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Post-Hadean transitions in Jack Hills zircon provenance: A signal of the Late Heavy Bombardment?

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ABSTRACT

Hadean Jack Hills (Western Australia) detrital zircons represent the best documented terrestrial resource with which to observe the pre-4 Ga Earth. The > 4 Ga component of this semi-continuous 4.38 to 3.0 Ga zircon record has been investigated in detail for age, δ^{18} O, Lu–Hf systematics, and Ti thermometry. The more abundant post-Hadean population is less well-characterized, but a previous study (Bell et al., 2011) suggests a more restricted range of δ^{18} O source materials together with a ca. 4.0-3.6 Ga discontinuity in Lu-Hf evolution. These differences could reflect a transformation in the character of the older zircon source region or their sourcing from different terranes entirely. The relative scarcity of 4.0-3.6 Ga zircons corresponds to a discontinuity in Lu-Hf evolution after which 176 Hf/ 177 Hf in zircon reverts to more radiogenic values relative to the > 4 Ga population. We present new oxygen isotope, titanium, and trace element results for 4.0-3.6 Ga Jack Hills zircons in a search for apparent transitions in petrological conditions. Post-3.8 Ga zircons show a marked decrease in the occurrence of heavy oxygen (> 6.5%), but remain close to the average of the Hadean distribution despite their restricted range. This may point to the decreased importance of sedimentary materials in post-3.8 Ga magmas. Ca. 3.9 Ga zircons fall into two categories: "Group I" displays temperatures and compositions similar to the Hadean zircons whereas "Group II" zircons have higher U and Hf, and lower (Th/U), Ce and P. Group II zircons also have anomalously low Ti, and are remarkably concordant in the U-Pb system. Group II's geochemical characteristics are consistent with formation by transgressive recrystallization (Hoskin and Black, 2000), in which non-essential structural constituents are purged during high-grade thermal metamorphism. The restricted age range of Group II occurrence (3.91–3.84) and its coincidence with the postulated intense bolide flux in the inner solar system (i.e., Late Heavy Bombardment; 3.95-3.85) may have causal significance.

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1. Introduction

The pre-3.6 Ga terrestrial rock record is sparse. Surviving rocks older than 4 Ga are even rarer and consist of components of the Acasta Gneiss (ca. 4.03 Ga, Bowring and Williams, 1999) and, possibly, amphibolites from the Nuvvuagittuq greenstone belt (ca. 4.3 Ga, O'Neil et al., 2008). Arguably the most complete record of the Hadean is found in detrital zircons from the Jack Hills, Western Australia, whose ages semi-continuously span the period 4.38–3.0 Ga (Compston and Pidgeon, 1986; Holden et al., 2009; Harrison, 2009). Investigations of these zircons have revealed the presence of heavy oxygen in some, perhaps reflecting evidence for sedimentary cycling and low-temperature water–rock interactions in the protolith (Peck et al., 2001; Mojzsis et al., 2001). Ti-in-zircon crystallization thermometry of Hadean zircons yields

apparent crystallization temperatures (T^{xlln}) that average ~700 °C (Fu et al., 2008; Watson and Harrison, 2005) suggestive of granitic minimum melting conditions (Watson and Harrison, 2005; cf. Fu et al., 2008). Rare earth element (REE) patterns and Lu–Hf systematics (Trail et al., 2007b; Harrison et al., 2008; Harrison, 2009) also suggest felsic igneous origins for the majority of the zircons. Although Kemp et al. (2010) argued for sourcing of the zircons from hydrous low-temperature remelting of a primary Hadean basaltic crust, they did not consider the full spectrum of constraints on their origin (see Harrison, 2009).

As a consequence of the sparse lithological record of early Earth, we currently have no clear view of the nature of the transition between conditions prevailing during the Earth's first few 100s of millions of years and those during the later, and more accessible, parts of the Archean—or indeed if globally there were significant differences between the two periods. The Jack Hills detrital record is an invaluable resource for investigating this poorly known time period as it provides a semi-continuous history of its source terrane(s) spanning more than a billion

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years. In this paper, we geochemically investigate this poorly understood transition and find significant differences between pre- and post-4 Ga zircons that may bear on the Earth's impact history.

2. Geologic transitions at the Hadean-Archean boundary

Jack Hills zircons are found in ca. 3 Ga metaconglomerates deposited in a deltaic environment (Spaggiari et al., 2007) sourced from mature clastic sediments. The range of protolith compositions and P-T histories experienced by Jack Hills zircons are likely representative of the catchment area of this drainage (barring selection effects of sedimentary transport, for instance if some of the zircons are polycyclic as suggested for some younger Jack Hills sedimentary units by Grange et al., 2010), but not necessarily of the whole Earth. Consequently, changes with time in the Jack Hills zircon record are potentially due to either changes to their local geological environment or possible planet-wide effects. Discerning positively whether the cause of a particular change in the Jack Hills provenance was global or local may not be possible. However, catastrophic meteorite bombardment-as in the hypothesized Late Heavy Bombardment—would be expected to have effects on both a local and a planet-wide scale.

2.1. Apparent geochemical transitions in Jack Hills zircons

Comparisons of pre-4 Ga and 3.6-3.4 Ga Jack Hills zircons show several apparent differences in formation conditions and protolith sources. Bell et al. (2011) found a $\delta^{18}O_{SMOW}$ distribution among the younger zircons that clustered around mantle equilibrium values (i.e., 5.3‰, Valley, 2003) with none containing unambiguously heavy oxygen (cf. Peck et al., 2001). By contrast, the Hadean record contains a significant proportion of zircons with heavy $\delta^{18} \rm O_{SMOW}$, consistent with incorporation of hydrous sediments (Mojzsis et al., 2001; Cavosie et al., 2005; Trail et al., 2007b). The most unradiogenic (with respect to CHUR) Hf isotopic signatures in Hadean zircons are generally not observed among the < 4 Ga zircons, such that even if the younger zircons are derived from broadly the same source terrane as their Hadean counterparts, some of the more unradiogenic source materials had either become inaccessible to protolith magmas or destroyed by 3.6 Ga (Bell et al., 2011).

Due to a paucity of detrital Jack Hills zircons between ca. 3.8 and 3.6 Ga, a prior survey (Bell et al., 2011) was unable to adequately sample that interval and thus did not document precisely when and how differences between Hadean and younger zircons began to be preserved (whether gradually or more suddenly). A sudden transition in δ^{18} O distribution, for instance, might signal a rapid change in geological conditions. Similarly, although Hadean and 3.6–3.4 Ga (the dominant peak in the Jack Hills zircon population) zircons yield similar Ti-in-zircon T^{xlln} distributions (Bell et al., 2011), any deviations from the prevailing, apparently granitic source during this period may also reflect changes in the sediment source during late Hadean–early Archean time.

2.2. The Late Heavy Bombardment

The Earth–Moon system, and likely the entire inner solar system, appears to have been subjected to an intense flux of impactors at ca. 3.9 Ga (Tera et al., 1974). The first recognition of this event came from isotopic disturbances seen in lunar samples (Tera et al., 1974). Specifically, Rb–Sr, U–Pb and K–Ar systems were reset at ca. 4.0–3.85 Ga (e.g., Tera et al., 1974; Turner, 1977; Maurer et al., 1978; Ryder et al., 2000; Kring and Cohen, 2002).

The hypothesis that emerged was of a discrete Late Heavy Bombardment (LHB) in the period 3.95–3.85 Ga (Tera et al., 1974), although it remains unclear whether this was instead the tail of a decreasing bolide flux (e.g., Hartmann, 1975). The lack of an identifiable signature in the fragmentary terrestrial rock record from the LHB era has limited the study of this period of solar system history almost entirely to extraterrestrial samples. Given its scaling to the Moon in terms of mass and surface area, the Earth should have experienced approximately 20 times the impact flux of the Moon (e.g., Grieve et al., 2006), leading to heating of a significant proportion of the crust.

As hypothesized (e.g., Gomes et al., 2005; Abramov and Mojzsis, 2009), the LHB would have been sufficiently pervasive and intense to create a distinctive set of geological conditions characterized by widespread metamorphism and hydrothermal alteration. For example, although the proportion of the crust predicted by Abramov and Mojzsis (2009) to have experienced thermal disruptions of > 1000 °C is small (ca. 2%), their model suggests that ~20% of the lithosphere would have been heated by 100 °C or more. More locally, large impacts would result in the generation of impact melt sheets.

Zircons grown from impact melt sheets are unlikely to crystallize at the predominantly minimum melting conditions inferred for Hadean detrital zircons (see Harrison, 2009), but instead form at significantly higher temperatures (Darling et al., 2009; Wielicki et al., 2012). Thermal metamorphism may or may not form new zircon (Hoskin and Schaltegger, 2003) depending on petrological conditions, but metamorphically grown and metamorphically overprinted zircons may be identifiable by their patchy internal zonation (Corfu et al., 2003), although this is not universal and some specific alteration mechanisms result in different internal structures. Low (Th/U) ratios are common among metamorphic zircons, whether newly grown (often < 0.01; cf. Wan et al., 2011) or recrystallized originally igneous zircons, which decrease in Th/U with respect to their protolith zircons but may not reach values as low as 0.01 (Hoskin and Schaltegger, 2003). Zircons recrystallized during metamorphic heating and/or fluid ingress show a variety of textural and chemical features (e.g., Pidgeon et al., 1998; Vavra et al., 1999; Hoskin and Black, 2000). Vavra et al. (1999) found zones of recrystallization in zircons from highgrade metamorphic rocks in the Ivrea Zone that showed bright regions of recrystallization under cathodoluminescence that had lost both Pb and U, resetting the U–Pb age. Pidgeon et al. (1998) observed that during metamorphism, zircons can develop both lobate low-U regions and trace element rich bands, cross-cutting previous zircon internal structures. Hoskin and Black (2000) found that zircons recrystallized under granulite-facies metamorphic conditions can contain recrystallized regions transgressing previous structures that are homogeneous or display faint relicts of magmatic textures. These transgressively recrystallized regions of their zircons typically display increased contents of trace elements compatible in the zircon lattice (e.g., U, Hf) and decreased contents of zircon-incompatible trace elements (e.g., P, LREE).

Unfortunately, much of the evidence of an LHB-type event would be indistinguishable from endogenic geological processes that operated at smaller spatial scales (e.g., regional metamorphism). Proof of a connection to a period of heavy bombardment may not be possible when considering the Jack Hills zircon record alone. That said, the absence of a distinctive signal consistent with a global impact cataclysm would argue against the source terrane having experienced LHB-related effects, so a partial hypothesis test of a terrestrial occurrence of the LHB may yet be possible. In this paper, we apply both the Ti-in-zircon crystallization temperature (T^{xlln}), an element of zircon petrogenesis that is wellestablished for the Hadean population, and other trace element analyses to 4.0–3.6 Ga zircons to seek evidence of some change or disruption in geological conditions with time in the Jack Hills source region(s).

3. Methods

Many U–Pb ages of zircons studied here were undertaken using the SHRIMP I instrument at the Australian National University and reported in Holden et al. (2009). Additional dating was carried out using UCLA's CAMECA *ims*1270 ion microprobe. All analytical results for those data are given in Table S1 of the Supplementary Online Materials (SOM) together with summarized ages for the previously analyzed samples. Oxygen isotope and trace element measurements were all carried out using the UCLA ion microprobe.

All samples were mounted in epoxy and polished to reveal a flat surface. At UCLA, Jack Hills detrital zircons were surveyed using a rapid (5–10 cycle) method that measured only the masses ²⁰⁴Pb, ²⁰⁶Pb, ²⁰⁷Pb, and ²⁰⁸Pb, providing a ²⁰⁷Pb/²⁰⁶Pb age estimate but no concordance information. Those zircons with apparent ages from 3.6–4.0 Ga were then more precisely analyzed using our standard U–Th–Pb protocol (Trail et al., 2007b). During the several analysis sessions at UCLA from June 2009 to May 2010 we used primary O⁻ beam intensities ranging from 8 to 13 nA corresponding to analysis spot sizes of 30 to 40 μ m. We used zircon U–Pb age standard AS3 (1099 ± 1 Ma; Paces and Miller, 1993) during all analysis sessions. In addition, some zircons analyzed for other variables were from the collection of Holden et al. (2009).

Ti measurements on 4.0–3.6 Ga zircons were carried out in multicollector (MC) electron multiplier mode detecting ⁴⁸Ti⁺ and ³⁰SiO⁺ under a 30–40 µm primary O⁻ beam of ~10 nA at high mass resolution power (MRP; $m/\Delta m \sim 8000$). The analyses were carried out in three sessions in August 2009, September 2009, and May 2010. The concentration of Ti was determined based on analysis of several standard materials, including the standard zircons AS3 and SL13 (22 ppm and 6.3 ppm, respectively; Aikman, 2007) as well as NIST610 glass. We determined T^{xlln} from the Ti measurements using the Ti-in-zircon thermometer (Watson and Harrison, 2005) as formulated by Ferry and Watson (2007).

Ti-in-zircon measurements were also undertaken in peak switching (PS) mode in the course of a more extensive analysis of trace elements (REE, Hf, Th, U, Ti) for a selected, smaller group of zircons at ca. 3.9 Ga, as well as several Hadean zircons (discussed in Section 4.2). These analyses were carried out using the CAMECA *ims*1270 ion microprobe at UCLA in one session during January 2011. Primary O⁻ beam intensities of ~15 nA were used, the spot size was 30 µm, and secondary ions were detected at low MRP ($m/\Delta m \sim 2000$) and high energy offset (-100 eV) using ⁴⁹Ti⁺. Only those analyses determined by later electron microscope imaging to not lie on cracks or inclusions were included in this study. NIST610 standard glass was used for calibration. We refer to these analyses as 'PS mode' (after the peak-switching protocol) to distinguish them from the multicollector ('MC') Ti measurements.

Oxygen isotope measurements were undertaken in two sessions during January and July of 2010. Analyses were made in Faraday multicollection mode with a Cs⁺ primary beam of ~1.5–2.2 nA focused into a ~30 μ m spot. For more details on the analytical method see Trail et al. (2007b). The AS3 zircon standard (5.34‰; Trail et al., 2007b) was used for sample-standard comparison.

4. Results

Zircons between 4.0 and 3.6 Ga broadly resemble the Hadean zircon population but differ in some important aspects of their trace element compositions. Ti-in-zircon temperatures and several other elements of interest reveal a group of zircons at ca. 3.9 Ga that differ substantially from the Hadean population.

4.1. Ti-in-zircon thermometry

154 T_{MC}^{MIn} measurements are displayed in Fig. 1 (and reported in Table S1 of the SOM). Statistics discussed herein are elaborated upon in Table S3 of the SOM. Calculated T^{xlln} vs. age for all samples from 4.0 to 3.6 Ga analyzed using the MC protocol are shown in Fig. 1a in the context of data previously generated from Hadean Jack Hills zircons (Harrison et al., 2008). Given the danger that the placement of ion probe analysis spots over cracks may yield an artificially high Ti measurement (Harrison and Schmitt, 2007), we have attempted to check the analysis spots for cracks through later imaging. Clearly imaged spots seen to be over cracks are excluded and were systematically higher in Ti than the clearly imaged spots with no cracks, which mostly display Hadean-like



Fig. 1. $T_{\rm M}^{\rm Min}$ vs. age for Jack Hills zircons. (a) All \geq 90% concordant samples from this study for the period 3.5–4.0 Ga, along with a Hadean dataset from Harrison et al. (2008). Rectangular area is the region of the plot shown in 1b. (b) Focusing on this study's data for the time period 3.70–4.05 Ga, with Hadean data excluded. The period 3.84–3.91 Ga—with many low-Ti zircons—is shaded for emphasis. Samples from this study are divided into "higher confidence" analyses, which have ion probe pits on demonstrably pristine surfaces, and "lower confidence" analyses, where the pits are not able to be identified with a pristine vs. cracked surface. There is no systematic difference between the two (see S3 of the SOM). Spots found to be on cracks were excluded due to the danger of artificially high Ti measurements (Harrison and Schmitt, 2007).

and lower temperatures (Fig. 1). Samples for which there is some question due to unclear imaging are marked in Fig. 1, but they are statistically indistinguishable from the well-imaged samples and we include them in our discussion. Both the clearly imaged and ambiguous datasets have a small high-temperature tail similar to that seen in the Hadean (Harrison et al., 2008; Watson and Harrison, 2005), with somewhat more in the poorly imaged samples.

Significant trends observed in the Ti survey formed the basis for subsequent targeting of trace element measurements. Although *T*^{xlln} among 4.0–3.6 Ga zircons ranges from similar to cooler than average Hadean T^{xlln} , one time period ~3.9 Ga stands out as distinct (shown in greater detail in Fig. 1b). A number of zircons with ages between 3.91 and 3.84 Ga display low Ti and apparent T^{xlln} that range well below 600 °C, as well as a scattering of higher-Ti zircons with apparent T^{xlln} above 700 °C. Zircons below 650 °C in this period are with one exception >90%concordant, whereas several higher-Ti zircons are > 10% discordant (discordance calculated as $100 \times (t_{207/206}/t_{206/238} - 1)$). As revealed by the Wilcoxon Rank Sum Test, the T^{xlln} distribution in the period 3.91-3.84 Ga is statistically distinguishable from both the Hadean distribution (Harrison et al., 2008; p-value of 0.01) and from the 3.84-3.6 and 3.91-4.0 Ga zircons analyzed in this study (both *p*-values \sim 0.02). The Wilcoxon test compares two samples of non-specified distribution in a particular variable and tests the hypothesis that their probability distributions are distinct (see McClave and Sincich 2006). The distributions of T^{xlln} in the age range 3.84–3.6 and 4.0–3.91 Ga both cluster about an average apparent $T^{\rm xlln}$ of \sim 690 °C and are statistically indistinguishable from the Hadean distribution (with *p*-values > 0.5). A few scattered zircons at 3.8–3.6 Ga fall at or below 600 °C but do not represent a robust population. On the basis of the distinctly low Ti distribution in the age range 3.91–3.84 Ga, trace element analyses were targeted in this time period to search for other distinctive geochemical differences.

4.2. Trace element results

Zircons from the period 3.91–3.84 Ga were targeted for comprehensive trace element analysis, including REE, Hf, Th, U, and a second Ti measurement in PS (peak-switching) mode. All trace element results for 3.91-3.84 Ga zircons and 14 Hadean zircons for comparison are compiled in Table S2 in the SOM. Various trace elements for the 30 zircons with accepted analyses in Table S2 are shown in Fig. 2. The 33 accepted analyses are those whose SIMS analysis pits were found to be free of cracks and inclusions (3 grains have 2 accepted analyses, which are similar and are averaged for interpretation). The zircon data appear to fall into two groupings within this time period (Group I and Group II), picked based on the two clusters in Fig. 2a (U_t vs. T^{xlln} ; X_t refers to quantity X corrected to time of formation). Fig. 3 shows chondrite-normalized REE results for the Group I and II zircons. Most zircons show the low LREE/HREE, positive Ce anomalies, and negative Eu anomalies common to most terrestrial zircons. There



Fig. 2. 3.91–3.84 Ga zircons classified into two groups (I and II) as defined in Section 4.2, plotted in various trace element quantities for which the groups are notably different. (a) U_t (age-corrected uranium concentration; see Section 4.2) vs. T_{PS}^{xlln} ; (b) U_t vs. $((Th/U))_t$ (time-corrected ²³²Th over time-corrected U); (c) Hf vs. T_{PS}^{xlln} ; (d) U_t vs. Ce.



Fig. 3. Rare earth element analyses for Group I and Group II zircons. The analyses resemble typical terrestrial continental zircons with prominent Ce and Eu anomalies and high HREE/LREE; elevated LREE in two analyses are unusual and may indicate the presence of microscopic phases not seen in our search for imperfections on the sample surface.

is little overall difference between the groups in HREE contents, but Group II is somewhat lower on average than Group I in several LREE, including Ce. Two zircons show elevated contents of some LREEs, which may point to the analysis pit overlapping small LREE-rich inclusions (e.g. phosphates), although the analysis pits show no visible evidence for this.

For the low-Ti MC measurements (< 650 °C), the two T^{xlln} estimates are typically consistent (Fig. 4). However, for the zircons that showed high Ti (> 700 °C) in the MC measurement, the PS estimate is often lower, leading to a Hadean-like distribution about apparent $T^{\text{xlln}} \sim 680$ °C (Harrison, 2009). The disagreeing Ti measurements may be due to inadvertent sampling of multiple Ti domains, and indeed five of the eight zircons with disagreeing Ti measurements reveal zonation in cathodoluminescence imaging (see Section 4.3). To reduce such a risk we attempted to place the measurement spots in the same structural domain as the age measurements; the few exceptions are noted in S2 of the SOM. It appears that the existence of a distinct low-Ti signature during this time period (now considered part of Group II) is robust, but a distinct high-Ti signature, relative to the Hadean distribution, is not.

The Wilcoxon Rank Sum Test (see McClave and Sincich, 2006) shows that Groups I and II are distinct in the variables U_t , $(Th/U)_t$, Hf, Ce, and P at the 95% confidence level (see SOM 3). Although Group I compositions are similar to those of Hadean Jack Hills zircons (see Fig. 5), Group II is distinct and apparently unique in the Jack Hills record. Group II U contents are higher than Group I and range from 50 to 480 ppm ($U_t = 100 - 1050$ ppm), with most grains having U > 200 ppm (Figs. 2a and 5). The high U contents displayed by Group II zircons contrast with the Hadean Jack Hills zircons, which typically have U below 200 ppm (e.g., Crowley et al., 2005; Harrison, 2009). (Th/U) ratios of the Group II zircons are typically below Group I (Fig. 2b) and (Th/U) appears to vary with U content. Another notable minor element is Hf (Fig. 2c), which is higher in Group II than Group I and covaries weakly with U (R^2 =0.42). Fig. 2d shows the light REE Ce, for which Group II displays lower values than Group I. Phosphorus behaves similarly to Ce in the two groups.

Discriminant analysis using the variables U_t , Hf, (Th/U)_t, P, and Ce and the discriminant function given in S3 (of the SOM) confirms these groupings, sorting all of the zircons in the 3.91–3.84 Ga age range into their respective groups based on our



Fig. 4. A comparison of the temperature estimates using Ti data from both multicollection (MC) and peak switching (PS) during the full trace element analysis.



Fig. 5. Group I and II zircons in U_t vs. Hf space, with a set of Hadean zircons also analyzed in this study for comparison (all PS trace element data in Table S2 of the SOM). Note the greater similarity with Group I than Group II of the 13 out of 14 studied Hadean zircons.

original estimated identifications from Fig. 2a. Leave-one-out cross-validation (to test the robustness of the discriminant classification; see, e.g., Klecka, 1980) also confirms this result. Trace element results for 14 Hadean Jack Hills zircons mostly fall within Group I (Fig. 5; U_t vs. Hf) and this is also shown by the discriminant analysis (see S3).

4.3. Imaging for morphologies and internal textures

Zircon morphologies range from irregularly shaped grains to those with at least one pyramidal termination. Zircons also range from angular to well-rounded. Many are highly cracked, although on most grains we were able to measure Ti on uncracked regions of the surface. Internal textures as shown by cathodoluminescence (CL) imaging include oscillatory zonation (common among magmatic grains), patchy zonation (commonly caused by metamorphic alteration), and concentric broad zones of an uncertain origin (but which may reflect altered or blurred oscillatory zonation). Many grains are homogeneous in CL. One grain



Fig. 6. Representative cathodoluminescence images of the 13 zircons in Group I. Each scale bar is 50 μ m unless otherwise specified. The locations of U/Pb analysis spots are labeled with their associated ²⁰⁷Pb/²⁰⁶Pb ages. The locations of trace element analyses are labeled with "REE" and their associated Ti-in-zircon temperatures. Several spots in which Ti alone was measured are labeled with their associated temperatures (these are the "MC" spots discussed in Section 4.1). The locations of oxygen isotope spots and their associated δ^{18} O values are also noted. Values in parentheses were later found to have been collected over a crack. Additional images for Group I zircons are shown in S4 (SOM).

(RSES73-3.7, 3831 \pm 35 Ma, T_{MC}^{xlln} =716 °C) shows possible sector zonation. Figs. 6 and 7 show representative CL images of zircons in Group I and Group II, respectively, along with SIMS analysis spots. Additional CL images for all grains in Groups I and II are found in S4 of the SOM.

4.4. Oxygen Isotopes

Fig. 8 shows δ^{18} O results for concordant 4.0–3.6 Ga zircons. All oxygen isotope data are tabulated in Table S1 of the SOM. Like the Ti_{MC} results, we imaged the spots and excluded those found to be collected on cracks. Higher-confidence measurements were collected on demonstrably pristine surfaces and lower-confidence measurement spots could not be imaged well enough for certainty, although there is no distinguishable difference between the two populations. Concordant zircons in this age range have an average $\delta^{18}O_{\text{SMOW}}$ of ~5.5%, similar to that of the Hadean population (see, e.g., Cavosie et al., 2005; Trail et al., 2007b; Harrison et al., 2008). Unlike the trace element record, the δ^{18} O distribution in the period 3.91-3.84 Ga is not distinct from the Hadean. After 3.8 Ga, however, the $\delta^{18}O_{SMOW}$ distribution is more restricted: there are few zircons with oxygen compositions resolvably heavier than the mantle value (5.3%, Valley, 2003), consistent with the findings of Bell et al. (2011) for post-Hadean Jack Hills zircons. The two exceptions are RSES72-1.3 (7.23 \pm 1.15‰ at 3.60 Ga) and RSES72-17.8 $(1.10 \pm 1.16\%)$ at 3.64 Ga), although the

highly imprecise measurement on sample RSES72-1.3 is within error of the prevailing \sim 4.5–6.5‰ population at this time period. Several discordant zircons (not pictured on Fig. 8 but listed in Table S1 of the SOM) also fall below the mantle value along with RSES72-17.8 between 3.8 and 3.6 Ga.

5. Discussion

The age distribution of the Jack Hills zircons is dominated by (a) a small population 4.3–3.8 Ga (peaking at 4.1 Ga) and (b) a dominant population 3.6–3.3 Ga (peaking at 3.4 Ga), with a sparsely populated age minimum in between (see Bell et al., 2011; Crowley et al., 2005; Holden et al., 2009). These two populations have somewhat different properties, indicating changes in provenance between the two time periods: despite similar T^{xlln} signatures, the more restricted δ^{18} O distribution among younger zircons points to a different magmatic environment (Bell et al., 2011).

Detailed investigation of zircons from the sparsely represented age range from 4.0 to 3.6 Ga sheds some light on this transition. Although the average δ^{18} O is not very different from that seen in previous studies of the Hadean zircons, the restricted range after 3.8 Ga (and lack of unambiguously heavy δ^{18} O) may point to a decreased importance of aqueous alteration or sediment inclusion



Fig. 7. Representative cathodoluminescence images of the 17 zircons in Group II. Values and analysis spot annotations for ${}^{207}\text{Pb}/{}^{206}\text{Pb}$ ages, T^{xlln} , and δ^{18} O are shown as in Fig. 6. Additional images for Group II zircons are shown in S4 (SOM).

in post-3.8 Ga Jack Hills protoliths. We expand further on the trace element results given in Section 4.2.

5.1. Group II: The case for a distinct origin

A distinct distribution of highly incompatible trace elements for some zircons ("Group II") suggests that many of these grains have a separate origin from the majority of other Jack Hills zircons in the variables U_t, (Th/U)_t, Hf, P, and Ce. Group II ²⁰⁷Pb/²⁰⁶Pb ages (of which 14 out of 17 grains are within 10% of concordia; all are within 15%) span the period 3.91–3.84 Ga. Other samples from the period 3.91 to 3.84 Ga ("Group I") have trace element signatures strongly resembling those of the Hadean Jack Hills zircons (see discriminant results in Section 4.2), such that a discriminant analysis based on the function and variables given in SOM S3 sorts the Hadean zircons into Group I. The 4.0–3.6 Ga distribution outside of this ~70 Ma period is indistinguishable from the Hadean distribution in apparent T^{xlln}.

5.1.1. Provenance interpretations

We interpret the two groups indicated by the discriminant analysis described in Section 4.2 as having separate origins, of which Group II is apparently unique in the Jack Hills record. Group I likely derives from similar provenance(s) as the Hadean zircons on the basis of T^{xlln} , U_t, Hf, and (Th/U)_t, Ce, and P, probably indicating a continuance of similar geological conditions in the

source region(s) at least until 3.84 Ga. Group I consists of zircons with both apparently magmatic, oscillatory zonation (4 of 13), patchy (apparently metamorphic or altered) internal features (7 of 13), and two zircons of more ambiguous internal structure: a homogeneous grain (RSES 54-15.11) and one displaying wide concentric banding of uncertain origins, which may be faded or blurred oscillatory zonation (RSES 55-5.13) (see Figs. 6 and S4 of the SOM). The zircons display typical igneous REE patterns of low LREE/HREE, positive Ce anomalies, and negative Eu anomalies (Hoskin and Schaltegger, 2003), although one does display somewhat unusually elevated LREE (see Fig. 3). $(Th/U)_t$ values of 0.27 ± 0.08 are within the range of typical igneous (Th/U) values (Hoskin and Schaltegger, 2003) and similar to if slightly lower than most Hadean Jack Hills zircons. Group I zircons are probably igneous in origin (or igneous with some later alteration, as with the patchily textured grains) and derive from a provenance(s) similar to the Hadean Jack Hills zircons.

Group II displays distinctly higher U_t and Hf than Jack Hills Hadean zircons and lower average $(Th/U)_t$, Ce, and P. The average $(Th/U)_t$ of 0.15 ± 0.05 is significantly below Group I and the Hadean zircons. Group II also contains both zircons with consistently low apparent T^{xlln} along with zircons that have conflicting (MC vs. PS) T^{xlln} estimates. REE patterns for the majority of these zircons appear to have all the characteristics of typical igneous zircon (as does Group I, though Group II has somewhat lower LREE as shown here by Ce abundances). Group II consists of 8 homogeneous and 7 patchy grains (see Fig. 7 and Table S2 of the



Fig. 8. δ^{18} O vs. age for U–Pb-concordant samples in this study, with earlier studies for comparison. After 3.8 Ga, zircons rarely fall above the mantle value (solid line; dashed lines are 1 σ above and below). As in Fig. 1, samples from this study are divided into "well imaged" and "poorly imaged" analyses. ¹The several previous studies include: Cavosie et al. (2005), Trail et al. (2007b), Harrison et al. (2008) (Hadean), and Bell et al. (2011) (post-Hadean).

SOM). Two zircons (RSES 56-10.17, RSES 59-6.12) display a wide concentric banding that is of uncertain origins, but may be faded or blurred oscillatory zonation. On the basis of REE and structural data, we conclude that most of these zircons are ultimately igneous in origin with variable amounts of later alteration.

5.1.2. Origins of Group II zircons

Several models for Group II petrogenesis are possible. If Group II zircons are igneous and relatively unaltered, then their higher U_t and Hf would suggest derivation from relatively more evolved or later-stage melts than those that yielded the Hadean and Group I zircons. Their very low Ti contents (and therefore low apparent *T*^{xlln}) are consistent with this, since rare (possibly subsolidus) zircons with apparent $T^{\text{xlln}} < 600 \,^{\circ}\text{C}$ are nearly always found in highly evolved felsic rocks (e.g., Fu et al., 2008). On first consideration, a relatively low degree of alteration for these zircons might be suggested by their high degree of concordancehomogeneous grains and grains with wide concentric zoning (possibly faded oscillatory zonation?) are mostly within 5% of concordia. By contrast, Holden et al.'s (2009) survey of Jack Hills zircons shows that during this time period only $\sim 60\%$ of the overall population are within 10% of concordia. However, the high degree of concordance for these high-uranium zircons, compared to the higher degrees of discordance found among other contemporary Jack Hills zircons, is puzzling. If Group II zircons are largely unaltered, it is likely that they resided in a higher temperature environment for much of their history between formation and deposition at ca. 3 Ga in order for accumulated radiation damage to be annealed, thus forestalling metamictization and Pb loss. The lack of clear igneous textures among Group II zircons is notable if an origin of the group as unaltered igneous zircons is to be seriously considered.

Another possible origin for Group II zircons is by metamorphic recrystallization of originally igneous zircons, perhaps even of similar or identical provenance to the prevailing 4.2–3.6 Ga population (though not necessarily so). Originally igneous zircons that subsequently recrystallized during metamorphism have distinct chemistries from neo-formed metamorphic zircon as well as different internal structures (Hoskin and Schaltegger, 2003). While several types of metamorphic recrystallization have been

identified that flush Pb from the zircon lattice and thus re-set the U-Pb clock (e.g., Hoskin and Black, 2000; Vavra et al., 1999), transgressive recrystallization (Hoskin and Black, 2000) is the type most likely to account for Group II. Transgressive recrystallization occurs under high-temperature conditions and involves the migration of recrystallization across a zircon (transgressing earlier structures), which results in the flushing of more incompatible trace elements (e.g., LREE, P, Th) from the lattice as well as an increase in more compatible elements (e.g., Hf, U), consistent with Group II chemistry. Many other types of alteration yield zircon with trace element chemistries at odds with the general trends for Group II: for instance. Pidgeon et al. (1998) found recrystallized regions with either low U or high levels of many trace elements including U, Pb, and P. Vavra et al. (1999) observed mostly CL-bright, U-depleted regions among their U-Pb disturbed zircon domains. Complete recrystallization tends to blur or erase original compositional zoning, often leading to transgressive dark, homogeneous regions of zircon (Hoskin and Black, 2000; Hoskin and Schaltegger, 2003), so that zircons with obviously altered/ metamorphic zoning (e.g., patchy) may represent only partially altered, rather than completely recrystallized, samples. Following this, CL-bright regions are also likely not transgressively recrystallized.

The chemistry of Group II is consistent with the general trends observed following transgressive solid-state recrystallization of zircon during high-grade metamorphism (e.g., Hoskin and Black, 2000; Hoskin and Schaltegger, 2003): cation pumping removes incompatible trace elements from the structure but tends to enhance more compatible elements, leading to increases in the concentrations of, e.g., Hf and U, in recrystallized areas. Less compatible elements in the zircon lattice tend to be expelled leading to recrystallized regions displaying lower Th/U ratios. The recrystallized zircons studied by Hoskin and Black (2000) displayed Th/U ratios lower than unaltered protolith zircons, but at the lower end of the magmatic range rather than the values < 0.01 often observed in neo-formed metamorphic zircon. Complete recrystallization will also reinitialize U-Pb ages by removing radiogenic Pb from the zircon crystal structure (e.g., Hoskin and Schaltegger, 2003). Group II's dark, homogeneous zircons are similar to what Hoskin and Black (2000) observed in recrystallized regions, although Group II zircons lack obvious alteration fronts and un-recrystallized areas for chemical comparison which would make their identification more certain. Some Group II zircons display patchy (if faintly so) regions that are probably not fully recrystallized via transgressive recrystallization or may have been subjected to other modes of alteration. It is significant that several of these patchy zircons are also among the most U-Pb discordant of the Group II grains.

Given the Group II zircons' U-Pb systematics, internal structures, and compositional traits, we consider transgressive recrystallization of originally igneous zircons to be the most likely scenario for Group II formation. The protoliths are unknown but could perhaps be a population similar to the Group I/Hadean lack Hills zircons. The trace chemical characteristics of Group II are consistent with its derivation from the Group I/Hadean population by transgressive crystallization, and the low degree of discordance despite the high U contents is explained by increased lattice stability and U-Pb clock resetting following cation pumping during recrystallization. The zircons with alteration structures were likely not completely recrystallized and radiogenic Pb was only partially lost. Under this interpretation, the unusually low Ti contents of Group II zircons do not reflect formation temperatures but instead cation-pumping during partial to total recrystallization. Higher-Ti domains sampled during MC analysis may represent zones that escaped thorough recrystallization; 3 out of the 6 Group II zircons with disagreeing MC and PS Ti measurements display patchy zonation indicative of

regions that escaped thorough recrystallization. For a population of protolith zircons with uniform age and similar (Th/U), transgressive recrystallization, as described by Hoskin and Black (2000), would be expected to lead to correlations between (Th/U) and apparent age. However, as the original igneous provenance of Group II zircon is likely highly inhomogeneous both in age and trace element contents (similar to the Group I/Hadean Jack Hills zircon population) then the lack of correlation between $(Th/U)_t$ and age is not a compelling argument against the transgressive recrystallization hypothesis. Given the likely multisource nature of the detrital zircons, it is unclear if the \sim 70 Ma period (from the range of Group II ages, 3.91–3.84 Ga) represents one long-duration thermal event, or a series of thermal events. The high degree of U-Pb concordance of Group II zircons indicates that it is unlikely that recrystallization occurred much more recently than the apparent grain ages, although given the nature of the recrystallization process and the possibility of only partial resetting (probably not significant, again, given the concordance of the zircons) the individual zircon ages may be slight overestimates for the period of resetting.

Hoskin and Black (2000) suggest that high concentrations of trace elements exert strain in the zircon crystal structure which is relieved by recrystallization. The higher U contents in Group II relative both to Group I and the prevailing 4.2–3.6 Ga population may suggest that these zircons were already high in trace element abundances. Higher U contents in particular also predispose a zircon to metamictization, which may facilitate recrystallization and other alteration. However, given that transgressive recrystallization also leads to increased U contents in recrystallized regions of the zircon, the original trace chemistry of these grains is unclear.

5.2. Are these observations consistent with an LHB signature?

If Group II zircons indeed recrystallized during a thermal event(s) at ca. 3.9 Ga in the Jack Hills zircon source(s) as discussed in Section 5.1.2, then the Late Heavy Bombardment provides a plausible, though not necessary, mechanism for the heating event(s). Expected effects of an intense meteorite bombardment of the magnitude proposed for the LHB (e.g., Abramov and Mojzsis, 2009) include low-grade metamorphism throughout much of the crust and high grade metamorphism-including temperature increases of \geq 300 °C through up to \sim 10% of the crust creating locally pervasive impact-related melting (Abramov and Mojzsis, 2009). Of these effects, metamorphism is most likely to be widespread enough to leave a signal in the detrital record. The inferred metamorphic event(s) suggested by Group II at ca. 3.91–3.84 Ga are consistent with the LHB, although endogenic causes for metamorphism cannot with the present data be excluded.

Although the detrital nature of our samples precludes examination of zircon protoliths, it does allow for a wide sampling of conditions in the Jack Hills source terrane ca. 3.9 Ga. One expected effect of bolide impact that is notably absent in the Jack Hills zircon record is the development of shock structures. The apparent absence of these in today's Jack Hills zircons may be due to preferential destruction of shocked grains during sedimentary transport. While Cavosie et al. (2010) documented the ability of shocked zircons to survive riverine transport from their basement source, the possibility of multi-cycle clastic sediments containing such zircons seems remote.

The existence of two distinct provenance groups among the ca. 3.9 Ga zircons, one distinct from the apparently dominant group from the Hadean, is interesting in light of an LHB origin model: Group I zircons represent a provenance contemporaneous with and not noticeably affected by the likely high-temperature conditions experienced by Group II and probably represent a continuation of the same petrogenetic processes ongoing in the Jack Hills source area prior to 3.91 Ga—probably intermediate to felsic magmatism near minimum melting conditions (e.g., Trail et al., 2007b; Watson and Harrison, 2005). At first glance, the continuity of Group I/Hadean-style zircon petrogenesis during the period 3.91–3.84 Ga seems problematic for a scenario in which Group II formed by transgressive recrystallization during heating. However, Group II zircons could have been derived from the portions of the source region that experienced higher temperatures—perhaps deeper in the crust or laterally closer to sources of heat at ca. 3.9 Ga—and Group I from areas that experienced less thermal intensity.

Lastly, we note that if our results are truly a consequence of the LHB, the observation of a unique zircon population bounded between 3.91 and 3.84 Ga would support the original hypothesis by Tera et al. (1974) of a relatively brief event at ca. 3.9 Ga rather than the termination of a protracted cataclysm (e.g., Hartmann, 1975).

5.3. Comparison of timing from other studies of the LHB

The concept of a Late Heavy Bombardment originated with the observation that U–Pb and Rb–Sr systems in Apollo and Luna samples were reset at ca. 3.95–3.85 Ga (Tera et al., 1974). ⁴⁰Ar/³⁹Ar dating of more randomly derived lunar meteorites has also been interpreted to indicate a Moon-wide cataclysm (Cohen et al., 2000) and the estimated ages of the largest lunar impact basins are restricted to ~3.82–4.0 Ga (Ryder, 2002). Meteorites from several large asteroid families (the mesosiderites, HED achondrites, and ordinary chondrites) also appear to have undergone impact degassing at ~3.9 Ga (Kring and Cohen, 2002).

In addition, several studies have identified a period at ca. 3.9 Ga when Jack Hills zircons grew epitaxial rims—likely due to a heating event. Trail et al. (2007a) found epitaxially grown rims on > 4 Ga Jack Hills zircons, with rim ²⁰⁷Pb/²⁰⁶Pb ages ranging from 3.85 to 3.97 Ga, permissively bracketing the Group II age range. These rims are in general highly discordant and have Th/U significantly different than the zircon cores. Recurring ages in the Trail et al. (2007a) study fall into the range 3.93-3.97 Ga, slightly older than Group II (but some rim ages are within error of 3.91 Ga). In a follow-up study, Abbott et al. (2012) found ca. 3.95-3.85 Ga rims grown on Hadean Jack Hills zircon cores. Abbott et al. (2012) extracted additional information from these rims by depth-profiling the zircons using a technique that combined traditional U-Th-Pb analysis (Trail et al., 2007a) with analysis of Ti, allowing for continuous profiles of both age and T^{xlln} . Most rims in the period 3.95–3.85 Ga displayed average apparent T^{xlln} \sim 850 °C, much higher than the Hadean average (ca. 680 °C) but consistent with prevailing T^{xlln} displayed by zircons formed in melt sheets associated with large impacts (Wielicki et al., 2012). This high- T^{xlln} signature is seen only in the period 3.85–3.95 Ga (Abbott et al., 2012), and is notably different than the lower T^{xlln} seen among many Group II zircons in the same period. This suggests that these rims probably formed by new zircon growth at 3.95-3.85 Ga under high temperature conditions, rather than by the solid-state, transgressive recrystallization of protolith zircon that we interpret in our Group II zircon cores. Cavosie et al. (2004) documented rims with ages of 3.7-3.4 Ga on > 4 Ga Jack Hills zircons; they did not find clear evidence for rims at ca. 3.9 Ga. However, they did not depth profile the zircons but collected multiple U-Pb spot analyses on each of several > 3.8 Ga grains. Rims on their zircons therefore had to be large to be noticeable; the $< 10 \,\mu m$ zones discovered by Trail et al. (2007a) would not be accessible to spot analysis. It appears that whatever event(s) occurred at ca. 3.9 Ga did not cause the noticeable growth of many rims larger than several µm in the preexisting Jack Hills zircons. Although there is no exact match between the periods of epitaxial rim formation (Abbott et al., 2012; Trail et al., 2007a) and apparent recrystallization of our Group II zircons, they do largely coincide and may point toward the same thermal event or series of events ca. 3.9 Ga in the Jack Hills source region(s). If Group II zircons display transgressive recrystallization, that likely points toward a high-temperature event: Hoskin and Black (2000) made the observations of this alteration type in granitoids that had undergone granulite-facies metamorphism. While this information is in itself insufficient to distinguish between a meteoritic vs. endogenic origins for this apparent period of heating in the lack Hills source terrane(s), the occurrence of a high-temperature metamorphic event ca. 3.9 Ga is an expected effect of the LHB and Group II Jack Hills zircons may be some of the first terrestrial evidence for it. Investigation of the few other localities on Earth where > 3.8 Ga rocks or zircons are found may shed further light on this important interval in Earth history.

6. Conclusions

The period between ca. 3.91 and 3.84 Ga appears unique in the > 3.6 Ga Jack Hills zircon record in having at least two distinct provenance groupings based on trace elements. The existence of a distinct high-U (and Hf), low-Ti (and Ce, P, Th/U) zircon provenance ("Group II") is specific to this era. Other zircons in this period (trace element "Group I") resemble the majority of Hadean zircons both in apparent T^{xlln} distribution and various other aspects of trace element chemistry. These patterns in trace element depletion and enrichment, the seemingly paradoxical coincidence of the highest U contents with high degrees of concordance, and the homogeneous nature or very faint zoning found in many Group II grains, lead us to interpret Group II as products of transgressive recrystallization at ca. 3.91-3.84 Ga (see Hoskin and Black, 2000; Hoskin and Schaltegger, 2003), likely resulting from a significant thermal event(s). Previously discovered ca. 3.9 Ga rims on older zircon cores (Abbott et al., 2012; Trail et al., 2007a) may also be related to this event. Group II makes up a large proportion of the ca. 3.9 Ga zircon record, and the existence of a prominent distinct group here (as compared to the rest of the 3.8-4.3 Ga Jack Hills record) suggests this event may have been unique in intensity during the Hadean and early Archean of the Jack Hills source terrane. The curious coincidence of an apparent thermal event with the time period suggested for the Late Heavy Bombardment (LHB) (i.e., ca. 3.9 Ga) suggests this portion of the Jack Hills detrital zircon record may be evidence of the LHB on Earth.

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Appendix A. Supplementary materials

Supplementary data associated with this article can be found in the online version at http://dx.doi.org/10.1016/j.epsl.2013.01.001.

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