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Mud Tank Zircon: Long-term Evaluation of a Reference Material for U-Pb Dating, Hf-Isotope analysis and trace element analysis

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Abstract

Zircon megacrysts from the Mud Tank carbonatite, Australia, are being used in many laboratories as a reference material for LA-ICP-MS U-Pb dating and trace element analysis, and LA-MC-ICP-MS determination of Hf isotopes. We summarise a database of > 10,000 analyses of Mud Tank zircon, collected from 2000 to 2018 during its use as a secondary reference material for simultaneous U-Pb and trace element analysis, and for Hf-isotope analysis. Trace element concentrations are highest in dark red-brown stones and lowest in colourless and gem-quality ones. Individual unzoned grains can be chemically homogeneous, while significant variations in trace element concentration are associated with oscillatory zoning. Chondrite-normalised trace element patterns are essentially parallel over large concentration ranges. A Concordia age of 731.0 ± 0.2 Ma ($2s$, $n = 2272$) is taken as the age of crystallisation. Some grains show lower concordant to mildly discordant ages, probably

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reflecting minor Pb loss associated with cooling and the Alice Springs Orogeny (450-300 Ma). Our weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ is 0.282523 ± 10 ($2s$, $n = 9350$); the uncertainties on this ratio reflect some heterogeneity, mainly between grains. A few analyses suggest that colourless grains have generally lower $^{176}\text{Hf}/^{177}\text{Hf}$. Mud Tank zircon is a useful secondary reference material for U-Pb and Hf-isotope analysis, but individual grains need to be carefully selected using CL imaging and tested for homogeneity, and ideally should be standardised by solution analysis.

Keywords: Mud Tank Zircon, trace element heterogeneity, U-Pb dating, Hf-isotope heterogeneity, geochemical reference materials.

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The Mud Tank zircon (hereafter MTZ) has been used as a reference material for U-Pb dating and trace element and Hf-isotope analysis in the Geochemical Analysis Unit (renamed Macquarie Geoanalytical in 2016) at Macquarie University since 2001, when its trace element composition was originally characterised by Belousova *et al.* (2002). It has gradually been adopted as a reference material by visitors to the laboratory and other users internationally, since it is readily available as large crystals, some of which have been well-characterised (e.g., Griffin *et al.* 2007, Woodhead *et al.* 2007, Yuan *et al.* 2008, Schweiters *et al.* 2009, Hu *et al.* 2012, Gain 2013, Horstwood *et al.* 2016, Gain *et al.* 2018). However, these and other studies have recorded chemical and isotopic differences that suggest variability within and between the crystals selected for analysis (Jain *et al.* 2007).

MTZ is not used in our laboratories as a reference material for calibration, but typically is included in measurement sessions involving zircon analysis, to monitor instrumental conditions and the accuracy of data. As a result, we have accumulated data from several thousand analyses of different crystals over 15 years, providing a basis to evaluate its chemical and isotopic homogeneity and reproducibility under routine analytical conditions. This contribution documents this comprehensive database, relevant to the use of MTZ as a reference material. To supplement this database, we also have carried out a detailed study of trace element variations as related to colour and internal structure (Gain 2013, this work).

Samples

The Mud Tank carbonatite intrudes rocks of the Strangways Range in the Arunta Inlier, in the southern part of the Northern Territory, Australia (Crohn and Moore 1984). The area, now known as the Strangways Metamorphic Complex, underwent granulite-facies metamorphism at 1815–1780 Ma, and localised amphibolite – and greenschist –facies regression is associated with shear zones developed during the intraplate Alice Springs Orogeny at 450–300 Ma. (Bendall 2000, Ahmad and Munson 2013). The latter orogeny exhumed the carbonatite intrusion and its country rocks prior to extensive erosion, silicification, and ferruginisation in the Tertiary.

During the Alice Springs orogeny metamorphic temperatures were high enough to reset isotopic systems in apatite (Green *et al.* 2006, Thomson *et al.* 2012) and biotite (Black and Gulson 1978, Crohn and Moore 1984). The dolomitic intrusive carbonatite is very unusual in its lack of mineral complexity and fenitisation, and the zircons have low contents of REE, U and Th, similar to zircon macrocrysts in many kimberlites. The carbonatite and its contacts are poorly exposed, and the body was originally discovered from colluvial concentrations of heavy minerals, including zircon. Today it is a recognised public fossicking site. The zircon is derived primarily from a magnetite-rich unit, one of three carbonate types that make up the intrusion (Crohn and Moore 1984). Confusion about the source of MTZ still prevails because past and present literature and media describe MTZ as found in the Harts Range, a location 70 km distant that hosts no carbonatite nor large zircon (see Ahmad and Munson, 2013).

MTZ occurs as euhedral to irregular crystals up to several kilograms in weight, but is usually found in gravels as mm- to cm-sized crystals and fragments. They are especially prized by fossickers for their gem clarity and a range of hues, from colourless to pale brown through orange-yellow and red-brown to purple (Brown *et al.* 1989, Faulkner and Shigley 1989, Kempe *et al.* 2006). Colours may partially reflect bleaching under strong sunlight, as colourless stones are relatively rare in excavated material. Inclusions comprising apatite, magnetite, carbonate and microscopic REE-rich phases are present but not abundant.

Cathodoluminescence (CL) images show colours from dark blue to pale blue to yellow, defining a variety of internal structures, from featureless to fine-scale sector and oscillatory zoning, and healed cracks (Figure 1).

Methods

Instrumentation

The database presented here contains analyses acquired from 2001 to 2018 for hafnium isotopes and from 2007 to 2018 for simultaneous determination of trace elements and U-Pb isotopes. Over these years, the GAU/MQGA instrumentation has evolved, so that this dataset represents a compilation of analyses acquired with various combinations of laser-ablation systems (e.g., New Wave and Photon Machines; 213 nm, 193 nm) and ICP-MS instruments (e.g., Agilent 7500, 7700; Nu Plasma, Nu Plasma II). A broad summary of the instrumentation setups used and their respective timelines of operation can be found in online supporting information Table S1.

Analytical methods

The analytical techniques used to build these datasets have been detailed in multiple GEMOC/CCFS publications over the last 20 years (e.g., Norman *et al.* 1998, Griffin *et al.* 2000, Jackson *et al.* 2004, Pearson *et al.* 2008). Therefore, only a basic overview of the methodology is provided here. However, it is important to note that while the techniques below are representative of the bulk of the datasets, subtle changes regarding instrumental conditions, new instrumentation and the evolution of best practice have also occurred throughout the years.

Trace element mass fractions: These were determined by LA-ICP-MS. Typical ablation conditions included beam sizes from 30 to 80 μm (static spot), with laser repetition rate of 5 Hz and energy densities from 6.23 to 12.15 J cm^{-2} (typically 7–8). Helium was used as the carrier gas at a total flow rate of 0.8 l min. A typical trace element run contained an average of ten zircon analyses and four analyses of reference materials used for quality control, bracketed by two analyses of the certified reference material NIST SRM 610 at the

beginning and end of each run. Measurements consisted of 60 s of background and 120 s of ablation. Trace element mass fractions were calculated from the raw signal data using the on-line software package GLITTER (Griffin *et al.* 2008; www.mq.edu.au/GEMOC). GLITTER calculates the element mass fractions and relevant isotopic ratios for each mass sweep and displays them as time-resolved data. This allows segments of the signal that represent chemically homogeneous material to be selected for integration, avoiding heterogeneity produced by for example inclusions or subsurface cracks. GLITTER then corrects the integrated ratios for ablation-related fractionation and instrumental mass bias by calibration of each selected time segment against the identical time-segments of the reference material (NIST SRM 610, with GeoReM values (Jochum *et al.* 2005)). Electron probe microanalyses of Hf mass fraction were used as the internal standard element to quantify trace element mass fractions, and USGS BCR-2G and synthetic NIST SRM 612 glasses were used as quality control materials. The GJ-1, 91500 and Mud Tank zircons were used as matrix-matched reference materials in a final check on data quality (Jackson *et al.* 2004, Elhlou *et al.* 2006). Lead mass fractions were derived by correcting the values derived by GLITTER for the measured relative isotopic abundances of ^{206}Pb , ^{207}Pb and ^{208}Pb , and summing the results.

Wiedenbeck *et al.* (2004) demonstrate that REE data for the 91500 zircon derived from LA-ICP-MS and SIMS show “only small systematic differences” and that “the use of the NIST SRM 610 glass as the calibrant introduces little or no systematic error into the results for zircon.” The mean and median values in a compilation of > 600 trace element measurement results for 91500, taken from the same runs used for U-Pb/TE analyses in our database (supporting information Table S2), show very good agreement with the interlaboratory means (both LA-ICP-MS and SIMS) presented by Wiedenbeck *et al.* (2004).

U-Pb analyses: These were performed by LA-ICP-MS. Typical ablation conditions included beam sizes from 30 to 50 μm , with pulse rate of 5 Hz and energy densities of typically 7–8 J cm^{-2} . Helium was used as the carrier gas at a total flow rate of 0.8 l min^{-1} . Measurements consisted of 60 s of background and 120 s of ablation. The isotopes monitored by ICP-MS were ^{206}Pb , ^{207}Pb , ^{208}Pb , ^{232}Th , ^{238}U and the operating conditions were optimised to minimise oxide formation ($^{248}\text{ThO}^+ / ^{232}\text{Th}^+ < 1\%$), while obtaining maximum

sensitivity on Pb and U. A typical U-Pb run contained on average ten unknowns bracketed by two analyses of the calibration zircon GJ-1 (Elhlou *et al.* 2006) at the beginning and at the end. Generally, each run also included analyses of the reference materials 91500 (Wiedenbeck *et al.* 1995, 2004), Mud Tank and Temora-2 (Black *et al.* 2004) for data quality control. The acquired data were processed on-line with GLITTER by integrating segments of the signal (see above) representing chemically homogeneous material.

***In situ* Hf isotope measurements:** These were obtained using a Nu Instruments MC-ICP-MS (Nu Plasma, Nu Plasma HR and Nu Plasma II). Typical ablation conditions include beam sizes from 30 to 50 μm , with pulse rate of 5 Hz and energy densities of typically 7–8 J cm^{-2} . Helium was used as the carrier gas at a total flow rate of 0.8 l min^{-1} . Analyses generally consisted of 30 s of background measurement and 150 s of sample ablation. Measurements were made at m/z 183, 180, 179, 178, 177, 176, 175 and 172, with instrumental mass bias correction calculated using the $^{179}\text{Hf}/^{177}\text{Hf}$ ratio and an exponential law. Values of $^{176}\text{Hf}/^{177}\text{Hf}$ calculated using only Hf or (Hf+Yb) to measure mass bias were identical within uncertainty ($y = 0.9989x + 0.0003$, $R^2 = 0.9945$, $n = 4568$). The corrections of ^{176}Lu and ^{176}Yb interferences on ^{176}Hf were respectively inferred from monitoring ^{175}Lu and ^{172}Yb . Runs typically include ten unknowns bracketed on each side by analyses of 91500, Mud Tank and Temora-2 in order to monitor analytical conditions and the effectiveness of the corrections for overlap of REE peaks on those of Hf isotopes. Data reduction was performed using the in-built time-resolved analysis software readily of the Nu Plasma instrument. In a similar fashion to GLITTER, data processing involved integrating segments of the signal representing chemically homogeneous materials.

Database construction

LA-ICP-MS data: 10,806 LA-ICP-MS runs with Glitter data reduction were compiled, covering the period 2007–2018. Each run contained either U-Pb or trace element data on MTZ, or both. For each run, the relevant data were extracted and separate databases for each type of run (i.e., U-Pb and trace elements) were made. The structure of each database and filtering principles are described below.

The trace element database contains the element mass fraction, its chondrite-normalised value (McDonough and Sun 1995) and respective 1s uncertainties. The elements monitored varied depending on operator choice, and the number of analyses depends on the specific element considered and range from 158 to 484. Data for seventy-nine elements in MTZ are recorded in the database. Table 1 summarises the data for elements with more than twenty-five individual analyses above the relevant detection limit. Among these elements, where more than one isotope was monitored, only the data derived from the most analytically appropriate stable isotope were retained. This procedure left twenty-three elements in the database. A more detailed study of the trace element composition of eleven colour-selected gem-quality zircons (Gain 2013, this work) is summarised below, with data presented in Table 2.

The U-Pb database (5932 unfiltered analyses) contains the ratios $^{207}\text{Pb}/^{206}\text{Pb}$, $^{206}\text{Pb}/^{238}\text{U}$, $^{207}\text{Pb}/^{235}\text{U}$ and $^{208}\text{Pb}/^{232}\text{Th}$, an age estimate for each ratio and 1s uncertainties directly exported from GLITTER output. In order to filter out unrepresentative analyses acquired during instrument tuning, or mislabelled analyses, the data were subjected to the following tests. For a given U-Pb run, if the age estimate of an MTZ analysis lay outside the 732 ± 10 Ma range for $^{206}\text{Pb}/^{238}\text{U}$ (i.e., recommended age $\pm 2s$, Black and Gulson (1978)) and another MTZ analysis that fell within the range was present, then only the latter was kept. If the only MTZ analysis was outside the accepted range, the same run was searched for an age estimate on the 91500 zircon. If the $^{207}\text{Pb}/^{206}\text{Pb}$ age estimate of the 91500 analysis lay within the range 1065.4 ± 10 Ma (Wiedenbeck *et al.* 1995), then the MTZ analysis was retained. Remaining data were then further filtered and only the analyses satisfying the following criteria were retained: (1) a $^{207}\text{Pb}/^{206}\text{Pb}$ age estimate between 700 and 760 Ma; (2) a $^{206}\text{Pb}/^{238}\text{U}$ age estimate between 715 and 745 Ma and (3) $^{208}\text{Pb}/^{232}\text{Th}$ age estimates between 650 and 800 Ma. These ranges represent the position of the normal distribution for each isotopic ratio, and include 92% of the data; they also include the anomalously low, but poorly documented, ages of Thompson *et al.* (2018). Reducing the range of data to these values allows a more accurate observation of the data distribution by use of relative-frequency histograms. The kernel density estimation reveals that reliable data are absent for lower and higher ages outside this range. This process left a total of 2272 analyses (i.e.,

38% of the total) in the filtered database; statistical data for the U-Pb and Th-Pb age estimates are summarised in Table 3.

LA-MC-ICP-MS data: Hafnium isotope data were collected by multiple users on three different Nu Plasma LA-MC-ICP-MS instruments (see Table S1). We report the isotopic ratios $^{176}\text{Hf}/^{177}\text{Hf}$, $^{176}\text{Lu}/^{177}\text{Hf}$, $^{176}\text{Yb}/^{177}\text{Hf}$, $^{178}\text{Hf}/^{177}\text{Hf}$ and $^{180}\text{Hf}/^{177}\text{Hf}$ for each instrument. The unfiltered database contains 12945 records, but many of these represent test analyses produced during tuning of the instrument, and are not representative of normal measurement conditions. The data for each ratio therefore were filtered using upper and lower thresholds representing the range of values realistically expectable for MTZ, based on the long-term precision (i.e. $0.2826 > ^{176}\text{Hf}/^{177}\text{Hf} > 0.2824$; $0.0002 > ^{176}\text{Lu}/^{177}\text{Hf} > 0.00003$; $0.012 > ^{176}\text{Yb}/^{177}\text{Hf} > 0.001$; $1.468 > ^{178}\text{Hf}/^{177}\text{Hf} > 1.4666$; $1.8875 > ^{180}\text{Hf}/^{177}\text{Hf} > 1.8855$). We retained only analyses that fell within these rather generous ranges for all five isotopic ratios. The three instruments have provided 6574, 2369 and 407 analyses, respectively, making a total of 9350 individual analyses (72% of the total) in the filtered Hf database (Table 4).

Plotting conventions

The ranges in elemental mass fractions and chondrite-normalised data were investigated using box-and-whisker plots (Figure 2). The boxes represent the first and third quartile (i.e., Q1 and Q3) and contain the median value of the dataset (McGill *et al.* 1978). The upper and lower limits of the notches framing the median represent its 95% confidence interval (McGill *et al.* 1978). The maximum lengths of the whiskers were defined as $Q1 - (1.5 \times (Q3 - Q1))$ and $Q3 + (1.5 \times (Q3 - Q1))$. The 1.5 value was chosen so that the whiskers represent 2.7s (99.3%) of the data for a normally distributed dataset. Outliers (individual red dots) are defined as data outside the whiskers range. In the box-and-whisker plots, only data that are above the instrumental detection limit are considered, because analyses below the detection limit contain no real data, and setting these values to zero is not statistically rigorous. Thus the mean and median values presented here represent upper estimates; this obviously affects low mass fraction elements (e.g., La, Pr) the most.

Age estimates and Hf-isotope ratios were investigated using relative frequency plots and kernel-density estimations produced by the IsoplotR software (Vermeesch 2018). For each series, the widths of bins were calculated using the formula of Scott (1979). The IsoplotR software was used to construct relative-frequency curves using the previously calculated bin widths, and to calculate weighted means and standard errors, as well as an overall Concordia age for the U-Pb data.

Results

Trace element measurements

Element abundance data for the overall dataset are compiled in Table 1, and are plotted in Figure 2a. Most of the trace element data reported here were collected simultaneously with U-Pb analysis. In this case only a subset of elements (REE, U, Pb, Th, Hf, Nb, Ta, Y, P, Ca, Si and Zr) was included in the run, in order to minimise mass sweep time, thus maintaining appropriate precision for both U-Pb dating and mass fraction determination. These trace element data are plotted normalised to chondrites (McDonough and Sun 1995) in Figure 2b. The mean pattern shows a strong positive Ce anomaly, depletion in the LREE and enrichment in the HREE. The HREE pattern is flatter than in zircons from most igneous rocks, (mean $\text{Yb}/\text{Sm}_{\text{CN}} = 30.5$) and is characteristic of zircons from some, but not all, carbonatites (Belousova *et al.* 2002, Hoskin and Ireland 2004).

Gain (2013) carried out a detailed study of offcuts from nine gem-quality coloured zircons, to investigate the factors that might influence colour. To supplement these data, we analysed two more crystals, one pale brown and one colourless. These studies found significant levels of a large range of elements including Sb, V, Cr, Ge, As, Fe, Mg, Al, Ti, Cu, P, B (Table 2); some of these show large ranges in mass fraction, especially in samples with marked oscillatory zoning (Figures 1, 3). Notably, the abundances of almost all elements determined in these gem-quality grains fall below, or barely within, the first quartile of the values in the main database, which is made up mainly of dark-red zircons. The REE contents are homogeneous in grains with little or no zoning, but vary by an order of magnitude across zircons with strong oscillatory zoning (Figure 3b) while the chondrite-normalised

patterns remain approximately parallel. Some of the analyses in Table 2 show weak negative Eu anomalies ($\text{Eu}/\text{Eu}^* 0.7\text{--}1.0$), but the mean pattern from the whole sample set (Figure 2) shows no significant anomaly.

It proved difficult to assign specific elements to specific colours, but in general, the highest trace element abundances were found in red-brown crystals, while the lowest abundances were typical of the lighter colours. The colourless zircon (YG-2) analysed here has trace element abundances approximately one order of magnitude lower than the median values for the main dataset (Figure 4). The main use of the MTZ in this laboratory is as a reference material for U-Pb and Hf-isotope analysis. This has led to the preferred use of the darker red-brown variety, which gives the highest signals for U, Pb and Hf, as well as most other trace elements. The low Lu/Hf ratios reported for colourless MTZ by Woodhead and Hergt (2005; see below) suggest that those zircons have low overall trace element contents similar to those of grain YG-2 (Table 2).

Gain (2013) identified several correlations between trace element abundances and CL intensity. High Hf concentrations typically coincide with zones of brighter CL, as observed by Woodhead and Hergt (2005). Similarly, areas with darker CL response have higher REE concentrations, while areas with lighter (brighter) CL response have lower REE contents (Figs 1, 3). This contradicts some previous studies (e.g., Marfunin 1979), and could reflect quenching of the normal CL response in most zircons by elements such as U, Hf and Y, all of which are relatively low in MTZ. Zones of lighter CL response also have lower concentrations of V, Ge, Pb, Th, U, Y and P, and higher concentrations of Al.

U-Pb dating

The summarised age data for our analyses of MTZ are given in Table 3 and Figures 5 and 6. We generally accept the weighted mean $^{206}\text{Pb}/^{238}\text{U}$, which takes uncertainties into account, as most reliable for zircons with ages < 1 Ga. This value, 731.0 ± 0.2 Ma (2 standard error uncertainty, $n = 2272$; Figure 5), and the mean value (730 ± 10 Ma, 2s; Table 3) are consistent with other LA-ICP-MS estimates. Schweiters *et al.* (2009) gave a LA-ICP-MS

Concordia age for MTZ of 729.0 ± 2.5 Ma ($2s$, $n = 35$), and Huan *et al.* (2008) reported $^{206}\text{Pb}/^{238}\text{U}$ ages for several instrument configurations, with a weighted mean of 731.7 ± 4.5 Ma ($2s$, $n = 19\text{--}27$).

Black and Gulson (1978) used five concordant to near-concordant solution-TIMS analyses and one strongly-discordant one ($^{206}\text{Pb}/^{238}\text{U}$ age = 439 Ma) to define a discordia line with an upper intercept of 732 ± 5 Ma, which they accepted as the age of crystallisation of the zircon (and the carbonatite). More recently, Horstwood *et al.* (2016) reported an ID-TIMS $^{206}\text{Pb}/^{238}\text{U}$ age of 731.8 ± 1.0 Ma.

Although our mean U-Pb age is concordant within its 1s uncertainties, the age distribution for $^{206}\text{Pb}/^{238}\text{U}$ is strongly skewed with mild bimodality; $^{207}\text{Pb}/^{235}\text{U}$ ages are less skewed and $^{207}\text{Pb}/^{206}\text{Pb}$ ages are nearly normally distributed (Figure 5). This pattern implies a degree of discordance, and is consistent with the minor discordance visible in the data of Black and Gulson (1978), and with the scatter of our data down the Concordia from the main age peak (Figure 6). The mean $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ages of Black and Gulson (1978) each lie at the extreme low end of our data, and help to explain some of the skewness of the $^{206}\text{Pb}/^{238}\text{U}$ age distribution, in particular. Among the zircons studied in detail by Gain (2013), several were concordant, but with $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ ages significantly lower than the main concordant group (down to 676 Ma), suggesting Pb loss not long after intrusion. Gain (2013) also found that the use of a larger spot size (120 μm vs. 60 μm) tended to give older ages. This is consistent with the presence of local zones affected by Pb loss, probably during the Alice Springs orogeny, which occurred 300–400 My after crystallisation of the Mud Tank carbonatite. This minor Pb loss may be related to healed fractures, like those seen in Figure 1a,b. Such Pb loss or redistribution, during post-magmatic cooling and/or the Alice Springs Orogeny, probably accounts for the wide range of ages reported (without uncertainties) by Thompson *et al.* (2018) from a small number of grains.

The $^{208}\text{Pb}/^{232}\text{Th}$ ages for MTZ have a nearly normal distribution, but the mean has higher uncertainties, which is not surprising given the low Th content of most Mud Tank zircon (Tables 1, 2).

Hf isotope measurements

The Hf isotope measurements are summarised in Table 4 (which includes data for each of three instruments) and Figure 7. The plots of $^{176}\text{Lu}/^{177}\text{Hf}$ show a strong negative skewness, and a bimodal pattern is visible in the largest data set (NP005, $n = 6574$). This reflects the observed small-scale compositional heterogeneity associated with visible CL patterns (Figure 1; see below), as well as grain-to-grain variability. Woodhead and Hergt (2005) reported a mean $^{176}\text{Lu}/^{177}\text{Hf}$ of 0.000042 for MTZ, mainly on colourless grains; this is close to the lower-Lu/Hf subpopulation in our data. A similar skewness is observed in the plots of $^{176}\text{Yb}/^{177}\text{Hf}$; this is expected from the scatter in $^{176}\text{Lu}/^{177}\text{Hf}$, since Lu, Yb and Hf tend to be closely correlated in the trace element data (Figure 2a). The variation among different grains is illustrated especially by the higher values from NP034 (Figure 7).

Our long-term value for the stable-isotope ratio $^{178}\text{Hf}/^{177}\text{Hf}$ is 1.46722 ± 36 (2s, $n = 9350$), within uncertainty of the nominal value of 1.46717; the mean $^{180}\text{Hf}/^{177}\text{Hf}$ is 1.88671 ± 49 (2s, $n = 9350$), compared with the nominal value of 1.88666.

Our weighted mean $^{176}\text{Hf}/^{177}\text{Hf}$ for all MTZ analyses is 0.282523 ± 10 , (2s, $n = 9350$), but the uncertainties on this ratio are greater than those on the stable isotope ratios, implying some heterogeneity. It is clear that this heterogeneity is mainly on the grain scale, a factor also recognised by Woodhead and Hergt (2005). The dataset for analyses run on NP256, using a single MTZ grain, shows much less scatter than the two larger datasets, and the mean is offset toward the less radiogenic end of the distributions seen in both datasets. Hf-isotope analyses of the nine zircons studied in detail for trace elements by Gain (2013) indicate that most individual grains are homogeneous within the 1s uncertainty of the mean values. Woodhead and Hergt (2005) show traverses across a finely zoned MTZ, in which individual values of $^{176}\text{Hf}/^{177}\text{Hf}$ oscillate between *ca.* 0.2827 and 0.2823, although the running-mean value fluctuates only by up to 0.0002 in some parts of the crystal.

Woodhead and Hergt (2005) gave a mean solution-TIMS value for $^{176}\text{Hf}/^{177}\text{Hf}$ of 0.282507 ± 3 . Their LA-MC-ICP-MS overall mean is 0.282504 ± 22 (all, $n = 158$), and the mean value for the colourless population is 0.282506 ± 13 . Judging from their figures, the mean and standard deviation for the coloured grains alone would be higher than this. Schweiters *et al.*

(2009) give a mean value for LA-MC-ICP-MS analyses of 0.282522 ± 19 ($n = 46$), and Hu *et al.* (2012) give a mean value for LA-MC-ICP-MS analyses of 0.282511 ± 20 ($n = 195$). Huan *et al.* (2008), using different spot sizes, reported mean values that ranged from 0.282507 ± 6 to 0.282520 ± 16 for their "Hf" method. Other combinations of simultaneous U-Pb, trace element and Hf-isotope analysis gave a mean value of 0.282506 ± 4 ($n = 51$). The GeoReM database (<http://georem.mpch-mainz.gwdg.de>; Jochum *et al.* 2005) contains 176 reports of $^{176}\text{Hf}/^{177}\text{Hf}$ on MTZ, ranging from 0.282426 to 0.282545, mean 0.282504 ± 30 (2s).

Our large datasets, collected over 18 years using three different LA-MC-ICP-MS instruments, suggest that most of these values are equally valid, and differences apparently related to particular methodologies probably can be ascribed to the observed heterogeneity within and between the varieties of MTZ.

Discussion and conclusions

The MTZ can in principle be used as a matrix-matched reference material for trace element analysis, since the trace element patterns are reproducible to the extent shown here. However, grains with strong oscillatory zoning should be avoided, and absolute abundances should be checked independently on the material to be used. The darker-coloured stones are more likely to have the higher trace element abundances desirable in a reference material. As noted above, colourless zircons may be restricted to surface-collected material, and the correlation between lack of colour and low trace element abundances suggests that zircons with low trace element contents are more susceptible to sunlight-UV bleaching. We have confirmed that all MTZ free of inclusions will lose its colour if gently heated above 400°C ; this treatment could aid in selection of crystals for use as reference materials.

The usefulness of MTZ as a reference material for U-Pb dating is limited to some extent by its low contents of U and Pb, but is enhanced by its age, as it is older than several commonly used reference materials (GJ-1, Temora, Plesovice). In particular, the large darker-coloured MTZ grains, with U levels above *ca.* $100\ \mu\text{g g}^{-1}$, provide a good secondary reference material for U-Pb dating. The work of Gain (2013) indicates that gem-quality stones typically have

lower contents of U, Pb and Th, but are more likely to be concordant at the accepted age. Pb loss has been noted in some grains, but is not a general feature. Such regions can be avoided by careful selection of samples using cathodoluminescence imaging, especially to avoid obvious cracks (Figure 1a, b). It also is recommended that stones with definite crystal shapes be used, as our experience suggests that some irregular fragments have experienced thermal effects or chemical modification.

As a reference material for Hf isotope measurements, MTZ is reliable within the limits shown here, and importantly, most grains appear to be internally homogeneous. One significant advantage over other zircon reference materials is the very low mass fractions of HREE, a feature that reduces the uncertainties involved in isotopic-overlap corrections. The work of Woodhead and Hergt (2005) suggests that colourless crystals show less inter-grain variation in $^{176}\text{Hf}/^{177}\text{Hf}$ than coloured stones, but this generalisation needs to be tested on a larger number of samples. Our experience indicates that grains with strongly zoned CL patterns should be avoided, and ideally solution-TIMS analysis should be used to establish a value for individual (unzoned) crystals.

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References

Ahmad M. and Munson T.J. (compilers) (2013)

Geology and mineral resources of the Northern Territory. **Special Publication 5, June 2013. Northern Territory Geological Survey, Northern Territory Government, NNNpp.**

Belousova E.A., Griffin W.L., O'Reilly S.Y. and Fisher N.I. (2002)

Igneous Zircon: Trace element composition as an indicator of host rock type. **Contributions to Mineralogy and Petrology, 143, 602–622.**

Bendall B. (2000)

Mid-Palaeozoic shear zones in the Strangways Range: A record of intracratonic tectonism in the Arunta Inlier, Central Australia. **PhD thesis (University of Adelaide), NNNpp.**

Black L.P. and Gulson B.L. (1978)

The age of the Mud Tank Carbonatite, Strangways Range, Northern Territory. **Journal of Australian Geology and Geophysics, 3, 227–232.**

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 $^{206}\text{Pb}/^{238}\text{U}$ microprobe geochronology by the monitoring of a trace element-related matrix effect: SHRIMP, ID-TIMS, ELA-EIP-MS and oxygen isotope documentation for a series of zircon standards. **Chemical Geology**, **205**, 115–140.

Brown G., Bracewell H. and Snow J. (1989)

Gems of the Mud Tank carbonatites. **Australian Gemologist**, **17**, 52–57.

Crohn P.W. and Moore D.H. (1984)

The Mud Tank Carbonatite, Strangways Range, Central Australia. **BMR Journal of Australian Geology and Geophysics**, **9**, 13–18.

Currie K., Knutson J. and Temby P. (1992)

The Mud Tank carbonatite complex, central Australia – An example of metasomatism at mid-crustal levels. **Contributions to Mineralogy and Petrology**, **109**, 326–339.

Elhlou S., Belousova E., Griffin W.L., Pearson N.J. and O'Reilly S.Y. (2006)

Trace element and isotopic composition of GJ-red zircon standard by laser ablation. **Geochimica et Cosmochimica Acta**, **70 (Supplement)**, A158.

Faulkner M.J. and Shigley J.E. (1989)

Zircon from the Harts Range, Northern Territory, Australia. **Gems and Gemology**, **25**, 207–215.

Gain S.E.M. (2013)

The geochemistry of gem-quality zircons from the Mud Tank carbonatite complex, Northern Territory. **BSc (Hons) thesis (Macquarie University)**, 118pp.

Gain S.E.M., Belousova E.A., Pearson N.J., Dainis I. and Griffin W.L. (2018)

Assessment of trace element homogeneity in gem quality zircons from Mud Tank, NT.

Geoanalysis 2018, Macquarie University, Sydney, 8-13 July.

Green P.F., Crowhurst P.V., Duddy I.R., Japsen P. and Holford S.P. (2006)

Conflicting (U-Th)/He and fission track ages in apatite: Enhanced He retention, not anomalous annealing behaviour. **Earth and Planetary Science Letters**, **250**, 407–427.

Griffin W.L., Pearson N.J., Belousova E.A. and Saeed A. (2007)

Reply to “Comment to short-communication ‘Comment: Hf-isotope heterogeneity in zircon 91500’ by W.L. Griffin, N.J. Pearson, E.A. Belousova and A. Saeed (Chemical Geology 233 (2006) 358–363)” by F. Corfu. **Chemical Geology**, **244**, 354–356.

Griffin W.L., Pearson N.J., Belousova E., Jackson S.E., O'Reilly S.Y., van Achterberg E. and Shee S.R. (2000)

The Hf isotope composition of cratonic mantle: LAM-MC-ICP-MS analysis of zircon megacrysts in kimberlites. **Geochimica et Cosmochimica Acta**, **64**, 133–147.

Griffin W.L., Powell W.J., Pearson N.J. and O'Reilly S.Y. (2008)

GLITTER: Data reduction software for laser ablation ICP-MS. In: **Sylvester P. (ed.), Laser ablation ICP-MS in the Earth sciences. Mineralogical Association of Canada Short Course Series**, **40**, 204–207.

Horstwood M.S.A., Kosler J., Gehrels G., Jackson S.E., McLean N.M., Paton C., Pearson N.J., Sircombe K., Sylvester P., Vermeesch P., Bowring J.F., Condon D.J. and Schoene B. (2016)
Community-derived standards for LA-ICP-MS U-(Th)-Pb geochronology – Uncertainty Propagation, age interpretation and data reporting. **Geostandards and Geoanalytical Research**, **40**, 311–332.

Hoskin P.W.O. and Ireland T.R. (2000)

Rare earth chemistry of zircon and its use as a provenance indicator. **Geology**, **28**, 627–630.

Hu Z., Liu Y., Gao S., Liu W., Zhang W., Tong X., Lin L., Zong K., Li M., Chen H., Zhou L. and Yang L. (2012)

Improved *in situ* Hf isotope ratio analysis of zircon using newly designed skimmer cone and jet sample cone in combination with the addition of nitrogen by laser ablation multiple collector ICP-MS. **Journal of Analytical Atomic Spectrometry**, **27**, 1391–1399.

Huan H.L., Gao S., Dai M.N., Zong C.L., Günther D., Fontaine G.H., Liu X.M. and Diwu C.R. (2008)

Simultaneous determinations of U-Pb age, Hf isotopes and trace element compositions of zircon by excimer laser-ablation quadrupole and multiple-collector ICP-MS. **Chemical Geology**, **247**, 100–118.

Jackson S.E., Pearson N.J., Griffin W.L. and Belousova E.A. (2004)

The application of laser ablation-inductively coupled plasma-mass spectrometry to in-situ U-Pb zircon geochronology. **Chemical Geology**, **211**, 47–69.

Jain J.C., Neal C.R. and Hanchar J.M. (2007)

Problems associated with the determination of rare earth elements of a “gem” quality zircon by inductively coupled plasma-mass spectrometry. **Geostandards and Geoanalytical Research**, **25**, 229–237.

Jochum K.P., Nohl U., Herwig K., Lammel W., Stoll B. and Hofmann A.W. (2005)

GeoReM: A new geochemical database for reference materials and isotopic standards. **Geostandards and Geoanalytical Research**, **29**, 333–338.

Kempe U., Trinkler M., Pöpl A. and Hincinschi C. (2006)

Coloration in natural zircon. **The Canadian Mineralogist**, **54**, 635–660.

McDonough W.F. and Sun S-S. (1995)

The composition of the Earth. **Chemical Geology**, **120**, 223–253.

McGill R., Tukey J.W. and Larsen W.A. (1978)

Variations of box plots. **The American Statistician**, **32**, 12–16.

Marfunin A.S. (1979)

Mineralogical chemistry: Chemistry, Physical and theoretical; Chemistry, Inorganic.

Springer-Verlag (Berlin, New York), 340pp.

Norman M.D., Griffin W.L., Pearson N.J., Garcia M.O. and O'Reilly S.Y. (1998)

Quantitative analysis of trace element abundances in glasses and minerals: A comparison of laser ablation ICP-MS, solution ICP-MS, proton microprobe, and electron microprobe data.

Journal of Analytical Atomic Spectrometry, **13**, 477–482.

Pearson N.J., Griffin W.L. and O'Reilly S.Y. (2008)

Mass fractionation correction in laser ablation-multiple collector ICP-MS: Implications for overlap corrections and precise and accurate in situ isotope ratio measurement. **In:**

Sylvester P. (ed.), Laser ablation-ICP-MS in the Earth sciences: Current practices and outstanding. Mineralogical Association of Canada Short Course, **40**, 93–116.

Schweikers J.B., Bouman C., Deerberg M., Wills J.D. and Gerdes A. (2009)

Simultaneous *in situ* analysis of U-Pb age and Hf isotopes of zircon by laser ablation sector-field (MC-) ICP-MS. **Thermo Scientific Application Note**, **30170**, 1–4.

Scott D.W. (1979)

On optimal and data-based histograms. **Biometrika**, **66**, 605–610.

Thompson J.M., Danyushevsky L.V., Meffre S. and Corfu F. (2018)

The Mud Tank zircon revisited: New ID-TIMS ages reveal complex crystallisation history.

Geoanalysis 2018, Macquarie University, Sydney, 8–13 July.

Thomson S.N., Gehrels G.E., Ruiz J. and Buchwald R. (2012)

Routine low-damage U-Pb dating of apatite using laser ablation-multicollector-ICP-MS.

Geochemistry, Geophysics, Geosystems, **13** [QOAA21].

Vermeesch P. (2018)

IsoplotR: A free and open toolbox for geochronology. **Geoscience Frontiers**, **9**, 1479–1493.

Wiedenbeck M., Corfu F., Griffin W.L., Meier M., Oberli F., von Quadt A., Roddick J.C.,

Spiegel W. and Todt W. (1995)

Three natural zircon standards for U-Th-Pb, Lu-Hf, trace element and REE analyses.

Geostandards Newsletter, **19**, 1–24.

Wiedenbeck M., Hanchar J.M., Peck W.H., Sylvester P., Valley J., Whitehouse M., Kronz A.,

Morishita Y., Nasdala L., Fiebig J., Franchi I., Girard J.-P., Greenwood R.C., Hinton R., Kita

N., Mason P.R.D., Norman M., Ogasawara M., Piccoli P.M., Rhede D., Satoh H., Schulz-

Dobrick B., Skår Ø., Spicuzza M.J., Terada K., Tindle A., Togashi S., Vennemann T., Xie Q.

and Zheng Y.-F. (2004)

Further characterisation of the 91500 zircon crystal. **Geostandards and Geoanalytical**

Research, **28**, 9–39.

Woodhead J.D. and Hergt J.M. (2005)

A preliminary appraisal of seven natural zircon reference materials for *in situ* Hf isotope

determination. **Geostandards and Geoanalytical Research**, **29**, 183–195.

Woodhead J.D., Hellstrom J., Hergt J.M., Greig A. and Maas R. (2007)

Isotopic and elemental imaging of geological materials by laser ablation inductively coupled

plasma-mass spectrometry. **Geostandards and Geoanalytical Research**, **31**, 331–343.

Yuan H.L., Gao S., Dai M., Zong C., Günther D., Fontaine G.H., Liu X. and Diwu C. (2008)

Simultaneous determinations of U-Pb age, Hf isotopes and trace element compositions of

zircon by excimer laser-ablation quadrupole and multiple-collector ICP-MS. **Chemical**

Geology, **247**, 100–118.

Supporting information

The following supporting information may be found in the online version of this article:

Table S1. Evolution of instrumentation in the Geochemical Analysis Unit, relevant to this work.

Table S2. Trace element data for zircon 91500.

This material is available from:

<http://onlinelibrary.wiley.com/doi/10.1111/ggr.00000/abstract>

(This link will take you to the article abstract).

Figure captions

Figure 1. Mud Tank Zircon. (a, b) Cold-cathode cathodoluminescence images illustrating internal zoning and healed fractures in two Mud Tank zircons used as reference materials in the GAU. (c) Micro-XRF image of Hf distribution in the sample shown in (a), showing preferential uptake of Hf on specific crystal faces. (d) Micro-XRF image of the distribution of REE elements in the sample shown in (a); "hot spots" along an interface boundary show REE-rich minerals.

Figure 2. Box-and-whisker plots of trace element data. (a) elemental abundances of twenty-three elements from the Mud Tank zircon in $\mu\text{g g}^{-1}$. Data considered as outliers are shown as red dots. (b) Element abundances normalised to Chondrite, for twenty-three elements from the Mud Tank zircon. Data considered as outliers are displayed as red dots. Further information on the plotting convention can be found in the text. Statistical data for these boxplots are provided in Table 1.

Figure 3. Chondrite-normalised REE data for two gem-quality Mud Tank zircons (a) MTD and (b) MTG, illustrating the greater heterogeneity in strongly zoned grains. Insets show the colours of the polished gems, and the locations of individual colour-coded analysis points superimposed on cathodoluminescence images.

Figure 4. Trace element data for two pale to colourless zircons, compared to the median values from Figure 2, and to the data from more strongly coloured gem zircons (Table 2).

Figure 5. Relative-frequency histograms of U-Pb and U-Th ages of Mud Tank zircons. Values for the mean (M), the weighted mean (WM and red line), the standard error (1SE) and the number of data (n) are presented for each dataset. Statistical data are summarised in Table 3.

Figure 6. Concordia plot of U-Pb data ($n = 2272$) from this database. Uncertainty ellipses represent 2s.

Figure 7. Relative-frequency histograms from Hf-isotope analyses of Mud Tank zircons: (a) $^{176}\text{Hf}/^{177}\text{Hf}$; (b) distribution of data relative to the mean value; (c) $^{178}\text{Hf}/^{177}\text{Hf}$; (d) $^{180}\text{Hf}/^{177}\text{Hf}$; (e) $^{176}\text{Lu}/^{177}\text{Hf}$; (f) $^{176}\text{Yb}/^{177}\text{Hf}$. Values for the mean (M), the weighted mean (WM and red line), the standard error (1SE) and the number of data (n) are presented for each dataset. Statistical data, including instrument-specific data, are summarised in Table 4.

Table 1.								
Statistical data for the elemental abundance box-and-whisker plots ($\mu\text{g g}^{-1}$)								
Element	Minimum	1st quartile	Median	3rd quartile	Maximum	Outliers	N detected	Below detection limit
P	16.5	48.4	63.6	96.2	283	3	271	0
La	0.00027	0.00615	0.0118	0.0295	1.19	19	158	364
Ce	0.161	1.98	2.81	3.99	20.3	8	465	0
Pr	0.00197	0.0272	0.0387	0.0556	1.15	21	365	28
Nd	0.0405	0.454	0.69	0.0995	10.2	12	446	0
Sm	0.06	1.05	1.53	2.19	8.34	14	465	0
Eu	0.0654	0.827	1.21	1.73	5.32	12	464	0
Gd	0.522	6.67	9.52	13.6	31.1	10	465	0
Tb	0.163	2.17	3.03	3.92	9.61	11	266	0
Dy	1.06	26.2	35.61	49.4	94.8	8	456	0
Y	14.1	216	277	374	951	11	484	0
Ho	0.484	8.34	11.1	15.2	29.8	8	456	0
Er	1.98	31.1	40	53.4	111	10	448	0
Tm	0.342	4.96	6.76	8.43	20.9	9	268	0
Yb	2.5	43.3	53.7	69.5	170	11	466	0
Lu	0.343	6.16	7.71	9.55	22.2	18	467	0
Hf	1.3	9080	11800	11900	34800	97	476	0
Ti	0.138	3.41	4.25	5.33	14.6	9	462	0
Nb	0.05	5.17	7.99	11.5	20.3	0	457	0
Ta	0.0037	5.11	7.33	9.87	22.2	2	457	0
Pb	0.129	3.53	5.86	8.85	16.3	0	468	0
Th	1.97	54.1	91.9	132	256	1	477	0
U	0.0043	77.2	103	141	308	3	478	0

Table 2.

Extended trace element mass fraction data (µg g⁻¹) for individual zircons as a function of their colour

Element	Orange		Red brown				Purple brown				Light purple				Purple				Pale brown				Colourless			
	MTG (n = 10)		MTB (n = 10)		MTT (n = 10)		MTG (n = 10)		MTD (n = 10)		MTG (n = 10)		MTG (n = 10)		MTG (n = 10)		MTT (n = 10)		MTG (n = 24)		YG-1 (n = 19)		YG-2 (n = 15)			
	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ	Mean	1σ
Li	0.14	0.03	0.17	0.05	0.05	0.01	0.16	0.16	0.08	0.01	0.09	0.03	0.15	0.13	0.09	0.03	0.05	0.02	0.05	0.02						
B	2.3	0.6	2.2	0.5	1.8	0.6	1.9	0.5	1.9	0.4	0.95	0.67	2.2	0.6	2	0.5	2.2	1.3								
Mg	0.024	0.009	0.021	0.01	0.41	0.65	0.1	0.11	0.03	0.02	0.022	0.006	0.04	0.009	0.11	0.05	0.17	0.09								
Al	0.66	0.18	1.4	0.2	0.98	0.51	1.2	0.5	0.53	0.1	0.63	0.47	0.45	0.11	1.3	0.1	0.90	0.36								
P	26	9	45	8	28	3	38	5	24	3	30	9	24	2	17	15	30	4			59	6	49	4		
Ca	34	25	34	21	23	24	77	37	36	22	34	31	19	20	31	32	45	29								
Ti	3.6	0.5	7.7	0.9	3.3	0.2	5.4	0.9	4.2	0.2	6.5	1.6	3.1	0.7	8.1	0.7	5.7	0.6								
V	0.051	0.006	0.14	0.01	0.04	0.01	0.09	0.02	0.003	0.006	0.15	0.07	0.04	0.01	0.06	0.01	0.07	0.02								
Cr	0.19	0.07	0.17	0.06	0.19	0.05	0.18	0.09	0.18	0.08	0.17	0.06	0.18	0.06	0.19	0.04	0.23	0.06								
Fe							15	19	2.7				0.75		1.5	0.2										
Cu	0.07	0.02	0.07	0.01	0.07	0.01	0.11	0.14	0.1	0.05	0.08	0.02	0.06	0.02	0.07	0.03	0.19	0.19								
Zn	0.06	0.03	0.06	0.02	0.06	0.04	0.13	0.17	0.1	0.12	0.19	0.09	0.07	0.03	0.06	0.02	1.1	1.6								
Ga	0.04	0.1	0.007	0.004	0.006	0.002	0.007	0.002	0.005	0.002	0.006	0.002	0.007	0.003	0.006	0.002	0.013	0.012								
Ge	0.2	0.04	0.29	0.04	0.19	0.04	0.27	0.04	0.19	0.04	0.36	0.06	0.17	0.05	0.15	0.04	0.29	0.08								
As	0.51	0.15	0.48	0.12	0.24	0.09	0.48	0.13	0.5	0.14	0.25	0.15	0.24	0.09	0.24	0.06	0.35	0.15								
Rb	0.012	0.004	0.012	0.003	0.014	0.005	0.014	0.003	0.012	0.004	0.014	0.004	0.013	0.006	0.014	0.003	0.027	0.023			0.23	0.02	0.23	0.01		
Sr	0.19	0.12					0.21	0.03	0.2				0.22	0.17												
Y	40	4	38	12	46	6	52	36	35	3	45	21	27	15	29	19	16	5			111	34	53	18		
Nb	1.2	0.2	1.3	0.3	1.7	0.2	1.4	0.4	0.94	0.16	1.7	0.5	1.8	0.3	1.8	0.3	0.99	0.08			2.1	0.6	1.3	0.3		
In	0.007	0.002	0.007	0.002	0.008	0.002	0.008	0.002	0.006	0.002	0.01	0.003	0.009	0.003	0.006	0.002	0.011	0.004								
Sn	0.2	0.04	0.18	0.03	0.15	0.04	0.19	0.05	0.16	0.04	0.15	0.06	0.18	0.05	0.16	0.03	0.3	0.2								
Sb	0.06	0.01	0.048	0.014	0.03	0.01	0.035	0.009	0.037	0.008	0.035	0.006	0.032	0.003	0.038	0.004	0.04	0.01								
La	0.0017	0.0011	0.0008	0.0004	0.0009	0.0009	0.0019	0.0004	0.0003	0.0002	0.002	0.0006	0.001	0.0004	0.0015	0.0006	0.005	0.004								
Ce	0.35	0.05	0.5	0.1	0.39	0.05	0.4	0.1	0.51	0.02	0.4	0.2	0.5	0.1	0.4	0.1	0.31	0.04			0.91	0.26	0.46	0.09		
Pr	0.064	0.001	0.006	0.005	0.005	0.001	0.01	0.01	0.004	0.0008	0.01	0.01	0.004	0.004	0.005	0.002	0.003	0.001								
Nd	0.09	0.02	0.12	0.03	0.1	0.02	0.5	0.2	0.09	0.02	0.2	0.2	0.06	0.04	0.12	0.05	0.05	0.02			0.34	0.22	0.12	0.03		
Sm	0.24	0.03	0.27	0.08	0.24	0.04	0.7	0.3	0.22	0.02	0.4	0.3	0.15	0.09	0.24	0.09	0.12	0.05			0.69	0.35	0.25	0.06		
Eu	0.17	0.02	0.2	0.05	0.19	0.02	0.5	0.2	0.17	0.01	0.3	0.2	0.12	0.07	0.18	0.07	0.10	0.03			0.51	0.22	0.2	0.06		
Gd	1.2	0.1	1.4	0.4	1.4	0.2	3	1.0	1.2	0.1	2	1	0.8	0.5	1.2	0.6	0.6	0.2			3.8	1.4	1.5	0.5		
Tb	0.38	0.04	0.4	0.1	0.42	0.05	0.7	0.2	0.34	0.03	0.5	0.2	0.1	0.2	0.18	0.06										
Dy	4.6	0.5	5	1	5.2	0.7	7	2	4.1	0.3	6	3.0	3.0	2	4	2	1.9	0.6			14.0	5	5.9	2.1		
Ho	1.4	0.2	1.4	0.5	1.6	0.2	2.0	0.6	1.3	0.1	1.7	0.9	0.9	0.5	1.0	0.7	0.6	0.2								
Er	5.8	0.7	6	2	7	1	7	2	5.2	0.4	7	3	4.0	2	4	3	2.2	0.7			17	5	8.5	3.1		
Tm	1.2	0.1	1.0	0.3	1.4	0.2	1.3	0.4	0.99	0.08	1.2	0.5	0.8	0.4	0.7	0.5	0.4	0.1								
Yb	11	1	9	3	13	2	11	5	9	1	10	4	7	4	6	4	3	1			22	5	13	5		
Lu	1.7	0.2	1.4	0.5	2.1	0.3	1.6	0.5	1.5	0.1	1.5	0.6	1.2	0.6	0.9	0.6	0.6	0.2			3.8	0.8	2.4	0.8		
Ta	0.84	0.09	1.2	0.3	1.2	0.1	1.3	0.3	0.7	0.06	1.6	0.6	1	0.3	1.6	0.5	0.69	0.07			2.4	0.5	1.7	0.5		
Pb	2.2	0.3	1.9	0.8	2.3	0.3	3	1	1.5	0.2	1.7	0.4	1.7	0.4	1.3	0.6	0.8	0.2			0.79	0.35	0.27	0.09		
Th	5.6	0.7	5	2	5.6	0.7	8	3	4.1	0.6	5	3	5	1	4	2	2.0	0.4			12.0	5	3.6	1.2		
U	17	2	15	6	18	2	17	10	12	2	12	6	14	3	10	5	6	1			28	8	15	4		

No error is shown if only one analysis was above the MDL.

Table 3.

Age estimates (in Ma) using U/Pb and T/Pbh isotopic systems

Ratio	Mean (Ma)	2σ	Weighted mean (Ma)	Standard error	N
²⁰⁷ Pb/ ²⁰⁶ Pb	738	45	737.8	0.62	2272
²⁰⁶ Pb/ ²³⁸ U	730	10	730.3	0.13	2272
²⁰⁷ Pb/ ²³⁵ U	732	13	732.2	0.15	2272
²⁰⁸ Pb/ ²³² Th	738	49	736.3	0.25	2272

Table 4.						
Statistical data for Hf/Hf, $^{176}\text{Lu}/^{177}\text{Hf}$ and $^{176}\text{Yb}/^{177}\text{Hf}$ ratios						
	Dataset	Mean	2s	Weighted mean	Standard error	N
$^{176}\text{Hf}/^{177}\text{Hf}$	NP005	0.282524	5.70E-05	0.282524	1.28E-07	6574
	NP034	0.282520	6.50E-05	0.282522	1.75E-07	2369
	NP256	0.282510	3.40E-05	0.282510	5.80E-07	407
	All data	0.282523	5.90E-05	0.282523	1.02E-07	9350
$^{178}\text{Hf}/^{177}\text{Hf}$	NP005	1.46718	3.10E-04	1.46718	2.93E-07	6574
	NP034	1.46734	4.20E-04	1.46731	4.99E-07	2369
	NP256	1.46727	1.00E-04	1.46727	1.19E-07	407
	All data	1.46722	3.60E-04	1.46722	2.47E-07	9350
$^{180}\text{Hf}/^{177}\text{Hf}$	NP005	1.88672	4.30E-04	1.88672	7.15E-07	6574
	NP034	1.88668	6.40E-04	1.88667	8.68E-07	2369
	NP256	1.88667	3.00E-04	1.88668	2.71E-07	407
	All data	1.88671	4.90E-04	1.88669	5.41E-07	9350
$^{176}\text{Lu}/^{177}\text{Hf}$	NP005	1.01E-04	6.90E-05	N/A*	N/A*	6574
	NP034	1.11E-04	6.10E-05	N/A*	N/A*	2369
	NP256	1.13E-04	4.60E-05	N/A*	N/A*	407
	All data	1.06E-04	6.80E-05	N/A*	N/A*	9350
$^{176}\text{Yb}/^{177}\text{Hf}$	NP005	4.61E-03	4.00E-03	N/A*	N/A*	6574
	NP034	6.01E-03	4.00E-03	N/A*	N/A*	2369
	NP256	4.73E-03	2.00E-03	N/A*	N/A*	407
	All data	4.99E-03	4.11E-03	N/A*	N/A*	9350
* Could not be calculated as the data do not represent a single population						