

# Establishing a provenance framework for sandstones in the Greenland-Norway rift from the composition of moraine/outwash sediments

## Analytical methods

### *Sample preparation*

The samples were immersed in water and cleaned by ultrasonic probe to remove and disperse any clay adhering to grain surfaces. They were then washed through a 63  $\mu\text{m}$  sieve and re-subjected to ultrasonic treatment until no clay passed into suspension. The samples were then wet sieved through 125  $\mu\text{m}$  and 63  $\mu\text{m}$  sieves, and the resulting >125  $\mu\text{m}$  and 63-125  $\mu\text{m}$  fractions were dried in an oven at 80°C. The 63-125  $\mu\text{m}$  fraction was placed in bromoform with a measured specific gravity of 2.8. Heavy minerals were allowed to separate under gravity, with frequent stirring to ensure complete separation. The heavy mineral residues were mounted under Canada Balsam for optical study using a polarising microscope, with a split retained for mineral chemical and isotopic studies.

### *Conventional analysis and ratio determination*

Heavy mineral proportions were estimated by counting 200 non-opaque detrital grains using the ribbon method [1]. Identification was made on the basis of optical properties, as described for grain mounts [2]. A qualitative assessment was also made of other components, such as diagenetic minerals, opaques and mica. Provenance-sensitive mineral ratios [3] were also determined using the ribbon counting method, ideally on the basis of a 200 grain count. It was not always possible to achieve the optimum 200 grain count because of the scarcity of some of the mineral phases.

### *Garnet and amphibole geochemical analysis*

Garnet and amphibole major element analysis was undertaken using electron microprobe analysis. Samples were selected on the basis of the results of the conventional optical analysis. Grains were picked with a needle from the dry residues during optical examination under a polarising microscope, placed on double sided adhesive tape, coated with carbon, and analysed using a Link Systems AN 10/55S energy-dispersive x-ray analyser attached to a Cambridge Instruments Microscan V electron microprobe at the University of Aberdeen. The count time was 30 seconds for each grain. The quality of each result was monitored to ensure that the stoichiometrically determined formula was approximately that of an ideal garnet or amphibole. Studies of North Sea detrital garnets have shown that intra-grain variations are usually negligible in grains between 63 and 125  $\mu\text{m}$  diameter (Morton, 1985; Morton *et al.*, 1989). Therefore, it is unlikely that compositional zoning has had a significant effect on the overall range of garnet compositions in any individual sample. Garnet compositions are expressed in terms of the relative abundance of the Mg,  $\text{Fe}^{2+}$ , Ca and Mn end members. Garnet assemblages were plotted on ternary diagrams with molecular proportions of  $\text{Fe}^{2+}+\text{Mn}$ , Mg and Ca as poles, calculated assuming all Fe is present as  $\text{Fe}^{2+}$  [4].

Classification of garnet into types A, B, C and D follows Morton *et al.* (2004), Jolley *et al.* (2007) and Mange and Morton (2007). Amphiboles are classified following the nomenclature of Leake *et al.* (1997).

#### *Rutile geochemical analysis*

Rutile trace element geochemistry was carried out by laser ablation inductively coupled plasma mass spectrometry in the School of Earth, Ocean and Planetary Sciences at Cardiff University, using a Thermo Elemental X(7) series ICP-MS coupled to a New Wave Research UP213 Nd:YAG 213 nm UV laser. The laser beam diameter was 30  $\mu\text{m}$  and the laser repetition rate set at 4 Hz. Helium gas was used for ablation initial transport from the laser cell and this was combined with argon outside the cell as the sample was transported to the ICP-MS. Thermo Elemental Plasmalab time-resolved analysis (TRA) data acquisition software was used with a total acquisition time of 60 s per analysis, allowing about 30 s for background followed by 25 s for laser ablation. Plasmalab was used for initial data reduction with post-processing in Excel. The calibration employed BIR-1G, BHVO-2G and BCR-2G (USGS basalt glass standards) to produce a 4 point (including the origin) calibration curve. The data have been normalised to Ti (98%  $\text{TiO}_2$ ) and adjusted accordingly. Instrumental drift was monitored by repeat analysis of BHVO-2G after every 25-30 grains. Discrimination of rutiles from metamafic and metapelitic provenances was achieved using Cr and Nb contents [5], with metamorphic temperatures estimated on the basis of Zr contents [6].

#### *U-Pb analyses of detrital zircons (Nu HR ICPMS)*

U-Pb analysis of zircon was conducted at the LaserChron Center at the University of Arizona. Zircon crystals were incorporated into a 1" epoxy mount together with fragments of a Sri Lanka standard zircon. The mounts were sanded down to a depth of ~20 microns, polished, imaged, and cleaned prior to isotopic analysis. U-Pb geochronology of zircons was conducted by laser ablation multicollector inductively coupled plasma mass spectrometry (LA-MC-ICPMS) [7, 8]. The analyses involved ablation of zircon with a Photon Machines Analyte G2 excimer laser equipped with a HeLEX ablation chamber, using a spot diameter of 30 microns. The ablated material was carried in helium into the plasma source of a Nu HR ICPMS, which is equipped with a flight tube of sufficient width that U, Th, and Pb isotopes are measured simultaneously. All measurements were made in static mode, using Faraday detectors with  $3 \times 10^{11}$  ohm resistors for  $^{238}\text{U}$ ,  $^{232}\text{Th}$ ,  $^{208}\text{Pb}$ - $^{206}\text{Pb}$ , and discrete dynode ion counters for  $^{204}\text{Pb}$  and  $^{202}\text{Hg}$ . Ion yields are ~0.8 mv per ppm. Each analysis consisted of one 15-second integration on peaks with the laser off (for backgrounds), 15 one-second integrations with the laser firing, and a 30 second delay to purge the previous sample and prepare for the next analysis. The ablation pit was ~15 microns in depth. For each analysis, the errors in determining  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  result in a measurement error of ~1-2% (at 2-sigma level) in the  $^{206}\text{Pb}/^{238}\text{U}$  age. The errors in measurement of  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{204}\text{Pb}$  also result in ~1-2% (at 2-sigma level) uncertainty in age for grains that are >1000 Ma, but are substantially larger for younger grains due to the low intensity of the  $^{207}\text{Pb}$  signal. For most analyses, the cross-over in precision of  $^{206}\text{Pb}/^{238}\text{U}$  and  $^{206}\text{Pb}/^{207}\text{Pb}$  ages occurs at c. 1000 Ma.  $^{204}\text{Hg}$  interference with  $^{204}\text{Pb}$  was accounted for by measurement of  $^{202}\text{Hg}$  during laser ablation and subtraction of  $^{204}\text{Hg}$  according to the natural  $^{202}\text{Hg}/^{204}\text{Hg}$  of 4.35. This Hg correction was not significant for most analyses because Hg backgrounds were low (generally ~150 cps at mass 204). Common Pb correction was accomplished by using the Hg-corrected

$^{204}\text{Pb}$  and assuming an initial Pb composition [9]. Uncertainties of 1.5 for  $^{206}\text{Pb}/^{204}\text{Pb}$  and 0.3 for  $^{207}\text{Pb}/^{204}\text{Pb}$  have been applied to these compositional values based on the variation in Pb isotopic composition in modern crystal rocks. Inter-element fractionation of Pb/U is generally ~5%, whereas apparent fractionation of Pb isotopes is generally <0.2%. In-run analysis of fragments of a large zircon crystal (generally every fifth measurement) with known age of  $563.5 \pm 3.2$  Ma (2-sigma error) has been used to correct for this fractionation. The uncertainty resulting from the calibration correction is generally 1-2% (2-sigma) for both  $^{206}\text{Pb}/^{207}\text{Pb}$  and  $^{206}\text{Pb}/^{238}\text{U}$  ages. Concentrations of U and Th were calibrated relative to the LaserChron Center Sri Lanka zircon, which contains ~518 ppm of U and 68 ppm Th. The resulting interpreted ages were plotted on Wetherill Concordia diagrams and ages are shown on kernel density estimation (KDE) plots, both generated using IsoplotR [10].

### *Amphibole age determination*

Amphibole  $^{40}\text{Ar}/^{39}\text{Ar}$  (Ar-Ar) geochronology was undertaken at the Lamont-Doherty Earth Observatory, Columbia University [11]. Amphibole grains were picked from the heavy mineral residues, and were co-irradiated with the Fish Canyon sanidine standard for 8 hours at the USGS Triga reactor in Denver. A J-value of  $0.0018941 \pm 2.77\text{e-}6$  was calculated based on a Fish Canyon sanidine age of 28.21 [12] that largely removes the ~0.7% apparent bias between U-Pb and Ar-Ar methods. Samples were run as individual grains because of the possibility of mixed ages. Because the sampled grains were very small, not all of them provided sufficient gas to obtain an age. Samples were fused with a  $\text{CO}_2$  laser and scrubbed of active gases with Zr-Al getters. Data were corrected for blanks, mass discrimination and nuclear interferences. Only grains that provided sufficient gas are reported here. The closure temperature for amphibole is ~500°C [13], but is somewhat variable depending on composition and crystal structure. Ages are shown on kernel density estimation (KDE) plots generated using IsoplotR [10].

## References

1. Galehouse, J.S., Point-counting, In *Procedures in Sedimentary Petrology*, R.E. Carver, Editor. 1971, Wiley-Interscience: New York, pp. 385-407.
2. Mange, M.A. and H.F.W. Maurer, *Heavy minerals in colour*. 1992, London: Chapman and Hall. 147.
3. Morton, A.C. and C.R. Hallsworth, Identifying provenance specific-features of detrital heavy mineral assemblages in sandstones. *Sedimentary Geology* **1994**, *90*, 241-256.
4. Droop, G.T.R. and B. Harte, The effect of Mn on the phase relations of medium grade pelites: constraints from natural assemblages and petrogenetic grid topology. *Journal of Petrology* **1995**, *36*, 1549-1578.
5. Meinhold, G., B. Anders, D. Kostopoulos, and T. Reischmann, Rutile chemistry and thermometry as provenance indicator: An example from Chios Island, Greece. *Sedimentary Geology* **2008**, *203*, 98-111.
6. Watson, E.B., D.A. Wark, and J.B. Thomas, Crystallization thermometers for zircon and rutile. *Contributions to Mineralogy and Petrology* **2006**, *151*, 413-433.
7. Gehrels, G., V. Valencia, and A. Pullen, Detrital zircon geochronology by laser-ablation multicollector ICPMS at the Arizona LaserChron Center. *The Paleontological Society Papers* **2006**, *12*, 67-76.

8. Gehrels, G.E., V.A. Valencia, and J. Ruiz, Enhanced precision, accuracy, efficiency, and spatial resolution of U-Pb ages by laser ablation–multicollector–inductively coupled plasma–mass spectrometry. *Geochemistry, Geophysics, Geosystems* **2008**, 9(3).
9. Stacey, J. and J. Kramers, Approximation of terrestrial lead isotope evolution by a two-stage model. *Earth and planetary science letters* **1975**, 26, 207-221.
10. Vermeesch, P., IsoplotR: A free and open toolbox for geochronology. *Geoscience Frontiers* **2018**, 9(5), 1479-1493.
11. Pierce, E., S. Hemming, T. Williams, T. van de Flierdt, S. Thomson, P.W. Reiners, G.E. Gehrels, S. Brachfeld, and S. Goldstein, A comparison of detrital U–Pb zircon,  $^{40}\text{Ar}/^{39}\text{Ar}$  hornblende,  $^{40}\text{Ar}/^{39}\text{Ar}$  biotite ages in marine sediments off East Antarctica: Implications for the geology of subglacial terrains and provenance studies. *Earth-Science Reviews* **2014**, 138, 156-178.
12. Kuiper, K., A. Deino, F. Hilgen, W. Krijgsman, P. Renne, Wijbrans, and JR, Synchronizing rock clocks of Earth history. *science* **2008**, 320(5875), 500-504.
13. McDougall, I. and T.M. Harrison, *Geochronology and Thermochronology by the  $^{40}\text{Ar}/^{39}\text{Ar}$  Method*. 1999: Oxford University Press on Demand.