# Methods

## Whole rock major and trace elements

Whole rock geochemistry was obtained from two laboratories, 11 samples were analysed at the ACMELabs in Vancouver, Canada ([www.acmelab.com](http://www.acmelab.com)), followed the analytical procedures termed “Group 4A and 4B - lithogeochemical whole rock fusion”. Three samples were analysed at the ACTLabs in Ontario, Canada (www.actlabs.com), following the analytical procedures termed “4Litho - Lithium Metaborate/Tetraborate Fusion - ICP and ICP/MS”

ACMElabs prepared samples were mixed with LiBO2/Li2B4O7 flux in crucibles and fused in a furnace. The cooled bead is then dissolved in ACS grade nitric acid. For “Group 4A” the total abundances of the major oxides and several minor elements are analysed for a 200 mg sample split by ICP-emission spectrometry following a lithium metaborate/tetraborate fusion and dilute nitric digestion. Loss on ignition (LOI) is determined by igniting a sample split at 1000°C then measuring the weight loss. “Group 4B” comprises two separate analyses for the total trace elements by ICP-MS. Rare earth and refractory elements are determined by ICP mass spectrometry following a lithium metaborate/tetraborate fusion and nitric acid digestion of a 200 mg sample. Additionally a separate 500 mg split is digested in Aqua Regia and analysed by ICP Mass Spectrometry to determine the precious and base metals. Fe valence was not determined and Fe2O3 thus refers to total Fe.

The GEUS in-house standard “Disko-1 basalt” was given a regular sample number and sent with each batch analysed at ACMELabs (21 runs over three years). The reported rare earth element (REE) contents for this standard were compared with data from GEUS’ ICP-MS lab (32 runs over 8 years). The results from the two laboratories agree well and are within analytical uncertainty as reported in Szilas et al. (2012).

Samples analysed at ACTLabs were mixed with a flux of lithium metaborate and lithium tetraborate and fused in an induction furnace. The molten melt is immediately poured into a solution of 5% nitric acid containing an internal standard, and mixed continuously until completely dissolved (~30 minutes). The samples are run for major oxides and selected trace elements (Code 4B) on a combination simultaneous/sequential Thermo Jarrell-Ash ENVIRO II ICP or a Varian Vista 735 ICP. Calibration is performed using 7 prepared USGS and CANMET certified reference materials. One of the 7 standards is used during the analysis for every group of ten samples. Samples fused under code 4B2 are diluted and analyzed by Perkin Elmer Sciex ELAN 6000, 6100 or 9000 ICP/MS. Three blanks and five controls (three before the sample group and two after) are analyzed per group of samples. Duplicates are fused and analyzed every 15 samples. Instrument is recalibrated every 40 samples. Fe valence was not determined and Fe2O3 thus refers to total Fe.

## Separation of zircon

Rocks were crushed and sieved (300-500 μm mesh), and the heavy minerals were separated by panning. Magnetic minerals were removed from the heavy mineral concentrate using a hand magnet. Zircon grains were picked from the final heavy mineral separate and were cast into epoxy resin and polished to expose a central cross-section of each grain. Transmitted light microscopy and Back Scattered Electron (BSE) imaging was applied to reveal internal structures. Energy Dispersive Spectroscopy (EDS) was applied to determine inclusion chemistry. BSE and EDS were carried out on a PHILIPS XL 40 SEM at GEUS.

## Laser ablation ICPMS analyses of zircon for U–Pb isotopes

The laser ablation inductively coupled plasma mass spectrometry (ICPMS) analyses were obtained at the Geological Survey of Denmark and Greenland in Copenhagen (GEUS) and acquired by a Thermo Scientific Element2 mass spectrometer coupled to a NewWave UP213 laser ablation system, following the procedures outlined by Gerdes and Zeh (2006) and Frei and Gerdes (2009). Standard bracketing was done by analysing the Geostandard zircon GJ1 (Jackson et al., 2004). Analytical sessions were started with six standards, followed by cycles of ten unknowns and three standards. The laser was operated with a 25-μm spot size at a repetition rate of 10 Hz with a nominal energy output of 45–50% of the maximum laser intensity, corresponding to a laser energy of about 0.025 mJ per pulse and a laser fluence of about 3 J/cm2. In each analysis the first 30 s were used to measure the gas blank (background), followed by 30 s of ablation and 20 s of washout time. Helium gas was used to flush the sample cell and was mixed downstream with the Ar sample gas before entering the plasma of the mass spectrometer. Measured masses were: 202Hg, 204(Pb + Hg), 206Pb, 207Pb, 208Pb, 232Th, 235U and 238U. The mass of 202Hg was measured to monitor the 204Hg isobaric interference on 204Pb. Data reduction was done with the GEUS in-house software (Zirchron) where the time-resolved isotope signal207Pb/206Pb and 206Pb/204Pb ratios were calculated as mean values, and 207Pb/235U,206Pb/238U and 208Pb/232U were drift-corrected by creating a least-squares fitting line, with an anchor point at the time the laser starts to ablate the zircon.

## Laser ablation multi-collector ICPMS analyses of zircons for Lu–Hf isotopes

Zircon Lu-Hf isotope analyses were done at two different laboratories. At the advanced Analytical Centre at James Cook University, Townsville, Australia, and at the analytical facilities at the Goethe University, Frankfurt, Germany.

At James Cook University, analyse were done by using a GeoLas 193-nm ArF laser and a Thermo Scientific Neptune multicollector ICPMS. The method is outlined by Kemp et al. (2009). Spot sizes were 31 μm, 42 μm and 58 μm with a 4-Hz laser pulse repetition rate. To counteract ArF degradation the power density at the sample was maintained at around 6–7 J cm−2, which translated into an estimated ablation rate of around 0.5 μm s−1. Ablation was conducted in He gas flow. The isotope ratios were derived from a 60-s ablation period, comprising 60 cycles of 1-s integration time. In the case of isotopic zoning or with intersecting cracks/inclusions, only the flattest, most stable portions of the time-resolved signal were selected for integration; this was done off-line using a customized Microsoft Excel spreadsheet. The correction for the isobaric interference of Lu and Yb on 176Hf was performed as advocated by Woodhead and Hergt (2005). For Yb, this involved monitoring the interference-free 171Yb during the analysis and then calculating the magnitude of the 176Yb interference using176Yb/171Yb = 0.897145 (Segal et al., 2003). The much smaller Lu correction is performed in the same way by measuring 175Lu, and using 176Lu/175Lu = 0.02655 (Vervoort et al., 2004). To correct for instrumental mass fractionation, Yb isotope ratios were normalized to 173Yb/171Yb = 1.130172 (Segal et al., 2003) and Hf isotope ratios to 179Hf/177Hf = 0.7325. The mass bias behaviour of Lu was assumed to follow that of Yb. The measured average 176Hf/177Hf from the Mud Tank reference zircon (MTZ) obtained over all analytical sessions was 0.282499(18) (where the error in parentheses is two standard deviations) and the ‘true’ (solution) value is taken as 0.282507(6) from (Woodhead and Hergt, 2005). A 176Hf/177Hf normalization factor of 1.000028, based on analyses of the MTZ, was applied to data from sample zircons. During the analytical sessions the Geostandard 91500, Temora2 and FC1 zircon were also repeatedly measured, for which normalized 176Hf/177Hf values are 0.282299(22) (*n* = 23), 0.282686(22) (*n* = 47) and 0.282178(26) (*n* = 38), respectively, where uncertainties are two standard deviations. The final analytical uncertainty for sample zircons was obtained by combining the MTZ reproducibility with internal error.

At the Goethe University, analyse were done by using a Resonetics M50 193 nm excimer laser and a Thermo Scientific Neptune multicollector ICPMS. The method is outlined by Gerdes & Zeh (2006, 2009). Data were collected during 40 s of ablation with a spot size of 40-60 μm. Time resolved profiles of the isotope ratios were processed offline to check the homogeneity of the ablated zircon zones. Nitrogen (∼0.005 l/min) was introduced into the Ar sample carrier gas. The isotopes 172Yb, 173Yb and 175Lu were simultaneously monitored during each analysis step to allow the correction of isobaric interferences between Lu and Yb isotopes on mass 176. The 176Yb and 176Lu were calculated using a 176Yb/173Yb of 0.796218 (Chu et al., 2002) and 176Lu/175Lu of 0.02658 (see below), and by taking the instrumental mass fractionation of each individual analysis into account. For instrumental mass bias correction Yb isotope ratios were normalized to 172Yb/173Yb of 1.35274 (Chu et al., 2002) and Hf isotope ratios to 179Hf/177Hf of 0.7325 using an exponential law. The mass bias behaviour of Lu was assumed to follow that of Yb. The 176Lu/175Lu of 0.02658 was obtained by the analysis of a natural Lu solution doped with Yb, and by using the Yb isotope composition of Chu et al. (2002). In fact the ratio obtained is only 0.09% higher than that obtained with the Yb isotope composition suggested by Segal et al. (2003). JMC 475 were used as the primary standard for 176Hf/177Hf normalisation. Secondary standard; GJ1 (*n* = 11) and Temora2 (*n* = 11) were included in the analytical session, and the obtained normalised mean 176Hf/177Hf values of these are 0.282002(24) and 0.282697(11), respectively.

The two reduction methods induce slight isotope differences due to differences in assumed Yb and Lu isotope composition and the slightly different approaches. To ensure consistency between the methods, the data obtained from the laboratory at the Goethe University have also been reduced by the method applied for the data from the James Cook University (the only difference is that 172Yb was measured instead of 171Yb). The two reduction and analytical methods induce variations in the mean GJ1 and Temora2 that is less than 1 epsilon Hf unit.

For CHUR we use the isotope ratios 176Lu/177Hf = 0.0336 and 176Hf/177Hf = 0.282785 (Bouvier et al. 2008) and for the 176Lu decay constant we used the value reported by Scherer et al. (2004) and Söderlund et al. (2004).

## Oxygen isotope ratios

These ratios were measured using a CAMECA IMS1270 ion microprobe (NordSIMS laboratory, Swedish Museum of Natural History) using a method similar to that described by Nemchin et al. (2006) and Whitehouse and Nemchin (2009) with the exception that, for this study, only 16O and 18O were measured. Briefly, a 20-keV Cs+primary beam (+10 kV primary, −10 kV secondary) of about 5 nA was used in aperture illumination mode to sputter a ~15-μm-diameter sample area, with a normal-incidence electron gun providing charge compensation. Fully automated runs comprised a 20-s pre-sputter period with a raster of 25 μm, field aperture, entrance slit and mass centring, using the 16O signal, followed by 240 s of data acquisition using two Faraday detectors in the multi-collector system operating at a common mass resolution of ~2,500. Data were normalized to measurements of the Geostandard zircon 91500, assuming a δ18O value of 9.86‰ determined by laser fluorination (Wiedenbeck et al., 2004). Reproducibility of 91500 during the sessions was 0.21.

## References

Bouvier, A., Vervoort, J. D. & Patchett, P. J. (2008). The Lu–Hf and Sm–Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implications for the bulk composition of terrestrial planets. Earth Planet. Sci. Lett. 273, 48–57.

Chu, N.C., Taylor, R.N., Chavagnac, V., Nesbitt, R.W., Boella, R.M., Milton, J.A., German, C. R., Bayon, G., 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 17, 1567–1574.

Frei, D. & Gerdes, A. (2009). Precise and accurate in situ U–Pb dating of zircon with high sample throughput by automated LA-SF-ICP-MS. Chem. Geol. 261, 261–270.

Gerdes, A. & Zeh, A. (2006). Combined U–Pb and Hf isotope LA-(MC-)ICP-MS analyses of detrital zircons: comparison with SHRIMP and new constraints for the provenance and age of an Armorican metasediment in Central Germany. Earth Planet. Sci. Lett. 249, 47–61.

Jackson, S., Pearson, N.J., Griffin, W. L. & Belousova, E.A. (2004). The application of laser ablation – inductively coupled plasma – mass spectrometry to in situ U–Pb zircon geochronology. Chem. Geol. 211, 47–69.

Kemp, A.I.S., Foster, G.L., Schersten, A., et al., (2009). Concurrent Pb–Hf isotope analysis of zircon by laser ablation multi-collector ICP-MS, with implications for the crustal evolution of Greenland and the Himalayas. Chem. Geol. 261, 244–260.

Ludwig, K.R., (2012). User’s manual for Isoplot 3.75. A Geochronological Toolkit for Microsoft Excel. Berkeley Geochronology Center Special Publication No. 5, 75 pp.

Nemchin, A.A., Whitehouse, M.J., Pidgeon, R.T., Meyer, C. (2006). Oxygen isotopic signature of 4.4–3.9 Ga zircons as a monitor of differentiation processes on the Moon. Geochim. Cosmochim. Acta 70, 1864–1872.

Szilas, K., Hoffmann, J.E., Scherstén, A., Rosing, M.T., Windley, B.F., Kokfelt, T.F., Keulen, N., van Hinsberg, V.J., Næraa, T., Frei, R., Münker, C. (2012). Complex calc-alkaline volcanism recorded in Mesoarchaean supracrustal belts north of Frederikshåb Isblink, southern West Greenland: Implications for subduction zone processes in the early Earth. Precambrian Research 208-211, 90-123.

Vervoort, J.D., Patchett, P.J., Söderlund, U., Baker, M. (2004). The isotopic composition of Yb and the precise and accurate determination of Lu concentrations and Lu/Hf ratios by isotope dilution using MC-ICPMS. Geochem. Geophys. Geosyst. 5Q11002.

Whitehouse, M.J. & Nemchin, A.A. (2009). High precision, high accuracy measurement of oxygen isotopes in large lunar zircon by SIMS. Chem. Geol. 261, 32–42.

Wiedenbeck, M. et al. (2004). Further characterisation of the 91500 zircon crystal. Geostand. Geoanalyt. Res. 28, 9–39.

Woodhead, J. & Hergt, J. (2005). A preliminary appraisal of seven natural zircon reference materials for in situ Hf isotope determination. Geostand. Geol. Res. 29, 183–195.

Scherer, E., Munker, C., Mezger, K. (2001). Calibration of the lutetium-hafnium clock. Science 293, 683–687.

Segal, I., Halicz, L. & Platzner, I. T. (2003). Accurate isotope ratio measurements of ytterbium by multi-collector inductively coupled plasma mass spectrometry applying erbium and hafnium in an improved double external normalisation procedure. J. Anal. At. Spectrom. 18, 1217–1223.

Söderlund, U., Patchett, J.P., Vervoort, J.D., Isachsen, C.E. (2004). The 176Lu decay constant determined by Lu-Hf and U-Pb isotope systematics of Precambrian mafic intrusions. Earth Planet. Sci. Lett. 219, 311–324.