APPENDIX 1: ZIRCON ANALYTICAL TECHNIQUES

Zircon crystals were obtained using magnetic and density separation, hand picking and were mounted in epoxy resin with standard zircons SL13 and QGNG (1850 Ma; Daly et al., 1998). The mount was polished to approximately half grain thickness to reveal zircon interiors. Transmitted, reflected light and cathodoluminescence (CL) images were taken prior to analysis and additional CL imaging was performed after analysis.

U-Pb zircon geochronology

All analyses were performed by SIMS using the SHRIMP I at the ANU. Analytical procedures for zircon are described in Compston et al. (1984), Williams and Claesson (1987) and Claoué-Long et al. (1995). The primary O^{2-} ion beam was in the range 2–3.5 nA for a spot diameter of 20–40µm. Ionised particles were extracted into the mass spectrometer with a 10 kV potential and counted by a single electron multiplier in peak skipping mode. The masses Zr_2O, Pb^{204}, background, Pb^{206}, Pb^{207}, Pb^{208}, U^{238}, ThO^{248} and UO^{254} were sequentially focused into the collector through stepping of the magnet. Each analysis represents the average of seven scans through the different mass stations.

Calibration of Pb/U ratios was by comparison to QGNG and its power law relationship between Pb^+/U^+ and UO^+/U^+. U and Th abundances were calculated with reference to SL13 (238 ppm U) and are subject to an uncertainty of at least ± 20%. Common Pb corrections were based on the individual measured ^{204}Pb abundances and the assumption of crustal common Pb of the same age in the zircons with the terrestrial Pb isotopic composition (Stacey and Kramers, 1975). Data reduction was carried out using SQUID and ISOPLOT (Ludwig, 1999, 2001). Individual analyses have uncertainties listed in Table 1 at 1σ level, and final ages are quoted in the text with 95% confidence limits.

Analyses of QGNG standard were interspersed with the unknowns at the rate of approximately one in four. QGNG analyses were also used as a monitor of the long-term stability of the $^{207}Pb/^{206}Pb$ ratios. An instrumental mass fractionation correction of 0.63% was applied to the measured $^{207}Pb/^{206}Pb$ ratios of each of the unknowns, based on values obtained on concurrent measurements of standard QGNG.

Zircon O isotopes

All oxygen isotope analyses were performed on SHRIMP II at the ANU, following procedures given by Ickert et al. (2008). Analyses were made on exactly the same spot locations as were previously analysed for U-Pb. All analyses were collected during the same analytical session with no correlation between $\delta^{18}O$ and analysis order, ruling out analytical problems relating to mount geometry or instrument tuning. A Cs^+ primary beam was used as the ionisation source and an electron gun employed to neutralise charge build up on the mount surface. The Kimball Physics ELG-5 electron gun streams electrons at a 45º incidence angle to the mount at a 20 mm working distance. The multicollector arrangement comprised two Faraday cups with a 1010 ohm resistor for the ^{16}O beam and a 1011 ohm resistor for the ^{18}O beam. Data were collected in two sets of 5 measurements each (with 10s integration times per measurement), with baselines measured prior to analysis. Possible isobaric interferences were resolved by operating at a mass resolution of ~2500 (source slit = 150 µm and collector slit = 300 µm). Secondary beam focussing was performed prior to data collection and between samples.

Data reduction was performed using the in-house program POXI written by Peter Lanc (ANU). Unknowns were bracketed by regular analyses of reference zircons FC1 (5.4‰, Ickert et al., 2008) and Temora 2 (8.2 ‰, Black et al., 2004). Calibrations included corrections for instrumental drift, gain corrections and electron-induced-secondary ion emission. Uncertainty on the standards over the full analytical session was 0.15 ‰ (σ), considered to be the best estimate of precision for the individual analysis.

Zircon Lu-Hf isotopes

Measurements of Hf isotopes were conducted by laser ablation multicollector inductively coupled plasma mass spectroscopy (LA-MC-ICPMS) using a ThermoFinnigan Neptune MC-ICPMS coupled with

a HelEx 193 nm ArF Excimer laser ablation system (Eggins, 2003; Eggins et al., 2005) at the ANU. Analyses were performed on the same spots previously analysed for U-Pb and O by SIMS. The laser spot diameter was 47 µm. The mass spectrometer was tuned to optimal sensitivity using zircon from the Monastery kimberlite. The following masses were measured simultaneously in static-collection mode: 171, 173, 174, 175, 176, 177, 178, 179, and 181. A laser line background was acquired every 10–12 analyses throughout the analytical session.

The laser was pulsed with a repetition rate of 5–8 Hz and applied fluence of ~5 J/cm^2. Data were acquired for 100 seconds, but in many cases only a selected interval with steady ^{174}Hf/^{177}Hf signals from the total acquisition was used in the data reduction. Several secondary standard zircons (Temora 2, Monastery and Mud Tank) were measured as a check on data quality. The precision and reproducibility (2se) on Hf reference materials was: Mud Tank 0.282491 ± 0.000017 (n = 11); Monastery 0.282714 ± 0.000017 (n = 11); Temora 2 0.282683 ± 0.000020 (n = 11), based on which a correction factor of 1.00005 was applied to all ^{177}Hf/^{176}Hf data. Measured signal intensity was typically ≈5–6 V ^{178}Hf at the beginning of ablation, and decreased over the acquisition time to 2 V or less.

Isobaric interferences of ^{176}Lu and ^{176}Yb on the ^{176}Hf signal were corrected by monitoring signal intensities of ^{175}Lu, ^{173}Yb, and ^{171}Yb. Interference of ^{174}Y on ^{174}Lu was also corrected from the monitored ^{173}Yb and ^{171}Yb isotopes. Lu and Yb isobar interferences were corrected using an exponential mass fractionation beta coefficient based on reference of the measured ^{173}Yb/^{171}Yb to the atomic ratio of 1.123456 (Thirwall and Anczkiewicz, 2004; Chu et al., 2002). In cases where zircon Yb contents were too low to measure ^{173}Yb/^{171}Yb to an internal precision better than 4%, the applied Yb and Lu beta coefficient was estimated from the measured Hf beta coefficient, based on the measured in-run ratio of the Yb and Hf beta coefficients. The latter was found to typically have a value near 1.30, consistent with the relationship reported by Chu et al. (2002). Interference corrected Hf isotope ratios were corrected for instrumental mass fractionation using an exponential law based on reference of the measured ^{179}Hf/^{177}Hf to the atomic ratio of 0.7325 (Thirwall and Anczkiewicz, 2004). The determined ^{174}Hf/^{177}Hf ratio was used to assess the veracity of the correction procedure applied to Lu and Yb isotope interferences on ^{174}Hf and ^{176}Hf. Data reduction was done using a custom ExcelTM spreadsheet written by S. Eggins. ε_{Hf} was calculated using the chondritic parameters of Blichert-Toft and Albaréde (1997) and the ^{176}Lu decay rate of Scherer et al. (2001), using the equation: $\varepsilon_{Hf} = (^{176}Hf/^{177}Hf_{T}/[0.282772 - (0.0332 * (e^{(0.01867 \times (Age(Ga)))}-1]-1) \times 10^4$.

SUPPLEMENTARY REFERENCES CITED

Black, L.P., Kamo, S.L., Allen, C.M., Davis, D.W., Aleinikoff, J.N., Valley, J.W., Mundil, R., Campbell, I.H., Korsch, R.J., Williams, I.S., and Foudoulis, C., 2004, Improved ^{206}Pb/^{238}U microprobe geochronology by the monitoring of a trace-element-related matrix effect; SHRIMP, ID–TIMS, ELA–ICP–MS and oxygen isotope documentation for a series of zircon standards: Chemical Geology, v. 205, p. 115–140, doi:10.1016/j.chemgeo.2004.01.003.

Blichert-Toft, J., and Albaréde, F., 1997, The Lu-Hf isotope geochemistry of chondrites and the evolution of the mantle-crust system: Earth and Planetary Science Letters, v. 148, no. 1–2, p. 243–258, doi:10.1016/S0012-821X(97)00040-X.

Chu, N.C., Taylor, R.N., Chavagnac, V., Nesbitt, R.W., Boella, R.M., Milton, J.A., German, C.R., Bayon, G., and Burton, K., 2002, Hf isotope ratio analysis using multi-collector inductively coupled plasma mass spectrometry: an evaluation of isobaric interference corrections: Journal of Analytical Atomic Spectrometry, v. 17, p. 1567–1574, doi:10.1039/b206707b.

Claoué-Long, J.C., Compston, W., Roberts, J., and Fanning, C.M., 1995, Two Carboniferous ages: a comparison of SHRIMP zircon dating with conventional zircon ages and 40Ar/39Ar analysis, *in* Geochronology, Time Scales and Global Stratigraphic Correlation: SEPM Special Publication 54, p. 3–21.

Compston, W., Williams, I.S., and Meyer, C., 1984, U-Pb geochronology of zircons from lunar breccia 73217 using a Sensitive High Mass-Resolution Ion Microprobe, *in* Proceedings of the 14th Lunar

and Planetary Science Conference, Part 2: Journal of Geophysical Research, v. 89, supplement, p. B525–B534, doi:10.1029/JB089iS02p0B525.

Daly, S.J., Fanning, C.M., and Fairclough, M.C., 1998, Tectonic evolution and exploration potential of the Gawler Craton, South Australia: AGSO Journal of Australian Geology & Geophysics, v. 17, p. 145–168.

Eggins, S.M., 2003, Laser ablation ICP-MC analysis of geological materials prepared as lithium borate glasses: Geostandards Newsletter, v. 27, p. 147–162, doi:10.1111/j.1751-908X.2003.tb00642.x.

Eggins, S.M., Grün, R., McCulloch, M.T., Pike, A.W.G., Chappell, J., Kinsley, L., Mortimer, G., Shelley, M., Murray-Wallace, C.V., Spötl, C., and Taylor, L., 2005, In situ U-series dating by laser-ablation multi-collector ICPMS: new prospects for Quaternary geochronology: Quaternary Science Reviews, v. 24, p. 2523–2538, doi:10.1016/j.quascirev.2005.07.006.

Ickert, R.B., Hiess, J., Williams, I.S., Holden, P., Ireland, T.R., Lanc, P., Schram, N., Foster, J.J., and Clement, S.W., 2008, Determining high precision, in situ, oxygen isotope ratios with a SHRIMP II: Analyses of MPI-DING silicate-glass reference materials and zircon from contrasting granites: Chemical Geology, v. 257, p. 114–128, doi:10.1016/j.chemgeo.2008.08.024.

Ludwig, K.R., 1999, Users Manual for ISOPLOT/Ex version 2.00. A geochronological tool kit for Microsoft Excel: Berkeley Geochronology Centre, Special Publication 1a.

Ludwig, K.R., 2001, SQUID 1.02. A users manual: Berkeley Geochronology Centre, Special Publication 2.

Scherer, E., Münker, C., and Mezger, K., 2001, Calibration of the Lutetium-Hafnium Clock: Science, v. 293, no. 5530, p. 683–687, doi:10.1126/science.1061372.

Stacey, J.S., and Kramers, J.D., 1975, Approximation of terrestrial lead isotope evolution by a two-stage model: Earth and Planetary Science Letters, v. 26, p. 207–221, doi:10.1016/0012-821X(75)90088-6.

Thirwall, M.F., and Anczkiewicz, R., 2004, Multidynamic isotope ratio analysis using MC-ICP-MS and the causes of secular drift in Hf, Nd and Pb isotope ratios: International Journal of Mass Spectrometry, v. 235, p. 59081.

Williams, I.S., and Claesson, S., 1987, Isotopic evidence for the Precambrian provenance and Caledonian metamorphism of high grade paragneisses from the Seve Nappes, Scandinavian Caledonides. II. Ion microprobe zircon U-Th-Pb: Contributions to Mineralogy and Petrology, v. 97, p. 205–217, doi:10.1007/BF00371240.