Supplementary Publication 18463 (Part 1)

Parent paper:

Parry, S. F., Noble, S. R., Crowley, Q. G. & Wellman, C. H. 2011. A high-precision U–Pb age constraint on the Rhynie Chert Konservat-Lagerstätte: timescale and other implications. *Journal of the Geological Society, London*, **168**, 863–872.

Analytical techniques

ID-TIMS U-Pb geochronology

Conventional ID-TIMS U-Pb geochronology was performed at the NERC Isotope Geosciences Laboratory (NIGL). Bulk samples of the Milton of Noth Andesite (RM-15 and RM-15XX) were first collected as described in the parent paper. These samples were thoroughly washed with water, allowed to dry naturally, then processed using standard crushing and mineral separation techniques. The resultant heavy mineral concentrates were split according to magnetic susceptibility using a Frantz[®] LB-1 Barrier Separator. Zircon and titanite were subsequently handpicked under ethanol, with only the highest quality, inferably magmatic grains and grain fragments being selected for analysis. Air abrasion (Krogh 1982) and chemical abrasion (Mattinson 2005 with modifications^{*}) were variously employed in an attempt to eliminate the effects of Pb-loss. The individual zircon and titanite fractions were sequentially washed then, having been either weighed or imaged, transferred to Teflon[®] dissolution vessels (Parrish-type micro-capsules (Parrish 1987) with the exception of fractions 2, 3 and 10, for which miniature Krogh-type bombs (Krogh 1973; Corfu & Noble 1992) were used) ahead of spiking and acidification. Two different isotopic tracer solutions were used during the course of this study: a ²⁰⁵Pb-²³⁵U solution (Krogh & Davis 1975) and a ²⁰⁵Pb-²³³U-²³⁵U solution (Parrish & Krogh 1987; see also Monaghan & Parrish 2006). The dissolved, spike-equilibrated fractions were, in general, subjected to ion-exchange procedures. Separation and purification of U and Pb were thus achieved on miniature ion-exchange columns (Corfu & Noble 1992) filled with Bio-Rad AG® 1-X8 (zircon U and Pb, titanite Pb) or Eichrom UTEVA[®] resin (titanite U), otherwise following the methods of Krogh (1973) with minor modifications (Corfu & Ayres 1984; Corfu & Andrews 1987; Parrish et al. 1992). In contrast, chemically-abraded single-grain zircon fractions 2, 3 and 10 underwent a twostage chloride conversion step (carried out on a hotplate), after which they received no further chemical treatment. U and Pb (\pm matrix elements) were loaded either separately or together along with silica gel and H₃PO₄ onto single outgassed rhenium filaments and analysed using a Thermo Scientific Triton mass spectrometer (fitted with an axial MasCom secondary electron multiplier) or a VG 354 mass spectrometer (equipped with an axial Daly system comprising a Philips photomultiplier

tube, an Ortec fast pre-amplifier, amplifier-discriminator and pulse counter, and a WARP[™] filter). The mass spectrometer output was scrutinized for statistical outliers and evidence of organic interferences using an in-house data evaluation program (Triton output), or done simply by eye (VG 354 output), and any offending data rejected. Thereafter, the measured isotope ratios were corrected for total procedural Pb and U blanks[†] of 1.2–20 pg and 0.50–3.9 pg, respectively, with the Pb composition deriving either from direct laboratory measurements or from the particulate dataset of Noble et al. (2008). Pb isotope ratios were further corrected for initial common Pb using a Stacey & Kramers (1975) model Pb composition equivalent to the interpreted age of the individual fractions (a 2 % uncertainty was assigned to these values). All data reduction and plotting were carried out using PBDAT version 1.24 (Ludwig 1993) and Isoplot version 3.00 (Ludwig 2003). The decay constants used were those proposed by Jaffey et al. (1971) (Steiger & Jäger 1977). Errors quoted for isotope ratios and ages are at either the 2σ or the 95 % confidence level (Ludwig 1980). Fully corrected analytical data are presented in Table 1 and depicted in Fig. 3 (see parent paper). We have attempted to make allowances for all sources of systematic error in our 'final age' calculations, and in accordance with this policy report the age of the Milton of Noth Andesite in the format: Age \pm X(Y)[Z] Ma, where X is the internal or analytical uncertainty in the absence of all systematic error (tracer calibration- and decay constant-related); Y includes the tracer calibration error (a conservative 2σ estimate of 0.10 % for the tracer's Pb/U ratio) and; Z also includes the ²³⁸U decay constant error of Jaffey et al. (1971).

^{*} The selected grains and grain fragments were annealed in small numbers (as opposed to in bulk) in quartz glass beakers at either 850 °C (fractions 6, 7, 8 and 9) or 900 °C (fractions 2, 3 and 10) for *c*. 60 hours. Leaching was subsequently carried out overnight (12–14 hours) at either 160 °C in Teflon[®] micro-centrifuge tubes (fractions 6, 7, 8 and 9) or 180 °C in 3 ml Savillex vials (fractions 2, 3 and 10) using 29 M HF + trace 8 M HNO₃. The grains/fragments were decanted into pre-cleaned PMP beakers, rinsed several times with Milli-Q[®] H₂O, then allowed to warm on a hotplate (*c*. 90 °C) in the presence of 3 M HCl for 3–4 hours. After further rinsing with Milli-Q[®] H₂O and also 8 M HNO₃, the grains/fragments were ready for full dissolution.

[†] For further details see Table SUP 1 below. The observed variation reflects fluctuations in the laboratory blank during the period over which these analyses were performed.

Fraction number	Pb blank (pg)	U blank (pg)
1.	7.0	0.60
2.	1.2	0.50
3.	1.2	0.50
4.	20	0.75
5.	1.7	3.9
6.	8.0	0.60
7.	8.0	0.60
8.	4.0	0.60
9.	4.0	0.60
10.	1.2	0.50

 Table SUP 1. Pb and U blanks for individual fractions

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Figure caption:

Fig. SUP 1. Photomicrographs (taken under ethanol) of zircon and titanite grains/grain fragments recovered from the Milton of Noth Andesite.

(a) Rounded, variably corroded zircons of mixed morphology. Large mineral inclusions and 'rust'-filled cracks are commonplace. Grains such as these are believed to be xenocrysts. (Sample RM-15)
(b) Morphologically variable pieces of essentially colourless zircon. Some mineral inclusions and cracks are observed. These grains/grain fragments are regarded as xenocrysts or suspect xenocrysts. (Sample RM-15)

(c) Further examples of xenocrystic zircon grains/fragments. Extensive cracks and mineral inclusions are observed in some of these. The rounded rim of a large inherited core is discernible in the well-faceted grain located towards the top of the field of view. (Sample RM-15)

(d) Fragments of morphologically simple, colourless, near-euhedral zircon prisms. Axial melt 'tubes' are conspicuous in three of these. Grains/fragments of this type are believed to represent primary zircon growth. The imaged fragments were not analysed, however, owing to the fact that they were reduced to a 'gravel' by the chemical abrasion process. (Sample RM-15)

(e) Fragments of colourless prismatic zircon. A melt inclusion is readily discernible in the lowermost of these. The four pictured fragments were analysed together as Fraction 1. (Sample RM-15).

(f) Colourless/slightly rust-coloured, morphologically simple zircon prisms/prism fragments. Four of these are regarded as xenocrysts or suspect xenocrysts, but the three euhedral/near-euhedral prisms located close to the centre of the field of view are examples of the grains which yield c. 411.5 Ma ages. (RM-15XX)

(g) Large, yellowish, yellowish brown or pale brown titanite fragments, one of which is notably well faceted. (Sample RM-15)

(h) Partially faceted, pale brown titanite fragments. Orangey red (?)rutile inclusions are discernible in two of these. (Sample RM-15)

Parry et al. Fig. SUP 1.















