaches the \([^{206}\text{Pb}/^{238}\text{U}]\) axis or an unexplained disequilibrium in the source melt.

![Diagram showing data trends](image)

**Figure 1:** Compiled TIMS data for monazite from Bananiera 1. The crystallization age is from \(^{207}\text{Pb}/^{235}\text{U}\) and \(^{208}\text{Pb}/^{232}\text{Th}\) data. The curve is descriptive, not modelled.

**IMPLICATIONS FOR SIMS ANALYSES**
Given the ready availability of monazite from Bananiera 1, it could provide widely-used reference material for SIMS. However, these new data illustrate the importance of thorough characterization and evaluation of the chemical and isotopic signatures and provenance of individual portions of megacrysts prior to their use in a given laboratory. Although the large overall variations in Th/U, magma/mineral fractionation behaviour and hence \(^{206}\text{Pb}/^{238}\text{U}\) isotopic ratios for Moacyr would appear to preclude its use as a calibration reference for SIMS analyses, correlation between \(^{206}\text{Pb}/^{238}\text{U}\) and \(^{208}\text{Pb}/^{206}\text{Pb}\) may enable a reference value to be determined post-analysis. The variations observed within cm-sized fragments are small, so within-laboratory corrections for variations in composition will be very small.
Figure 2: Compiled TIMS data for monazite from Bananiera. The crystallization age falls below the range of the $t^{206}_{206\text{Pb}}/^{238}\text{U}$ axis. The trend line relates to GSC data, ignoring two high outliers. Sample identification as in Figure 1.

ACKNOWLEDGEMENT

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What is the source of Hadean zircons?

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The moon (possibly).

All published attempts to explain the existence of Hadean zircons on Earth carry the implicit assumption that they are of terrestrial origin. Although this is an obvious proposition, it has several difficulties: there are no known source rocks; their age distribution places awkward constraints on the processes that generated their source rocks; they require preservation for up to 400 Myr in a hostile environment; and they require transport to much younger continental surfaces. The moon is a known repository of zircons of similar age which does not have these limitations. It is a possible source of at least some of Hadean zircons found on Earth.
In situ dating of zircon in micro-tuff supports a Proterozoic ‘snowball Earth’

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At the Beijing SHRIMP workshop we presented data, including some from microtuffs in the lower sequence of the Timeball Hill Formation of the Transvaal Supergroup, South Africa, which were interpreted to show that there were only three identified Proterozoic ‘global’ glaciations in the Huronian Supergroup and Transvaal Supergroup, and that the youngest was too old (~2.31 Ga) to be correlated with equatorial flood basalts, thus undermining previous arguments for a fourth, ‘snowball Earth’, glaciation at ~2.22 Ga.

Subsequent study has identified two additional microtuff bands (<2 cm thick) in the upper sequence of the Timeball Hill Formation, below the contentious diamictite. Ages of ~2.26 Ga and 2.27 Ga for these show that a previously unrecognised and visually minor discontinuity in the Timeball Hill Formation actually records a >40 Myr unconformity. The Timeball Hill diamictite is younger than the three glaciations preserved in the Huronian Supergroup. A depositional age of ≤2.26 Ga for the Timeball Hill and correlated Makganyene glacial deposits strengthens previous arguments for a low-latitude glaciation at ~2.22 Ga.
Zircon from iron-ore, Middleback Ranges, South Australia: isotopic resetting and the age of supergene fluid-alteration?

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INTRODUCTION

Despite the extensive resources, ongoing mining activity and economic importance of iron-ore in Australia, the genesis of iron-ore and particularly its timing, remains relatively poorly understood. Most iron-ore in Australia is interpreted to originate as Banded Iron Formation (BIF) that has subsequently experienced one or more fluid leaching events in which silica is removed, leaving the residual rock highly enriched in iron (Morris and Kneeshaw, 2011). While this general model appears relatively well established, questions remain regarding whether iron-enrichment typically occurs over one or more events, the timing of such events, and the controls on fluid movement leading to iron enrichment.

Here we report textural observations and U-Pb isotopic results from zircon extracted from hematite ore from the Iron Knob mine in the Middleback Range, South Australia. The U-Pb ages have yielded unexpected results that are interpreted to indicate at least some fluid interaction and iron enrichment in the Middleback Range occurred in multiple stages through the Paleozoic and Mesozoic. Such timing is unexpected given the local geological context, but may in part be explained by early Paleozoic tectonic events in the Adelaide Fold Belt (Delamerian Orogeny), ~100 km to the east, having played a role in mobilising supergene fluids within the adjacent margin of the Gawler Craton.

GEOLOGICAL SETTING

Situated near the eastern margin of the Gawler Craton, South Australia, the Middleback Range on northern Eyre Peninsula is the site of the oldest iron-ore mining in Australia and contains several operating iron-ore mines including Iron Knob, Iron Baron and Iron Duke. Iron-ore in the Middleback Range is hosted in a sequence of Banded Iron Formation (BIF) intercalated with dolomite and schist that is collectively known as the Middleback Subgroup (Parker et al., 1993). Both the depositional age of the BIF protoliths in the Middleback Range and the age of subsequent iron-enrichment are poorly constrained. The Middleback Subgroup has been assigned to the Hutchison Group (Parker et al., 1993) and interpreted to have been deposited in the Paleoproterozoic between ~2000 and ~1850 Ma. Recent work has shown that local granitic basement to the Middleback Subgroup is much older than previously thought at ~3250 to 3150 Ma (Fraser et al., 2010; Reid and Jagodzinski, 2011), and Szpunar et al. (2011a) have presented detrital zircon ages from the Cook Gap Schist of the Middleback Subgroup that yield a maximum depositional age of ~2560 Ma. While not definitive, these recently-published results suggest the possibility of an older, Neoarchean depositional age for the Middleback Subgroup that would in turn allow correlation of the Middleback Range BIF with BIF from the northern Gawler Craton and Hamersley Group of the Pilbara Craton (Szpunar et al., 2011a, b). Rocks of the eastern Gawler Craton, including those of the Middleback Subgroup, were tightly folded, sheared and variably metamorphosed during the Paleoproterozoic Kimban Orogeny (~1730–1690 Ma). The northern Eyre Peninsula region has remained relatively undisturbed at upper crustal levels since the early Mesoproterozoic, as indicated by the extensive cover of flat-lying and...
largely undeformed ~1590 Ma Gawler Range Volcanics (Fanning et al., 1988; Creaser and Cooper, 1993).

RESULTS
In order to improve age constraints on the history of the Middleback Range iron-ore, zircon was extracted from a hematite-rich ore sample from the Iron Knob mine, and analysed via SHRIMP IIe at Geoscience Australia. Approximately 100 zircons were retrieved from the sample and mounted in a conventional epoxy SHRIMP mount. Optical, secondary electron and cathodoluminescence imaging reveals a suite of rounded zircons that exhibit a range of internal compositional zoning, including oscillatory and sector zoning, and core and overgrowth relationships. In many cases internal zoning patterns are truncated by grain boundaries. On the basis of morphology and internal zoning these zircons are interpreted to be detrital in origin, presumably incorporated as part of a minor clastic component into the protolith BIF.

A total of 72 U–Pb analyses reveal a range of near-concordant apparent ages from ~3140 Ma to ~98 Ma. Four ages are Archean, at ~3140 Ma, ~2860 Ma, ~2850 Ma and ~2750 Ma. A single analysis yields a Paleoproterozoic age of ~2335 Ma. The remaining 67 analyses include: six ages between ~1200 and 800 Ma; 43 ages ranging between ~700 and 500 Ma; four ages between ~415 and 405 Ma; five ages between ~350 and 305 Ma; seven ages between ~255 and 245 Ma, and individual ages at ~150 Ma and ~98 Ma.

DISCUSSION
Based on the morphological interpretation of these zircons as being detrital in origin, it was expected that the ages of these zircons would provide constraints on the ages of clastic sedimentary source materials and a maximum depositional age for the Middleback Range BIF. Instead, local geological constraints, including the overlying ~1590 Ma Gawler Range Volcanics and the deformation of the Middleback Subgroup attributed to the Kimban Orogeny (~1730–1690 Ma), suggest that all but the oldest five of these zircon ages are too young to reflect the age of detrital zircon in the Middleback Subgroup. Instead, most zircons from the Iron Knob hematite-rich ore sample appear to have been isotopically reset, and the local geological history would suggest that such resetting has taken place in the near-surface environment, presumably via interaction with fluids. The predominance of zircon ages between ~700 Ma and 500 Ma broadly coincides with a period of late Neoproterozoic extension and sedimentation in the Adelaide Rift Complex to the east of the Gawler Craton, followed by basin inversion during the ~515–490 Ma Delamerian Orogeny in the Adelaide Fold Belt. Ductile deformation associated with the Delamerian Orogeny is largely restricted to the region east of the Torrens Hinge Zone, approximately 100 km east of the Middleback Ranges. The zircon age results presented here, however, suggest significant isotopic resetting of zircon occurred to the west of the Torrens Hinge Zone, in the marginal parts of the Gawler Craton. The presence of post-Delamerian zircon ages extending to as young as Mesozoic is even more surprising as there are no major tectonic events known in the region at this time.

Another intriguing feature of the zircons extracted from the Iron Knob ore is the presence of numerous grains with embayed margins and a variably-developed, discontinuous replacement crust. This crust has been demonstrated to be baddeleyite, using EDS compositional analyses. It is highly unlikely that these delicate crusts could have survived any sedimentary transport and they are thus interpreted as in situ secondary replacement textures, whereby zircon was replaced by baddeleyite presumably in the presence of a Si-poor fluid.

The results from the Iron Knob ore sample are interpreted to indicate that multiple fluid flow events in the near surface environment induced isotopic resetting of zircon and replacement of zircon by baddeleyite, and that these fluid events were related to supergene iron enrichment of the ore.
Figure 1: Representative zircon images and U–Pb isotopic results from Iron Knob hematite-ore (sample 1999697). a) transmitted light, b) cathodoluminescence, c) secondary electron image of zircons. Note: (i) the relic oscillatory zoning in several zircons in part b, and (ii) the discontinuous crusts of baddeleyite around zircon, seen as irregular dark patches around several grains in part c. d) Concordia diagram showing U–Pb results of all 72 zircon analyses. e) Concordia diagram showing U–Pb results of 67 zircon analyses that are younger than 1300 Ma. All of these apparent ages are interpreted as having been isotopically reset. f) Probability density diagram showing results from all 72 zircon analyses, with $^{207}\text{Pb}/^{206}\text{Pb}$ ages older than 1500 Ma plotted in red, and $^{206}\text{Pb}/^{238}\text{U}$ ages younger than 1500 Ma plotted in blue.
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SHRIMP remote control and MC-ICP-MS at the University of Hong Kong

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The SHRIMP (Sensitive High Resolution Ion Microprobe) specializes in in situ analysis of geological materials. It is a particularly powerful technique for uranium-lead and oxygen isotope studies due to its high resolution and non-destructive nature (e.g., Williams et al., 2006; Ickert et al., 2008; Pidgeon et al., 2010; Castro et al., 2011; Compston and Gallagher, 2012; Lu et al., 2012; White and Ireland, 2012). The SHRIMP remote control at the University of Hong Kong (HKU) was installed in November 2010 and is a collaborative project with the Beijing SHRIMP Center. To date, nearly one hundred samples have been analysed.

In addition to the SHRIMP remote control, a Nu Plasma HR MC-ICP-MS (Nu Instruments, UK, High Resolution Multiple Collector Ion Coupled Plasma Mass Spectrometer), coupled to a 193 nm excimer laser ablation system (RESOlution M-50, Resonetics LLC, USA) was installed at HKU in October 2009. Since its installation, thousands of analyses have been conducted. Our MC lab performs: (1) routine in situ zircon U–Pb and Hf analysis (Xia et al., 2011); (2) newly developed techniques, such as Mg isotope and in situ Sr isotope analysis, and (3) potential methodology development, including Li and Nd isotope analysis.

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In situ Sm isotopic analysis of neutron-irradiated materials

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INTRODUCTION

In situ Sm isotopic analysis by SHRIMP is applicable for the detection of integrated neutron flux (neutron fluence) in samples which have experienced nuclear reactions in nature, from the isotopic shift of $^{149}\text{Sm}$ to $^{150}\text{Sm}$ due to the neutron capture reaction $^{149}\text{Sm}(n,\gamma)^{150}\text{Sm}$, because $^{149}\text{Sm}$ has a very large thermal neutron capture cross section ($\sigma = 4.2 \times 10^4 \text{ barn}$).

Sm has seven stable isotopes with mass numbers 144, 147, 148, 149, 150, 152, and 154. Among the seven isotopes, only two isotopes, $^{147}\text{Sm}$ and $^{149}\text{Sm}$, have no isobaric interferences from the neighbouring elements such as Nd and Gd. Therefore, in this study, isotopic deficiency of $^{149}\text{Sm}$ relative to $^{147}\text{Sm}$ is monitored as isotopic evidence for neutron irradiation experience of the materials in nature. The samples analysed in this study are from natural fission reactors, aubritic meteorites, and lunar surface regolith.

CASE STUDY 1: THE OKLO NATURAL FISSION REACTORS

Parts of the Oklo uranium deposit in the Republic of Gabon, central Africa, functioned as natural fission reactors. Large-scale fission chain reactions occurred spontaneously in 16 separate areas in the deposit, and were sustained intermittently for $2.4 \times 10^4$ to $3.0 \times 10^5$ years. Many elements in the natural reactor samples show variations in their isotopic compositions caused by a combination of nuclear fission, neutron capture and radioactive decay. The major concerns are when and how the fission products migrated from the reactors. Since some kinds of fission products are heterogeneously distributed in uranium matrices, microscopic isotopic observation on the Oklo samples is meaningful for better understanding of the geochemical behaviour of fission products (DeLaeter and Hidaka, 2007).

Uraninite generally contains high amounts of REE including Sm (a few hundred to a few thousand ppm). Therefore, in situ Sm isotopic analyses within 0.3 to 0.5% precision at 2\(\sigma\) of standard error level can be performed by SHRIMP. As shown in Table 1, isotopic depletions of $^{149}\text{Sm}$ in the Oklo samples are large enough to identify neutron capture effects even from in situ analysis by SHRIMP. The neutron fluxes estimated from the Sm isotopic data correspond to the range of $10^{20}$ to $10^{21}$ n cm$^{-2}$ (Horie et al., 2004).

CASE STUDY 2: EXTRATERRESTRIAL MATERIALS (METEORITES AND LUNAR REGOLITH)

Cosmic rays in space penetrate a few meters into the surface of planetary materials, and produce secondary nuclides, so called cosmogenic nuclides, in the materials. The exposure history of meteorites has been characterized by several cosmogenic nuclides. Cosmogenic nuclides such as long-lived radioisotopes (e.g., $^{10}\text{Be}$, $^{26}\text{Al}$, $^{36}\text{Cl}$) and stable noble gas isotopes (e.g., $^{3}\text{He}$, $^{21}\text{Ne}$, $^{36}\text{Ar}$, $^{38}\text{Ar}$) have been widely used to determine the cosmic-ray exposure (CRE) ages of meteorites in space. Sm isotopic shifts by neutron capture reactions also provide useful information for understanding the cosmic-ray exposure records of meteorites.
Most enstatite achondrites (aubrites) generally show longer CRE ages (3x10^7 to 1.1x10^8 years) than any other stony meteorites. On the other hand, lunar surface materials (regolith) collected from the Apollo 15, 16, and 17 landing sites also show intensive neutron irradiation evidence with CRE ages over 5x10^8 years (Russ et al., 1972; Curtis and Wasserburg, 1975; Sands et al., 2001). Previous studies on Sm isotopic analyses of extraterrestrial materials by TIMS show large depletions of ^149Sm isotopic abundance - from a white clast of the Norton County aubrite (^149Sm/147Sm = 0.913507 ± 0.000126; Hidaka et al., 2012) and lunar regolith sample 60001.98 (^149Sm/147Sm = 0.915569 ± 0.000028; Hidaka and Yoneda, 2007). It is expected to identify the deficiency of ^149Sm isotopic abundance in the extra terrestrial samples from \textit{in situ} isotopic analysis if the analytical precision with <0.9–1.1% can be performed on the Sm isotopic measurements of individual samples. However, in case of meteorite samples, it is generally difficult to provide such high precision isotopic data by \textit{in situ} analysis because of low elemental abundances of REE. In the case of aubrites, oldhamite (CaS) is known as a major REE carrier, and contains Sm of a few tens ppm (Floss and Crozaz, 1993). Several oldhamite grains sized more than 10 µm in some aubrites have been found for SHRIMP analysis: 2 from Cumberland Falls, 2 from Mayo Belwa, 5 from Norton County, 5 from Pena Blanca Springs, and 4 from Shallowater. Preliminary results from two oldhamite grains of Pena Blanca Springs and Norton County are shown in Table 1. Unfortunately the analytical precisions of these two data are not high enough to identify the deficiency of ^149Sm over the analytical errors. Sm isotopic studies on several grains from the Apollo lunar regolith are also now in progress.

Table 1: \(^{149}\text{Sm}/^{147}\text{Sm}\) isotopic data by SHRIMP analyses.

<table>
<thead>
<tr>
<th>SAMPLE</th>
<th>(^{149}\text{Sm}/^{147}\text{Sm})</th>
</tr>
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<tbody>
<tr>
<td>NIST SRM610 (standard glass)</td>
<td>0.9240 ± 0.0040</td>
</tr>
<tr>
<td>Mistamisk (standard uraninite)</td>
<td>0.9180 ± 0.0045</td>
</tr>
<tr>
<td>Chardon (standard uraninite)</td>
<td>0.9218 ± 0.0014</td>
</tr>
<tr>
<td>Faraday Mine (standard uraninite)</td>
<td>0.9220 ± 0.0190</td>
</tr>
<tr>
<td>Oklo (RZ10, D81-13 uraninite)</td>
<td>0.0162 ± 0.0002</td>
</tr>
<tr>
<td>Oklo (RZ13, SD37-S2/CD, uraninite)</td>
<td>0.00706 ± 0.00007</td>
</tr>
<tr>
<td>Pena Blanca Springs (aubrites, oldhamite)</td>
<td>0.9232 ± 0.0047</td>
</tr>
<tr>
<td>Norton County (aubrites, oldhamite)</td>
<td>0.9187 ± 0.0054</td>
</tr>
</tbody>
</table>

*Analytical errors are shown in 2σ of the mean (n = 40–50).

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SHRIMP contributions to the geology of the Sør Rondane Mountains in Antarctica: the crossing of Late Neoproterozoic / Cambrian collision zones in Gondwana


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INTRODUCTION

The assembly of the supercontinent Gondwana has attracted controversy amongst geologists. Although the consensus is that the western part of Gondwana was united by the amalgamation of Africa and South America at c. 600 Ma (e.g., Trompette, 1997), the assembly of eastern Gondwana has been the subject of many, often contradictory, studies (e.g., Fitzsimons, 2000, 2003; Boger et al., 2001; Harley, 2003; Meert, 2003; Jacobs et al., 2003; Grantham et al., 2008; Boger, 2011). Orogenic zones of differing age have been recognized in eastern Gondwana: components of 750–620 Ma (e.g., East African Orogen) and 570–500 Ma (e.g., Kuunga Orogen). The former older events have been reported mainly from eastern Africa, whereas younger ages dominate in south-eastern Africa through India, Sri Lanka, East Antarctica to western Australia (e.g., Meert, 2003). In the East Antarctic Shield, pervasive 550–500 Ma high-grade metamorphic terranes comprise the main orogenic routes, with 700–600 Ma metamorphic ages restricted to a few minor areas. The Sør Rondane Mountains (SRM) is one such area where two metamorphic age components of c. 650–600 Ma and c. 560–550 Ma have been reported (e.g., Shiraishi et al., 2008), and is of potential significance for unravelling the two orogenic routes presumably crossing at this part of Antarctica.

THE SØR RONDANE MOUNTAINS OF EAST ANTARCTICA

The SRM have been divided into two metamorphic zones, based on geological studies during the Japanese Antarctic Research Expedition (JARE) from the 1980s to early 1990s (e.g., Asami et al., 1992; Osanai et al., 1992; Shiraishi et al., 1997 and references therein). These are the granulite-facies NE Terrane and the amphibolite-facies SW Terrane. SHRIMP zircon U–Pb studies imply formation during different metamorphic events dated at c. 650-600 Ma for the NE Terrane and c. 560–550 Ma for the SE Terrane of the SRM (Shiraishi et al., 2008). Expanding on this work, a three year geological field program was conducted by the JARE geology group during 2007–2010. Progressive changes of the metamorphic grade increasing from south-southwest to north-northeast and at least three distinctive metamorphic P-T patterns were recognised (e.g., A-, B- and L-types from the central-northern part of the SRM; Adachi, 2010). Both A- and B-type rocks recorded granulite-facies peak metamorphism, but markedly different P-T trajectories: clockwise (CW) P-T path for the A-type and counter-clockwise (CCW) for the B-type. The A-type rocks predominate in the north-northeastern area and the B-type rocks are found in the northwest-central area, although the boundary between these two zones is not clear due to sparse outcrop. The L-type rocks occur dominantly in the central-southern area and preserve amphibolite-facies peak metamorphic conditions without any CW or CCW P-T signature.
SHRIMP U–Pb AND REE CONSTRAINTS

Utilizing the ion microprobe at NIPR, we and our collaborators have conducted extensive zircon U–Pb dating along with selective REE analysis of various metamorphic and magmatic rocks from the SRM. Accumulated zircon ages demonstrate that Mesoproterozoic-Neoproterozoic (1150–800 Ma) juvenile magmatic components and coeval sediments comprise the main part of the SRM. Zircon U–Pb dates interpreted as metamorphic events are scattered in the range of >700–550 Ma, and those combined with REE data suggest the dominant high-grade metamorphic event occurred at 640–630 Ma for both A- and B-type granulite-facies zones. The L-type rocks recorded c. 550 Ma metamorphic ages and typically lack c. 600 Ma metamorphic zircon. This indicates the concurrent development of both CW and CCW metamorphic P-T processes in the granulite-facies zones, and we speculate that the A-type area was thrust over the B-type area during collision at c. 640–630 Ma (e.g., Adachi, 2010). Details of the temporal-spatial relationships of the c. 640–630 Ma age-event, and the geological implications of the subsequent c. 550 Ma event in this area are yet to be clearly understood. The project is ongoing, and we believe that the accumulated zircon, monazite and other dates combined with REE and other trace element data in these high-grade gneisses and related magmatic rocks will provide insights into the development of metamorphic and fluid regimes throughout the long-lived (700–550 Ma) amalgamation of Gondwana, and the unravelling of Late Neoproterozoic and Cambrian collision zones within the supercontinent.

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New calibration method for Hf in zircon: simultaneous analysis of Hf content with U–Pb dating

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INTRODUCTION
Hafnium (Hf) and zirconium (Zr) have nearly identical chemistry, and most of the crust has near-chondritic Zr/Hf ratios of ~35–40 (Ahrens and Erlank, 1969; Hoskin and Schaltegger, 2003). Zircon (ZrSiO₄), essentially a zircon-hafnon (HfSiO₄) solid solution, contains up to 2 wt% HfO₂ (Claiborne et al., 2006 and references therein) and is the major reservoir for Hf in the Earth’s crust. Therefore, zircon growth controls the Hf composition of any melt. As zircon grows, both the Zr and Hf concentrations in the melt will decrease; zircon preferentially incorporates Zr over Hf, which leads to a decrease in the Zr/Hf ratio of the remaining melt. This process leads to increasing Hf concentration in growing zircon crystals that corresponds to increasing fractionation of the melt (Claiborne et al., 2006, 2010). Consequently, Hf zoning in magmatic zircons can provide useful information about melt evolution.

Generally, SHRIMP determination of the Hf content in zircon is obtained through rare earth element analysis, with counts of ¹⁸⁰Hᶠ⁺ referred to counts of ⁹⁶Zr⁺ derived from the zircon matrix. However, this approach makes it difficult to obtain Hf contents and U–Pb age data concurrently, due to the large magnetic field sweeps required to accommodate extremes at ⁹⁶Zr⁺ and ²⁵⁴UO⁺ (or higher). An alternative approach is to analyse hafnium oxide ions (e.g., ¹⁹⁶HfO⁺ or ²¹²HfO₂⁺) or other polymer ions (e.g., ²⁰⁸HfSi⁺), referred to ¹⁹⁶Zr₂O⁺ as the matrix ion, during the U–Pb dating process. Although this method produces simultaneous Hf-content and U–Pb age data, session-to-session comparison of Hf data is problematic because oxide ion yields are dependent on instrumental operating conditions. This study establishes a new method for calibrating Hf concentration in zircon, which permits concurrent collection of Hf-content and U–Pb age data, and is applicable over a wide range of instrumental conditions.

PROCEDURES
The reference material used for calculation of Hf concentration was 91500 zircon (~5588 ppm Hf; Wiedenbeck et al., 1995). Three unknowns were tested: TEMORA2 zircon (8310 ppm Hf; Black et al., 2004), Mud Tank zircon, and OT4 zircon, which was obtained from quartz diorite of the Unazuki plutonic complex in Japan. In addition to the collection of mass peaks typically used for U–Pb dating, the SHRIMP run-table included the peaks ¹⁸⁰Hf⁺ and ¹⁹⁶HfO⁺, as well as ¹⁸⁰Zr₂O⁺ and ²⁰⁸DyO⁺, which were used to monitor peak centering during analyses, and for the correction of interference on the ¹⁸⁰Hf⁺ peak.

RESULTS AND DISCUSSION
In order to be applicable over a wide range of operating conditions, the Hf concentration relationship utilises a correlation between ln(¹⁹⁶Zr₂O⁺/¹⁸⁰Hf⁺) and ln(¹⁹⁶HfO⁺/¹⁸⁰Hf⁺), analogous to the widely adopted U concentration relationship proposed by Claoué-Long et al. (1995) on the basis of the correlation between ln(¹⁹⁶Zr₂O⁺/²³⁸U⁺) and ln(²⁵⁴UO⁺/²³⁸U⁺). Two different analytical sessions (July 2011 and January 2012) are both characterised by (1) good correlation between ¹⁹⁶Zr₂O⁺/¹⁸⁰Hf⁺ and ¹⁹⁶HfO⁺/¹⁸⁰Hf⁺, and (2) less variation in ¹⁹⁶HfO⁺/¹⁸⁰Hf⁺ than is observed in ¹⁹⁶Zr₂O⁺/¹⁸⁰Hf⁺ (Figure
1). The precision of the concurrent U–Pb data is unaffected by the presence of the Hf-related peaks, and the analytical uncertainty of each Hf analysis is about 6.6%.

The average Hf concentration of TEMORA2 zircon obtained by this procedure (8218 ± 460 ppm; SD) is consistent with that obtained by previous studies. The Mud Tank zircon yielded a mean Hf concentration of 9126 ± 213 ppm (SD). The Hf contents of the OT4 zircons span the range 7779–9385 ppm, with an average of 8651 ± 466 ppm (SD), and a relatively small spot-to-spot uncertainty in Hf concentration (5.4%) that is comparable to that calculated from the TEMORA2 dataset (5.6%), and indicates little variation in Hf concentration from grain to grain. The Hf contents obtained by this method are consistent with those obtained via rare earth element analysis, which suggests that the Hf calibration presented herein is reasonably robust.

![Figure 1: Correlation between $^{196}\text{ZrO}_2{}/^{180}\text{Hf}^+$ and $^{196}\text{HfO}_2{}/^{180}\text{Hf}^+$ obtained from two separate sessions. The first and second sessions were carried out in July 2011 and January 2012, respectively.](image)

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SQUID-2 compatibility problem for non-English speaking countries

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It is known that SQUID-2 is not compatible with the recent versions of Excel, later than Excel 2003, and with non-English versions of Excel such as Japanese versions. The problem right now for us Japanese is that older and foreign versions of the software, especially the English version of Excel 2003, are no longer available for purchase in Japan and probably in other non-English speaking countries, however, there are ever increasing numbers of new SHRIMP users. We wonder how common this kind of problem is, especially among the SHRIMP and SQUID Development Consortium groups from non-English speaking countries. We would like to know the situation in other SHRIMP laboratories and to seek help in obtaining a compatible version of Excel from the SHRIMP community until SQUID-2 is updated to be compatible with the latest version of Excel.
SHRIMP apatite analysis and data reduction

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INTRODUCTION
Apatite [Ca₅(PO₄)₃(OH, F, Cl)] is a common accessory mineral in almost all rocks. Apatite, and its extra-terrestrial relatives, merrilite and whitlockite, readily accept trace elements, and contain sufficient U, Th, and the REE, to allow their use in TIMS geochronology; these minerals have provided critical age constraints on early solar system processes (Amelin and Krot, 2007), and Lunar evolution (Grange et al., 2009). SIMS and LA-ICP-MS U–Th–Pb isotope micro-analysis of apatite, both in separated minerals and in situ, is under-utilised (Ireland and Williams, 2003). The SHRIMP ion microprobe, which allows U–Th–Pb isotope analysis at a spatial resolution of 5–20 microns, can expand the application of apatite geochronology into complexly zoned apatite that may contain inherited components (Figure 1A).

SHRIMP ANALYSIS OF APATITE
Successful SHRIMP analysis of any variable composition, solid solution mineral, requires (1) the careful assessment of analytical effects that can produce spurious data, and (2) the development of data reduction methods that correct for any bias in the data and produce accurate and reproducible results with the smallest real uncertainties. To date apatite by SHRIMP we must:

- Have homogeneous, well-characterised reference materials of suitable age and composition, with sufficient U, Th and Pb
- Be able to measure with sufficient accuracy and precision the initial Pb composition
- Measure Instrumental Mass Fractionation (IMF) with sufficient accuracy and precision to allow correction for any bias in this data
- Identify any chemical matrix effects
- Identify any crystallographic orientation effects
- Identify the best U–Pb and Th–Pb calibration schemes (2D or 1D)
- Cross check our calibration results by independent means

The above requirements are covered in the sections below.

REFERENCE MATERIAL
Since SIMS and LA-ICP-MS are comparative methods there must be well-characterised natural reference material (RM) available. TIMS Inter-lab comparison can also benefit from the use of high quality RM. Large faceted gems and crystals of apatite are relatively cheap and readily available through the Internet. Faceted gems have already been assessed for clarity and colour, and this is helpful. Unfortunately, apatite often has very low U and Th, and/or high initial Pb, and >85% of the material we have examined is unusable as reference material. Even so, we have identified a number of apatites that may be useful as RM. We have characterised two Ordovician and three Proterozoic apatites. They are from Madagascar (AFB1 and AFG2), Canada (OL2) and Brazil (BR2 and BR5) and they have ages ranging from ~470 Ma to ~2060 Ma. These apatites have low to moderate U (45–140 ppm), moderate to high Th (500–5000 ppm) and moderate to low fractions of initial Pb (²⁰⁶Pb/²⁰⁴Pb = 250–1000, and ²⁰⁸Pb/²⁰⁴Pb = 1000–4000). SHRIMP data from these apatites show good homogeneity.
Multiple (up to 10), single chip, TIMS U–Pb analysis of each apatite has been completed at Boise State University and the University of Geneva. The TIMS analyses show the individual chips of apatite are isotopically heterogeneous, due to variable amounts of initial Pb and minor disturbance. The initial Pb composition is derived from a 3D Total Pb–U isochron (Figure 1B). After correction for initial Pb, the radiogenic Pb compositions of the different apatites are less heterogeneous. For example, the ten TIMS analyses of AFG2 have a radiogenic $^{206}\text{Pb}/^{238}\text{U}$ age range that is $<$1 Ma, and a $^{207}\text{Pb}/^{206}\text{Pb}$ age range of $<$3 Ma. AFG2 is the least heterogeneous apatite we have identified and it has a Concordia age of 478.69 ± 0.45 Ma ($\sigma$, including $\lambda$ uncertainties), with a MSWD = 1.4 (Figure 1C), and a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 478.47 ± 0.26 Ma (95% confidence limit, MSWD = 0.63).

INITIAL Pb IN APATITE
The Ca$^{2+}$ crystallographic site in apatite readily accepts a Pb$^{2+}$ ion, which has the same charge and an almost identical ionic radius. This means that many apatites have high percentages of initial Pb relative to radiogenic Pb (i.e., low $^{206}\text{Pb}/^{204}\text{Pb}$). An accurate radiogenic Pb composition can only be calculated if the composition of the initial Pb is accurately known. This difficulty is compounded when both the unknowns and RM have low $^{206}\text{Pb}/^{204}\text{Pb}$. In some instances, the initial Pb composition is close to the value derived from the Stacey and Kramers Pb evolution curve (Stacey and Kramers, 1975). However, this is not the case for many apatites. Our TIMS data has provided initial Pb compositions for all of the possible apatite RM we have characterised.

INSTRUMENTAL MASS FRACTIONATION
We have not identified a RM for high precision monitoring of $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in apatite. Apatite separates from Archean rocks with ‘predictable’ apatite ages (OGC1: 3465 Ma, A41: 3465 Ma, and Strelley: 2835 Ma) have been used to assess IMF under typical analytical conditions. Within our uncertainties we have not seen evidence of any consistent bias in measured $^{207}\text{Pb}/^{206}\text{Pb}$ ratios that can be attributed to IMF (Figure 1D).

CHEMICAL MATRIX EFFECTS
Apatite readily accepts a variety of elements into its structure. It can contain CO$_3$, Fe, Mn, Mg, Sr, Ba, Y, Si and S at minor element levels, and there is a complete isomorphous solid solution series in natural apatite containing OH, F and Cl. Chemical variation can produce changes in ion yields during SHRIMP analysis (Fletcher et al., 2010). The major (P, Ca, and F), minor (Si, Cl and S) and trace elements (Th, U, and REE) vary slightly in our RM apatite and this has allowed us to look for chemical matrix effects. Our data suggest that an isobaric interference on $^{204}\text{Pb}^+$ may exist for high Th apatite.

ORIENTATION EFFECTS
In a number of minerals crystallographic orientation relative to the incident primary ions affects secondary ion yields and isotope ratios (Wingate and Compston, 2004). In rutile, for example, crystallographic orientation is a major control on secondary ion yields (Taylor et al., 2012). This effect is greatest for molecular ion species. We have measured ion yields for a number of molecular species for apatite, and none show any discernable relationship with orientation. We have sectioned a Brazilian apatite perpendicular and parallel to the C crystallographic axis. The data sets for these two sections are identical within our uncertainties.

CALIBRATION SCHEMES
To compare different U–Pb and Th–Pb calibration schemes we have collected data sets containing 12 or 13 secondary ion species that include: a reference peak (typically a molecular species containing isotopes of Ca, P and O), $^{197}\text{Au}^+$, $^{204}\text{Pb}^+$, a background peak, $^{206}\text{Pb}^+$, $^{207}\text{Pb}^+$, $^{208}\text{Pb}^+$, $^{206}\text{Pb}^+\text{H}^+$, $^{238}\text{U}^+\text{O}^+$, $^{238}\text{U}^+\text{O}_2^+$, $^{232}\text{Th}^+\text{O}^+$ and $^{232}\text{Th}^+\text{O}_2^+$.
CROSS CHECKING RESULTS
Ages calculated using SQUID2 U–Pb and Th–Pb calibration schemes are compared with the age from (1) $^{207}\text{Pb}/^{204}\text{Pb} - ^{206}\text{Pb}/^{204}\text{Pb}$, (2) $^{206}\text{Pb}/^{204}\text{Pb} - ^{238}\text{U}/^{204}\text{Pb}$ and (3) $^{208}\text{Pb}/^{204}\text{Pb} - ^{232}\text{Th}/^{204}\text{Pb}$ isochrons.

**Figure 1:** (A) complexly zoned apatite; (B) Total U–Pb isochron for RM Ol2; (C) Radiogenic Pb Concordia diagram for RM AFG2; (D) Pb–Pb isochron for Strelley apatite.

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Late Permian to Early Triassic arc magmatism and Middle-Late Triassic thermal overprint in southeastern Korea: SHRIMP U–Pb zircon geochronology and Nd isotope geochemistry

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Triassic continental collision between the North and South China blocks and subsequent subduction of the paleo-Pacific plate are two main tectonic events that have governed the Phanerozoic crustal evolution of the Korean Peninsula. The relationship between these events and their linkage to metamorphic or magmatic episodes are, however, still poorly constrained. Nevertheless, geochronological and geochemical data recently reported from granitic rocks in southeastern Korea (Cheong et al., 2002; Park et al., 2005; Yi et al., 2012) provide new insights in understanding the complexity of tectonomagmatic evolution in an active margin at the periphery of the paleo-Asian continent. Here we present detailed SHRIMP U–Pb zircon ages and geochemical and Nd isotopic data for metagranitoids, xenoliths and metasedimentary rocks in the Andong, Cheongsong and Yeongdeok areas situated along the border between the Precambrian Yeongnam massif and the Cretaceous to Paleogene Gyeongsang Basin (Figure 1).

Figure 1: Geologic map of the Andong-Cheongsong-Yeongdeok area and tectonic province of the Korean Peninsula. Abbreviations: N: Nangrim massif; P: Pyeongnam basin; NCB: North China Block, and SCB: South China Block.
Zircon grains from tonalitic gneisses distributed near Andong city have oscillatory-zoned cores and thin overgrowth rims showing dark cathodoluminescence (CL). The former yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 250.5 ± 1.2 Ma ($n = 63$, MSWD = 3.9; Figure 2a), indicating the emplacement of the magmatic protolith during the transitional Permian–Triassic. The latter, clustering at 223.4 ± 2.0 Ma ($n = 5$, MSWD = 0.22), yielded low Th/U ratios (0.04–0.08) indicative of a metamorphic origin. Two samples of metasedimentary xenoliths have detrital zircon grains showing a wide age spectrum from Late Archean to Paleozoic (Figures 3a, b). Weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of the youngest population of detrital zircons broadly overlap each other within uncertainties: 417 ± 10 Ma ($n = 20$, MSWD = 21) and 434 ± 7 Ma ($n = 13$, MSWD = 4.7). Dark CL rims mantling detrital zircon grains yielded $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from ca. 250 Ma to 230 Ma and, together with relatively low Th/U ratios (0.02–0.13), imply that these grains have experienced thermal events associated with tonalitic magmatism and Triassic recrystallisation.

The Cheongsong pluton, typically occurring as porphyritic hornblende-biotite granodiorite to the southeast of Andong city, commonly contains xenoliths of variable size. Its oscillatory-zoned zircons yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 202.9 ± 1.2 Ma ($n = 18$, MSWD = 1.02, Figure 2b) and Th/U ratios ranging from 0.51 to 1.19. This Late Triassic emplacement age is slightly older than the U–Pb titanite age of 195.9 ± 2.0 Ma previously reported by Sagong et al. (2005). Zircon grains from a monzonitic gneiss xenolith in the Cheongsong pluton have inherited cores with oscillatory, sector and banded zones and structureless rims of moderate to dark CL emission, yielding weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 248.6 ± 1.5 Ma ($n = 19$, MSWD = 1.5) and 234.3 ± 1.1 Ma ($n = 18$, MSWD = 0.89), respectively (Figure 2c). A few overgrowth rims were dated at ca. 200 Ma, corresponding to the emplacement age of the Cheongsong pluton. Zircon grains from a trondhjemitic gneiss xenolith are composed of oscillatory- and sector-zoned cores yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 247.1 ± 2.0 Ma ($n = 36$, MSWD = 2.9), and structureless rims with bright CL emission forming a slightly younger cluster at 237.1 ± 2.1 Ma ($n = 15$, MSWD = 0.94, Figure 2d). In the Cheongsong area, the emplacement age of the magmatic protolith to the monzonitic and trondhjemitic gneiss xenoliths, estimated from the inherited zircon cores, is indistinguishable within uncertainty from that of the tonalitic pluton in the nearby Andong area. Metamorphic overgrowth of zircon, however, is older by ca. 10 Ma in the Cheongsong area than in the Andong area.

One sample of biotite gneiss in the Cheongsong area has detrital zircon grains showing an age spectrum (Figure 3c) similar to that of the metasedimentary xenolith in the tonalitic gneiss from the Andong area. Dark CL metamorphic overgrowth rims with low Th/U ratios (<0.1) yielded $^{206}\text{Pb}/^{238}\text{U}$ ages ranging from 263 Ma to 216 Ma.

In the easternmost part of the study area, diorite xenoliths are present in the adakitic Yeongdeok pluton which was dated at ca. 250 Ma (Yi et al., 2012). Zircons from two xenolith samples yielded identical weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 265.0 ± 2.2 Ma ($n = 20$, MSWD = 1.5, Figure 2e) and 264.7 ± 2.9 Ma ($n = 10$, MSWD = 0.99, Figure 2f) with Th/U ratios ranging from 0.34 to 1.01.

In summary, our SHRIMP U–Pb zircon ages indicate that the protoliths of metagranitoids in the Andong and Cheongsong areas were emplaced at ca. 250 Ma. Zircon grains in these metagranitoids are overgrown by thin rims dated at 237–223 Ma. Zircons from metasedimentary xenoliths and a biotite gneiss in the Cheongsong area were overgrown during the emplacement of tonalitic magma and subsequent Triassic metamorphism. On the other hand, Permian diorite was emplaced at ca. 265 Ma in the Yeongdeok area, prior to the emplacement of the Yeongdeok pluton at ca. 250 Ma; here the Triassic overgrowth of zircon was not recorded.
Figure 2: Tera-Wasserburg concordia diagrams for zircons from (a) Andong tonalitic gneiss, (b) Cheongsong pluton, (c) monzonitic gneiss xenolith in the Cheongsong pluton, (d) trondhjemitic gneiss xenolith in the Cheongsong pluton, (e) and (f) diorite xenoliths in the Yeongdeok pluton. Filled and open ellipses represent the analytical points from the oscillatory-zoned core and overgrowth rim of zircons, respectively. Error ellipses are at 1σ level and the calculated ages are at 95% confidence. Dashed ellipses are outliers noted by statistical t-test in the calculation of weighted mean ages. The diagrams were plotted using the estimation of common lead with 206Pb-corrected ratios of 206Pb*/238U and 206Pb*/207Pb*. 
Tonalitic and trondhjemitic magmas are considered to be typically generated in an arc environment. All metagranitoid rocks in the Andong and Cheongsong areas show geochemical characteristics of subduction-zone magmas, such as the depletion in high field strength elements and the enrichment in large ion lithophile elements. They also show moderate LREE/HREE ratios with slightly negative Eu anomalies. Tonalitic gneiss samples in the Andong area show $\varepsilon_{\text{Nd}(t)}$ values ranging from −7.9 to −3.3, indicating some contribution from recycled crustal materials. The monzonitic and trondhjemitic gneiss xenoliths in the Cheongsong pluton have $\varepsilon_{\text{Nd}(t)}$ values of −4.7 and −3.9, respectively, which are similar to those of tonalitic gneisses in the Andong area. It is worth noting that the $\varepsilon_{\text{Nd}(t)}$ values of these rocks are considerably higher than those reported for granitoids in the Gyeonggi massif and Okcheon belt (Figure 4), suggesting significant contribution of primitive components during the magma generation in the former. The $\varepsilon_{\text{Nd}(t)}$ value of a diorite xenolith in the Yeongdeok pluton is as high as 4.3.

Recently, Yi et al. (2012) suggested that arc-related magmatism was prevalent in the Yeongdeok area during the Permian-Triassic transition period before the continental collision presumed to occur in central Korea during the Middle-Late Triassic. Our SHRIMP ages of zircon cores from the tonalitic and trondhjemitic gneisses in the Andong-Cheongsong area (ca. 250 Ma) confirm that this subduction-zone magmatism is widespread in southeastern Korea. In fact, the initiation of a subduction system could have occurred in the Middle Permian according to our SHRIMP zircon ages of ca. 265 Ma for the diorite xenoliths in the Yeongdeok pluton.

The distribution patterns of detrital zircon ages for a biotite gneiss and metasedimentary xenoliths in the Andong-Cheongsong area are comparable with those for the Taean Formation in the western Gyeonggi massif (Cho et al., 2010). This result corroborates the occurrence of Upper Paleozoic sequences which were long considered to be lacking throughout the Korean Peninsula.

Our SHRIMP U–Pb zircon ages and geochemical data reveal that the geochronological scheme and source characteristics of arc magmatism distinctly differ between the southeastern and central regions in the Korea Peninsula. This dissimilarity suggests that the two regions may have experienced separate tectonic episodes. Furthermore, our new findings of a subduction system since the Middle Permian and the presence of Upper Paleozoic sedimentary sequences in the southeastern Korea, provide new insights on the Phanerozoic tectonomagmatic evolution of the Korean Peninsula.
Figure 4: $\varepsilon_{Nd}(t)$ versus emplacement age diagram for the Permian to Jurassic (meta)granitoids in southeastern Korea. The ancient crust line is constructed on the basis of a $^{147}$Sm/$^{144}$Nd value of 0.11 and a present $\varepsilon_{Nd}$ value of -25, typical for the Precambrian basement rocks in Gyeonggi and Yeongnam massifs (Cheong et al., 2000; Lee et al., 2003). For reference, previous results on the granitoids in Gyeonggi and Yeongnam massifs, Okcheon belt and Gyeongsang basin are also shown (data from Cheong and Chang, 1997; Cheong et al., 2002; Williams et al., 2009; Kee et al., 2010; Kim, J. et al, 2011; Kim, S.W. et al., 2011).

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SHRIMP zircon geochronology of Late Cretaceous to Oligocene granitoid plutons in the eastern part of the Gyeongsang Basin, Korea

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The Korean Peninsula is an important tectonic link between eastern China and the Japanese arc (Figure 1). Widespread occurrence of Phanerozoic granitoids in the peninsula is considered to have been closely related to the subduction of the paleo-Pacific Plate since the late Permian (Sagong et al., 2005; Kee et al., 2010; Yi et al., 2012). The Cretaceous arc system developed in southeastern Korea, referred to as the Gyeongsang Arc System by Chough and Sohn (2010), was an extension of the Japanese arc formed by the subduction of the Izanagi Plate under the Asian continent.

Figure 1: Distribution of Phanerozoic granitoids in the Gyeongsang Basin, SE Korea with the locations of dated plutons. The inset figure shows the distribution of Phanerozoic granitoids in the southern Korean Peninsula and southwest Japan (Jahn, 2010; Cheong and Kim, 2012). Permian to Jurassic granitoids are shown in grey; Cretaceous to Paleogene granitoids are in black.
Precise age data for granitoid plutons comprising the arc platform are crucial for understanding the tectonomagmatic evolution of Korea and Japan, but are currently limited. Here we present new Sensitive High Resolution Ion Microprobe (SHRIMP) zircon ages for eleven granitoid plutons in the eastern part of the Gyeongsang Basin, southeastern Korea; from north to south, the Ocheon, Hoam, Kwonyiri, Oryuri, Daebonri, Bonggilri, Ijeonri, Gadaeri, Banggeojin, Daejeonri and Seosaeng plutons (Figure 1).

Tera-Wasserburg plots for the analysed zircon samples are shown in Figure 2. Zircons yielded weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 48.15 ± 0.45 Ma (n = 16, MSWD = 0.86) and 50.84 ± 0.44 Ma (n = 15, MSWD = 2.7) for the Ocheon and Hoam plutons, respectively. These emplacement ages are similar to the Rb–Sr whole rock age of 49.7 ± 0.1 Ma reported for the adjacent A-type Namsan pluton (Kim and Kim, 1997). Older (112 Ma, 83 Ma, 64 Ma) cores were found in zircons from the Ocheon pluton. Zircons from the Kwonyiri pluton yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 27.06 ± 0.25 Ma (n = 21, MSWD = 1.3). Until now, this Chattian age represents the youngest granitoid intrusion in South Korea. Inherited core ages of zircons from the Kwonyiri pluton range from 72 Ma to 62 Ma. Zircons yielded weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 64.60 ± 0.46 Ma (n = 20, MSWD = 1.9) and 67.02 ± 0.48 Ma (n = 26, MSWD = 2.4) for the Oryuri and Daebonri plutons, respectively. Zircons from two samples of the Bonggilri pluton gave reproducible weighted mean ages of 74.8 ± 1.3 Ma (n = 13, MSWD = 3.1) and 74.28 ± 0.60 Ma (n = 16, MSWD = 1.9). Silurian (443 Ma) and Jurassic (184 Ma) cores were found in zircons from the Bonggilri pluton. Zircons yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 86.04 ± 0.44 Ma (n = 13, MSWD = 1.14) for the Ijeonri pluton, 69.32 ± 0.77 Ma (n = 24, MSWD = 1.9) for the Gadaeri pluton and 57.24 ± 0.56 Ma (n = 16, MSWD = 1.3) for the Bangeojin pluton. In zircons from the Gadaeri pluton, a Permian (244 Ma) core was found. The Daejeonri and Seosaeng plutons in the southern part of the study area were dated at 57.54 ± 0.48 Ma (n = 16, MSWD = 2.6) and 68.56 ± 0.55 Ma (n = 24, MSWD = 2.6), respectively.

Previous Rb–Sr whole rock ages reported for the Hoam (39.7 ± 0.1 Ma), Daebonri (42.2 ± 0.1 Ma) and Oryuri (59.5 ± 0.1 Ma) plutons (Kim et al., 1995) are significantly younger than the SHRIMP zircon ages in this study. This discrepancy is probably a function of incomplete initial homogenization of Sr isotopes and/or later isotopic disturbance of the Rb–Sr system. Assuming a closure temperature of 500°C, and calculated cooling rates from previous Rb–Sr studies on biotite (KHNP, 2003), the Ijeonri (79.4 ± 0.4 Ma), Gadaeri (65.3 ± 0.3 Ma) and Banggeojin (51.9 ± 0.3 Ma) plutons yield very rapid cooling rate ranging from 75°C/Ma to 124°C/Ma. This supports the conventional idea that granitoid plutons in the Gyeongsang Basin are shallow intrusives (Chough et al., 2000).

The Silurian to Jurassic zircon core ages within the Bonggilri and Gadaeri plutons are distinctly younger than the Neoarchean to Paleoproterozoic protolith ages of the basement rocks from the two Precambrian massifs (Gyeonggi and Yeongnam) in South Korea (Cheong et al., 2000). This Phanerozoic age range supports a relatively short crustal residence time of basement rocks beneath the Gyeongsang Basin, also suggested by Sm–Nd isotope data (Cheong et al., 2002; Yi et al., 2012).

In summary, our SHRIMP zircon ages reveal that there were nearly continuous magmatic pulses in the eastern part of the Gyeongsang Basin from the late Cretaceous to Oligocene. Ages of inherited zircon cores from the Ocheon and Kwonyiri plutons are comparable with emplacement ages of other plutons in the Gyeongsang Basin and thus could also be considered to represent magmatic pulses. Extensive granitic magmatism appears to have ended in the early Eocene (c. 50 Ma) with the intrusion of A-type granites, with reoccurrence in the late Oligocene (c. 27 Ma).

Further chemical and Sr-Nd isotopic analyses will be undertaken for the comparison of dated plutons with Cretaceous to Paleogene granitoids from southwest Japan. Proto-Japan converted to an island arc isolated from the Asian continent (Maruyama et al., 1997). Our geochronological and geochemical data may have important implications for the paleogeographic correlation between southeastern Korea and southwest Japan.
Figure 2: Concordia diagrams for zircons from the dated plutons. Error ellipses are at 1σ level and the calculated ages are at 95% confidence. Dashed ellipses are outliers noted by statistical t-test in the calculation of weighted mean ages. The diagrams were plotted using the estimation of common lead with 208Pb-corrected ratios of 206Pb*/238U and 206Pb*/207Pb*.

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Geochronology of granitoids from the Eastern Dharwar Craton, India

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The Dharwar Craton in southern India consists of three main rock units: 1) early to middle Archean (3400–3000 Ma) tonalite, trondhjemite and granodiorite (TTG) basement, widely known as the Peninsular Gneissic Complex; 2) two generations of volcano-sedimentary greenstone belts at 3580–3200 Ma and 3000–2500 Ma; and 3) Late Archean (2600–2500 Ma) calc-alkaline K-rich granitic intrusions (Jayananda et al., 2000, 2009). Based on the differences in the nature and degree of regional metamorphism, the craton is divided by the Chitradurga shear zone into two parts: the Western Dharwar Craton (WDC), dominated by older Peninsular gneisses with broad sediment-rich greenstone belts; and the Eastern Dharwar Craton (EDC), dominated by late Archean granitic rocks with minor TTG and narrow greenstone belts. The WDC probably acted as a nucleus onto which Late Archean and Proterozoic terranes were accreted from the east. The whole craton was affected by ca. 2.5 Ga shearing and greenschist to granulite-facies metamorphism.

Here we present new zircon U–Pb ages (Figure 1) for granitoid samples collected from a traverse through the Eastern Dharwar Craton. Zircon grains from TTG in the Chitradurga corridor yield ca. 3280 Ma ages, indicating earliest crustal accretion. Zircons from monzogranite from the western part of the Eastern Dharwar yield ca. 2545 Ma ages, whereas the anatectic granite yields ages of 2530 Ma, with 3328 Ma xenocrysts. Two banded tonalitic gneisses from the central part have an age range of ca. 2600–2565 Ma. Monzogranites from the central part of the corridor record zircon ages from 2565–2525 Ma; porphyritic monzogranite from the western corridor are ca. 2546 Ma, and quartz-monzonite ages extend from 2575–2565 Ma. These data reveal two episodes of crustal growth at ca. 3.3–3.2 Ga and 2.6–2.5 Ga. The lower intercepts on concordia indicate a Pan-African thermal event that affected the margins of the EDC. The older TTG gneiss has low magnesium and calcium and high Na/K, Ni and Cr contents, whereas the younger tonalitic gneisses exhibit higher Mg, Ca, Ni and Cr. The latest granites have the chemical characteristics of high-Mg sanukitoids. The changes in chemical characteristics between 3.3 and 2.5 Ga can be attributed to changes in geodynamic processes, particularly increasing subducting slab angle, depth of melting and interaction of slab melts with overlying mantle.
Figure 1: Selected CL images of zircons from analysed samples; top row: granite (A) and tonalitic gneiss (B and C); middle row: TTG (D and F) and tonalitic gneiss of younger generation (E); bottom row: monzodiorite (G and I) and porphyritic granite (H).

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Pb isotopes in zircon by ion imaging

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High resolution secondary ion mass spectrometry was used in scanning mode to generate Pb isotope and age maps of zircon grains. The complexities of internal structure and age were not predictable from CL imaging of these grains, which are mostly dark and lacking in detail. Imaging reveals zonation of Y and U characteristic of magmatic zircons, together with a patchy distribution of Pb and Ti that does not correspond to growth zonation or cracks. Multicollector imaging of $^{204}$Pb, $^{206}$Pb and $^{207}$Pb show similar patchiness, which is best displayed in the scanning ion image of the $^{207}$Pb/$^{206}$Pb, which is positively correlated with Pb counts in micro-domains. Our results confirm ancient radiogenic lead redistribution as a product of high-grade Neoarchean metamorphism of Eoarchean zircon. Careful consideration should be taken when interpreting Pb–Pb age data from similar grains.
Mesozoic granitic rocks are widespread in the Korean Peninsula, covering more than one third of the total landmass. Precise age data for their emplacement and subsequent metamorphic imprints are crucial in understanding the Phanerozoic tectonomagmatic evolution of the peninsula. Here we present Sensitive High Resolution Ion Microprobe (SHRIMP) U–Pb mineral ages from Mesozoic calc-alkaline granitoid plutons (namely the Baekrok, Cheongsan, Boeun and Sokrisan plutons) in the central part of the Okcheon belt that separates the Precambrian Gyeonggi and Yeongnam massifs in South Korea.

The zircon grains yielded $^{206}\text{Pb}/^{238}\text{U}$ ages in close agreement with previous dating results: 225.6 ± 1.8 Ma (n = 11, MSWD = 0.98) for the Baekrok pluton (previous SHRIMP zircon U–Pb age = 226.0 ± 3.9 Ma; Kim et al., 2011), 224.7 ± 1.8 Ma (n = 13, MSWD = 1.4) for the Cheongsan pluton (previous SHRIMP zircon U–Pb age = 224.8 ± 1.7 Ma; Williams et al., 2009), 171.2 ± 2.2 Ma (n = 13, MSWD = 1.7) for the Boeun pluton (previous thermal ionization mass spectrometry (TIMS) titanite U–Pb age = 171.7 ± 1.4 Ma; Ree et al., 2001), and 94.2 ± 2.1 Ma (n = 18, MSWD = 0.49) for the Sokrisan pluton (previous TIMS whole rock Rb–Sr age = 91 ± 6 Ma; Cheong and Chang, 1997). These zircon ages once again confirm the occurrence of episodic magmatism in central Korea during the Late Triassic, Middle Jurassic and Late Cretaceous (Sagong et al., 2005; Cheong and Kim, 2012).

Titanites from the Baekrok and Boeun plutons are relatively clean with few inclusions, whereas those from the Cheongsan pluton show various and complicated textural relationships with monazite, allanite, ilmenite, rutile, and calcite. SHRIMP analysis of separated titanite grains is being conducted to evaluate the validity of previous TIMS U–Pb dating. The results will be discussed during the presentation.

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Insights into provenance pathways on the North West Shelf, Australia

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Australia’s North West Shelf has been the premier hydrocarbon exploration and production province for over 30 years. Despite the large number of geological studies completed in this region, numerous questions remain to be answered such as the provenance of reservoir units and how this relates to reservoir quality, extent and correlation. Complementary methods of isotopic analysis on detrital zircon have been applied to a range of samples collected from recent exploration drilling programs across the Exmouth Plateau and Browse Basin.

U–Pb age results have identified potential provenance and sedimentary transport pathways of reservoir facies and revealed that the relatively proximal Pilbara, Yilgarn and Kimberley Archean cratons were not major proto-sources of sediments during the Late Triassic. A Triassic volcanic signature in the Mungaroo Formation has also been identified. The source remains enigmatic, but textural characteristics of the grains suggest a provenance proximal to the Exmouth Plateau. Provenance studies elsewhere in South East Asia point toward possible Triassic correlations that may refine future paleogeographic reconstruction models.

Analytical work has also extended into the Canning and Perth basins, to investigate potential sedimentary transport pathways from Mesoproterozoic to Cambrian zircon proto-sources. Of particular interest is tracing the singular source of material seen in samples from the Brewster Sands from the Browse Basin, which is presumed to have a transport pathway through the Canning Basin. However, results remain ambiguous, probably indicating the complex evolution of the Canning Basin.
Pb sensitivity dependence on primary ion impact energy

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In preparation for the SHRIMP IV, standard U–Pb zircon geochronology was performed with a primary beam energy ranging from 3 to 15 kV. Typical calibration lines were generated at all energies above 5 kV. Pb sensitivity peaked between 7.5 and 10 kV, at just over 30 cps/ppm/nA. Useful yield increased continuously to lower energies, with the 3 kV analyses having a useful yield of approximately 1.5%. The use of an \(^{18}\text{O}_2\) primary beam allowed oxygen in the UO and UO\(^2\) calibration species to be labelled as oxygen from the zircon crystal structure or oxygen from the primary beam. These results suggest that all UO in energies above 5 kV is a product of atomic recombination, as no evidence of intact UO or ThO molecules from the zircon crystal structure is detected. As a result, the U\(^{18}\text{O}/\text{U}^{16}\text{O}\) ratios can be used to calculate sputtered volume directly.

The Pb sensitivity and useful yield curves are consistent with oxygen activity at the sputtering site being the primary control on Pb ionization. The low sensitivity, high U\(^{18}\text{O}/\text{U}^{16}\text{O}\) ratios, and high useful yields at energies below 7.5 kV are consistent with smaller collision cascades per incoming ion. The drop in sensitivity at high energies appears to continue after the collision cascade reaches its maximal value, suggesting that some other factor may be important. The results of these experiments suggest to us that the SHRIMP IV should be given the capability to operate at impact energies below 15 kV if it is to be used for geochronology.

Figure 1: Pb sensitivity, useful yield, apparent primary beam current (PBM), and true beam current for primary (impact) energies between 3 and 15 kV.
The Closepet Granite: a transcrustal magma chamber?

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The Closepet Granite in the Dharwar Craton of southern India is described by Moyen et al. (2003) as a 400 km x 20 km batholith, often considered as the boundary between the western Dharwar and eastern Dharwar cratons (Naqvi, 2005). It is exposed at different crustal levels over its length, corresponding to paleopressures from 7–8 kbar in the south to 2–3 kbar in the north. The current outcrop of the batholith and its host rocks is considered to be an oblique section of Neoarchean continental crust. Exposed in the south is the ‘root zone’ within migmatitic source rocks. The central part of the batholith is described as the ‘magma transfer zone’, and to the north are the ‘northern intrusions’. The characteristics of each zone are gradational from inclusion-rich and primitive compositions in the south to fractionated true granites in the north. A key question is whether this elongate batholith was emplaced over a short time interval as a single, transcrustal magma chamber, or was the batholith an Archean example of a typical subduction zone-related batholith. We address this question with SHRIMP-based geochronology.

The importance of the Closepet Granite is more than academic. The batholith lies subparallel to the shear zone boundary between the East and West Dharwar Craton (EDC and WDC), and two world-class orogenic gold deposits lie immediately to the east of the batholith (viz. Kolar and Hutti). The age of gold mineralisation at Hutti is ~2547 Ma (Sarma et al., 2008), whereas gold mineralisation events to the west are ~2520 Ma (Sarma et al., 2011). Given the obvious crustal heat anomaly imposed by the emplacement of the Closepet Granite, and the possible geometric relationship between the batholith and world-class ore bodies, the age or ages of batholith emplacement take on economic significance.

The available published age data for this vast batholith is complicated by high U-contents in their magmatic zircons. This appears to be ubiquitous, and yields a high proportion of discordant data corresponding to radiation-damaged zircons. This is further complicated by high grade metamorphic overprints at ~2.5 Ga and ~600 Ma, particularly towards the south. Published ages of ca. 2.52 Ga from zircons are considered to be the emplacement age of the batholith.

We have dated zircons from samples from the Closepet Granite and produced similar results to published studies. However, following our experience in other cratons where Neoarchean granites (s.s.) typically host high-U zircons, we have also dated coexisting titanite (see technical note below) and monazite (method described by Fletcher et al., 2010), where present, and obtained ages of ~2.54–2.52 Ga for the ‘northern intrusions’, which are the least affected by later overprints. We consider these to be reliable emplacement ages. Together with other known felsic magmatism as old as 2.56 Ga in the region, we consider that the Closepet Granite has a longevity similar to modern subduction zone-related batholiths and was emplaced over tens of millions of years. As the main orogenic gold deposits of the EDC are coeval with part of this history, it is inferred they formed above subducted crust, implying east-dipping subduction.
**Technical note: Titanite geochronology**

SHRIMP analysis of titanites suffers from broad-spectrum noise in the Pb-isotope mass range, which significantly degrades $^{207}\text{Pb}/^{206}\text{Pb}/^{204}\text{Pb}$ data. We have tested and employed the use of the retardation lens, which successfully removes this noise but may introduce Pb-isotope fractionation. Concurrently, we have characterised a potential Archean titanite standard, ORBA, which is anticipated to provide a homogeneous reference standard for U/Pb, and a monitor of Pb-isotope fractionation via measurement of the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio. It is also an adequate reference for U-content. Our preliminary results indicate ORBA is as uniform in Pb/U as the Khan titanite, currently used as a reference standard. We are currently obtaining TIMS data on ORBA.

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Cratonic Source Codes

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Cratonic Source Codes (CSCs) are a temporal fingerprint, in the form of a sequence of population ages, preserved in detrital minerals found in Archean (meta)sedimentary rocks. Simplistically, they indicate the ages of source rocks exposed at the time of sedimentation. In detail, however, the issues of reworking previous sedimentary rocks and recycling detrital grains, the effect of overprints such as metamorphism on primary age preservation in some detrital minerals, and Pb-loss accompanying metamictisation, all conspire to complicate the understanding and application of CSCs.

Dealing in the first instance with zircons, SHRIMP-derived age data from sedimentary rocks are filtered for quality (i.e. discordance, common Pb correction), and then used to identify the age (and associated uncertainty) of each source component. Building the source code for a craton (or other geological domain) involves the accumulation of detrital zircon population ages from multiple samples. As the CSC for a particular craton matures with sufficient data, each source age from detrital zircons should correspond to a known source from that craton (i.e., a marker in the Cratonic Code – CC). More detailed tests of zircon texture and geochemistry (trace elements and isotopes) can subsequently be used to assess the correlation between each age population from the CCS and CC.

The increasing amount and improved quality of available zircon age data from several cratons (e.g., Pilbara and Yilgarn cratons, Australia) makes such comparisons possible. Cratonic Codes for these cratons, and perhaps others, can be constructed now. In the future, these CCs will be improved and refined, and CCs for other cratons created as the data becomes available.

The applications of CSCs are many, and may be either positive or negative. The presence of a detrital population with the same age as zircons in a potential source terrain is positive, although their absence need not be negative (e.g., if that zircon source was not exposed at the time of sediment deposition). However, a more powerful criterion applies when a detrital population age is not found in a potential source region or craton. This may signal the presence of cratonic rocks that have yet to be identified or reliably dated, or possibly rules out that craton as a source for that component, with possible implications for Archean plate reconstructions or the like.

Other datable minerals in sedimentary rocks, such as rutile, titanite, monazite and xenotime are less abundant than zircon but nonetheless provide the opportunity to test time-links between CSCs and CCs. Source rocks of high metamorphic grade, in particular, may display characteristic metamorphic ages which are faithfully preserved in their detritus.

In this presentation we utilise new SHRIMP age data from detrital minerals in late basins and cratonic rocks from the Dharwar Craton, southern India, to assess the India-Australia link in the Archean.
Radiation damage in the TEMORA zircon standard

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The crystal structure of zircon gradually breaks down over time as a result of damage caused by the alpha decay of uranium and thorium. One possible concern is that at the time of SHRIMP measurement the target zircons can have a variable degree of radiation damage, sometimes within the same grain, and this can be different from the radiation damage of the standard being used. The effect of the degree of radiation damage on the sputtering behaviour of the zircon has not been investigated. In earlier times radiation damage was determined from XRD analyses that required milligram sized samples. Recently, the micro-measurement of radiation damage in zircons has been revolutionised by the application of Raman spectroscopy. Using this technique the degree of radiation damage can be measured on a one micron laser spot on the surface of a zircon grain. One aspect of the possible problem of the effect of radiation damage on SHRIMP measurements is the degree of radiation damage of the zircon standards. For standards such as CZ3, a large flawless Sri Lankan gem zircon, the radiation damage for all chips is constant over the grain. Radiation damage in Sri Lankan zircons has been extensively studied since the 1950’s (e.g., Holland and Gottfried, 1955) using XRD and recently on a micro-scale using Raman spectroscopy (e.g., Palenik et al., 2003). However for standards like TEMORA, where separate zircon grains are used, each grain can have a different concentration of U and Th and a different degree of radiation damage. There is currently no knowledge of the radiation damage of the TEMORA standard and the purpose of this contribution is to discuss Raman results combined with SHRIMP measurements of the U and Th concentrations on the range of radiation damage in the TEMORA zircons (Figures 1 and 2). We compare this to the spectrum of damage described by Palenik et al. (2003). Using these data we also consider evidence that the TEMORA zircon radiation damage has been subjected to an early annealing. This leads to a further application of the results to the history of uplift or heating of the TEMORA zircon parent rock.

![Figure 1: Raman shift position in wave numbers versus arbitrary height of peaks in a typical Raman spectrum of a TEMORA zircon.](image-url)
Figure 2: Range of radiation damage of Raman zircons with U and Th contents ranging from 663 and 344 ppm to 75 and 24 ppm respectively as measured from the FWHM and position measurements of the $B_{1g}(n_3)$ peak of the Raman spectrum. The results show an essentially linear relationship between increasing peak width and wave length with increasing dose.

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An experience of Pleistocene-Pliocene zircon
and perovskite dating: application to paleoarchaeology


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Volcanic ashes and tuffs are the main targets in Pleistocene-Pliocene paleoarchaeological dating. K/Ar and Ar/Ar bulk mineral analyses are mainly used for this purpose. Samples from two such archaeology-related sites using different mineral-geochronometers (zircon and perovskite) were studied in the Centre of Isotopic Research of Russian Geological Research Institute by the spatially selective secondary ionization mass spectrometry technique (SIMS SHRIMP II).

The first is the recently discovered Early Paleolithic site located at Karakhach, in the Northern Armenian Highland. The stratigraphic sequence includes volcanic ash layers where zircon autocrysts (up to 4500 ppm U), are suitable for SIMS U–Pb dating (Presnyakov et al., 2012). Pleistocene U–Pb ages are affected by initial disequilibrium in the U-series and therefore have been corrected on the basis of the algorithm outlined in Schmitt et al. (2003). Disequilibrium-corrected zircon crystallization ages of 1.947 ± 0.045 Ma, 1.804 ± 0.030 Ma, 1.799 ± 0.044 Ma and 1.750 ± 0.020 Ma may date the enclosed Early Acheulian lithic artefacts.

Zircons from each of four studied ash-bearing layers at Karakhach yielded a single ‘young’ age population, suggesting that the layers were formed during multiple eruptions without any reworking. Since accidental (captured) zircons of an ‘older’ age occurred in some layers, zircon genesis was also estimated on the basis of isotopic Hf-Nd systematics, following the approach described in Lokhov et al. (2009). The U–Pb ages of the zircons were used to calculate εHf(T) for the Lu–Hf system in the zircons and εNd(T) for the Sm–Nd system in the ash. Crystals with ages ranging from 1.7 Ma to 1.95 Ma fit into the magmatic field (Terrestrial Array, see Vervoort and Blichert-Toft, 1999) and correspond to the volcanic event responsible for ash formation. All others are clearly inherited, since their positions are below the field for magmatic zircons (see Figure 1). The ages obtained identify Karakhach as the oldest Early Acheulian site outside Africa.

The second site is the Sadiman volcano, located in northern Tanzania (Crater Highlands area), next to the Gregory rift. It is believed to be the source of the Laetoli tuffs where famous hominid footprints with an age of about 3.8–3.5 Ma are imprinted (Leakey and Hay, 1979; Leakey, 1981). The Sadiman volcano consists of phonolitic tuffs, tuff breccias and nephelinitic lava flows (Zaitsev et al., 2011). Perovskite is a principal phenocryst phase in the Sadiman tuffs, and was extracted for U–Pb dating. The procedure for SIMS U–Pb perovskite dating was similar to that described by Ireland et al. (1990). Eleven perovskite grains (sixteen spots altogether) from Sadiman tuffs were analyzed by SIMS SHRIMP II with Tazheran skarn perovskite (463 Ma) as a standard. Measured U–Pb data uncorrected for common Pb were plotted on the Tera-Wasserburg diagram, and defined a
lower intercept of 6.1 ± 2.2 Ma. Unfortunately, the high error overlaps all known K/Ar and Ar/Ar ages for Sadiman nephelinite lavas: 4.5 Ma (Bagdasaryan et al., 1973), 3.7 Ma (Hay, 1976) and an age of 3.3 Ma reported by P.C. Manega (Foster et al., 1997). The relatively large uncertainty is explained by the low (40–100 ppm) U content of the crystals, and the resulting low radiogenic Pb content represent only a small proportion of the total measured Pb. Consequently, the uncorrected perovskite analyses plot relatively close to the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio for modern common Pb, and significant extrapolation is required to define the lower intercept.

Thus, our data illustrate the applicability of perovskite dating of Pleistocene-Pliocene objects in principle, but in this case, do not allow us to determine unequivocally whether the Sadiman volcano is a source of the Laetoli tuffs. A search for more U-rich crystals is required.

Figure 1: Hf-Nd isotope systematics of zircons from the Karakhach site.

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Paleozoic activation of the Salmi rapakivi batholith (Baltic Shield) revealed by SIMS SHRIMP zircon dating

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Modern in situ isotope techniques, like SIMS and LA-ICP-MS, have a high spatial resolution and allow us to reveal information beyond the reach of the ID-TIMS technique. Recently, we have found several cases of latent Phanerozoic events, recorded in radiogenic Pb-loss (Sergeev et al., 2008), as well as in new zircon growth (Goltsin et al., 2010; Akhmedov et al., 2011; Lokhov et al., 2011), in zircons from Precambrian granitic complexes in Russia.

The Salmi Batholith is an A-type rapakivi granite complex that intruded along the Archean-Proterozoic boundary in the Ladoga region of northwestern Russia at 1540 Ma. In the North Ladoga area some Precambrian magmatic rocks (e.g., Valimjaki gabbro, Pitkaeranta pegmatites) contain both concordant and highly discordant zircons, the latter corresponding to a young, ca. 250 Ma, thermal event. A similar case has been observed in small late-magmatic potassium granite and pegmatite satellites of the Salmi rapakivi batholith (e.g., Hopunvaara, Torpussuo, Nietjaervi), which, along with 1480–1520 Ma magmatic zircons, have 230–500 Ma individual zircon grains. These young zircons have an excess of radiogenic hafnium (Sundblad et al., 2011), and their model depleted mantle Hf age is younger than their U–Pb age, suggesting a low-temperature metasomatic origin (Lokhov et al., 2011; Sundblad et al., 2011).

The presence of young individual zircons in such rocks and the apparent absence of grains with old cores and young rims led us to check rapakivi granite samples from the main Salmi rapakivi pluton, and nearby satellite intrusions. SIMS SHRIMP data show that the most altered rapakivi zircons have low-U (30–50 ppm) inner cores and 150–600 ppm-U outer rims. The U–Pb system is near-concordant, common Pb is low (<0.7%) and Th/U = 0.4–0.8. The weighted mean 207Pb/206Pb age is 1541 ± 12 Ma, in full agreement with ID-TIMS data (Amelin et al., 1997). A few zircons exhibit tiny (<15 µm) rims, dark in cathodoluminescence images. They are very discordant and have up to 40% common Pb, 4500–9500 ppm U and low Th/U (0.09–0.15).

All data may be approximated by a Discordia line (MSWD = 0.16) with upper and lower intercepts of 1540 ± 15 Ma and 444 ± 15 Ma, respectively (Figure 1). We suggest the younger age corresponds to a real geological event, which was not recognised earlier by ID-TIMS, possibly due to selection of the least-altered material for analysis. We suggest that the thin zircon rims were completely recrystallized during the regional hydrothermal Caledonian Event (~490–390 Ma), which we consider probably affected most Precambrian complexes of the Baltic Shield.
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U–Pb SHRIMP IIe dating of zircon from the Santa Catarina Quartzite, Luiz Alves Craton, South American Platform


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The South American Platform covers an area of about 15 million square kilometers, some 40% of which is exposed in the Precambrian shields: the Guiana, Central Brazil and Atlantic Shields. About 80% of the continental crust exposed in these shields was formed during the Paleoproterozoic and Archean. At the end of the Neoproterozoic, the South American Platform consisted of several plates or independent cratonic nuclei, most of which are still aggregated to their African counterparts. The most important cratons of the South American Platform are the Amazonian, Sao Francisco, and Rio de La Plata. The basement of these cratons consists essentially of medium- and high-grade metamorphic rocks, in addition to granite-greenstone belt type associations and numerous granitoid plutons. Fragments of Archean medium- to high-grade metamorphic rocks occur as inliers in the Proterozoic mobile belts (Dardene and Schobbenhaus, 2000).

The Luiz Alvez Microplate (Basei et al., 1998) is considered to be a continental segment composed of high-grade metamorphic rocks of regional expression, the basement of which is formed by the Santa Catarina Granulitic Complex. The high-grade rocks are predominantly orthogneisses with a subordinate contribution of kinzigitic paragneiss, quartzite and calc-silicate gneiss, in addition to local occurrences of banded iron formation. Compositionally they are predominantly depleted charno-enderbites; chemically very similar to the granulites of the Lewisian Complex in Scotland.

Sample 2BBV40 was collected from quartzite gneiss located near the Barra Velha region, Santa Catarina State. Two different zircon populations (transparent and dark grains) were identified in transmitted light (TL). Here we discuss only the small transparent zircon grains, which display well-preserved igneous characteristics. They are generally 80–400 µm in the largest dimension, and are predominantly needle shaped and inclusion-free. Cathodoluminescence (CL) images typically reveal simple broad zoning parallel to the crystallographic c-axis, or sector zoning in more equant grains. U concentrations range from 30 to 425 ppm (mean value = 205 ± 80 ppm) and Th/U ratios from 0.10 to 1.75 (mean value = 0.60 ± 0.30).

SHRIMP ANALYTICAL SETUP

Primary Beam:
Kohler aperture = 120µm, spot size = 30 µm and O₂⁻ beam density around 4nA.

Secondary Beam:
Source Slit = 80 µm; mass resolutions for 196(Zr₂O), 206Pb, 207Pb, 208Pb, 238U, 248(ThO) and 254(UO) were >5000 (1%) with residuals less than 0.025; no energy filtering.

Acquisition table:
Raster: 2 minutes with 2 minutes of burning time and spot size = 120µm; SL13 was used for the uranium concentration calibration (238 ppm); data acquisition parameters as shown in Table 1.
Table 1: SHRIMP data acquisition parameters.

<table>
<thead>
<tr>
<th>Mass</th>
<th>Zr2O</th>
<th>Pb</th>
<th>204.1</th>
<th>206Pb</th>
<th>207Pb</th>
<th>208Pb</th>
<th>238U</th>
<th>254ThO</th>
<th>248UO</th>
</tr>
</thead>
<tbody>
<tr>
<td>Delay (s)</td>
<td>5</td>
<td>3</td>
<td>1</td>
<td>2</td>
<td>1</td>
<td>1</td>
<td>2</td>
<td>2</td>
<td>2</td>
</tr>
<tr>
<td>Counting time (s)</td>
<td>2</td>
<td>10</td>
<td>10</td>
<td>20</td>
<td>2</td>
<td>10</td>
<td>5</td>
<td>5</td>
<td></td>
</tr>
<tr>
<td>Mass Auto Center</td>
<td>ON</td>
<td>OFF</td>
<td>OFF</td>
<td>ON</td>
<td>OFF</td>
<td>OFF</td>
<td>ON</td>
<td>ON</td>
<td>ON</td>
</tr>
</tbody>
</table>

Primary autotune:
(enabled): Src Steering Y and Src Steering Z.

Secondary autotune:
(enabled): QT1Y and QT1Z; Auto run selector: 254(UO); Auto center method: 50% peak height; Analytical cycle number: 5; All raw count rates have been corrected for a collection system dead time of 25ns; Analytical rate among standard and sample: 1 standard to 4 zircon samples.

Acquisition and data processing:
SHRIMP software: LabVIEW – 8.5 and SHRIMP – SW version 2.1; Calibration method: Ln(Pb/U) vs Ln(UO/U); Common lead correction utilised = 204Pb; Mass fractionation: not used; Data reduction software: SQUID 1.06 and Isoplot 4; Common lead correction is done by 204Pb; TEMORA2 was used as the 206Pb/238U age reference (416.78 Ma).

RESULTS
Three methods were used to date sample 2BBV40: Thermal Ionization Mass Spectrometer (TIMS), Laser Ablation-Ion Coupled Plasma-Mass Spectrometer (LA-ICP-MS) and Sensitive High Resolution Ion Microprobe (SHRIMP).

![Figure 1: U concentration histogram.](image)

The TIMS analytical procedures are based on the Krogh (1973) technique, with small modifications including the use of mixed 205Pb – 235U spike and anion exchange columns. The U–Pb results yielded a Concordia age of 2182 ± 9 Ma. LA-ICP-MS analyses employed the GJ1 zircon (600 Ma) as the U/Pb isotopic reference material (600 Ma), and sample 2BBV40 yielded a Concordia age of 2199 ± 16 Ma, which is similar to the TIMS age.

One hundred and nine zircon crystals were analysed by SHRIMP. Uranium concentrations range from 30 to 470 ppm with a mean value of 205 ± 0.85 ppm (Figure 1) and 232Th/238U ratios from 0.1 to 1.70 (Figure 2). Eighty-five of the 109 spots are concordant and yield a concordia age of 2193 ± 5.7 Ma (Figure 3). The 207Pb/206Pb weighted average age is 2191.9 ± 2.5 Ma (mean of 102 spots), within error of the concordia age.
**CONCLUSION**

Transparent zircon crystals from sample 2BBV40 show a quite homogeneous U–Pb isotopic composition and a $^{207}$Pb/$^{206}$Pb weighted average age of 2192 Ma. Additional work is in progress to test if 2BBV40 can be used as a Paleoproterozoic Brazilian internal laboratory standard.

**REFERENCES**


SQUID in the Clouds – what is next for SHRIMP data processing?

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SHRIMP data processing has a long and varied history with several software applications being developed over the last thirty years. Many of these applications have been developed in-house at various laboratories, and while individual applications are often widely used, they have often been dependent on specific platforms, development environments, and a very limited number of developers to provide support. These dependencies limit the ability of users to modify the applications for new purposes or require new systems to be built altogether, further complicating the situation. The impact of these issues is not simply academic. The potential for significantly different results between applications and even within versions of the same application can bring the validity of the methodology into question.

A BRIEF HISTORY OF SQUID

The original SQUID package was developed by Ken Ludwig of the Berkeley Geochronology Center as a Visual Basic for Applications (VBA) add-on to Microsoft Excel (Ludwig, 2001) and built on the popular Isoplot package (Ludwig, 1999). The use of the familiar spreadsheet environment as an interface made SQUID popular among both expert and non-expert users. However, the restrictions imposed by a fixed input data format and inability to adapt the underlying algorithms, especially with the development of new mineral and isotopic techniques, led to the development of SQUID-2 from 2005. Development by Ken Ludwig was supported by Geoscience Australia and several other SHRIMP labs in a consortium.

A major aim of the development was to provide tools to modify data input, processing and graphing (the ‘tasks’) and this was successfully implemented (Ludwig, 2009). As the custodians of the source code, Geoscience Australia made it freely available on the web-based source code repository, SourceForge (sourceforge.net/projects/squid2/). This reflects Australian Federal Government policy about the dissemination of computer software and is good practice supporting the transparency and reproducibility of the scientific process (Barnes, 2010; Merali, 2010; Ince et al., 2012).

SQUID HAS DEPENDENCY ISSUES...

Despite considerable technical achievement, the additional complexity of SQUID-2 further highlighted dependency issues. The application is particularly dependent on the MS Windows-only English native version of Microsoft Office Excel 2003 and even slight alterations to the operating environment can cause problems. Installation of the add-in is a complex and frequently unsuccessful process to ensure that previous versions and their associated files do not interfere with the new version. The use of Excel-based interface forms stored as propriety format modules along with the text-based VBA code makes version control in development and delivery phases additionally complex. More broadly, there have been criticisms of the precision and accuracy of statistical functions in Excel 2003 (McCulloch and Wilson, 2005) although Microsoft has worked to improve this in Excel 2010 (Oppenheimer, 2010).

The major challenge facing continued use of SQUID-2 is the increasingly common usage of the Microsoft Windows 7 and Office 2010 with mixed reports about the stability and accuracy of the
current versions of SQUI

D-2 in these environments. Geoscience Australia is reviewing the SQUI

D-2 application and options for continuing use ahead of a major change in the standard operating

environment on computer workstations across the entire organisation in the second half of 2012. Beyond technical coding issues, the review is highlighting broader questions about the future directions of SHRIMP data processing in general (Table 1).

<table>
<thead>
<tr>
<th>OPTION</th>
<th>POSITIVE OUTCOME</th>
<th>NEGATIVE OUTCOME</th>
</tr>
</thead>
<tbody>
<tr>
<td>Do nothing</td>
<td>Very easy to implement</td>
<td>• Current operating environments will become increasingly obsolete and difficult to maintain • Risk of low reproducibility across versions damaging reputation of method</td>
</tr>
</tbody>
</table>
| Maintain working copies of SQUI

D-2 | Simple to implement | • Potential bottleneck in workflows • Distribution and installation issues remain • Stand-alone systems will become increasingly obsolete and difficult to maintain |
| Maintain working copies of SQUI

D-2 | Accessible via web • Common utility for all users • Reduced distribution/installation issues | Licensing in virtual/cloud environment will mean on-going regular costs per user |
| Update SQUI

D-2 for Office 2010 | Bring application up-to-date with commonly used environment • Encourage use by non expert users | Requires reformation of consortium and payments to developer/s |
| New application: | Reduce dependency on Windows/Excel environment • Opportunity to engage new users and developers | Requires review of potential languages/environments • Creates new dependencies • Requires reformation of consortium and payments to developer/s • Will take several years • May require radical change for users |
| New application: | Use existing application, reduce costs | May create new environment and developer dependencies • Review period required |
| New application: | Accessible via web • Common utility for all users, reduced distribution/installation issues | Licensing costs if using propriety applications (e.g., Microsoft) • Will take several years |

FUTURE OPPORTUNITIES

Other geochronology and geochemistry communities are working with similar data handling issues. Driven by a desire for greater precision, reproducibility and calibration between laboratories and methods, groups such as EARTHTIME (www.earth-time.org) and Cyber Infrastructure Research & Development Lab for the Earth Sciences are developing workflows and platform-independent and open-source applications such as the U–Pb Redux software for TIMS (cirdles.org; Bowring et al., 2011). The ICP-MS community have also formalised development efforts and are meeting regularly (e.g., Horstwood et al., 2010). Similar initiatives are also occurring in the broader disciplines of geochemistry (www.earthchem.org). There are opportunities to learn from these developments and the first SHRIMP-focused inter-laboratory calibration exercise is the first step in a similar path for the ion probe community that will likely highlight the issues with inconsistent data processing.
There are also ample prospects to adapt tools and technologies used in larger scientific fields such as computational biology and biotechnology. Workflow management systems such as Taverna (www.taverna.org.uk) and Kepler (www.kepler-project.org) are widely used in bioinformatic research to capture and share data acquisition, processing and visualisation tasks that range from a local hard-drive to web services and large internet based data archives. These have the potential to be adapted for more specialised data processing tasks and provide a way to reveal internal algorithms for verification and document any modifications.

While new concepts and technologies such as ‘open-source’ and ‘cloud computing’ are exciting they should always be approached with a long-term view that new tools and technologies need to be carefully assessed beyond their novelty and hype for their true cost and sustainability. Importantly, the new technology does not avoid the greatest challenges to new development – the so-called ‘soft issues’ of people and project management, the logistics of shared resourcing, and in-grained institutional or group cultures around data management (e.g., Barton et al., 2010). Developing modern, integrated and sustainable applications has moved well beyond ‘hero-coding’ by part-time programmers; however, the organisationally intense project management processes and tools used in large-scale software development need careful tuning for specialised, small-scale and complex projects such as geochronology data management.

CONCLUSION
There are several issues challenging the future use of the SQUID-2 data processing application, but there are also several opportunities for further development. The overall strategy proposed by Geoscience Australia is incremental change with maintenance and upgrade of the existing Excel-based SQUID-2 in the short-term while exploring options for a longer term solution with emerging technologies. Further discussion among the SHRIMP community is needed to list the needs and priorities for further development and re-establish procedures for funding that work.

REFERENCES
Experiments visualising detrital zircon age data with bumps and barcodes

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The increasing ability to acquire large sets of detrital zircon data via ion probe and laser ablation in situ methods has not necessarily been matched by advances in the best tools to visualise both individual and large collections of samples. On an individual sample level, Veermeesch (2012) has noted the statistical flaws of the conventional probability density distribution (PDD) and has developed a tool (http://densityplotter.london-geochron.com/) for the display of detrital zircon data using kernel density estimation (KDE). However, regardless of the method creating the distributions, large numbers of samples quickly overwhelm meaningful visual interpretation (Sircombe and Hazelton, 2004). Perhaps a simple adjustment of perspective, as illustrated in Figure 1, might help improve visualisation of large detrital datasets and any inherent similarity patterns.

Figure 1: Experimenting with detrital zircon age distributions from north Western Australia. The darkness of the stripes reflects the distribution density or the ‘height’ of the distribution in a conventional plot. Does it make it easier to ‘see’ the patterns of similarity?

REFERENCES


Development of motorized O$_2$ feed valve control system II

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A motorized oxygen feed valve control system has been developed at NIPR, which was presented at the SHRIMP Workshop in Beijing (Tachikawa et al., 2010). We are now advancing the system in order to realize fully-automatic control of the Duoplasmatron, which includes detection of arc dropout and recovery of arcing. In order to detect arc dropout, an electric current for the arc current meter on the Primary Column table can be used, but it is not easy to directly measure the current because the meter is in high voltage. A DC current sensor (Model: DCS-20-05-AS) manufactured by U.R.D. Co., Ltd, Japan (Figure 1), has been utilized to overcome the difficulty of being in high voltage. The sensor operates with 12 V DC and takes a non-contact measurement of a current with rated input currents of ± 500 mA. The measured current values are linearly converted to output voltages of 2 V for −500 mA and 10 V for 500 mA by the sensor, which means that no input current, (i.e., arc dropout), gives the output voltage of 6 V (Figure 2). The output voltage range and the offset voltage can be easily converted to any range and offset by using an operational amplifier. For example, 0 A (arc dropout) gives output voltage of 0 V and 100 mA gives 10 V. By integrating the output voltage into the oxygen valve control system, detection of arc dropout followed by automatic re-establishment of arc discharge should be feasible, provided that an appropriate program code can be developed. The arc current is usually optically monitored by a CCD camera in many SHRIMP laboratories, but the conversion of the current values in high voltage into the voltage values at ground also enables us to put the output voltage into a DAQ device (e.g., NI PCI-6221), which allows us to monitor the arc current on the PC for meters.

REFERENCE


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**Figure 1:** Photograph of a DC current sensor, DCS-20-05-AS, manufactured by U.R.D. Co., Ltd, Japan. Dimensions (mm): 53 W × 51 H ×14 T.

**Figure 2:** Output characteristics of DCS-20-05-AS, whose rated currents are ± 0.5 A. Zero current gives a voltage of half of power supply voltage: 6 V for power supply voltage.
Application of zircon REE patterns

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Rare earth elements (REE) have been commonly used as one of the useful indicators of zircon characterization. CI chondrite-normalized REE patterns for various settings of zircon are shown in Figure 1a. REE distribution in zircon is primarily controlled by crystal structure constraining the ionic radii compatible with zircon and the REE composition of the source melt. Zircon generally prefers heavy REE (HREE) to light REE (LREE), resulting in high within-group fractionation, namely a high HREE/LREE ratio. The degrees of fractionation between HREE and LREE, Ce anomalies, and Eu anomalies are thought to reflect those of source melts. Ce anomalies are derived from contribution of Ce⁴⁺, whereas the Eu anomalies can be explained by plagioclase fractionation.

In the case of metamorphic zircons, REE patterns are controlled by coexisting minerals. For example, the overgrowth rim of zircon coexisting with garnet shows a lower HREE/LREE ratio and a flat REE pattern, particularly the HREE (Figure 1a), which indicates that distribution coefficient between zircon and garnet in HREE ($D_{\text{zrn/grt}}$) is less than 1 (e.g., Hokada and Harley, 2004). REE partitioning between zircon and melt/garnet is also investigated by experimental approaches (e.g., Rubatto and Hermann, 2007). On the other hand, zircon coexisting with monazite is characterized by a higher HREE/LREE ratio and depletion of LREE and middle REE (MREE). This depletion suggests consumption of LREE and MREE by monazite during crystallization.

Interesting REE distributions are found in zircons affected by hydrothermal fluids (e.g., Hoskin, 2005). During interactions between zircon and low-temperature hydrothermal fluids, Pb is released from zircon through volume diffusion and non-formula elements such as Ca, Al, Mn, and Fe are incorporated into zircon (e.g., Geisler et al., 2002). The altered zircon shows a lower HREE/LREE ratio and enrichment of LREE (e.g., Geisler et al., 2003; Horie et al., 2006), which suggests that preferential incorporation of LREE occurs together with incorporation of Ca. Therefore, the REE abundance in zircon affected by hydrothermal interaction can provide information on the disturbance of the U–Pb system.

The Duluth Complex anorthositic series (AS3) zircon is one of the U–Pb geochronological reference materials. However, some of these zircon grains show discordant U–Pb data, and it is proposed that these discordant data reflect Pb diffusion (Schmitz et al., 2003). Some REE patterns of AS3 show a lower HREE/LREE ratio and enrichment of LREE (Figure 1b), which is similar to those of zircon affected by hydrothermal alteration. There is the possibility that the variation of the REE abundance relates to the disturbance of the U–Pb system in AS3. Therefore, zircon REE patterns are potentially valuable tools in revealing the crystallization process and history of zircons.
Figure 1: CI chondrite-normalized REE patterns for (a) typical zircons and (b) AS3 zircon. Data in (a) derived from: Grt-Bt-Sil gneiss in the Sør Rondane Mountains (‘with garnet’, red square; Hokada, unpublished data), augen gneiss in Busan gneiss complex (‘with monazite’, green diamond; Horie, unpublished data), and tuff affected by chlorite alteration in Bidoudouma (‘altered’, grey triangle; Horie et al., 2006).

REFERENCES
SHRIMP-RG $^{238}\text{U} - ^{230}\text{Th}$ dating of late Pleistocene allanite

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U–Th DATING OF ALLANITE

Technique and standardization

Allanite is a Th-rich epidote-group mineral that occurs in a variety of silicic rocks and may be an excellent chronometer for dating the crystallization history of young magmas. We describe a refinement of analytical technique and standardization for $^{238}\text{U} - ^{230}\text{Th}$ disequilibrium dating of allanite, as well as its application to resolving the ages of late Pleistocene-Holocene rhyolitic tephras and lavas in the western United States. Using the USGS-Stanford SHRIMP-RG, measurements of the relative $^{238}\text{U} - ^{230}\text{Th} - ^{232}\text{Th}$ compositions of allanite were made with a 15–20 nA O$_2$ primary beam, mass resolution of 8000–9000, and energy selection slit set to minimize tailing onto $^{230}\text{Th}^{16}\text{O}^+$ from lower mass molecules. Energy filtered $^{230}\text{Th}^{16}\text{O}^+/\text{background}$ ratios ranged from ~10 (in secular equilibrium allanite) to ~100 in young (late Pleistocene) allanite.

Measurement of secular equilibrium (atomic $^{230}\text{Th} / ^{238}\text{U} = 1.694\times10^{-5}$) during allanite dating is important because it provides a measure of relative U/Th ionization during sputtering as well as the ability to resolve the ages of ‘old’ crystals. However, secular equilibrium in allanite is challenging to measure because U concentrations are typically <300 ppm. Consequently, ‘old’ allanite in $^{238}\text{U} - ^{230}\text{Th}$ secular equilibrium typically yields weak (~0.1 cps/nA) $^{230}\text{Th}^{16}\text{O}^+$ signals. We investigated several potential standards for precisely measuring secular equilibrium by analyzing large single crystals derived from pegmatite localities including: 1) Pacoima Canyon, California, 2) Mitchell County, North Carolina, 3) Cerbat Mountains, Arizona, and 4) Arendal, Norway. Results indicate that Arendal allanite is most promising because it contains atypically high U concentrations (~1000 ppm) along with ThO$_2$ concentrations of ~3 wt.%, and allows characterization of secular equilibrium to ± 1.5% precision. Using Arendal allanite, we find that session or mount specific factors for relative U/Th ionization are 0.88 ± 0.01 to 0.92 ± 0.02, similar to those derived from $^{208}\text{Pb} / ^{206}\text{Pb}$ vs. ThO$^7$/UO$^+$ in ca. 1.2 Ga Pacoima Canyon allanite during the same sessions. In addition, investigation of mass spectra for these allanites reveals that the intensity and position of molecular guide peaks for $^{230}\text{Th}^{16}\text{O}^+$ used in past studies (e.g., Vazquez and Reid, 2004) can vary significantly depending on REE, Ti, and Fe concentrations.

Dating the eruption of late Pleistocene tephras using allanite rims

The U/Th variation of allanite from a particular magma is typically limited (~10%), which precludes the derivation of precise ages simply from internal isochrons. Consequently, allanite U-Th ages are typically modelled from an assumed initial Th-isotope composition or derived from multi-phase isochrons using coexisting minerals or glass. We derive relatively precise (± ~5%, 2σ) U–Th isochron ages from the unpolished rims of pumice-derived allanite and coexisting zircon from late Pleistocene Wilson Creek Formation tephras in eastern California whose ages are controversial and have been difficult to resolve by Ar/Ar dating due to the pervasive presence of sanidine xenocrysts. For analyses of unpolished rims, allanite and zircon were embedded into indium-filled troughs within standard epoxy mounts. To monitor for surface contamination and the significant generation of $[^{32}\text{Th}^{16}\text{O}^{12}\text{C}]^{2+}$ that interferes with $^{230}\text{Th}^{16}\text{O}^+$, we monitored $^{230}\text{Th}^{15}\text{C}^+$ as a proxy for this Th-O-
C molecule. Cleaning of mounts with soapy water and dilute acid prior to gold coating sufficiently cleaned rim surfaces. However, we observe that adhered pumiceous glass on rim surfaces often contains elevated concentrations of carbon, and should be avoided. Allanite and zircon rims from Ashes 7–19 in the lower portion of the Wilson Creek Formation yield stratigraphically consistent isochron ages of 26.8 ± 2.1 (2σ, MSWD = 1.02, n = 18) and 61.6 ± 1.9 ka (2σ, MSWD = 0.7, n = 20), respectively. A minority of crystals in each tephra are identifiable as xenocrysts because they yield model ages of ca. 90–100 ka. Tephra deposited during the Laschamp geomagnetic excursion yields an isochron age of 40.8 ± 1.9 ka (2σ, MSWD = 1.2, n = 22), which is indistinguishable from an independent age of 40.7 ± 0.9 ka (Singer et al., 2009) derived at the excursion’s type locality in France. The results are in excellent agreement with a previously determined chronology derived from magnetostratigraphy (Zimmerman et al., 2006).

REFERENCES
Concerning conodonts

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BACKGROUND

The publication of the results of SHRIMP II oxygen analyses of Ordovician conodonts four years ago (Trotter et al., 2008) was significant for several reasons. Not only was it the first major study of stable isotopes in biominerals using SHRIMP II, it was the first study of oxygen isotopes in conodonts by SIMS. The principal technical achievement of the study was to demonstrate that conodont oxygen compositions could be measured reproducibly from one analytical session to another with high precision and accuracy. The principal scientific achievement was to demonstrate that, at least for the early Paleozoic, the oxygen isotopic composition of conodont bioapatite is a much more reliable indicator of sea surface temperatures than the oxygen isotopic compositions of calcitic brachiopods.

The headline emphasis of the Trotter et al. (2008) paper was the implications of the measured conodont compositions for climate change through the Ordovician and its impact on biodiversity and biomass. Because it was the first study of its type, however, this was underlain by several tests of the validity of the technique. A major concern at an early stage of the work was whether a mineral apatite standard (Durango) could be used as a reference material for analysing conodont carbonate fluorapatite. To complicate matters further, the crown of conodont elements can consist of two tissue types, hyaline and albid (Figure 1), the relative abundance of which varies through time and the evolution of conodont lineages; albid is plentiful in early Paleozoic forms, whereas later lineages are typically only hyaline. Hyaline consists of well-aligned, elongate micro-crystals containing both CO₃ and PO₄ and numerous nanopores. Albid, on the other hand, consists of large (>100 µm) crystals containing only PO₄ (Trotter et al., 2007). As a result of these different structures, albid is much less permeable than hyaline, is more resistant to post-mortem uptake of trace elements, and is more likely to retain primary geochemical signatures (Trotter and Eggins, 2006).

Figure 1: Transmitted and reflected light images of a complete conodont (left) then sectioned in a SHRIMP mount (right), showing the two crown tissue types.
RELIABILITY TESTS
To test the reliability of measuring bioapatite against a mineral apatite standard, the oxygen isotopic composition of the enamel from a modern shark tooth was analysed by SHRIMP II and shown to be within analytical uncertainty of the composition determined by conventional GIRMS analysis. Further, the oxygen composition measured by SHRIMP II on conodonts from two Early Ordovician samples from Australia was the same within uncertainty as that measured conventionally on a bulk conodont sample of similar age from the USA (Bassett et al., 2007). To test the effects of differences in matrix, both hyaline and albid tissues were analysed within individual conodont elements. No systematic difference in the measured $\delta^{18}$O was found. To test for differences in composition between genera, up to three different genera were analysed from some samples, yet there were no systematic differences apparent. Finally, samples of similar age and paleolatitude but from different localities in geographically disparate continents (Canada and Australia) gave consistent results.

This range of tests and cross-checks, although far from comprehensive, was considered sufficient to validate the method and has served as the basis for a subsequent expanded conodont study supported by funding from the ARC. That work, currently under way, aims to develop a robust record of changes in sea surface temperature from the Late Cambrian to the Late Triassic, with a particular focus on periods of biotic crisis and environmental change.

SOME CONCERNS
A recent series of abstracts by Wheeley et al. (2010a; b; c), however, has cast doubt on the reliability of conodont oxygen analyses by SIMS. Having used the Edinburgh Cameca 1270 to analyse 69 Ordovician and Silurian conodonts for their oxygen isotope compositions, Wheeley et al. (2010a) concluded that 1) $\delta^{18}$O can vary by as much as 4‰ within the hyaline crown tissue of individual conodont elements, 2) $\delta^{18}$O varies systematically across some conodont elements, implying an underlying microstructural control, 3) $\delta^{18}$O can differ by as much as 3‰ between different taxa from the same sample, and 4) the difference between SIMS and conventional analyses of some taxa can be as much as 1‰. They also found that even low burial temperatures (<90°C) were sufficient to shift the measured $\delta^{18}$O by up to 2.5‰, and that separating the conodonts from the host rock using formic, rather than acetic, acid could introduce shifts in measured $\delta^{18}$O of up to 3.5‰.

SOME CONCERNS ADDRESSED
All conodonts that we have studied so far have a very low Colour Alteration Index (CAI), and all have been separated using acetic acid, so we have no data bearing on the last two points. We do, however, have a large data set (>1000 specimens, most with 3 to 12 analyses per specimen) with which to assess intra-element variability, including possible differences in measured $\delta^{18}$O relating to tissue type, and inter-species differences. We consistently undertake multiple analyses of each specimen and usually analyse 5 specimens per sample. Although there is some compositional variation between specimens and within single conodont elements, as would be expected from any animal presumably living through at least one seasonal cycle, we find that it is not systematic. Thus in good quality conodonts intra-element compositions are internally consistent, and conodonts of different genera or species extracted from the same rock sample commonly give consistent $\delta^{18}$O within the sub-permil analytical uncertainty (Figure 2). Exceptions are rare, but have significant geological implications. Examples illustrating these findings will be presented and discussed.
Figure 2: SHRIMP II oxygen isotopic analyses of 90 conodonts, representing 15 species from 18 closely-spaced Late Triassic stratigraphic units deposited in the Sicani Basin, Sicily, showing the close similarity in composition between species (data from Rigo et al., 2012).

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Recent technical development of triple oxygen isotopic analysis using SHRIMP-IIe/MC

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For in situ measurement of triple oxygen isotopic compositions in planetary and meteoritic specimens, we have developed the technique using the SHRIMP-IIe/MC recently installed at the Korea Basic Science Institute. In addition to our previous report, the analytical results were significantly improved by: 1) the method of sample storage using a nitrogen chamber, 2) a newly manufactured collector slit for central Faraday, and 3) very precise alignment of height of the three collector slits. Preliminary data were obtained with analytical uncertainties of 0.1 to 0.2 ‰ for internal errors of individual measurements and ~1.5‰ for reproducibilities. More details will be presented at the workshop.