Geochronology of Hadean zircon grains from the Jack Hills, Western Australia
constrained by quantitative scanning ion imaging

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Abstract

Five Hadean (>4 Ga) aged zircon grains from the Jack Hills metasedimentary belt
have been investigated by a secondary ion mass spectrometry scanning ion image
technique. This technique has the ability to obtain accurate and precise full U-Pb
systematics on a scale <5 µm, as well as document the spatial distribution of U, Th and
Pb. All five of the grains investigated here have complex cathodoluminescence patterns
that correlate to different U, Th, and Pb concentration domains. The age determinations
for these different chemical zones indicate multiple reworking events that are preserved
in each grain and have affected the primary crystallized zircon on the scale of <10 µm,
smaller than conventional ion microprobe spot analyses. In comparison to the spot
analyses performed on these grains, these new scanning ion images and age
determinations indicate that almost half of the spot analyses have intersected several age
and chemical domains in both fractured and unfractured parts of the individual crystals.
Some of these unfractured, mixed domain spot analyses have concordant ages that are
inaccurate. Thus, if the frequency of spot analyses intersecting mixed domains here is
even close to representative of all other studies of the Jack Hills zircon population, it
makes the interpretation of any trace element, Hf, or O isotopic data present in the
literature tenuous. Lastly, all of the grains analysed here preserve at least two
distinguishable ²⁰⁷Pb/²⁰⁶Pb ages. These ages are preserved in core-rim and/or complex
internal textural relationships in unfractured domains. These secondary events took place
at ca. 4.3, 4.2, 4.1, 4.0, 3.7, and 2.9 Ga, which are coincident with previously determined
statistically robust age peaks present in this zircon population.

1. Introduction

Zircon (ZrSiO₄) is an extremely robust mineral, which hosts three, independent long-
lived radiogenic isotopic systems: ²³²Th→²⁰⁸Pb, ²³⁸U→²⁰⁶Pb, and ²³⁵U→²⁰⁷Pb. While

41 zircon readily incorporates the parent isotopes (Th and U), it includes very little to no
42 daughter product (Pb) making it a very reliable geochronometer. Therefore, in a perfect
43 setting, the chemical and physical robustness of the mineral would preserve the full U-Pb
44 and Th-Pb systematics and provide three accurate, concordant ages from three decay
45 chains within an individual mineral grain or even part of a grain. Additionally, when used
46 in conjunction with other isotopic or trace element systematics (i.e., Hf, O, Ti, and, rare
47 earth elements), zircon presents evidence by which to study the time resolved behavior of
48 crustal differentiation, temperature regimes, and the potential interaction with a
49 hydrosphere throughout Earth's history. The property for a zircon to have coupled
50 geochronology and other isotopic systematics is especially important in the Hadean eon
51 (> 4.0 Ga) on Earth, because there are few other proxies to understand crust formation
52 and crustal processes ongoing during that time (e.g., Bell et al., 2011, 2013, 2014,
53 Carvoise et al., 2005, 2006, Harrison et al., 2005, 2008, Kemp et al., 2010, Mojzsis et al.,
54 2001, Nemchin et al., 2006, Wilde, et al., 2001 and references therein). However, despite
55 the robust physical characteristics of zircon, these grains are still susceptible to
56 overprinting events postdating their original crystallization. In some cases, multiple
57 events can be preserved in individual grains, often resulting in complexities observed in
58 the U-Pb system. As a result, the complex U-Pb systematics of some individual zircon
59 grains has been interpreted to represent partial recrystallization, replacement, resetting,
60 and variable damage of the crystal lattice by radioactive decay. All of these post-
61 crystallization processes have the ability to affect the U-Pb and Th-Pb systems
62 differently, resulting in multiple types of discordance. Recent studies (e.g., Bellucci et al.,
63 2016, Kusiak et al., 2013a,b, Whitehouse et al., 2014) indicate that this variability and

64 mixing between U, Th, and Pb can occur on the scale of a few nanometers to several
65 micrometers. Consequently, the correct interpretation of U-Pb and Th-Pb chronology and
66 subsequent trace element or other isotopic information requires an understanding of
67 processes that might affect the chemistry and/or internal structure of zircon on an
68 appropriate scale. Understanding the internal heterogeneity of a single crystal is
69 especially important when combining multiple analyses in a single area of a potentially
70 heterogeneous grain.

71 Ancient zircon grains, like those from metasedimentary rocks in the Jack Hills region
72 of Western Australia, are the only direct source of information about the Hadean Earth
73 (>4.0 Ga) and its evolution. As a result, this zircon population has been extensively
74 investigated for more than a decade, generating vast datasets of U-Pb ages, Ti
75 thermometry, trace element concentrations, O and Hf isotope compositions (Bell et al.,
76 2011, 2013, 2014, 2016, Cavosie et al., 2005, 2006, Harrison et al., 2005, 2008, Kemp et
77 al., 2010, Mojzsis et al., 2001, Nemchin et al., 2006, Whitehouse et al., 2017, Wilde, et
78 al., 2001 and references therein). Despite the large amount of data, there are two
79 opposing views regarding the Hadean Earth. Light REE patterns, Ti thermometry in
80 zircon, heavy O isotope compositions, and some Hf isotope analyses have been used to
81 suggest that zircon crystallised from a granitic magma, which may have assimilated
82 sedimentary rocks that had interacted with surface water in a modern style plate tectonic
83 setting (Harrison et al., 2005, Hopkins et al., 2008, Peck et al., 2001, Wilde et al., 2001).
84 This point of view also implies presence of enriched crust that is rather similar to modern
85 continental crust. In contrast, there exists an alternate interpretation, based on the study of
86 Jack Hills zircon grains and other approaches (e.g., Shirey et al., 2008), that the Earth's

87 surface was far less temperate and had a basaltic crust that formed a stable lid for an
88 extended period of time, preventing modern-style subduction recycling (Coogan and
89 Hinton, 2006, Kamber et al., 2005, Kemp et al., 2010). Since both hypotheses are
90 supported from the study of zircon, their applicability to understanding the Hadean Earth
91 are explicitly contingent on the accuracy/concordance of the U-Pb and Th-Pb chronology
92 and chemical homogeneity for all other trace elements and isotopic information in the
93 areas analysed. This issue of grain scale heterogeneity is exemplified by the fact that the
94 Jack Hills zircon population appears to have been affected by both ancient and modern
95 Pb loss, the latter also accompanied by potential U loss/gain, and/or Th loss/gain. These
96 effects imply that each analysis in a zircon grain may encompass Pb that has evolved in
97 several different ways, making it impossible to demonstrate convincingly, which part of
98 the data set represents a primary magmatic signature without any later overprint.

99 This study aims to demonstrate a way to overcome this problem and better constrain
100 the accurate chronological history of Jack Hills zircon grains by analysing the spatially
101 resolved U-Th-Pb systematics in some already recognized ancient (>4 Ga) and complex
102 grains from the Jack Hills zircon population (ages determined earlier by conventional
103 SIMS spot analyses, Whitehouse et al., 2017). The cathodoluminescence (CL) features in
104 the grains here show a range of internal structures consistent with the complexity of the
105 Jack Hills population recorded in previous studies (e.g. Cavosie et al., 2005, Dunn et al.,
106 2005, Nemchin et al., 2006). The five selected zircon grains have been analysed here by a
107 Secondary Ion Mass Spectrometry (SIMS) scanning ion imaging technique (SII). This
108 technique provides chemical and isotopic imaging in 70 x 70 μm domains for U, Th, and
109 Pb, after which regions of interest (ROIs) can be assigned and full U-Pb systematics

obtained (after Bellucci et al., 2016). Similar SII investigations have been shown to be invaluable in understanding the micrometer distribution of some trace elements but have yet to be applied to chronology (i.e., Ti, Harrison and Schmidt, 2007). Therefore, the specific aims of this study are to: 1) visually compare the new scanning ion images with CL imaging to assess the viability of CL images in determining where to place conventional spot analyses; 2) visually and quantifiably evaluate the effects of ancient and/or recent U-Th-Pb mobility on U-Pb systematics; 3) compare the results from conventional spot analyses to the SII domains and explain mixing relationships and the effect it would have on geochronology performed with spot analyses; 4) assess the scale of age heterogeneities present; and 5) accurately determine the history of some of the most ancient terrestrial zircon grains available.

2. Analytical Methods

Five grains were chosen for analysis based on previously obtained CL images and initial U-Pb ages determined by conventional SIMS spot analyses (Figure 1). Additional CL and BSE images were collected using a Tescan MIRA3 FE-SEM at the Microscopy and Microanalysis Facility (John de Laeter Centre) at Curtin University in Perth, Western Australia. Images were collected at an acceleration voltage of 12 kV. Prior to scanning ion image acquisition, the zircon grains were prepared as mineral separates in an epoxy mount and were cleaned in mild acid and base washes followed by alternating ultrasonic baths of ethanol and distilled water. After the sample was cleaned it was coated with 30 nm of Au. Similar procedures were followed for the epoxy mount containing standard zircon grains.

All SIMS SII analyses were performed using a CAMECA IMS1280 large-geometry ion microprobe located at the NordSIMS facility, Swedish Museum of Natural History, Stockholm, Sweden, modified from those described by Bellucci et al., (2016), Kusiak et al. (2013a, b) and Whitehouse et al. (2014). Prior to the start of each SII analysis, an area of 80 x 80 μm was sputtered for 10 minutes using a $\sim 20\ \mu\text{m}$, $\sim 10\ \text{nA}$ O_2^- primary beam to effectively remove surface gold coating and minor residual surface contamination. To obtain high spatial resolution for the ion images of the standards and unknowns, a 50 μm primary beam aperture was used, resulting in a projected beam diameter of $\sim 5\ \mu\text{m}$ on the sample surface and a beam current of $\sim 250\ \text{pA}$. This spot size, which corresponds to a surface area of $20\ \mu\text{m}^2$, defines the minimum spatial resolution at which the technique can confidently resolve individual, non-mixed zircon chemical domains. The secondary ion beam from the rastered area was processed using the dynamic transfer optical system (DTOS), a synchronized raster in the transfer section of the instrument that deflects the ions back onto the ion optic axis of the instrument regardless of their original point of sputtering from the sample, allowing both image acquisition and collection of secondary ions at high mass resolution, in this case 4860 $\text{M}/\Delta\text{M}$. Secondary ions of ^{204}Pb , ^{206}Pb , ^{207}Pb , and ^{208}Pb were measured simultaneously using the multi-collector array, while ions of $^{90}\text{Zr}_2^{16}\text{O}$, ^{238}U , $^{232}\text{Th}^{16}\text{O}$, and $^{238}\text{U}^{16}\text{O}_2$ were measured in subsequent peak hops. As with conventional SIMS U-Pb spot analyses in zircon, oxygen was introduced into the sample chamber increasing its pressure to $\sim 2 \times 10^{-5}$ mbar to double Pb sensitivity (Schuhmacher et al., 1993). All ion-counting detectors used in this study were low-noise discrete dynode Hamamatsu R4146-04 electron multipliers, with typical backgrounds of $<0.005\ \text{cps}$, which precluded the need for any background correction. Prior to image

acquisition, the secondary ion beam was centered in the field aperture, optimized for
 maximum energy distribution in a 45 eV energy window, and mass calibrated using the
 zircon matrix $^{90}\text{Zr}_2^{16}\text{O}$ signal. Count times for the ions of $^{90}\text{Zr}_2^{16}\text{O}$, simultaneous Pb
 isotopes, ^{238}U , $^{232}\text{Th}^{16}\text{O}$, and $^{238}\text{U}^{16}\text{O}_2$ were 2, 12, 5, 2, and 2 seconds, respectively, and
 images were integrated over 60 scans, resulting in a total analysis time of 34 minutes.
 Ions of $^{90}\text{Zr}_2^{16}\text{O}$, ^{238}U , $^{232}\text{Th}^{16}\text{O}$, and $^{238}\text{U}^{16}\text{O}_2$ were measured in the same detector as the
 ^{208}Pb ions in order to minimize aging on detectors used for the geochronometrically
 critical radiogenic Pb isotopes, ^{206}Pb and ^{207}Pb , as well as unradiogenic ^{204}Pb . Images
 were processed using the CAMECA WinImage2 software package. Regions of interest
 (ROIs) were selected in each of the seven images based on elevated concentration areas
 of ^{206}Pb , $^{232}\text{Th}^{16}\text{O}$, or ^{238}U images for each image (Figure 2). The same ROI outlines were
 then applied to eight images of the 91500 zircon standard (6 images before unknowns and
 2 images after) and two images of an external zircon standard, QGNG. Once the ROIs
 were determined for each image, the isotope ratios of $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, $^{204}\text{Pb}/^{206}\text{Pb}$,
 $^{206}\text{Pb}/^{238}\text{U}$, $^{238}\text{U}^{16}\text{O}_2/^{238}\text{U}$, $^{232}\text{ThO}/^{238}\text{U}$, and $^{90}\text{Zr}_2^{16}\text{O}/^{238}\text{U}$ were calculated in WinImage2
 and exported to a spreadsheet where all isotope ratios were corrected for gain differences
 between the electron multipliers and U/Pb elemental fractionation as described below.

A single, linear correction factor that accounts for Pb isotope mass fractionation
 and gain differences between electron multipliers was determined by performing
 conventional spot analyses of USGS basaltic glass reference material BCR-2G (~11 $\mu\text{g/g}$
 Pb) before the imaging session, following the methods described by Bellucci et al. (2016)
 using an ~20 μm , ~10 nA O_2^- primary beam. All spot analyses were conducted in multi-
 collector mode at a mass resolution of 4860 ($M/\Delta M$), using an NMR field sensor in

regulation mode to control the stability of the magnetic field. Gain correction values were then determined by comparison to the accepted Pb isotope ratios (Woodhead and Hergt, 2000). External precision in this session for ratios $^{207}\text{Pb}/^{206}\text{Pb}$, $^{208}\text{Pb}/^{206}\text{Pb}$, and $^{204}\text{Pb}/^{206}\text{Pb}$ were 0.5%, 0.4%, and 0.6%, respectively (2σ). The $^{206}\text{Pb}/^{238}\text{U}$ was corrected for detector differences by using a gain correction factor determined from the inverse of $^{208}\text{Pb}/^{206}\text{Pb}$. External uncertainty estimates were propagated through to all unknown Pb isotopic ratios and the gain corrected $^{206}\text{Pb}/^{238}\text{U}$ ratio.

Determining the correct $^{238}\text{U}/^{206}\text{Pb}$ ratio from the secondary ion elemental-ratio ($^{238}\text{U}^+ / ^{206}\text{Pb}^+$) is essential for accurate U-Pb age determinations (e.g., Jeon and Whitehouse, 2015). For this study, the $^{206}\text{Pb}/^{238}\text{U}$ vs. $^{238}\text{U}^{16}\text{O}_2 / ^{238}\text{U}$ power law relationship was applied. The $^{206}\text{Pb}/^{238}\text{U}$ vs. $^{238}\text{U}^{16}\text{O}_2 / ^{238}\text{U}$ was determined for each ROI in each image and a ROI-specific correction factor to convert $^{206}\text{Pb}/^{238}\text{U}$ vs. $^{238}\text{U}^{16}\text{O}_2 / ^{238}\text{U}$ to $^{206}\text{Pb}/^{238}\text{U}$ was determined by fitting a power law regression through eight different ROI-specific analyses of zircon 91500, assuming an accepted age of 1065.4 ± 0.3 Ma (Wiedenbeck et al., 1995). This correction factor was then applied to each specific unknown ROI, compensating for any U/Pb fractionation differences across the imaged area. The accuracy of the fractionation factor determined from 91500 was assessed by applying the fractionation factor for each ROI to two images of the secondary zircon standard, QGNG (Supplementary Figure 1) which has an accepted isotope-dilution TIMS age of 1849.8 ± 1.1 Ma (Compston, 2001, Daly et al., 1998). The uncertainty (std. dev.) in the power law relationship between the eight 91500 ROIs was propagated through to the final, corrected U/Pb ratios. In summary, the final, reported uncertainties on the corrected isotopic ratios combine Poisson's counting statistics (internal uncertainty), the

external gain, and the external error associated with the U/Pb vs. UO_2/U power law correction. Lastly, common Pb (given in Table 1 as $f_{206}\%$), which likely results primarily from sample preparation, was monitored using ^{204}Pb and corrected assuming the present-day terrestrial Pb composition of Stacey and Kramers, (1975). After the gain, U/Pb fractionation, and common Pb corrections were made for each ROI, its U, Pb, and Th concentrations were determined, as well as $^{207}\text{Pb}/^{206}\text{Pb}$ and $^{206}\text{Pb}/^{238}\text{U}$ ages (ages calculated with the U decay constant recommendation of Steiger and Jäger, 1977 and isotopic ratio $^{238}\text{U}/^{235}\text{U}$ of 137.88), and weighted average calculations and Concordia diagrams were made with Isoplot 4.15 (Ludwig, 2012).

3. Results

3.1 QGNG

All ROIs applied to both images of QGNG are concordant and accurate in $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages within uncertainty of the accepted age of 1849.8 ± 1.1 Ma (Supplementary Figure 1, Supplementary Table 1). Pooling all ROIs from QGNG-analysis 1 yields a Concordia age of 1853 ± 10 Ma (2σ , $n=68$) and QGNG-analysis 2 yields a Concordia age of 1851 ± 10 Ma (2σ , $n=68$) (Supplementary Figure 1). Moreover, the small systematic bias towards older $^{206}\text{Pb}/^{238}\text{U}$ ages previously observed to be associated with the SII technique (Bellucci et al., 2016) has been resolved by the increase in the number of standards (2 vs 8).

3.2 Grain A32

The center of Grain A32 has a progression from a mostly structureless or patchy zircon to regular fine oscillatory zoning. This central part is partly resorbed and overgrown by a CL bright zone with a less regular sector to cross-bedded zoned rim followed by CL dark outer zircon, which appears to have an internal pattern similar to that of the CL bright zone. Two U-Pb spot analyses, which include one within the oscillatory zoned zircon that possibly has a slight overlap with the CL bright zone and one within CL dark and CL bright zone, but probably slightly overlapping oscillatory zones, yielded two concordant ages with $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 4366 ± 8 and 4269 ± 8 Ma, respectively (Black ellipses, Figure 3). The third spot analysis is discordant in its U-Pb system. It overlaps both the oscillatory zoned and CL bright zircon and has a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4326 ± 8 Ma, likely representing a mix between the two areas in the zircon with different ages.

The imaged area in grain A32 is located mostly within the oscillatory-zoned central part as visible in CL (Figure 1). This zoning is also visible in U, Th, and Pb, although elemental maps are of lower resolution (i.e., less sharp) compared to the CL image. Additionally, there is a sharp boundary through the oscillatory zoning resulting in a brighter and darker region in CL that corresponds to lower and U, Th, and Pb intensities (Figure 2, Image 1). Imaging reveals several elongated regions with a strong Th enrichment also identifiable by a more subtle U enrichment. These regions can be directly linked to the fractures visible in CL. A single ROI selected over two of these areas show strongly discordant U-Pb ages (80 and 43%, Image 1, ROIs 4 and 9 respectively). Two other ROIs (Image 1, 7 and 14) selected next to each other are also discordant (17 and 18%) although they do not appear to be associated with any significant increase in Th and

U content visible in the SII or fractures evident in CL. Nevertheless, their $^{207}\text{Pb}/^{206}\text{Pb}$ Their average $^{207}\text{Pb}/^{206}\text{Pb}$ ages define an average of 4353 ± 16 Ma (2σ , MSWD 1.5, $p = 0.13$, Figure 3) which is similar to those of other ROIs data from the central oscillatory zoned part (Image 1, ROIs 1, 2, 3, 5, 6, 11, 12, 13, 15, 16) and likely indicates modern Pb loss. This age is in agreement with the previous spot analysis $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4366 ± 8 (black ellipse, Figure 3) and also within uncertainty of the previously identified oldest Jack Hills zircon between 4.36 and 4.37 Ga (Holden et al., 2009, Nemchin et al., 2006, Valley et al., 2014). The dark area in the oscillatory-zoned central region of the grain was also sampled (Image 1, Figure 3). Two ROIs (Image 1, 8 and 10) placed within this zone define an age of 4259 ± 29 Ma (2σ , MSWD = 3.6, $p = 0.06$) are in agreement with the second concordant spot analysis at 4269 ± 8 Ma (Black ellipses in Figure 3).

3.3 Grain A79

Grain A79 has dark grey CL inner part with faint relatively thick linear zones (Figure 1). This inner part is overgrown by a CL bright zone along a curved boundary, probably representing a break in zircon growth and partial dissolution. The bright CL zone is in turn overgrown by a sector to cross-bedded outer zone. One spot analysis of the inner part of the grain is concordant with a $^{207}\text{Pb}/^{206}\text{Pb}$ age at 4205 ± 10 Ma, while analyses of the outer zone are discordant and have $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 4017 ± 8 and 4029 ± 12 Ma (Black ellipses, Figure 3). However, all spot analyses for this grain intersect multiple chemical boundaries and therefore, should not be used for accurate age determinations (Figure 1).

Similar to grain A32, imaging of grain A79 reveals linear features and increasing Th and U content correlated with the fractures visible in CL. One of the ROIs partially including one of these features has a discordant U-Pb system. Two ROIs (Figure 2, Image 8, ROIs 4,5) have been defined in the CL dark core, which is free of cracks, and can be used to define a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4256 ± 22 (2σ), although a high MSWD = 4.2 and low $p = 0.04$ (Figure 3) may indicate some ancient redistribution of Pb within these two ROIs. The CL bright area surrounding the core (Figure 2, Image 8 ROIs 1,2,3,6) can be used to define a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3963 ± 27 Ma (2σ , MSWD = 0.44, $p = 0.72$).

3.4 Grain A11

Zircon A11 has a patchy internal structure with some remnants of linear zoning inside some parts of the grain and CL grey homogenous areas. The inner part of the grain is embayed from several sides where bright and dark CL zircon is developed along the curved boundaries with the inner parts of the grain. Three analyses of the patchy inner zircon are concordant with $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 4022 ± 30 , 4011 ± 10 , 4014 ± 6 Ma. A further three analyses intersect boundaries between different zones, are discordant and have $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 3865 ± 8 , 3799 ± 12 , and 3711 ± 16 Ma (Black ellipses, Figure 3).

SII analysis of Grain A11 (Figure 2, Images 5,6) indicate that both cracks in the zircon and dark areas in CL are enriched in U, Th, and Pb. Meanwhile, bright areas in CL are depleted in U, Th, and Pb (Figure 2, Images 5,6). The grain is crosscut by multiple fractures especially where Image 5 was taken and although care has been taken to avoid

these fractures when selecting ROIs, three of the seven ROIs (2, 6, and 7) in this image show 10-11% discordance in the U-Pb data. The remaining ROIs in the main (embayed) part of the grain (Image 5 ROIs 1, 3, 5 and 7 and Image 6 ROIs 1, 5, and 6) define an average $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3977 ± 16 Ma (2σ , MSWD = 1.05, $p = 0.40$), while two ROIs in the zircon occurring within the embayed regions (ROIs 2 and 4, Image 6) determine a partial resetting age of 3742 ± 40 Ma (2σ , MSWD = 3.0, $p = 0.08$). The third ROI (ROI 3, Image 6) in this part of the grain includes a fracture and has 16% discordant U-Pb data.

3.5 Grain A114

Zircon A114 shows a transition from CL darker sector zoned inner parts towards the CL brighter fir-tree to cross bedded zoning in the tip of the grain. The tip shows extremely bright CL where zoning, if present, is masked by CL intensity. Similar bright CL regions, often disrupting primary zoning, are common in many zircon grains formed in variety of environments (e.g., Corfu et al. 2003), although usually they are only minor features present in the grains. The opposite side of grain A114 contains several fractures and displays what appears to be more “spongy” zircon developed along these fractures. Although CL contrast in this part of the grain is very subtle, the “spongy” zircon appears to transgress over some primary growth zones. Four spot analyses made in this grain are concordant with $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 4150 ± 15 , 4170 ± 20 , 4150 ± 10 Ma for the sector zoned zircon and 4081 ± 18 Ma age in the brighter tip (Black ellipses, Figure 3).

As with earlier described grains, ion imaging shows an increased concentration of Th and U along the fractures. In addition it appears that a band overriding primary zoning,

cutting across the grain and formed by “spongy” zircon, which is very dark in CL. The distribution of ages is not consistent through the obvious texture differences grain. This is exemplified in Image 4, ROIs 1, 5, and 7, which define a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4064 ± 16 Ma (2σ , MSWD = 6.6, $p = 0.001$, Figure 3). High MSWD and low probability may indicate that three ROIs represent a mixture of not completely separated primary and secondary zircon. The remaining five ROIs (Image 4, 2,6,3,4,8) determine a statistically much better defined older age of 4155 ± 7 Ma (2σ , MSWD = 2.8, $p = 0.064$, Figure 3). These ROIs also seem to correspond the different sectors defined by bright and dark regions in CL.

3.6 Grain A74

Grain A74 has a core with a smoothly curved boundary. The core has remnants of lighter grey CL zircon lingering in and being replaced by the dark grey CL “spongy” zircon and is surrounded by a relatively thin bright CL rim with sector to cross-bedded zoning. Four spot analyses in the core yielded strongly discordant data with $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 3836 ± 24 , 3821 ± 10 , 3298 ± 72 , and 3866 ± 16 Ma (Black ellipses, Figure 3).

Imaging of the grain highlights multiple fractures emphasized by high Th and U concentrations. Extensive fracturing appears to result in the majority of ROIs defining strongly discordant U-Pb data. The only exception is ROI-2 located in the rounded zircon core (Image 3) representing most pristine part of the grain. U-Pb data for the other two ROIs (Image 3, 1 and 10) placed in the core are also among the least discordant (15 and 18% discordance). The rest are 30 to 80% discordant showing decreasing $^{207}\text{Pb}/^{206}\text{Pb}$ ages correlated with degree of discordance, which indicates ancient Pb loss. The time of

this loss can be estimated as 2931 ± 42 Ma (2σ , MSWD 0.81, $p = 0.49$) from the ROIs defining lowest statistically similar $^{207}\text{Pb}/^{206}\text{Pb}$ ages (Figure 2, Image 2, ROIS 2,3,4,6). This age is similar to the ages of the youngest zircon grains ever recovered from conglomerate samples at the location of the sample investigated here (e.g., Grange et al., 2010). The three most concordant ROIs define the best estimate for the age of the grain at 4155 ± 68 (2σ , MSWD = 2.8, $p = 0.064$)

4. Discussion

4.1 Comparison of SII vs. CL imaging

There is a general agreement between the CL imaging and the variation of Pb, U and Th visible in SII. Specifically, the brighter CL regions have less U, Th, and Pb than the darker regions. One of the features clearly visible in the SII is the unequivocal association of Th and U enrichment with the fractures in zircon grains. Similar changes associated with the cracks in Jack Hills zircon grains have been observed for LREE by Bell et al. (2016). The U and Th enrichment is generally accompanied by higher Pb content in all grains, although this Pb has an increased proportion of common Pb evident from the calculations made for selected ROIs placed in these areas. This leads to a conclusion that Pb in the fractures is not accumulated *in situ* from U and Th decay, which is also reflected in the strong discordance of U-Th-Pb ages calculated for the same ROIs, pointing towards a recent migration of all elements in and/or out of the cracks. Although in general, fractures in the grains can be identified from the SII, close investigation of ROIs placed over the cracks reveals that U, Th, and Pb in these areas are not correlated

(Figure 5). All of these regions are enriched in U, however the overall range of Th/U is similar to that of un-fractured domains. This behavior suggests that the process responsible for increased content of U, Th and Pb in the cracks is more complex than simultaneous and correlated addition of these elements into fractures. Regardless of the detailed mechanism of U, Th and Pb mobility, it is clear that these ROIs cannot be used to extract primary information about ages or chemistry of investigated zircon grains. A similar conclusion probably applies to the five ROIs selected in the “spongy” dark grey CL zircon parts of grain A74 (Image 2, ROIs 7, 8, 12 and 13) and grain A79 (Image 5, ROI 7). These areas are not associated with the major cracks, but appear to contain possible micro-fractures identifiable in CL.

A different process, although one that is probably related to the recent mobility of elements in zircon, is recorded by the ROIs-1, 2, 3 and 10 in Image 3 of grain A74, which shows the most broken internal structure in CL. Although these ROIs are selected to avoid visible cracks, they have higher Th/U ratios than all other investigated grains (Figure 5, Table 1). In addition, this is the only grain in the investigated group where Th/U calculated using $^{207}\text{Pb}/^{206}\text{Pb}$ age and measured $^{208}\text{Pb}/^{206}\text{Pb}$ is significantly lower than the measured Th/U estimated from the counts obtained for the selected ROIs (Table 1), indicating significant discordance of Th-Pb and U-Pb systems and mobility of the elements in the bulk zircon volume.

Mostly primary features are recorded in four of the five investigated grains, which show a range of internal structures compatible with the complexity of the Jack Hills population recorded in the previous studies (e.g. Cavosie et al., 2005, Dunn et al., 2005, Nemchin et al., 2006). None of these structures can be uniquely interpreted as reflecting

zircon crystallisation from the melt, with a possible exception of the core in grain A32, showing concentric (oscillatory) zoning that is commonly attributed to magmatic crystallisation (e.g., Corfu 2003, and references therein). Features that can be potentially viewed as discontinuous remnants of oscillatory zoning could also be identified in the core of the grain A79 and some areas of grain A11. Relatively thick concentric CL bright and CL dark zones in the outer parts of grain A79 as well as cross-bedded zoning in the rims of the grains A32 and A79 can be also attributed to magmatic or late magmatic crystallisation. However, similar features are frequently found in metamorphic grains (or overgrowths) associated with both amphibolite and granulite facies metamorphism (e.g., Vavra, 1996). Sector to fir-tree to cross-bedded zoning observed in grain A114 is most commonly found in high-grade metamorphic zircon grains, while embayment filling zircon in grain A11 can be explained by metamorphic or late fluid/melt recrystallization or dissolution re-precipitation reactions (Corfu, 2003). In general, grains A32 and A79 show more features that can be attributed to magmatic processes, while grains A114 and A11 are dominated by internal structures that are more likely associated with a metamorphic origin or reworking of a magmatic grain. The grains that have more magmatic textures appear to have a slightly elevated Th/U compared to the grains that have textures more commonly attributed to metamorphism (Figure 6, Table 1). This subtle difference may be viewed as an additional indication of a different origin for these grains. While there are clearly not enough grains investigated here to make any firm constraints, further investigation of these textural and chemical differences could provide an additional way for a detailed reconstruction of the origin(s) of different groups of grains within the Jack Hills population

402

403 ***4.2 Comparison of SII ages vs. spot analyses***

404 A total of twenty conventional spot analyses have been made in the five grains
405 investigated here. Eight of the analytical spots (all of those in grain A74, three in grain
406 A11 and one in grain A32) appear to intercept fractures revealed in the post analysis
407 imaging (Figure 1). Similarly, some of the spot analyses also appear to cross boundaries
408 between different un-fractured CL domains in the grains. The data from these spots have
409 an extremely discordant U-Pb system and/or have intermediate, meaningless $^{207}\text{Pb}/^{206}\text{Pb}$
410 ages when compared to data from the other spot analyses and SII ages (Figure 3).

411 Data from the two remaining spot analyses in grain A32 (Figure 1) appear to
412 intercept CL boundaries even though they are placed in the crack free areas.
413 Nevertheless, the ages determined for these spots agree with those defined from nearby
414 ROIs. The resulting age difference between the oldest and youngest ages in this grain is
415 ca. 100 Ma. All three spot analyses in grain A79 cross CL boundaries (Figure 1),
416 however, the spots with $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 4017 and 4029 Ma are located within the part
417 of the zircon with consistent ages determined from the ROIs in SII. Thus, the CL
418 boundary overlap had no effect on the $^{207}\text{Pb}/^{206}\text{Pb}$ ages of these spots. The third spot with
419 a $^{207}\text{Pb}/^{206}\text{Pb}$ age of 4205 Ma, however, shows a $^{207}\text{Pb}/^{206}\text{Pb}$ age intermediate to older and
420 younger ages determined from the ROIs and clearly overlaps different age and chemistry
421 domains. Three spots in grain A11 are placed within homogenous CL and SII domains
422 (Figure 1) and show concordant ages that agree with the data obtained from the SII
423 (Figure 3). Finally, the four spots in grain A114 have all intersected different regions
424 revealed by CL and SII. However, given the texture of this grain, these sectors were

likely formed by partial recrystallization that developed through the middle part of the grain, which resulted in similar age determinations between the spot analyses and SII. Importantly, in the instances where concordant spot analyses have overlapped unfractured but mixed chemical domains (e.g., Grain A79), it is impossible to say for certain if those ages are real or intermediate/mixed without SII. This is especially crucial for multiple isotopic or trace element analyses for a certain spot, which without SII would appear to be concordant and accurate but in reality, will be meaningless in terms of its age. This decoupling of isotope systems in unfractured but mixed domains makes interpretation of these coupled analyses impossible.

The comparison of data from the spot analyses and SII indicates that the ages determined from the spot analyses that do not cross CL boundaries, SII chemical boundaries, and/or fractures agree completely with the ROI results within analytical uncertainty. While the precision of spot analyses is generally better than that of an individual ROI, SII provides an unparalleled capability to avoid overlapping CL or heterogeneous U, Th, or Pb domains as well as fractures within an individual zircon grain. While some fractures can and should be avoided during the spot analyses, some may be hidden or too small to see. Furthermore, the boundaries between different CL domains are not visible under the Au coating with the reflected light camera during the selection of analytical points, increasing probability of inadvertently analysing mixed zircon domains. This becomes increasingly important when these CL or chemical zones are comparable in size to conventional spots, which is clearly demonstrated here.

4.3 Potential Implications for the Hadean Earth

Despite the small sample size of zircon grains ($n=5$) investigated here, an important outcome of this imaging study of Jack Hills zircon is that every analysed grain records two ages that are distinguishable outside of analytical uncertainty. In three of the grains, these ages are clearly associated with the cores and rims, while the two other grains appear to have experienced post-formation modification and/or recrystallization of some of the original zircon. While rare rims have been reported in the previous studies of the Jack Hills zircon population, they all are 3.8 to 3.4 Ga in age (e.g. Cavosie et al., 2004, Valley et al., 2014 and references therein). In contrast, the three grains investigated here record secondary events happening in the Hadean (older than 4.0 Ga). Although rims have not been readily identified in previous studies, variable ages determined by multiple spot analyses or in depth profile in individual grains are very common (e.g., Abbott et al., 2012, Bell and Harrison, 2013, Cavosie et al., 2004; Nemchin et al., 2008, Valley et al. 2014). Similarly, multiple domains of trace element concentrations have been observed in these grains (Abbott et al., 2012, Bell and Harrison, 2014, Trail et al., 2007a,b). The presence of secondary ages in all of the zircon grains investigated here raises the very distinct possibility that all previous occurrences of variable ages in Jack Hills zircon grains result from unrecognised core-rim domains, or otherwise complex partial recrystallization relationships in these zircon grains, rather than simple Pb-loss. An explicit advantage of the technique presented here, in contrast to previous studies (e.g., depth profiling, multiple spot analyses) is that homogeneity can be assessed in an almost completely non-destructive manner.

Additionally, there appears to be a regular overlap between core and rim ages of different grains (Figure 4). The best estimate for the age of the core in grain A32 is

4353±16 Ma, which is amongst the oldest grains recorded in the Jack Hills population (e.g., Holden et al., 2009, Nemchin et al., 2006, Valley et al., 2014, Whitehouse et al., 2017) but its rim has an age defined as 4269±12 Ma, which is similar to the age of the core in grain A79 estimated as 4256±22 Ma. The 3963±27 Ma rim of grain A79 is, in turn, similar to the core of grain A11 (3977±16 Ma), which has a Late Archaean rim of 3742±40 Ma. In contrast, the two remaining grains, A74 and A114, appear to have cores with similar ages of 4155±68 Ma and 4155±7 Ma, respectively, but very different secondary ages of 2931±42 and 4064±16 Ma, although the former is not entirely reliable as it is based on a set of highly discordant data.

Despite the very limited number of grains analysed here, these results suggest that a consistent pattern may emerge within the Jack Hills zircon population with analyses from additional grains. It is already clear that some of the secondary events preserved in the rims of zircon grains are occurring simultaneously with the generation of new zircon. This age constraints of these processes generally agrees with the major age peaks seen in the most recent compilation of the Jack Hills age distribution (Whitehouse et al., 2017). Lastly, since there exists a strong possibility of unrecognised core-rim or otherwise complicated internal structures in previous analyses of the Jack Hills zircon population, caution must be applied when interpreting data from multiple isotopic systems within a potentially heterogeneous grain. The structures shown here would explicitly affect the interpretation of results from similar studies of the trace element distributions (i.e., Ti and REE) in these grains. Extrapolating from the frequency of mixed domain spot analyses from this study indicates that approximately half (the frequency observed here) of published trace element and Hf/O isotope data also may represent mixed values. If this

value even remotely approaches the frequency of mixed data sets in other studies, it becomes extremely problematic to accurately interpret the isotopic and trace element record preserved in these zircon grains. The issue of mixed domains has even greater implications for Hf-isotopic data, where analyses require larger volumes of zircon compared to that used by ion probe during U-Pb, O-isotope and trace element analyses (Whitehouse et al., 2017). While the metamorphic or recrystallization events recorded in the U-Pb ages reported here are unlikely to change the Hf isotopic composition of the zircon, the interpretation of Hf data is explicitly tied the U-Pb age of the zircon analysed. Specifically, if the U-Pb age is disturbed, a Hf model age calculated using the apparent U-Pb age could be erroneously interpreted as having true geological significance rather than as an artifact (e.g., Vervoort and Kemp, 2016). Thus, the probability of mixed U-Pb ages and subsequent decoupling of all other isotope systems from ‘real ages’ creates a strong hindrance in interpreting the correct isotopic record of the Hadean Earth. SII offers a novel way in overcoming this hindrance in providing a relatively non-destructive imaging technique to assess ages and homogeneity of a zircon prior to other more destructive analyses (e.g., Hf). Hopefully, with future studies these techniques can be used in conjunction to provide a reliable and accurate contextualized isotopic record for the Hadean Earth.

5. Conclusions

Results from this study demonstrate the nature and origin of the complex age distribution of some Hadean grains from the Jack Hills zircon population. Of the five zircon grains analysed, each one exhibits correlated internal variability of CL, U, Pb, and

$^{207}\text{Pb}/^{206}\text{Pb}$ (ancient Pb loss) and $^{206}\text{Pb}/^{238}\text{U}$ ages (recent Pb loss or U gain). The mixing end members defined here by five grains, and in one instance a single grain, encompass almost the entire variability of the previously analysed population suggesting that every Jack Hills grain contains this complexity and that one or two spot analyses per grain do not define the true ages of these crystals. It also suggests that previously reported trace elements, O, and Hf isotope data could represent mixing of different primary and secondary components with diverse origins and may have not been correlated with accurate ages. The SII technique applied here provides a useful technique to distinguish between primary zircon and areas in the same grain influenced by secondary processes, both ancient and recent. This technique can help to identify areas in the grains containing primary age information, which can then be targeted to obtain O and Hf isotope data, which, unlike trace elements and U-Pb ages, cannot be obtained using a SII approach. Lastly, the age distribution, core-rim relationships, and/or internal structures in the grains here indicates several Hadean (> 4 Ga) thermal events resulting in multiple resetting or zircon crystallization events.

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Figures

Figure 1. Cathodoluminescence images of the zircon grains for this study. Yellow circles represent locations of spot analyses (20 µm in diameter; ages in Ma), while red boxes represent locations for image analyses (70 x 70 µm).

Figure 2. CL and corresponding scanning ion images of U, Th, and Pb and regions of interest (ROIs) for each image superimposed on the SII image of U distribution.

Figure 3. Concordia diagrams and weighted average for young and old parts of each analyzed grain. Numbers in weighted averages correspond to ROIs in each image. Blue ellipses represent analyses included in the old age calculation. Red ellipses represent analyses included in the youngest part of the grain calculation. Dotted ellipses were excluded from any age calculations for intersecting multiple domains (in spot analyses) or obvious cracks in SII or CL. Black ellipses represent spot analyses. ROIs for each analysis listed in the weighted averages in $^{207}\text{Pb}/^{206}\text{Pb}$ ages.

Figure 4. Summary of age determinations for the oldest and youngest age for each grain. Reported uncertainties are 2σ .

Figure 5. Pb, Th, and Th/U vs. U for all ROIs in this study. ROIS that encompass cracks have elevated U and disturbed Pb, Th, and Th/U.

Figure 6. Th/U vs. U for assumed primary zircon in this study. Samples are divided by typical metamorphic and igneous textures.

Grain A11 Image 5,6

Grain A74 Image 2,3

Grain A79 Image 8

Grain A32 Image 1

Grain A114 Image 4

Red Boxes are 70 μm x 70 μm
Yellow circles are 20 μm

Figure 2 Grain A32, Image 1

Grain A79 Image 8

Grain A11 Image 5

Grain A11 Image 6

Grain A114 Image 4

Grain A74, Image 2

Grain A74, Image 3

Figure 3

Figure 4

$^{207}\text{Pb}/^{206}\text{Pb}$ age

Figure 5

Figure 6

Table 1. U-Pb and U,Th,Pb concentration data

Image #	Sample #	ROI #	$\frac{^{207}\text{Pb}}{^{235}\text{U}}$	$\pm\sigma$
				%
Image 1	Grain A32	1	62.4	4.7
		2	69.1	5.6
		3	67.4	6.5
		4	8.5	7.7
		5	57.5	6.2
		6	61.9	5.7
		7	53.3	4.9
		8	55.2	6.7
		9	29.1	10.1
		10	57.6	8.1
		11	74.3	7.5
		12	54.6	7.8
		13	55.8	11.4
		14	50.9	7.4
		15	57.7	4.9
		16	60.5	7.0
Image 8	Grain A79	1	39.6	6.6
		2	39.5	5.1
		3	31.8	7.4
		4	64.4	3.4
		5	50.9	6.2
		6	35.9	18.8
		7	15.5	3.9
Image 5	Grain A11	1	45.7	4.8
		2	36.0	7.4
		3	42.8	11.0
		4	41.0	5.9
		5	41.0	8.9
		6	31.9	10.4
		7	35.9	6.3
		8	34.4	11.2
Image 6	Grain A11	1	43.9	11.3
		2	32.8	4.9
		3	27.6	11.9
		4	28.7	10.1
		5	44.9	3.7
		6	46.6	4.3
Image 4	Grain A114	1	47.9	3.6

Background dataset for online publication only

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