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A 4463 Ma apparent zircon age from the Jack Hills resulting from ancient Pb mobilization --Manuscript Draft--

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Abstract:	Hadean (≥ 4.0 Ga) zircon grains provide the only direct record of the first half billion years of Earth's history. Determining accurate and precise crystallization ages of these ancient zircons is a prerequisite for any interpretation of crustal evolution, surface environment and geodynamics on the early Earth, but this may be compromised by mobilization of radiogenic Pb due to subsequent thermal overprinting. Here we report a detrital zircon from the Jack Hills (Western Australia) with 4486 - 4425 Ma concordant ion microprobe ages that yield a concordia age of 4463 ± 17 Ma (2σ). These are the oldest zircon ages recorded from Earth. However, scanning ion imaging reveals that these >4.4 Ga apparent ages resulted from incorporation of micrometre-scale patches of unsupported radiogenic Pb with extremely high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios corresponding to >4.5 Ga $^{207}\text{Pb}/^{206}\text{Pb}$ ages. These patches likely resulted from redistribution of radiogenic Pb into nanometer-scale domains in a ~ 4.3 Ga zircon during a ~ 3.8 Ga or older event. This highlights that even a concordia age can be spurious and should be carefully evaluated before being interpreted as the crystallization age of ancient zircon.
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A 4463 Ma apparent zircon age from the Jack Hills
resulting from ancient Pb mobilization

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ABSTRACT

Hadean (≥ 4.0 Ga) zircon grains provide the only direct record of the first half billion years of Earth's history. Determining accurate and precise crystallization ages of these ancient zircons is a prerequisite for any interpretation of crustal evolution, surface environment and geodynamics on the early Earth, but this may be compromised by mobilization of radiogenic Pb due to subsequent thermal overprinting. Here we report a detrital zircon from the Jack Hills (Western Australia) with 4486 – 4425 Ma concordant ion microprobe ages that yield a concordia age of 4463 ± 17 Ma (2σ). These are the oldest zircon ages recorded from Earth. However, scanning ion imaging reveals that these >4.4 Ga apparent ages resulted from incorporation of micrometre-scale patches of unsupported radiogenic Pb with extremely high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios corresponding to >4.5 Ga $^{207}\text{Pb}/^{206}\text{Pb}$ ages. These patches likely resulted from redistribution of radiogenic Pb into nanometer-scale domains in a ~ 4.3 Ga zircon during a ~ 3.8 Ga or older event. This highlights that even a concordia age can be spurious and should be carefully evaluated before being interpreted as the crystallization age of ancient zircon.

Keywords: Hadean zircon; Jack Hills; Pb mobilization; scanning ion imaging; ion microprobe

INTRODUCTION

Zircon (ZrSiO_4) is a superlative geochronometer because it is abundant in many crustal rocks and is physically and chemically robust under most geological conditions. It incorporates moderate amounts of U and Th in the crystal lattice (but excludes Pb), which provide three independent radiogenic decay schemes (^{238}U to ^{206}Pb , ^{235}U to ^{207}Pb , and ^{232}Th to ^{208}Pb) that enable evaluation of internal consistency (i.e. concordance) of the ages derived from each scheme. A concordant age, or more reliably, a *concordia* age calculated from multiple concordant analyses (Ludwig, 1998), is generally interpreted as the time of zircon crystallization. However, as radiogenic Pb (Pb^*) is incompatible in the zircon lattice, it can be mobilized during later tectonothermal events, resulting in variable degrees of Pb^* loss or, more rarely, Pb^* gain (local Pb^* enrichment) producing, respectively, discordant or reversely discordant U-Pb ages spread along a discordia (Williams et al., 1984; Wetherill, 1956). This effect can be easily recognized in most cases, but it can be difficult to discern for ancient zircons that experienced Pb^* mobilization shortly after crystallization, because in this case the resultant discordia is subparallel to the concordia curve and the U-Pb data remain concordant, within analytical uncertainties, despite significant Pb^* loss or gain, thereby producing spurious ages that are significantly younger or older than the crystallization age (Kusiak et al., 2013; Whitehouse et al., 2017).

It is particularly important to recognize ancient Pb^* mobilization in Hadean zircons, since they experienced complex, protracted post-crystallization histories (e.g.,

Cavosie et al., 2007; Harrison, 2009; Nebel et al., 2014; Whitehouse et al., 2017). Ancient Pb* loss has been invoked to explain along-concordia spread of U-Pb ages of some Hadean zircons, and thus the oldest concordant (or concordia) ages were considered as the minimum crystallization ages (e.g., Compston and Pidgeon, 1986; Wilde et al., 2001; Nemchin et al., 2006; Pidgeon et al., 2017). However, the possibility of ancient Pb* enrichment has rarely been considered. Recently, nanometer-scale Pb* enriched domains (PEDs) have been documented in Hadean and younger zircons using atom probe tomography (Valley et al., 2014; Peterman et al., 2016; Piazzolo et al., 2016; Reddy et al., 2016), scanning ion imaging (Kusiak et al., 2013; Whitehouse et al., 2014) and transmission electron microscopy (TEM) (Kusiak et al., 2015; Whitehouse et al., 2017). These PEDs have high Pb* contents and high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios, and if overlapped during in-situ spot analyses, can compromise analytical precision and produce spurious $^{207}\text{Pb}/^{206}\text{Pb}$ ages that may be hundreds of million years older than the crystallization ages (Kusiak et al., 2013, 2015). Clearly, to determine accurate and precise crystallization ages of ancient zircons, it is essential to evaluate whether Pb* loss or gain occurred and, if it did, to what extent it has affected the U-Pb systematics.

Here we discuss these issues with respect to a Hadean detrital zircon (grain 14041) from the Jack Hills (Western Australia) that yielded the oldest $^{207}\text{Pb}/^{206}\text{Pb}$ ages recorded from Earth.

RESULTS

Structure of Grain 14041

Grain 14041 is a $\sim 180 \times 120$ μm reddish-brown, oval zircon obtained from metaconglomerate at the W74 site, where Hadean detrital zircons were first reported from the Jack Hills supracrustal belt (Compston and Pidgeon, 1986; Wilde et al., 2001). Five serial surfaces were exposed by progressive polishing, effectively providing information from successive 1-2 μm sections through the zircon. Cathodoluminescence (CL) images show that surface 1 is relatively dark and homogeneous (Fig. DR1 in the GSA Data Repository¹), but more detailed internal structures were revealed on surfaces 2 – 5 (Fig. 1; Fig. DR1b – DR1e). Surface 2 is dominated by sector or irregular domains with variable CL intensities in the central part, which are characterized by either fine lamellae or homogenous structure (Fig. 1A). These are cross-cut near the tips of the grain by relatively irregular CL-bright domains possibly formed by recrystallization, which are further surrounded by 10 – 20 μm thick, CL-dark rims (Fig. 1A). Surfaces 3 – 5 are generally similar to surface 2, but a CL-bright annular band of variable thickness appears in the central part of the grain on surface 3 (Fig. 1A), and a CL-dark core was gradually revealed in the centre on surfaces 4 and 5 (Fig. DR1d; Fig. 1C). The shape and size of these domains gradually change with polishing depth. In addition, Electron Backscatter Diffraction (EBSD) mapping shows that this grain has only undergone minor ($<2^\circ$) internal deformation (Fig. DR2). Although a y-shaped fracture was exposed on surfaces 3 – 5 (Figs. DR1, DR2), ion microprobe dating and imaging (see

below) indicate that this has no effect on the U-Pb isotopic system.

Greater than 4.4 Ga ion microprobe ages

Thirty-eight U-Pb spot analyses were made using a SHRIMP II ion microprobe during seven analytical sessions on different polished surfaces (see above and DR1). Six >4.4 Ga ages were obtained during four analytical sessions from slightly different locations near the centre of the grain on surfaces 2 – 5 (Fig. 1; Fig. DR1). The $^{207}\text{Pb}/^{206}\text{Pb}$ ages range from 4486 ± 17 to 4425 ± 55 Ma (1σ) and are concordant within analytical uncertainty (Table DR1). These six analyses are statistically indistinguishable and yield a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4464 ± 15 Ma (2σ , MSWD = 1.01) and a concordia age of 4463 ± 17 Ma (2σ , MSWD of concordance and equivalence = 0.82; Fig. 2). Other analyses on domains with fine lamellae or homogeneous structure yielded concordant to slightly discordant ages ranging from 4374 ± 77 to 4227 ± 51 Ma, and two concordia ages were calculated: 4369 ± 30 Ma and 4277 ± 16 Ma (2σ , MSWD of concordance and equivalence = 0.46 and 1.3, respectively; Fig. 2). Analyses on, or partly overlapping, the CL-bright recrystallized domains and the CL-dark rims yielded $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 4130 – 3860 Ma with variable degrees of discordance. Except for 4 spots located on, or mixed with, the CL-dark core and rim, other analyses on grain 14041 reveal low U (average 28 ppm) and Th (average 3 ppm) contents, as well as low Th/U ratios (average 0.12; Table DR1), relative to typical Hadean zircons from the Jack Hills (Cavosie et al., 2007). Most analyses have higher uncertainties in $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ ratios and ages than standard ion microprobe analyses of ancient zircons. This is due to large within-run

variations of ^{207}Pb and, to a lesser extent, ^{206}Pb counts (Fig. DR3), implying heterogeneous distribution of Pb isotopes with increase in sputtering depth.

Unsupported ancient Pb* revealed by ion imaging

Because the 4463 ± 17 Ma concordia age would make this zircon significantly older than any previously recorded from Earth (Wilde et al., 2001; Valley et al., 2014), the Moon (Nemchin et al., 2009), or Mars (Humayun et al., 2013), it is essential to evaluate whether it represents the crystallization age of the grain. Scanning ion imaging and dating were therefore carried out over a $70 \mu\text{m} \times 70 \mu\text{m}$ area using a CAMECA IMS1280 ion microprobe (see DR1). This technique (Bellucci et al., 2016; Kusiak et al., 2013; Whitehouse et al., 2014) enables not only mapping of the U-Th-Pb isotopes with high spatial-resolution down to $\sim 2 \mu\text{m}$ but also calculation of $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages for any regions of interest (see DR1). The results show that abundant PEDs occur as $\leq 5 \mu\text{m}$ ‘hotspots’ or as larger patches (Fig. 3; Fig. DR4). The distribution of these hotspots and patches seems to follow the boundary between the recrystallized domain and the domain with fine lamellae, as well as the conjunction of different sectors within the domain with fine lamellae (Fig. 1C; Fig. 3). High Pb* concentration is also present in the CL-dark (high-U) core of the grain. However, line scans show that, unlike the core, the elevated Pb* in the PEDs is not supported by elevated U, and ^{207}Pb is significantly enriched compared to ^{206}Pb , resulting in very high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios and extremely old $^{207}\text{Pb}/^{206}\text{Pb}$ ages (Fig. 4A). Age calculations for $\sim 5 \mu\text{m}$ ellipses located on the PEDs yielded 4.5 – 5.1 Ga $^{207}\text{Pb}/^{206}\text{Pb}$ ages, which mostly have even older $^{206}\text{Pb}/^{238}\text{U}$ ages (i.e. are reversely discordant) but intercept the concordia because of the

large $^{206}\text{Pb}/^{238}\text{U}$ uncertainties (Fig. 3C; Fig. 4B; Table DR2). Ellipses similar to the SHRIMP spots that include, or partly overlap, the PEDs yielded 4500 – 4400 Ma apparently concordant ages (Fig. 3C; Fig. 4B; Table DR2), establishing that the >4.4 Ga SHRIMP spot ages resulted from incorporation of these PEDs.

To further constrain the growth and recrystallization history of grain 14041, large polygons that broadly follow individual domains seen in CL images were selected for age calculations from the ion images (Fig. 3D; Table DR2). The CL-dark core yielded a concordant age of 4.32 Ga, consistent with the results for the ellipses. The domains with fine lamellae or homogeneous structure yielded concordant or nearly concordant ages of 4.29 – 4.27 Ga, although one homogeneous domain yielded a slightly younger concordant age (4.20 Ga), which is consistent with 4.22 – 4.20 Ga concordant ages obtained from ion images of the CL-bright domains surrounding the core and near the tip (Fig. 3D; Fig. 4B). The outer rim has a concordant age of 3.89 Ga. These data indicate that this grain probably crystallized between 4.32 and 4.27 Ga, consistent with the 4277 ± 16 Ma concordia age from the majority of SHRIMP analyses. This was probably followed by complex recrystallization between 4.2 and 3.8 Ga, resulting in local redistribution of Pb* within the crystal. The areas with the PEDs also yielded consistent ages, suggesting that they formed in a closed system within individual domains.

DISCUSSION AND CONCLUSION

The 4463 ± 17 Ma concordia age obtained in this study would have significant implications for the timing of major events that shaped the early Earth if interpreted as the crystallization age of the zircon, with wider implications for the Moon and other terrestrial planets. However, from the characteristics of the ion microprobe spot analyses and the ion images, we consider that the >4.4 Ga ages from this grain resulted from local enrichment of ancient radiogenic Pb and are thus geologically meaningless. Evidence for ancient Pb* mobilization from ion microprobe spot analyses from this and other studies (Kusiak et al., 2013; Whitehouse et al., 2014) includes: 1) large within-run variations of ^{207}Pb and ^{206}Pb counts from cycle to cycle (Fig. DR2), resulting in higher analytical uncertainties than in standard analyses; 2) large within-grain variations of apparent $^{207}\text{Pb}/^{206}\text{Pb}$ ages even for the same domains or same spot locations on different surfaces; and 3) reverse discordance of at least some analyses, especially the oldest ones. Scanning ion images confirm the heterogeneous distribution of Pb* and demonstrate that the >4.4 Ga SHRIMP ages result from incorporation of PEDs.

The formation mechanism of PEDs in zircon remains elusive. Recent ion image (Whitehouse et al., 2014), atom probe (Valley et al., 2014; Peterman et al., 2016) and TEM (Kusiak et al., 2015; Whitehouse et al., 2017) results reveal that most PEDs occur as 10–30 nm spheres or clusters in zircons of different ages, but their Pb* concentration is extremely variable. Several mechanisms have been proposed for their formation,

including: 1) volume diffusion of Pb* through crystalline zircon during a later thermal overprint into nanoclusters related to α -recoil damage (Valley et al., 2014); 2) deformation-induced trace element redistribution into migrating dislocations and misorientation boundaries (Peterman et al., 2016; Piazzolo et al., 2016; Reddy et al., 2016; Timms et al., 2011); and 3) metallic Pb nanospheres trapped as melt inclusions due to thermal annealing of interconnected radiation-damage (Kusiak et al., 2015; Whitehouse et al., 2017). The Pb nanoclusters formed by the first process have relatively low Pb* concentrations (<0.2 atom%) and are homogeneously distributed, so cannot explain the spurious ages and the compromised precision of ion microprobe spot analyses. EBSD mapping (Fig. DR2) indicates that deformation (mechanism 2) can also be excluded. The third mechanism is also unlikely because the calculated α -decay dose, and thus degree of radiogenic damage, of grain 14041 ($0.54 - 0.88 \times 10^{15}$ /mg at present, $0.12 - 0.20 \times 10^{15}$ /mg at 3.8 Ga) is much lower than those for the grains from which metallic Pb nanospheres were reported ($\geq 1 \times 10^{15}$ /mg) (Kusiak et al., 2015; Whitehouse et al., 2017). The fact that most PEDs in grains 14041 seem to follow the margin of the recrystallized domains suggests that mobilization of incompatible elements (including Pb*) at the recrystallization front, enhanced by fluid infiltration during metamorphism (Geisler et al., 2007), may be a more likely process for the formation of the PEDs in grain 14041.

Regardless of the exact formation mechanism, PEDs in zircons documented in this and previous studies (Kusiak et al., 2015, 2013; Valley et al., 2014; Whitehouse et al.,

217 2014; Peterman et al., 2016; Whitehouse et al., 2017) represent Pb* locally
 218 concentrated during a later overprinting event. Some of the conventional spot analyses,
 219 as well as various regions selected from ion images, are a mixture of concentrated
 220 ancient Pb* and Pb* produced by subsequent U decay. Theoretically, the isotopic
 221 composition of ancient Pb* (I_0) can be calculated, and the time of Pb* mobilization and
 222 the proportion of PEDs involved in mixing can be modelled (Fig. 4C – 4D, see DR1).
 223 Assuming a crystallization age of ~4.3 Ga for grain 14041 (U = 30 ppm), as constrained
 224 by several ion images and spot analyses, 4.5 – 4.4 Ga concordant ages with ~3% errors
 225 (1σ , average for SHRIMP analyses) can be produced by mixing with ~0.0015 vol.%
 226 (assuming pure metallic Pb (Kusiak et al., 2015; Whitehouse et al., 2017)) or ~0.3 vol. %
 227 (assuming ~4,600 ppm Pb for Pb*-rich nanoclusters (Valley et al., 2014)) of PEDs
 228 formed during a ~3.8 Ga or older event (Fig. 4D). This also explains the along-
 229 concordia spread of ion microprobe ages. Mixing with PEDs formed during later events,
 230 e.g., the ~2.65 Ga metamorphism recorded by some inclusions in Jack Hills zircons
 231 (Rasmussen et al., 2011), would produce significantly discordant ages (Fig. 4D). The
 232 modelled volume percent of PEDs corresponds to about ~1100 metallic Pb nanospheres
 233 (Kusiak et al., 2015; Whitehouse et al., 2017) or $\sim 2.3 \times 10^5$ Pb-rich nanoclusters (Valley
 234 et al., 2014) (assuming 20 nm in diameter) in an ion microprobe spot (assuming 20 μm
 235 circular spot, 1 μm in depth), or a density of ~3.6 or ~720 per μm^3 , respectively. The
 236 fact that the precision of the ion microprobe spot analyses was compromised implies
 237 that the distribution of these nanoclusters or nanospheres is heterogeneous at the
 238 micrometer scale. Assuming better precision for uncompromised ion microprobe

analyses (e.g., 1% for $^{207}\text{Pb}/^{206}\text{Pb}$ and 2% for $^{206}\text{Pb}/^{238}\text{U}$, 2σ), statistically concordant >4.4 Ga ages can still be obtained with the same proportion of PEDs (inset in Fig. 4D).

This case study highlights that apparently concordant U-Pb ages up to 200 Ma older than the crystallization ages can be obtained from ancient zircon grains during ion microprobe spot analysis. This is an important finding because the dating of the oldest zircons has significant implications for crustal evolution on Earth, as well as on the other terrestrial planets and the Moon. Specifically, a single concordant age, or even a concordia age calculated from multiple concordant analyses, should now be treated with caution. Scanning ion imaging and dating (Bellucci et al., 2016) provides a powerful tool to verify Pb* redistribution and to extract meaningful ages from such zircons, provided Pb* redistribution occurred within a closed system. We recommend it becomes a routine technique in any future studies of ancient zircons.

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FIGURE CAPTIONS

Figure 1. Selected cathodoluminescence images and SHRIMP ages. Ages shown are $^{207}\text{Pb}/^{206}\text{Pb}$ ages (in Ma) with 1σ errors and discordance (in brackets). See Fig. DR1 and Table DR1 for details. Letters in italics refer to internal structures described in the text: ab – annular band; c – core; fl – fine lamella; hm – homogeneous domain; rc – recrystallized domain; r – rim. Note that analyses 30 – 34 are on surface 4 (Supplementary Fig.S1d), but are superimposed on surface 5 in C to compare spot positions. Dashed square in (C) shows the area of scanning ion imaging. Scale bars are 20 μm .

Figure 2. Terra–Wasserburg diagram showing SHRIMP U-Pb ages. Note the along-concordia spread and large errors in the data. Data are colour-coded according to $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Three concordia ages (thick black ellipses) were calculated based on consistence and concordance of the ages (dashed green ellipses were not included in the calculation). The dashed blue line is the discordia of a 4.3 Ga zircon that experienced 3.8 Ga Pb* mobilization.

Figure 3. Selected scanning ion images and calculated $^{207}\text{Pb}/^{206}\text{Pb}$ ages. A: ^{206}Pb image. B: ^{207}Pb image. Note the hotspots and patches of elevated ^{207}Pb and ^{206}Pb . Dashed line (abc) identifies the position of the profile shown in Fig.4A. C: ^{207}Pb image showing calculated $^{207}\text{Pb}/^{206}\text{Pb}$ ages (in Ma) for $\sim 5\ \mu\text{m}$ (solid white) and ~ 20

μm (dashed yellow) ellipses that locate on, or partly overlap, the hotspots and patches. D: ^{207}Pb image showing calculated $^{207}\text{Pb}/^{206}\text{Pb}$ ages for large areas that broadly follow individual domains (see Fig. 1C). Scale bars are 20 μm .

Figure 4. Ion imaging dating and modelling. A: line scan through the CL-dark core and the PEDs showing that, unlike the core, the elevated ^{207}Pb and ^{206}Pb counts and high $^{207}\text{Pb}/^{206}\text{Pb}$ ratios in the PEDs are not supported by elevated U. See Fig. 3A and 3B for location. **B:** Terra-Wasserburg diagram showing calculated U-Pb data for different regions of interest shown in Fig. 3C and 3D. **C:** calculated $^{207}\text{Pb}/^{206}\text{Pb}$ ratio (I_0) of ancient Pb^* plotted as a function of duration between the time of zircon crystallization (t_1) and Pb^* mobilization (t_2). The inset shows the definition of t_1 , t_2 and I_0 in the Terra-Wasserburg diagram (Tera and Wasserburg, 1972). Dashed line indicates 4.4 Ga apparent $^{207}\text{Pb}/^{206}\text{Pb}$ age. Diamond shows the $^{207}\text{Pb}/^{206}\text{Pb}$ ratio measured by atom probe in a $\sim 4,370$ Ma zircon overprinted at ~ 3.4 Ga ((Valley et al., 2014)); filled cycles show I_0 values used for the modelling in D with $t_2 = 3.8$ Ga (orange) and $t_2 = 2.65$ Ga (green). **D:** modelled U-Pb ages resulting from mixing of ancient Pb^* (in PEDs) of a 4.3 Ga zircon (yellow star) that experienced Pb mobilization at 3.8 Ga (orange) and 2.65 Ga (green), and Pb^* produced by U decay after Pb mobilization. Numbers indicate modelled volume percent of PEDs assuming metallic Pb (100%) for the PEDs (Kusiak et al., 2015; Whitehouse et al., 2017). Error ellipses are average values of SHRIMP analyses (3.0% for $^{207}\text{Pb}/^{206}\text{Pb}$ and 2.7% for $^{206}\text{Pb}/^{238}\text{U}$, 1σ). Inset shows the same modelling

393 for $t_2 = 3.8$ Ga but with higher precision (1% for $^{207}\text{Pb}/^{206}\text{Pb}$ and 2% for $^{206}\text{Pb}/^{238}\text{U}$,
394 2σ).

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396

397 1GSA Data Repository item 201Xxxx, DR (Methods), Figure DR1 – DR4
398 (supplementary figures), Tables DR1 (SHRIMP data) and Table DR2 (scanning ion
399 imaging data), is available online at www.geosociety.org/pubs/ft20XX.htm, or on
400 request from editing@geosociety.org or Documents Secretary, GSA, P.O. Box 9140,
401 Boulder, CO 80301, USA.

Figure1

Figure2

[Click here to download Figure Fig2-14041-concordia.pdf](#)

Figure3

Figure4

[Click here to download Figure4-ion imaging ages.pdf](#)

DR1: METHODS

SHRIMP U-Th-Pb spot analyses

Zircon grains were extracted from a meta-conglomerate sample from the W74 site at Jack Hills using a high voltage pulsed power fragmentation system (SelFrag), and were mounted along with standard zircons in epoxy resin. The mount was polished, gold-coated, and imaged under reflected and transmitted light and by scanning electron microscopy. Cathodoluminescence (CL), backscattered electron (BSE) and Electron Backscatter Diffraction (EBSD) images were collected using a TESCAN MIRA3 scanning electron microscope at the Electron Microscopy and Microanalysis Facility (John de Laeter Centre), Curtin University, Perth. Electron backscatter patterns (EBSPs) were collected in orthogonal grids (maps). EBSD mapping were undertaken with a 20 kV acceleration voltage and step size of 0.5 μm using a Nordlys Nano high-resolution detector and Oxford Instruments Aztec acquisition system, and the data were processed with Channel 5.12 software. In-situ zircon U–Th–Pb analyses were carried out in seven sessions (Nov. 2016 – Jun. 2017) using a SHRIMP II ion microprobe at Curtin University, following standard procedures described in (De Laeter and Kennedy, 1998). The mount was re-polished after each session (except between sessions 2 and 3) to remove previous sputtering pits (1 – 2 μm), and optical and/or CL/BSE images were taken before and after each session to precisely determine each spot position and check the pits for cracks or inclusions. A primary O^{2-} ion beam with intensity of ~ 2 nA and spot size of ~ 20 μm was used. Each analysis site was rastered for 120 seconds to remove

surface contamination. Six scans (seven for session 5) were made for each spot analysis. Standard zircon BR266 ($^{206}\text{Pb}/^{238}\text{U}$ age = 559 Ma, U = 909 ppm, (Stern, 2001)) or CZ3 ($^{206}\text{Pb}/^{238}\text{U}$ age = 563.9 Ma, U = 550 ppm, (Nasdala et al., 2004)) was analyzed for every 3 – 4 unknowns to calibrate Pb/U isotopic fractionation and elemental concentrations. The assigned 1-sigma external error of the Pb/U ratio for the standard zircons was between 0.5 and 1.4 % during this study. A secondary standard, OGC or OG1, was analyzed as an unknown and yielded a weighted mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3467.0 ± 2.0 Ma (2σ , MSWD = 0.98, $n = 29$), consistent with the ID-TIMS age (3465.4 ± 0.6 Ma, (Stern et al., 2009)). BR266 and CZ3 analyzed as unknowns yielded weighted mean $^{206}\text{Pb}/^{238}\text{U}$ ages of 559.0 ± 2.9 Ma ($n = 9$, MSWD = 0.95) and 565.3 ± 3.1 Ma ($n = 10$, MSWD = 1.01), respectively. Common lead was corrected using the measured ^{204}Pb and the present-day common lead composition given by (Stacey and Kramers, 1975). Data reduction was performed using SQUID 2.5 ((Ludwig, 2009)). Data were plotted using Isoplot 4.15 ((Ludwig, 2008)).

Scanning ion imaging and dating

Scanning secondary ion imaging and U-Pb dating were carried out using a CAMECA IMS1280 ion microprobe at the NordSIM Facility, Swedish Museum of Natural History, Stockholm. Detailed analytical procedure is described in (Bellucci et al., 2016; Kusiak et al., 2013; Whitehouse et al., 2014), and only a brief outline is given below. Prior to ion imaging, the mount was re-polished and gold coated. The selected area was first rastered for 10 minutes using a ~ 20 μm , ~ 10 nA O_2^- primary beam to remove surface gold coating and enhance secondary ion yield. A ~ 5 μm primary beam with a beam

current of ~ 250 pA was then rastered over a $\sim 70 \times 70$ μm area on the sample surface. The secondary ions were processed using the dynamic transfer optical system (DTOS) that deflects the ions back onto the optical axis of the instrument, allowing acquisition of both position information and ion intensity without compromising mass resolution capability. The secondary ions of ^{207}Pb , ^{206}Pb , ^{204}Pb and ^{208}Pb were measured simultaneously in multi-collector mode using low-noise (<0.003 cps) ion-counting multipliers, while $^{96}\text{Zr}^{18}\text{O}$, ^{238}U , $^{238}\text{U}^{16}\text{O}_2$ and $^{232}\text{Th}^{16}\text{O}$ were measured in subsequent peak-hopping mode. The integration time was 12s for Pb isotopes, 5s for ^{238}U , and 2s for other masses. Each image was integrated over 60 cycles. As with conventional analysis, the sample images were bracketed by multiple images of the standard zircon 91500 ($^{206}\text{Pb}/^{238}\text{U}$ age = 1065 Ma, (Wiedenbeck et al., 1995)). Ion images were processed using the CAMECA WinImage2 software, where various regions of interest (ROIs) were defined and isotopic ratios were calculated for each ROI. U/Pb mass fractionation was corrected by fitting a power law Pb/U – UO_2/U correction curve for each ROI using data from the bracketing 91500 analyses for the same ROI. Common Pb correction was neglected because the more precise spot analyses indicate that common Pb is negligible for most parts of the grain. The ^{204}Pb image also shows insignificant ^{204}Pb counts (Supplementary Fig. S3d). The higher apparent $f^{206}\text{Pb}_c$ from the imaging data (average 1.33% compared to 0.06% for the spot analysis) likely resulted from relatively much lower counts of ^{207}Pb and ^{206}Pb in imaging mode, and in any case corresponds to $<0.5\%$ correction to the $^{207}\text{Pb}/^{206}\text{Pb}$ age for most ROIs, insignificant compared to the precision of the current method. One 91500 and one OGC zircon were processed as unknowns

and yielded a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 1067 ± 22 Ma (2σ , MSWD = 0.47, $n = 37$) and $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3475 ± 12 Ma (2σ , MSWD = 1.3, $n = 30$), respectively.

Isotopic modelling

The $^{207}\text{Pb}/^{206}\text{Pb}$ ratios of ancient Pb^* (I_0) can be calculated using the following equation:

$$\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}}\right)_{I_0} = \frac{^{235}\text{U}}{^{238}\text{U}} \cdot \frac{(e^{\lambda_{235}t_1}-1)-(e^{\lambda_{235}t_2}-1)}{(e^{\lambda_{238}t_1}-1)-(e^{\lambda_{238}t_2}-1)} = \frac{1}{137.88} \cdot \frac{e^{\lambda_{235}t_1}-e^{\lambda_{235}t_2}}{e^{\lambda_{238}t_1}-e^{\lambda_{238}t_2}} \quad (1)$$

where t_1 and t_2 are the age of zircon crystallization and Pb^* mobilization, respectively; λ_{235} and λ_{238} are the decay constants of ^{235}U and ^{238}U , respectively. This ratio corresponds to the intercept of a discordia through t_1 and t_2 with the ordinate in the Terra-Wasserburg diagram (Tera and Wasserburg, 1972) (Fig. 4c). The $^{207}\text{Pb}/^{206}\text{Pb}$ ratios (1.2 ± 0.05) of Pb^* -rich nanoclusters measured by atom probe in a ~4370 Ma zircon overprinted at 3.4 Ga ((Valley et al., 2014)) are identical to the calculated value (1.1998), confirming Pb^* redistribution in a closed system (zircon lattice). According to this equation, over 4.4 Ga apparent $^{207}\text{Pb}/^{206}\text{Pb}$ ages can be produced in zircons as young as 3.0 Ga that experienced Pb^* enrichment immediately following crystallization (Fig. 4c). Likewise, ancient Pb^* concentrated in a 4370 Ma detrital zircon of the Jack Hills would have $^{207}\text{Pb}/^{206}\text{Pb}$ ratios as high as 1.73, corresponding to an apparent $^{207}\text{Pb}/^{206}\text{Pb}$ age of 6.0 Ga (Fig. 4c). The $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{238}\text{U}/^{206}\text{Pb}$ ratios produced by mixing of PEDs and the matrix zircon after PED formation can be calculated using the following equation:

$$\left(\frac{^{207}\text{Pb}}{^{206}\text{Pb}}\right)_{\text{mixed}} = \frac{^{235}\text{U} \cdot (e^{\lambda_{235}t_2}-1)(1-p) + C \cdot I_0 / (1+I_0) \cdot p}{^{238}\text{U} (e^{\lambda_{238}t_2}-1)(1-p) + C \cdot 1 / (1+I_0) \cdot p} \quad (2)$$

$$\left(\frac{^{238}\text{U}}{^{206}\text{Pb}}\right)_{\text{mixed}} = \frac{^{238}\text{U} \cdot (1-p)}{^{238}\text{U} (e^{\lambda_{238}t_2}-1)(1-p) + C \cdot 1 / (1+I_0) \cdot p} \quad (3)$$

where C and p are Pb^* concentration and proportion (volume percent) of PEDs,

respectively; ^{235}U and ^{238}U are present-day contents of U isotopes in the zircon.

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Supplementary figures

Fig. DR1. SEM and optical images of grain 14041. (a) – (e) CL images showing internal structures, SHRIMP analytical sites and $^{207}\text{Pb}/^{206}\text{Pb}$ ages (in Myr) with 1σ

errors and discordance (in brackets) on five different surfaces with increasing polishing depth. Spots are numbered to match data presented in Table S1 and colour-coded according to $^{207}\text{Pb}/^{206}\text{Pb}$ ages. Note the changing internal structures with increasing polishing depth. See text for descriptions. (f) BSE image of surface 3; (g) reflected light photograph of surface 4; (h) transmitted light photograph of surface 4. A fracture is visible on surfaces 3 – 5 (c – f, h), but is not present on surfaces 1 and 2 (a, b). Analyses intentionally located on the fracture in (d) yielded comparable results with those on other parts of the grain. Scanning ion images show no enrichment or depletion of U, Th or Pb isotopes along the fracture (Fig 3 and Fig S3). These observations indicate that this fracture was exposed during polishing and does not affect the U-Pb isotopic system. Scale bars are 20 μm .

Fig. DR2. EBSD data of surface 5. (a) texture component map; (b) local misorientation map; (c) pole figure (equal area projection, lower hemisphere). The grain shows little ($<2^\circ$) internal deformation except for a small portion at the margin and the centre. The straight lines are scratches induced during polishing.

Fig. DR3. Within-run variations of the ^{207}Pb , ^{206}Pb , ^{238}U and ^{248}ThO counts and $^{207}\text{Pb}/^{206}\text{Pb}$ ratio relative to the first cycle for selected analyses, showing large variations of ^{207}Pb and ^{206}Pb counts and $^{207}\text{Pb}/^{206}\text{Pb}$ ratios for the >4.4 Ga analyses compared to normal analyses (e.g., OGC-4), whereas ^{238}U and ^{248}ThO remain relatively uniform. This implies heterogeneous distribution of radiogenic Pb as the sputtering depth increases for each cycle (by $\sim 0.1 \mu\text{m}$). Numbers in (b) – (d) show apparent $^{207}\text{Pb}/^{206}\text{Pb}$ ages (in Myr) for each cycle.

Fig. DR4. Scanning ion images of (a) ^{238}U ; (b) $^{232}\text{Th}^{16}\text{O}$; (c) ^{208}Pb and (d) ^{204}Pb for the 70 μm x 70 μm area investigated using the CAMECA IMS1280. Scale bars are 20 μm.

Table DR SHRIMP U-Th-U isotopic data and ages for the detrital zircon grain (14041) with >4400 Myr apparent

Spot Name	U	Th	Th/U	$f^{206}\text{Pb}_c$	Isotopic ratios (^{204}Pb corrected)					
	ppm	ppm	%		$^{238}\text{U}/^{206}\text{Pb}$	1 σ	$^{207}\text{Pb}/^{206}\text{Pb}$	1 σ	$^{207}\text{Pb}/^{235}\text{U}$	1 σ
session 1 (Nov 14, 2016)										
14041.1	31	3	0.09	-0.27	1.15	2.29	0.5174	3.77	62.3	4.41
14041.2	30	3	0.08	-0.15	1.08	3.72	0.4628	5.96	59.1	7.03
14041.3	46	11	0.24	0.05	1.30	4.26	0.4230	2.66	44.9	5.02
14041.4	17	2	0.11	0.00	1.12	3.31	0.5131	0.91	63.2	3.44
session 2 (Dec 11, 2016)										
14041.4-1	25	3	0.11	0.21	1.15	1.88	0.4496	0.70	53.8	2.00
14041.5	25	2	0.09	0.00	1.02	1.84	0.5143	2.58	69.8	3.17
14041.6	25	3	0.13	0.00	1.00	1.88	0.5456	2.46	75.1	3.09
14041.7	25	2	0.09	-0.11	1.02	2.88	0.5475	5.27	74.2	6.01
14041.8	26	2	0.08	0.14	1.13	1.79	0.5075	5.15	61.7	5.45
14041.9	23	2	0.11	-0.02	1.13	4.73	0.4448	5.20	54.4	7.03
14041.10	25	3	0.12	0.05	1.03	1.93	0.5170	2.29	69.4	3.00
session 3 (Jan 21, 2017)										
14041.11	23	3	0.11	0.14	1.11	2.22	0.5164	1.22	63.9	2.53
14041.12	31	3	0.10	0.04	1.15	2.19	0.5289	3.53	63.3	4.16
14041.13	22	2	0.09	0.40	1.21	3.71	0.4677	6.89	53.5	7.82
14041.14	95	187	1.97	1.12	3.34	4.66	0.5050	0.80	20.8	4.73
session 4 (Feb 05, 2017)										
14041.6R	39	6	0.14	-0.07	0.95	3.86	0.5838	0.74	84.7	3.93
14041.6R2	42	6	0.15	-0.08	0.99	2.16	0.5684	1.97	78.9	2.93
14041.6R3	41	6	0.15	0.00	1.01	2.17	0.5738	1.36	78.1	2.56
14041.7R	29	3	0.09	0.05	1.29	2.33	0.4070	3.85	43.6	4.50
session 5 (Mar 12, 2017)										
14041.15	23	3	0.15	0.13	1.12	2.11	0.4996	3.05	61.7	3.71
14041.16	21	2	0.11	0.03	1.07	2.23	0.5142	1.79	66.5	2.86
14041.17	25	3	0.11	-0.02	1.01	2.07	0.5909	1.14	80.3	2.36
14041.18	30	3	0.09	-0.02	1.05	2.99	0.5333	3.88	70.2	4.90
14041.19	31	3	0.09	0.07	1.07	2.01	0.4953	3.44	64.1	3.99
14041.20	24	3	0.13	-0.04	1.14	2.26	0.5130	4.39	62.3	4.94
14041.21	30	3	0.12	0.00	1.01	3.24	0.5403	2.43	73.5	4.05
14041.22	41	3	0.08	0.14	1.17	3.08	0.4243	1.78	50.0	3.56
14041.23	25	4	0.15	0.17	1.05	2.08	0.5025	1.91	66.2	2.82
14041.24	20	2	0.09	-0.14	1.41	2.32	0.3864	0.92	37.9	2.49
14041.25	134	714	5.33	0.28	3.05	1.44	0.3996	1.20	18.1	1.88
session 6 (May 27, 2017)										
14041.27	22	34	1.54	0.21	1.24	2.07	0.4548	0.93	50.7	2.27
14041.29	24	3	0.12	0.12	1.05	1.91	0.5071	3.61	66.8	4.08
14041.30	65	18	0.27	-0.03	1.12	3.70	0.5114	6.13	62.9	7.16
14041.31	22	3	0.14	-0.04	1.02	2.09	0.5733	4.53	77.2	4.99
14041.32	26	2	0.08	-0.09	1.18	7.44	0.4220	7.42	49.2	10.51
14041.33	29	4	0.15	0.04	1.02	2.09	0.5413	1.50	73.2	2.58
14041.34	33	5	0.16	0.00	1.07	1.97	0.5136	1.63	66.2	2.55
session 7 (Jun 04, 2017)										
14041.35	29	5	0.16	0.07	1.00	1.88	0.5668	3.74	78.4	4.18
secondary standard										
OGC-1.1	296	295	1.00	0.00	1.47	1.37	0.2986	0.24	28.1	1.39

OGC-1.2	147	105	0.71	0.01	1.48	1.46	0.2999	0.35	27.9	1.50
OGC-2.1	131	60	0.46	0.01	1.43	1.48	0.2996	0.35	28.8	1.52
OGC-3.1	170	115	0.68	0.04	1.45	1.66	0.3006	0.32	28.6	1.69
OGC-4	179	133	0.74	0.01	1.40	1.42	0.2999	0.46	29.5	1.49
OGC-5.1	263	243	0.92	0.02	1.42	1.36	0.2979	0.36	28.9	1.41
OGC-6.1	156	78	0.50	0.03	1.44	1.42	0.3002	0.31	28.8	1.45
OGC-7.1	266	180	0.68	0.01	1.42	1.36	0.2988	0.22	29.0	1.38
OGC-8.1	156	67	0.43	0.01	1.43	1.42	0.2990	0.29	28.9	1.45
OGC-8.2	146	64	0.44	0.02	1.40	1.43	0.2988	0.57	29.4	1.54
OGC-4	296	242	0.82	0.01	1.43	0.74	0.2975	0.46	28.7	0.87
OGC-1	168	123	0.73	0.00	1.45	0.83	0.2985	0.32	28.3	0.89
OGC-3	153	72	0.47	-0.01	1.43	0.87	0.2995	0.66	28.8	1.09
OGC-5	123	61	0.49	-0.02	1.45	0.94	0.2996	0.38	28.5	1.01
OGC-7	133	96	0.72	0.00	1.46	0.95	0.3002	0.40	28.4	1.03
OGC-2	179	153	0.86	-0.01	1.44	0.84	0.3008	0.33	28.8	0.90
OGC-6	144	103	0.71	-0.01	1.49	0.91	0.3019	0.59	27.9	1.08
OGC-7	262	263	1.00	0.01	1.44	0.73	0.2985	0.27	28.5	0.78
OGC-8	178	161	0.91	0.00	1.46	0.91	0.2996	0.34	28.3	0.97
OGC-9	131	54	0.42	0.04	1.49	0.90	0.3005	0.38	27.9	0.98
OG1-1.3	193	76	0.40	0.04	1.64	0.88	0.2937	0.31	24.7	0.94
OG1-2.3	108	57	0.53	0.03	1.47	1.08	0.2985	0.43	28.0	1.17
OG1-3.2	154	59	0.39	-0.02	1.43	0.93	0.2990	0.34	28.8	0.99
OG1-3.3	193	92	0.48	0.00	1.43	0.91	0.2999	0.33	28.9	0.97
OG1-3.4	119	55	0.47	0.02	1.42	0.94	0.2990	0.34	29.0	1.00
OG1-1.1	133	52	0.39	-0.01	1.43	0.98	0.3015	0.37	29.0	1.05
OG1-1.2	161	81	0.50	0.01	1.43	0.93	0.2986	0.36	28.7	1.00
OG1-2.1	103	78	0.76	-0.01	1.40	1.10	0.2997	0.43	29.5	1.18
OG1-2.2	102	77	0.75	0.01	1.46	1.03	0.3017	0.42	28.4	1.11
OG1-3.1	180	61	0.34	-0.02	1.40	0.87	0.2980	0.32	29.3	0.93

Note:

$f^{206}\text{Pb}_c$: percent of common ^{206}Pb in total ^{206}Pb ; negative values indicate below detection;

ρ : error coefficient = percent error of $^{206}\text{Pb}/^{238}\text{U}$ /percent error of $^{207}\text{Pb}/^{235}\text{U}$

Disc.: Discordance = $(^{207}\text{Pb}/^{206}\text{Pb} \text{ age}/^{206}\text{Pb}/^{238}\text{U} \text{ age} - 1) \times 100$

ages from the Jack Hills (western Australia)

			Age (^{204}Pb corrected)				
$^{206}\text{Pb}/^{238}\text{U}$	1σ	ρ	$^{206}\text{Pb}/^{238}\text{U}$	1σ	$^{207}\text{Pb}/^{206}\text{Pb}$	1σ	Disc.
%							%
0.87	2.29	0.52	4045	69	4292	55	+8
0.93	3.72	0.53	4227	115	4127	88	-3
0.77	4.26	0.85	3683	120	3993	40	+10
0.89	3.31	0.96	4114	101	4279	13	+5
0.87	1.88	0.94	4028	56	4084	10	+2
0.98	1.84	0.58	4416	59	4283	38	-4
1.00	1.88	0.61	4461	60	4370	36	-3
0.98	2.88	0.48	4413	92	4374	77	-1
0.88	1.79	0.33	4075	54	4263	76	+6
0.89	4.73	0.67	4092	143	4068	77	-1
0.97	1.93	0.64	4381	61	4290	34	-3
0.90	2.22	0.88	4131	68	4289	18	+5
0.87	2.19	0.53	4028	66	4324	52	+9
0.83	3.71	0.47	3891	108	4143	102	+8
0.30	4.66	0.99	1687	69	4256	12	+68
1.05	3.86	0.98	4634	127	4468	11	-5
1.01	2.16	0.74	4490	70	4429	29	-2
0.99	2.17	0.85	4426	70	4443	20	+1
0.78	2.33	0.52	3705	66	3935	58	+8
0.90	2.11	0.57	4124	64	4240	45	+4
0.94	2.23	0.78	4266	69	4282	26	+1
0.99	2.07	0.88	4423	66	4486	17	+2
0.96	2.99	0.61	4322	94	4336	57	+0
0.94	2.01	0.50	4268	63	4227	51	-1
0.88	2.26	0.46	4070	68	4279	65	+7
0.99	3.24	0.80	4424	104	4355	36	-2
0.86	3.08	0.87	3984	91	3998	27	+0
0.96	2.08	0.74	4323	65	4248	28	-2
0.71	2.32	0.93	3460	62	3857	14	+13
0.33	1.44	0.77	1830	23	3908	18	+61
0.81	2.07	0.91	3819	60	4101	14	+9
0.96	1.91	0.47	4323	60	4262	53	-2
0.89	3.70	0.52	4109	112	4274	90	+5
0.98	2.09	0.42	4391	66	4442	66	+2
0.85	7.44	0.71	3949	220	3990	111	+1
0.98	2.09	0.81	4407	67	4358	22	-2
0.93	1.97	0.77	4255	61	4281	24	+1
1.00	1.88	0.45	4478	61	4425	55	-2
0.68	1.37	0.99	3354	36	3463	4	+4

0.68	1.46	0.97	3326	38	3470	5	+5
0.70	1.48	0.97	3414	39	3468	5	+2
0.69	1.66	0.98	3382	44	3473	5	+3
0.71	1.42	0.95	3469	38	3470	7	+0
0.70	1.36	0.97	3431	36	3459	6	+1
0.69	1.42	0.98	3401	38	3471	5	+3
0.70	1.36	0.99	3431	36	3464	3	+1
0.70	1.42	0.98	3426	38	3465	5	+1
0.71	1.43	0.93	3473	38	3464	9	-0
0.70	0.74	0.85	3419	20	3457	7	+1
0.69	0.83	0.93	3377	22	3462	5	+3
0.70	0.87	0.80	3409	23	3468	10	+2
0.69	0.94	0.93	3384	25	3468	6	+3
0.69	0.95	0.92	3371	25	3471	6	+4
0.69	0.84	0.93	3400	22	3474	5	+3
0.67	0.91	0.84	3311	24	3480	9	+6
0.69	0.73	0.94	3397	19	3462	4	+2
0.69	0.91	0.94	3368	24	3468	5	+4
0.67	0.90	0.92	3316	23	3473	6	+6
0.61	0.88	0.94	3070	22	3437	5	+13
0.68	1.08	0.93	3347	28	3462	7	+4
0.70	0.93	0.94	3419	25	3465	5	+2
0.70	0.91	0.94	3415	24	3470	5	+2
0.70	0.94	0.94	3432	25	3465	5	+1
0.70	0.98	0.94	3415	26	3478	6	+2
0.70	0.93	0.93	3412	25	3463	6	+2
0.71	1.10	0.93	3470	29	3469	7	-0
0.68	1.03	0.93	3358	27	3479	7	+4
0.71	0.87	0.94	3470	23	3460	5	-0

Table DR2 U-Th-Pb isotopic data and ages calculated from ion images

Sample/ spot #	U ppm	Th ppm	Th/U	f ₂₀₆ %	$\frac{^{238}\text{U}}{^{206}\text{Pb}}$	$\pm \sigma$ %	$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	$\pm \sigma$ %
<i>~5 μm ellipses</i>								
14041-1-1-1	24	2	0.09	0	1.133	14.59	0.6298	4.90
14041-1-1-2	25	3	0.14	3.07	0.871	20.54	0.6721	4.54
14041-1-1-3	23	3	0.14	0	0.889	17.40	0.7225	4.38
14041-1-1-4	21	4	0.17	0	1.059	21.01	0.7395	6.07
14041-1-1-5	24	3	0.14	0	0.781	20.80	0.6085	4.45
14041-1-1-6	19	3	0.16	0	1.051	24.80	0.6909	5.65
14041-1-1-7	14	2	0.14	2.46	0.960	19.17	0.6610	5.76
14041-1-1-8	13	2	0.12	2.37	0.710	29.56	0.6620	5.65
14041-1-1-9	12	2	0.13	0	0.498	29.20	0.8828	5.64
14041-1-1-10	16	2	0.14	0	0.746	23.57	0.6312	6.15
14041-1-1-11	142	62	0.43	1.04	1.144	19.90	0.5371	4.00
<i>SHRIMP spot-sized ellipese</i>								
14041-1-2-1	24	3	0.12	1.71	1.074	7.24	0.5670	1.81
14041-1-2-2	21	3	0.12	0.95	1.066	5.73	0.5616	1.92
14041-1-2-3	25	5	0.21	1.82	1.162	7.56	0.5651	2.63
14041-1-2-5	16	2	0.13	0.94	1.089	6.85	0.5601	2.19
14041-1-2-6	13	2	0.13	2.43	0.903	9.66	0.5969	2.66
14041-1-2-7	14	2	0.14	1.89	0.935	8.97	0.5577	2.40
14041-1-2-8	98	43	0.44	0.52	1.057	5.27	0.5236	1.70
<i>individual growth zone seen in CL</i>								
14041-1-4-1	21	4	0.19	2.27	1.131	6.25	0.4851	2.33
14041-1-4-2	17	5	0.32	3.33	1.086	9.88	0.5165	2.13
14041-1-4-3	15	2	0.12	2.11	1.117	3.34	0.4926	1.17
14041-1-4-4	16	2	0.15	3.75	1.226	7.21	0.3940	2.46
14041-1-4-5	90	41	0.46	0.27	1.031	4.23	0.5262	1.49
14041-1-4-6	23	3	0.12	1.33	1.156	3.51	0.5092	1.07
14041-1-4-7	21	5	0.23	1.05	1.156	5.94	0.4865	2.42

Note:

disc: discordance = $(^{207}\text{Pb}/^{206}\text{Pb} \text{ age} / ^{206}\text{Pb}/^{238}\text{U} \text{ age} - 1) \times 100$;

PED: Pb* (radiogenic Pb) enriched domain;

Data are not corrected for common Pb.

$\frac{^{207}\text{Pb}}{^{206}\text{Pb}}$	$\pm\sigma$	$\frac{^{206}\text{Pb}}{^{238}\text{U}}$	$\pm\sigma$	disc.	domain
4578	69	4078	457	12	PED
4672	64	4930	750	-5	PED
4776	63	4858	623	-2	PED
4809	87	4285	694	12	PED
4528	63	5316	801	-15	PED
4712	81	4311	831	9	PED
4648	81	4602	663	1	PED
4650	79	5664	1223	-18	PED
5062	80	7103	1398	-29	PED
4582	86	5480	935	-16	PED
4347	57	4049	628	7	core
4426	26	4242	229	4	PED
4412	28	4267	181	3	PED
4421	38	4002	229	10	PED
4408	32	4201	215	5	PED
4500	38	4806	336	-6	PED
4401	35	4688	306	-6	PED
4309	25	4292	167	0	core
4197	34	4084	192	3	
4289	31	4208	313	2	
4219	17	4121	102	2	
3887	37	3845	212	1	rim
4316	22	4371	136	-1	core
4268	16	4019	106	6	
4201	35	4019	180	5	