

## Hadean Zircon Petrochronology

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### INTRODUCTION

The inspiration for this volume arose in part from a shift in perception among U–Pb geochronologists that began to develop in the late 1980s. Prior to then, analytical geochronology emphasized progressively lower blank analysis of separated accessory mineral aggregates (e.g., Krogh 1982; Parrish 1987), with results generally interpreted to reflect a singular moment in time. For example, a widespread measure of confidence in intra-analytical reliability was conformity to an MSWD (a form of  $\chi^2$  test; Wendt and Carl 1991) of unity. This approach implicitly assumed that geological processes act on timescales that are short with respect to analytical errors (e.g., Schoene et al. 2015). As *in situ* methodologies (e.g., Compston and Pidgeon 1986; Harrison et al. 1997; Griffin et al. 2000) and increasingly well-calibrated double spikes (e.g., Amelin and Davis 2006; McLean et al. 2015) emerged, geochronologists began to move away from interpreting geological processes as a series of instantaneous episodes (e.g., Rubatto 2002). At about the same time, petrologists developed techniques that permitted *in situ* chemical analyses to be interpreted in terms of continuously changing pressure–temperature–time histories (e.g., Spear 1988). The recognition followed that specific mineral reactions yielded products that could be directly dated or interpreted in terms of protracted petrogenetic processes. Part of this shift was due to an appreciation that trace elements in accessory phases could identify the changing nature of modal mineralogy during crystal growth (e.g., Pyle et al. 2001; Kohn and Malloy 2004) and thus potentially relate petrogenesis to absolute time. The transition to petrochronology was complete upon recognition that high MSWDs were in fact the expected case for most metamorphic minerals (Kohn 2009).

One of the great frontiers for fundamental discovery in the geosciences is earliest Earth (DePaolo et al. 2008). However, investigations of the first five hundred million years of Earth history—known as the Hadean eon (Cloud 1972, 1976)—are limited by the lack of a rock record older than 4.02 Ga (Bowring and Williams 1999; Mojzsis et al. 2014; Reimink et al. 2016; cf. O’Neil et al. 2008). This potentially leaves only a single strategy—the examination of Hadean detrital or inherited minerals—to directly assess the geophysical conditions, and therefore habitability, of early Earth. Not having access to the rock context in which a mineral geochronometer formed does reduce opportunities to understand its growth medium and the forces acting on it during crystallization. However, all is not lost. Virtually every accessory phase contains both trace element signatures and inclusions of coexisting minerals that were incorporated during its formation. Thus we can stand what seems to be a limitation on its head by viewing, for example, a detrital zircon as both a micro-rock encapsulation system and an elemental partition mirror of the magma from which it grew.

In this chapter, we review the petrochemical and -chronological systems in zircon and their application to detrital grains from the Jack Hills regions, enumerate the thirteen presently known localities from which Hadean zircons have been documented, review their age and geochemical properties, and discuss the results in context of possible and unlikely sources. For our purposes, we arbitrarily define the Hadean as the period of Earth history prior to formation of the oldest documented rock (i.e., older than the age of the Acasta metatonalite at 4.02 Ga). We conclude that, in contrast to the longstanding paradigm of a hellish early Earth devoid of oceans, continents and life, the Hadean zircon record, and the micro-rocks that they encapsulate, largely grew under a range of conditions far more similar to the present than once imagined.

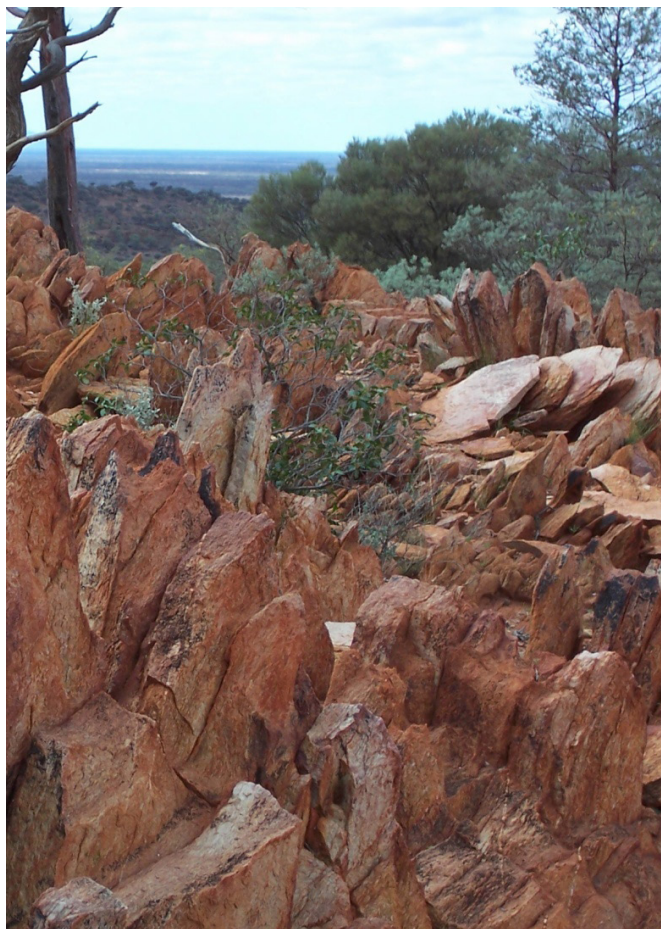
### WHY STUDY HADEAN ZIRCONS?

Due to zircon's inherent resistance to alteration by weathering, dissolution, shock, and diffusive exchange, and its enrichment in U and Th relative to daughter product Pb (Hanchar and Hoskin 2003), the U–Pb zircon system has long been regarded as the premier crustal geochronometer. While highly valued in that role, the trace element and isotopic compositions of zircon have become recognized as valuable probes of environmental conditions experienced during crystallization. Even in cases where zircon has been removed from its original rock context, such as detrital grains in clastic rocks, inclusions, trace element patterns and isotopic signatures can yield important information regarding source conditions if the record is undisturbed. Having emphasized the remarkably refractory nature and resistance to diffusive exchange of zircon (Cherniak and Watson 2003), it is important to note its Achilles heel. Zircon is sensitive to radiation damage and can degrade into heterogeneous microcrystalline zones encompassed by amorphous material (Ewing et al. 2003). Nature has, to some degree, already weeded out those grains most susceptible to metamictization from detrital zircon populations as high U and Th grains are unlikely to survive sediment transport (e.g., Hadean Jack Hills zircons with original U concentrations >600 ppm are exceedingly rare). Thus care must be taken to ensure that effects of post-crystallization alteration are not mistaken as primary features.

The importance of Hadean zircons is then in the coupling of their great antiquity with their amenability to U–Pb dating and capacity to retain geochemical information. Although first documented at nearby Mt. Narryer (Froude et al. 1983), the vast majority of investigations of > 4 Ga zircons sampled heavy-mineral-rich quartz-pebble conglomerates from a locality in the Erawondoo region of the Jack Hills (Fig. 1) (Compston and Pidgeon 1986; Maas et al. 1992; Spaggiari et al. 2007). Zircons are typically extracted from these rocks using standard separatory methods based on their high density and low magnetic susceptibility, handpicked and secured in an epoxy mount which is then polished and analyzed using the  $^{207}\text{Pb}/^{206}\text{Pb}$  ion microprobe dating approach (see Holden et al. 2009).

Over 200,000 of these grains have been  $^{207}\text{Pb}/^{206}\text{Pb}$  dated in this fashion with over 6,000 yielding ages older than 4 Ga. Most of the ~3% of the analyzed grains that are > 4 Ga were then U–Pb dated using an ion microprobe, with several found to be as old as 4.38 Ga (Compston and Pidgeon 1986; Holden et al. 2009; Valley et al. 2014).

Although zircon is dominantly a mineral of the continental crust, its formation is not restricted to that environment nor, for that matter, to Earth. However, zircons of continental affinity can be readily distinguished from those derived from the mantle or oceanic crust by trace element characteristics (e.g., U/Y vs. Y) and significantly lower crystallization temperatures (Grimes et al. 2007; Hellebrand et al. 2007). Lunar and meteoritic zircons can be distinguished from terrestrial counterparts by their REE signature (e.g., lack of a Ce anomaly; Hoskin and Schaltegger 2003). Furthermore, apparent crystallization temperatures for lunar zircons range from 900 to 1100 °C (Taylor et al. 2009) in contrast to terrestrial Hadean zircons which are restricted to 600–780 °C (Harrison et al. 2007; Fu et al. 2008). Thus it is amply clear that the vast majority of Hadean



**Figure 1.** Quartz-pebble conglomerates on Erawondoo Hill, Jack Hills region of Western Australia. Samples collected within ~100 m of this site have produced >95% of all Hadean zircons yet documented (Photo credit: Bruce Watson).

zircons are derived from terrestrial continental lithologies. Furthermore, textural characteristics of Hadean zircons from Jack Hills (e.g., growth zoning, inclusion mineralogy) indicate that most are derived from igneous sources (e.g., Cavosie et al. 2004; Hopkins et al. 2008).

Geochemical studies using upwards of half of the total Hadean grains thus far documented have inspired a variety of interpretations. However, there is a broad consensus that evidence derived from these ancient zircons implies abundant water at or near Earth's surface during that era (e.g., Wilde et al. 2001; Mojzsis et al. 2001; Rollinson 2008; Shirey et al. 2008; Harrison 2009). This represents a dramatic reversal from the conception of an uninhabitable, hellish world from which this time period gets its name (Solomon 1980; Smith 1981; Maher and Stevenson 1988; Abe 1993; Ward and Brownlee 2000).

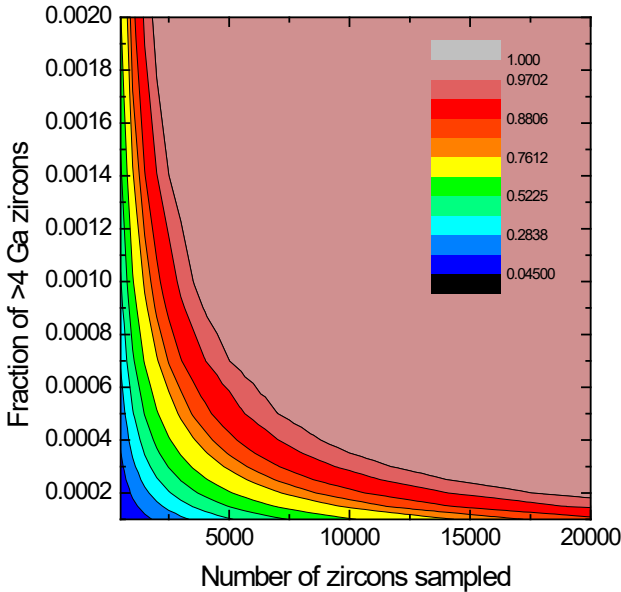
We note at the outset that the intrinsic limitations (including preservation bias) of the Hadean zircon record could prevent 'smoking gun' conclusions about earliest Earth from ever being drawn. For example, the 70% of the Earth's surface that is today covered by MORB contributes essentially nothing to the archive of detrital or xenocrystic zircons. This concern is sure to diminish as Hadean zircons are documented from a growing number of globally diverse locations.

## Modes of investigation

Most investigations of Hadean zircons to date have emphasized ion microprobe analysis to minimize the volume of mineral excavated during age surveys, thus maximizing the signals in our subsequent analyses (i.e.,  $\delta^{18}\text{O}$ ,  $^{176}\text{Hf}/^{177}\text{Hf}$ , Ti, etc.). This made sense for early studies of Jack Hills zircons (e.g., Compston and Pidgeon 1986; Mojzsis et al. 2001) as there were then no serious alternatives to the ion microprobe. Typical practice was to handpick individual zircons and mount them on double-sided adhesive tape in systematic grids together with zircon standards. This enabled the most ancient grains identified by the  $^{207}\text{Pb}/^{206}\text{Pb}$  age survey to be easily located for subsequent analysis. When we began the program to date over 100,000 Jack Hills zircons in 2001, this laborious mounting process was not the rate limiting step in creating a large archive of Hadean zircons as then no ion microprobe yet had automated analysis capability. Indeed, that project led to the development of the automated stage on the SHRIMP instruments, followed shortly thereafter by CAMECA's 'chain analysis' tool. Arguably the most remarkable analytical development over the subsequent 15 years has been the development and refinement of laser ablation, inductively-coupled mass spectrometry (LA-ICP-MS). Effective yields have increased by over an order of magnitude dropping both analytical time and the mass of material needed to attain a specified precision. This in turn has decreased costs dramatically. While the ion microprobe remains the ultimate tool for *in situ* U–Pb dating, it is perhaps no longer cost effective in undertaking large (i.e.,  $\geq 5,000$  U–Pb zircon) age surveys. Where once zircons were largely evaporated to attain an LA-ICP-MS U–Pb age, modern multicollector instruments can obtain a U–Pb with  $\pm 2\%$  precision from a  $\sim 1000\ \mu\text{m}^3$  volume (Ibanez-Mejia et al. 2014) which begins to compare favorably with the  $\sim 150\ \mu\text{m}^3$  volume long attainable using the ion microprobe. Even lower cost, quadrupole LA-ICP systems can attain similar precision from  $\sim 6,000\ \mu\text{m}^3$  ablation craters, which still represents only  $\sim 4\%$  of a typical Hadean zircon mass (i.e.,  $\sim 1\ \mu\text{g}$ ). However, a common Pb correction based on  $^{204}\text{Pb}$  is problematic for LA-ICP instruments owing to near ubiquitous background at  $^{204}\text{Hg}$  leading to seemingly precise but potentially inaccurate U–Pb ages.

**Age distributions.** Numerous age studies of Jack Hills detrital zircons all show a characteristic bimodal distribution with peaks close to 3.4 and 4.1 Ga with some grains as old as nearly 4.4 Ga (Compston and Pidgeon 1986; Maas et al. 1992; Amelin 1998; Amelin et al. 1999; Mojzsis et al. 2001; Cavoise et al. 2004; Trail et al. 2007; Holden et al. 2009; Bell et al. 2011, 2014; Bell and Harrison 2013).

How abundant are Hadean zircons on Earth? Most of the dozen or so localities for which at least one  $>4$  Ga zircon has been documented were not targeted for that purpose but rather discovered serendipitously. Ancient metasediments and orthogneisses for which 10s to 100s of zircons have been U–Pb dated without identifying at least one Hadean zircon must fall into one of two categories: 1) those in which  $>4$  Ga zircons are present at a level of less than  $\sim 1\%$  but have not yet been detected, and 2) those in which they are simply absent. How many zircons should be dated to ascertain to which category a sample belongs? The probability of detecting at least a single  $>4$  Ga zircon as a function of abundance is shown in Fig. 2. A reasonable assumption is that the ca.  $3\%$   $>4$  Ga zircon abundance in the Jack Hills (Holden et al. 2009) is anomalously high for most Archean quartzites and thus we examine the detection probabilities where abundances are between one and two orders of magnitude lower (i.e.,  $0.2$ – $0.02\%$ ). From Fig. 2, we can see that at the 95% confidence level (bright red band), diminishing returns are achieved following analysis of  $\sim 5000$  zircons, corresponding to an effective abundance limit of  $\sim 0.05\%$ . To our knowledge, only the Erawondoo locality in the Jack Hills has had more than 5000 zircons dated and thus intercomparisons are as yet of limited value.



**Figure 2.** Plot showing the probability of identifying at least one Hadean zircon from populations with a range of assumed occurrence rates of >4 Ga grains as a function of number of dated grains. Note that achieving 89–93% confidence in detecting a Hadean zircon from a population in which 1-in-2000 are >4 Ga requires U–Pb dating ~5000 grains.

Indeed, the significance of Hadean zircons is sometimes dismissed by their seeming rarity—with less than a handful of these grains (the total mass acquired is less than 6 g), how can one begin to articulate the nature of early Earth? Our view is that this type of question is akin to asking how the Big Bang could possibly be characterized by capture of a vanishingly small fraction ( $<10^{-70}$ ) of the photons in the observable universe. That is, observations on rare materials can lead to profound insights. There are two principal factors that inform this view. The first is, we do not expect to preserve a significant proportion of early formed crust on a dynamic planet. Assuming that Earth has recycled crust since formation at least as efficiently as we recognize it has throughout the Phanerozoic, only a few percent at most would likely remain (Armstrong 1981). The second is that we simply have not tried hard enough to find these remnants; we have sampled considerably less than  $10^{-17}$  of the continental crust for geochronology, and support for reconnaissance dating surveys (i.e., “fishing trips”) is notoriously difficult to obtain.

**Isotope geochemistry.** Several elements abundant in zircon comprise isotopic systems relevant to petrogenesis and have a significant role in defining conditions not only during the Hadean but throughout Earth history. The  $^{18}\text{O}/^{16}\text{O}$  of magmas contains information regarding their sources with primary variations often reflecting incorporation of aqueously altered materials. Mantle-derived magmas display a narrow range of  $^{18}\text{O}/^{16}\text{O}$ , corresponding to zircons with an average  $\delta^{18}\text{O}_{\text{SMOW}}$  of  $5.3 \pm 0.3$  ( $1\sigma$ ) (Valley et al. 1998). Aqueous alteration at low temperatures results in clay-rich sediments with higher  $\delta^{18}\text{O}$ , whereas hydrothermal alteration generally imparts lower  $\delta^{18}\text{O}$  values. Incorporation of these altered materials into later magmas results in significant deviation from the mantle average value (e.g., O’Neil and Chappell 1977) which is reflected in the compositions of all silicate and oxide phases present, including zircon. That some Hadean Jack Hills zircons are significantly above the mantle value suggests abundant liquid water in the surface or near-surface environment as early as ca. 4.3 Ga (e.g., Mojzsis et al. 2001; Peck et al. 2001).

The Lu–Hf system is based on the decay of  $^{176}\text{Lu}$  to  $^{176}\text{Hf}$  ( $t_{1/2} = 37$  Ga; Söderlund et al. 2004). Lu and Hf are fractionated during partial melting, such that higher Lu/Hf ratios form in depleted mantle and lower Lu/Hf ratios form in continental crust. Over Earth’s history,

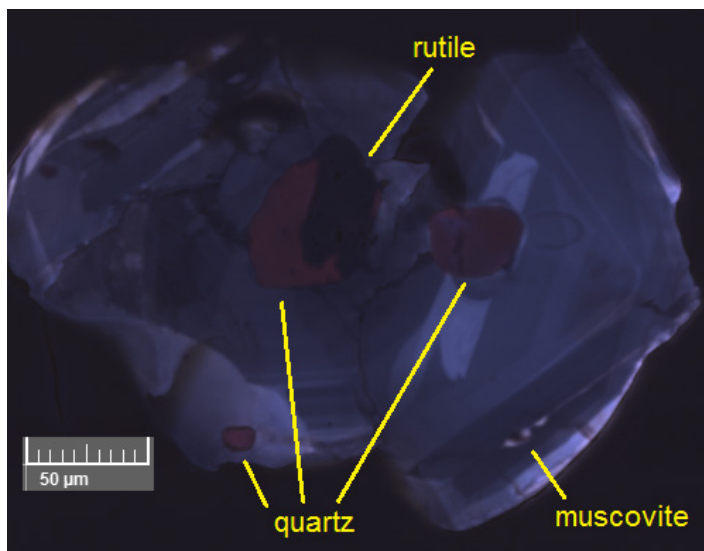


this leads to differences in  $^{176}\text{Hf}$  relative to the stable, primordial isotope  $^{177}\text{Hf}$  (represented by  $\epsilon_{\text{Hf}}$ ) in these two reservoirs. The spread in  $\epsilon_{\text{Hf}}$  between the continental crust and depleted mantle allows for the calculation of a model age of mantle extraction for igneous rocks. This isotopic system is useful on the level of individual zircons due to the incorporation of abundant (up to several weight percent) Hf in zircon and the lesser, ca. 100 ppm-level incorporation of Lu (e.g., Hoskin and Schaltegger 2003), which allows zircon to preserve the original magma  $\epsilon_{\text{Hf}}$  with very little age-correction for  $^{176}\text{Lu}$  ingrowth. Hadean Jack Hills zircons show dominantly negative (i.e., old crustal)  $\epsilon_{\text{Hf}}$  with some grains requiring separation of very low-Lu/Hf (i.e., felsic) reservoirs by ca. 4.5 Ga (Harrison et al. 2008; Bell et al. 2014).

**Mineral inclusions.** As zircon crystallizes in the solid state or from magmas, it almost invariably traps exotic phases such as crystals and melt or other fluids (e.g., Maas et al. 1992; Chopin and Sobolev 1995; Tabata et al. 1998; Liu et al. 2001; Fig. 3). Coupled with the capacity for accurate U–Pb dating of the zircon host, these inclusions are a potentially rich source of information about petrogenetic conditions of formation and/or provenance.

Although mineral inclusions in magmatic zircon can record diagnostic information about the environment in which they formed, the extent to which the mineralogy and chemistry of zircons and their inclusion can be used to reconstruct petrogenesis and provenance is only now becoming clear. Darling et al. (2009) concluded that mineral inclusions in zircons grown in intermediate to felsic melts within the Sudbury impact melt sheet imply somewhat more felsic melt conditions than the associated whole rock in terms of the modal proportions of quartz, alkali feldspar, and plagioclase. However, Jennings et al. (2011) showed that the chemistry of igneous apatite and mafic phases is typically similar between crystals included in zircon and those in the whole rock.

Establishing the primary nature of inclusions and contamination introduced during sample preparation are potentially serious concerns that need to be explicitly addressed. For example, reports of abundant diamonds and graphite in Hadean Jack Hills zircons (Menneken et al. 2007; Nemchin et al. 2008) were later determined to be contaminants introduced during sample preparation (Dobrzhinetskaya et al. 2014).



**Figure 3.** Cathodoluminescence image of Hadean Jack Hills zircon RSES77-5.7. This  $4.06 \pm 0.1$  Ga concordant grain contains likely primary inclusions of quartz, rutile and muscovite permitting reliable Ti thermometry and phengite barometry which can then be used to infer near surface thermal structure.

Mineral inclusions coupled with the chemistry of their host zircon are an underexploited resource for establishing internally consistent evidence for host rock character. The advent of the Ti-in-zircon thermometer, for instance, underscored the potential for thermodynamic relationships between included phases and elements partitioned into the zircon structure. Similarly, the incorporation of aluminous and carbonaceous inclusions into zircon (Hopkins et al. 2008; Rasmussen et al. 2011; Bell et al. 2015b; Harrison and Wielicki 2015) raises the possibility of calibrating trace elements in zircon as an indicator of host melt chemistry or volatile content.

**Zircon geochemistry.** Zircon incorporates many elements at the trace or minor level during crystallization, some of which are useful petrologic indicators. For example, the content of Ti in zircon serves as a crystallization thermometer given knowledge of the melt  $a_{\text{SiO}_2}$  and  $a_{\text{TiO}_2}$  (Watson and Harrison 2005; Ferry and Watson 2007).  $\text{Ce}/\text{Ce}^*$ , or the excess in Ce over the other light rare earth elements (LREE) La and Pr, is a proxy for magma  $f_{\text{O}_2}$  (Trail et al. 2011a). Th/U can generally be used to distinguish magmatic from metamorphic zircons, with metamorphic zircons typically  $<0.07$  and igneous zircon at higher values (Rubatto 2002, 2017). Other trace element concentrations have less quantitative ties to petrogenesis but may have the potential to yield important information.

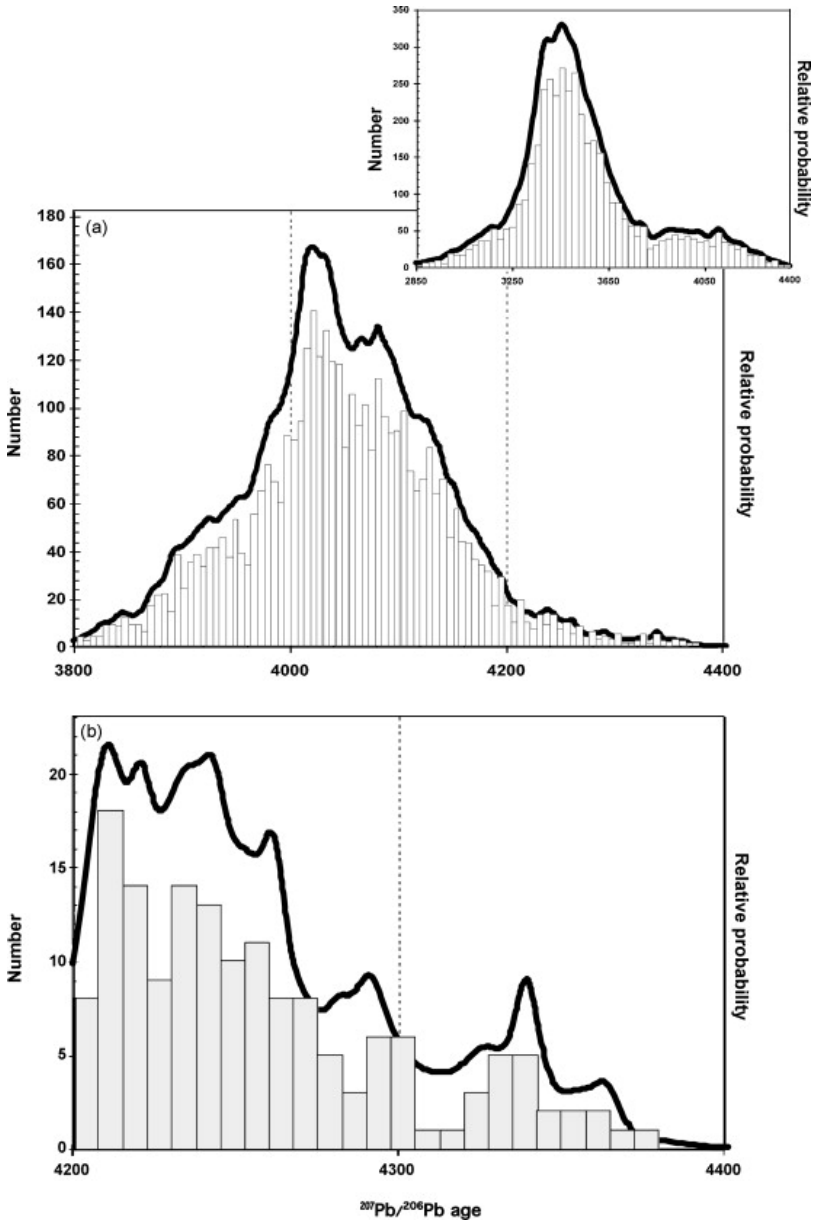
Rare earth elements (REE) occur in terrestrial zircon with a characteristic chondrite-normalized abundance pattern characterized by relatively low LREE and increasingly abundant REE with increasing Z (e.g., Hoskin and Schaltegger 2003). Two exceptions to this rule include the aforementioned excess in Ce ( $\text{Ce}/\text{Ce}^*$ ) which is seen among virtually all unaltered terrestrial zircons and a deficit in Eu ( $\text{Eu}/\text{Eu}^*$ ). The steady increase in compatibility with increasing atomic mass for most REE in the zircon lattice results from the steady decrease in ionic radius coupled with the trivalent oxidation state in which most REE are found in the crustal and surficial environment. Significant amounts of tetravalent Ce (which is more compatible in zircon) and divalent Eu (largely taken up by plagioclase) lead to their respective anomalous contents. However, interpreting REE patterns in terms of zircon petrogenesis requires distinguishing pristine from altered zircon chemistry, and hydrothermal alteration of zircon is usually accompanied by an increase in LREE relative to the other REE and a flattening of the LREE pattern, obscuring the  $\text{Ce}/\text{Ce}^*$  and potentially the  $\text{Eu}/\text{Eu}^*$ .

## JACK HILLS ZIRCONS

### Isotopic results

**U–Pb age.** Various age surveys of detrital zircons from the Erawondoo Hill discovery site conglomerate (e.g., Crowley et al. 2005; Holden et al. 2009) generally show the zircons to have a bimodal age distribution with major peaks at ca. 3.4 and 4.1 Ga. Concordant zircons older than ca. 3.8 Ga make up approximately 5% of the population, and zircons become much less abundant with age older than ca. 4.2 Ga (Holden et al. 2009; Fig. 4). The remaining 95% of the population is mostly concentrated between 3.3 and 3.6 Ga, with a deficit of zircon ages between 3.6 and 3.8 Ga (Bell and Harrison 2013).

The confidence with which one can interpret the meaning of a U–Pb date of a  $>4$  Ga zircon is challenged by the potential for later fluid alteration and thermal disturbances. While the concordance of U–Pb analyses (or lack thereof) can be used to assess the robustness of an interpreted age, this is generally insensitive to early Pb loss. Therefore, assessing the general reliability of ion microprobe U–Pb ages is an open challenge, especially given that most Hadean Jack Hills zircons contain multiple age domains. Valley et al. (2014) examined the possibility of Pb redistribution in a 4.38 Ga zircon core, imaged using atom probe tomography, encompassed by a ca. 3.4 Ga, 10–20  $\mu\text{m}$  rim. In this analytical technique, a zircon sliver extracted using a focused ion beam was field evaporated and the emergent ions mass analyzed with a spatial



**Figure 4.** Histograms and probability-density curves for concordant Jack Hills zircons. (a) Histogram of rapid initial survey of individual  $^{207}\text{Pb}/^{206}\text{Pb}$  ages undertaken to identify the  $>3.9$  Ga population. Inset shows the whole population of 4500 rapidly scanned  $^{207}\text{Pb}/^{206}\text{Pb}$  ages. (b) Histogram and probability density for the concordant  $>4.2$  Ga zircons. The small peak at 4.35 Ga may be the oldest surviving crustal remnant. Reprinted from Peter Holden et al. Mass spectrometric mining of Hadean zircons by automated SHRIMP multicollector and single collector U/Pb zircon age dating: The first 100,000 grains, *International Journal of Mass Spectrometry* 286(2–3):53–63 (2009), with permission from Elsevier.



resolution of <1 nm. Results from their analysis show Pb redistribution into “nanoclusters” with ~10 nm diameter and spacing of ~10–50 nm. The  $^{207}\text{Pb}/^{206}\text{Pb}$  age of the zircon outside of the “nanoclusters” is ~3.4 Ga and ~4.4 Ga for the entire analyzed volume. These data are consistent with an event at 3.4 Ga that mobilized radiogenic Pb that had accumulated since the zircon’s crystallization at 4.38 Ga. The mobilized Pb migrated into “nano clusters” on a length scale of <50 nm, which is below the lateral spatial resolution of an ion microprobe. This finding supports the view that due to the generally slow diffusion of Pb in zircon and zircon’s resistance to alteration, concordant U–Pb analyses likely record actual zircon crystallization ages.

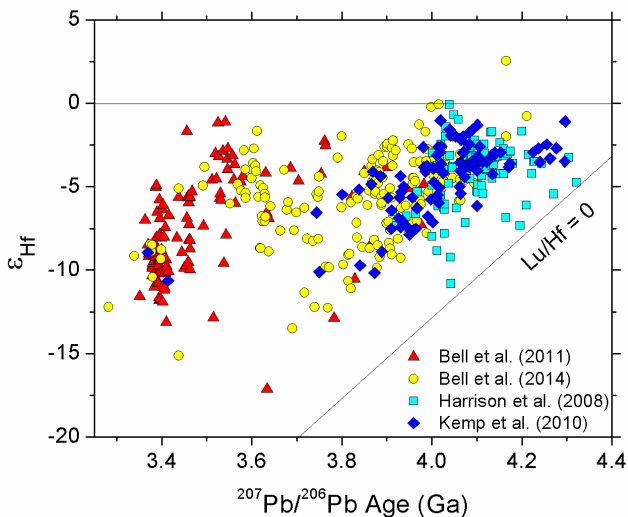
**Oxygen isotopes.** Elevated values of  $\delta^{18}\text{O}_{\text{SMOW}}$  observed in Hadean Jack Hills zircons led two independent groups to simultaneously propose (Mojzsis et al. 2001, Wilde et al. 2001) that the protolith of these grains contained  $^{18}\text{O}$ -enriched clay minerals, in turn implying that liquid water was present at or near the Earth’s surface by ~4.3 Ga. Numerous follow-up measurements (e.g., Cavosie et al. 2005, Trail et al. 2007, Harrison et al. 2008; Bell et al. 2016) confirmed that a significant fraction of Hadean Jack Hills zircons contain  $^{18}\text{O}$ -enrichments 2 to 3‰ above the mantle zircon value of 5.3‰ (Valley et al. 1998). As the oxygen isotope fractionation between zircon and granitoid melt is approximately –2‰ (Valley et al. 1994, Trail et al. 2009),  $\delta^{18}\text{O}$  values of the melt from which the zircons crystallized are inferred to have been up to +9‰.

Phanerozoic granitoids derived largely from orthogneiss protoliths (I types) tend to have  $\delta^{18}\text{O}$  between 8–9‰, whereas those derived by melting of clay-rich (i.e.,  $^{18}\text{O}$  enriched) metasedimentary rocks (S types) have higher  $\delta^{18}\text{O}$  (O’Neil and Chappell 1977). Granitoids with  $\delta^{18}\text{O}$  values significantly less than 5‰ likely reflect hydrothermal interaction with meteoric water (Taylor and Sheppard 1986) rather than weathering. In general, S-type granitoids form by anatexis of metasediments enriched in  $^{18}\text{O}$ , compared with I-type granitoids that form directly or indirectly from arc processes (Chappell and White 1974). Jack Hills zircons enriched in  $^{18}\text{O}$  thus provide evidence indicating the presence in the protolith of recycled crustal material that had interacted with liquid water under surface, or near surface, conditions (i.e., at low temperature).

A limitation to this interpretation is the possibility of oxygen isotope exchange under hydrous conditions, even at post-depositional temperatures experienced by Jack Hills zircons (i.e., ~450 °C). For example, the characteristic diffusion distance for oxygen in zircon at 500 °C for 1 Ma is ~1 μm, assuming a high water activity (Watson and Cherniak 1997). Thus it is conceivable that oxygen isotope exchange during protracted thermal events could have introduced the heavy oxygen signature. This concern is somewhat mitigated by the relative improbability that hydrothermal fluids were highly  $\delta^{18}\text{O}$  enriched. However, it does not preclude isotopic equilibration from having occurred prior to deposition at ca. 3 Ga.

**Lutetium–Hafnium.** Studies of initial  $^{176}\text{Hf}/^{177}\text{Hf}$  in >4 Ga Jack Hills zircons show large deviations in  $\varepsilon_{\text{Hf}(T)}$  from bulk silicate Earth (Kinny et al. 1991; Amelin et al. 1999; Harrison et al. 2005, 2008; Blichert-Toft and Albarède 2008; Bell et al. 2011, 2014; Kemp et al. 2010) that have been generally interpreted to reflect an early major differentiation of the silicate Earth (Fig. 5). Modeling these data by associating  $\varepsilon_{\text{Hf}(T)}$  with the range of  $^{176}\text{Lu}/^{177}\text{Hf}$  observed in large datasets of analyzed crustal rocks are consistent with the formation of crust occurring essentially continuously since 4.5 Ga. Several data (Harrison et al. 2008; Bell et al. 2014) yield  $\varepsilon_{\text{Hf}(T)}$  within uncertainty of the solar system initial ratio (Iizuka et al. 2015) requiring that the zircon protoliths had been removed from a chondritic uniform reservoir (CHUR) by 4.5 Ga. Harrison et al. (2005) initially reported several Hadean Jack Hills zircons with positive  $\varepsilon_{\text{Hf}(T)}$ , but subsequent *in situ* studies have not confirmed significantly positive values. This likely reflects complications arising from the lack of simultaneous age and Hf isotope analysis, as described by Harrison et al. (2005).

The most robust aspect of this now large dataset is the cluster of results along a line corresponding to a Lu/Hf ≈ 0.01, a value characteristic of continental crust. Such a low-Lu/Hf reservoir at ~4 Ga is consistent with either early extraction of this very felsic crust or its



**Figure 5.**  $\epsilon_{\text{Hf}}(T)$  vs.  $^{207}\text{Pb}/^{206}\text{Pb}$  age of Jack Hills zircons. Reference  $^{176}\text{Lu}/^{177}\text{Hf}$  ratios for continental crust (0.01) is shown along with value for Bulk Earth (0.034) and primordial  $^{176}\text{Hf}/^{177}\text{Hf}$  (i.e.,  $\text{Lu}/\text{Hf}=0$ ). These data are consistent with the formation of continental crust occurring essentially continuously since 4.5 Ga (modified from Bell et al. 2014).

generation by remelting of a primordial more basaltic reservoir, but in either case extrapolation of this trend yields a present-day  $\epsilon_{\text{Hf}(T)}$  of approximately -100. This is substantially lower than the most negative value yet measured ( $\epsilon_{\text{Hf}(T)} = -35$ ; Guitreau et al. 2012). The lack of such a signal suggests substantial recycling of crust into the mantle during the early Archean (Bell et al. 2011, 2014). More specifically, zircons with  $\epsilon_{\text{Hf}(T)}$  consistent with continuing evolution of this reservoir appear absent from the Jack Hills record after 3.7 Ga (Bell et al. 2014). Combined with Hf isotopic evidence for juvenile mantle melts at ca. 3.9–3.7 Ga at both Jack Hills (Bell et al. 2014) and the nearby Mt. Narryer site with similarly aged zircon (Nebel-Jacobsen et al. 2010), these observations likely point to a recycling event ca. 3.9–3.7 Ga which resembles the Hf isotopic evolution of modern subduction-related orogens (e.g., Collins et al. 2011) and so may have additional tectonic significance.

**Plutonium–Xenon.** The meteorite record reveals that  $^{244}\text{Pu}$  was present in the early solar system with an initial Pu/U abundance of  $\sim 0.007$  (Ozima and Podosek 2002). However, its use as a geochemical tracer is restricted by its relatively short half-life ( $t_{1/2} = 82$  Ma). As the only known relics of the Earth's earliest crust, analysis of Xe in Hadean zircons offers a way to determine terrestrial Pu/U ratios and potentially investigate Pu geochemistry during early crust forming events. Because these ancient zircons are detrital and of unknown provenance, it is essential that individual grains be analyzed. Turner et al. (2004) discovered the first evidence of extinct terrestrial  $^{244}\text{Pu}$  in individual 4.15–4.22 Ga Jack Hills zircons. These measurements yielded initial Pu/U ratios ranging from chondritic ( $\sim 0.007$ ) to essentially zero. The latter results were first interpreted to be due to Xe loss during later metamorphism. This assumption was tested by irradiating 3.98–4.16 Ga zircons with thermal neutrons to generate Xe from  $^{235}\text{U}$  neutron fission to determine Pu/U simultaneously with U–Xe apparent ages. Comparison of U–Pb and U–Xe ages showed varying degrees of Xe loss, but about a third of the zircons yield  $^{207}\text{Pb}/^{206}\text{Pb}$  and U–Xe ages that are concordant within uncertainty (Turner et al. 2007).

Given that U becomes oxidized to the soluble uranyl ion ( $\text{UO}_2^{2+}$ ) under even mildly oxidized aqueous conditions while the solubilities of essentially all Pu species are generally much lower, variations in Pu/U has been suggested as a potential indicator of aqueous alteration in the Jack Hills zircon protoliths (Harrison 2009). To test this hypothesis, Bell (2013) collected a multivariate dataset on eleven zircons, including analysis of Xe isotopic

ratios, U–Pb age, trace element contents, and  $\delta^{18}\text{O}$ , to look for correlations (e.g.,  $\delta^{18}\text{O}$  vs. Pu/U) expected from aqueous processes. With the exception of Nd/U, none were found. High-Nd/U zircons display only low Pu/U, while low Nd/U zircons show more heterogeneous Pu/U. The high-Nd/U group appears less magmatically evolved than other Hadean zircons, has REE patterns suggestive of some degree of alteration, either by hydrothermal fluid interaction or phosphate replacement, and consists of solely low-Pu/U zircons with a range of Hadean to Proterozoic U–Xe ages. The higher diversity of Pu/U among the rest of the population may reflect more heterogeneous processes, including possible primary Pu/U variations from a variety of processes that were not well-constrained. Thus the early promise that Pu/U variations might record aqueous fractionation events in the Hadean may not be realized.

**Lithium.**  $\delta^7\text{Li}$  analyses of Hadean Jack Hills zircons range from  $-19$  to  $+13\text{‰}$  (Ushikubo et al. 2008). These authors interpreted highly negative values to reflect zircon crystallization from a source that experienced intense weathering, thus placing the protolith at one time at Earth's surface. A limitation of this interpretation is that Li diffuses readily in zircons at relatively low temperatures (Cherniak and Watson 2010) and thus could have exchanged with hydrogen species during metamorphism (Trail et al. 2011b). Ushikubo et al. (2008) speculated that Li migration might be limited by coupling with the very slow REE diffusion in zircons thus limiting its geological transport rate. Recently Trail et al. (2016) examined just this relationship and found no detectable link between Li and REE diffusion.

### Inclusions in zircon

The plentiful mineral inclusions preserved in detrital zircons from the Jack Hills, western Australia, have been the subject of several studies beginning with Maas et al. (1992) who recognized their dominantly granitic character.

**Muscovite.** Hopkins et al. (2008, 2010) followed up the Maas et al. (1992) study by examining  $>1700$  inclusion bearing zircons from Jack Hills. Their examination revealed that quartz and muscovite are the principal inclusion phases, potentially pointing to aluminous granitic sources; see example in Fig. 3). Hopkins et al. (2010) used a thermodynamic solution model for celadonite substitution in muscovite (White et al. 2001) to estimate pressures for muscovite inclusions in magmatic zircons. In all cases, pressures greater than 5 kbar (unsurprising given the presence of magmatic muscovite) were obtained which, coupled with the relatively low host zircons crystallization temperature (ca.  $700^\circ\text{C}$ ), implies remarkably low near surface heat flows ( $\leq 80\text{ mW/m}^2$ ). This stands in stark contrast to previous model estimates of  $160\text{--}400\text{ mW/m}^2$  (Smith 1981; Sleep 2000). By analogy to modern Earth, this led them to suggest formation in an underthrust, or subduction-like, environment (Hopkins et al. 2008, 2010). However, the primary nature of these inclusions was brought into question by Rasmussen et al. (2011), who surveyed 1000 Jack Hills zircons from 4.2 to 3.0 Ga and showed that some inclusions fall on cracks in their host zircons and that phosphate inclusions generally record post-depositional U–Pb ages. They suggested that much of the mineral inclusion record was due to secondary mineralization.

However, a closer look at the Jack Hills mineral inclusion record reveals complexities not well explained by a largely secondary origin and argues for the preservation of many primary inclusions. Inclusions that intersect cracks in their host zircons display a different modal mineralogy than those isolated from cracks (Bell et al. 2015a). Muscovite inclusions record a wide range of silica substitution with Si-per-formula-unit (12 oxygen basis) ranging from 2.9 to 3.4, unlikely to all form from the same metamorphic fluid. The assemblage that intersects cracks is roughly intermediate between the isolated assemblage and the assemblage of secondary phases seen filling void space along cracks, probably showing partial replacement (Bell et al. 2015a). The isolated and likely primary assemblage is muscovite-dominated with abundant quartz, still suggestive of aluminous granitic protoliths, and minor phases such as biotite, apatite, and feldspars vary in abundance with zircon age (Bell et al.

2015a). Certain phases present in the isolated assemblage and absent in the crack-intersecting assemblage probably point to selective destruction of the minerals apatite and feldspar. Because of the relatively low numbers of identified rare phases (e.g., aluminosilicates), it is difficult at present to determine their significance for zircon provenance or for identifying the nature of the altering fluids that invaded the zircons along cracks over geologic time.

In many instances where a sound case for a preserved primary inclusion assemblage can be made, analyses cannot currently be effected due to size limitations. Indeed, only 6 of the 31 muscovites documented in the Hopkins et al. (2008) study could be reliably analyzed using EMPA due to their small ( $<2\ \mu\text{m}$  on shortest dimension) size and the effects of secondary fluorescence. Typically, the oldest zircons ( $>4.2$ ) contain the smallest white mica inclusions. For example, we have identified a zircon as old as 4.34 Ga containing white mica that, except for its size, is a candidate for thermobarometric analysis.

**Fe oxides.** The development of textural criteria for identifying primary inclusions (Bell et al. 2015a) opens up possibilities for recognizing zircons' changing provenance with time and investigating their post-depositional alteration history. One intriguing aspect of zircon provenance that could be further understood through the inclusion record is that of protolith magma  $f_{\text{O}_2}$  and its evolution. As described in more detail in the next section, Trail et al. (2011a) demonstrated that the Ce anomaly of a zircon ( $\text{Ce}/\text{Ce}^*$ ) is a quantitative estimate for host magma  $f_{\text{O}_2}$ , and furthermore that Hadean Jack Hills zircons show a range in  $f_{\text{O}_2}$  with an average near the fayalite–magnetite–quartz (FMQ) buffer, i.e., similar to the modern upper mantle. Granitoids form at a range of  $f_{\text{O}_2}$ , controlled both by source region and assimilation of wall rock material during ascent. Characteristic series of granites with contrasting  $f_{\text{O}_2}$  in accretionary environments are identified by their accessory Fe–Ti oxides, with more oxidized granites dominated by magnetite and more reduced granites dominated by ilmenite (Ishihara 1977).

Fe–Ti oxides occur commonly as inclusions in zircon (Rasmussen et al. 2011) and appear to be a robust if minor component of the Hadean primary assemblage (Bell et al. 2015a). Primary Fe-oxide inclusions may preserve geomagnetic information and multiple groups are currently investigating whether such signals are the oldest known records of a Hadean dynamo. Knowing when the geodynamo arose potentially constrains the Earth's early thermal structure and potential for atmospheric loss, as well as when compositionally-driven core convection began. At present, the oldest reliable determination of the terrestrial magnetic field is 3.45 Ga (Biggin et al. 2011).

Tarduno et al. (2015) interpreted Jack Hills zircons as containing magnetite inclusions that retained primary remanent magnetization as old as 4.2 Ga (cf. Weiss et al. 2015) but failed to demonstrate whether they had been remagnetized by thermal processes subsequent to formation. Tarduno et al. (2015) argued that their zircons had not experienced high-temperature metamorphism, as Pb would be redistributed in an inhomogeneous fashion at the nm-scale (Valley et al. 2014). This process would result in non-systematic Pb/U variations during SIMS depth profiling, which they did not observe. That view misrepresents their ion microprobe capability in three ways: 1) the sputtering process mixes near surface atoms at the  $\sim 10\text{nm}$ -scale, 2) the SHRIMP instrument they used cannot truly depth profile as sputtered atoms from both crater bottom and surface are simultaneously accelerated into the mass spectrometer, and 3) the 10–20  $\mu\text{m}$  diameter spot they used is three orders of magnitude larger than would be needed to reveal such heterogeneities, even if they existed. As described below, Trail et al. (2016) suggested that zircons exhibiting Li concentration heterogeneities, including oscillatory zoning, could be calibrated in this role as a peak temperature geothermometer for paleomagnetic studies.

**Biotite.** Biotite inclusions in magmatic zircon are relatively common (Rasmussen et al. 2011) and appear to reflect the composition of biotite in the host (Jennings et al. 2011), which varies considerably among granitoids (e.g., Buda et al. 2004; Abdel-Rahman 1994). Biotite shows characteristic variations in FeO, MgO, and  $\text{Al}_2\text{O}_3$  contents that can discriminate among

calc-alkaline, peraluminous, and alkaline anorogenic granitoids (Abdel-Rahman 1994). Thus, identifying and analyzing primary Hadean biotite inclusions could better constrain the nature of Hadean melt compositions that may have tectonic implications. In addition, rare sulfide (Mojzsis 2007) and carbonaceous (see next section) phases have also been identified in Hadean zircons. A systematic survey for these and other rare phases will further illuminate the volatile contents of Hadean magmas and their source materials.

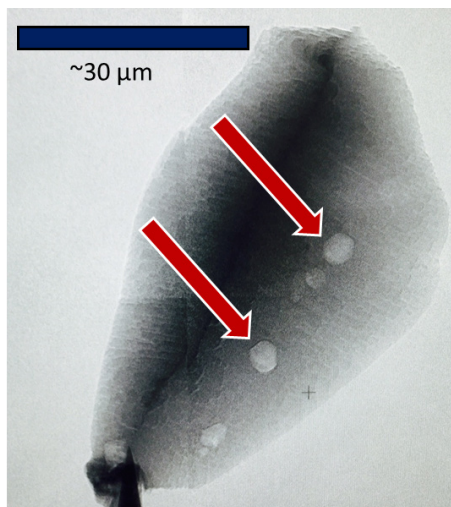
**Graphite.** A key challenge in pondering the existence of life elsewhere is that we know of only one occurrence. While Earth is the only planet on which life is known to have emerged, we remain largely ignorant of the conditions, timing and mechanisms by which this occurred. A broad array of morphological and isotopic evidence supports the view that by 3.8 to 3.5 billion years (Ga) ago our planet hosted microbiota, including some with relatively sophisticated metabolisms (e.g., Mojzsis et al. 1996; Rosing 1999; McKeegan et al. 2007; Schopf 2014; Brasier et al. 2015).

As noted earlier, geochemical studies of Hadean Jack Hills zircons have led several authors to suggest relatively clement conditions on earliest Earth (e.g., Mojzsis et al. 2001; Wilde et al. 2001; Harrison 2009). This leaves open the possibility that our planet became habitable, and life emerged, during the first 500 million years of Earth history. Knowing when and under what conditions life emerged could tell us a great deal about the likelihood of life elsewhere. Were conditions clement or hellacious? Did life emerge virtually immediately or only after a half billion years of planetary preparation?

Thus reports of abundant diamond and graphite inclusions in the Jack Hills zircons (4% of each in the zircons investigated) and the spectrum of light carbon isotopic compositions they contained (Menneken et al. 2007; Nemchin et al. 2008) was met with both excitement and skepticism; the latter reflecting the seeming inconsistency of the presence of diamonds with the many inferences drawn from other zircon inclusions (e.g., their derivation from crustal melts; Mojzsis et al. 2001; Peck et al. 2001; Watson and Harrison 2005; Hopkins et al. 2010; Bell et al. 2015). Recently, the diamonds were shown definitively to be contamination from the polishing compound that was used during sample preparation (Dobrzhinetskaya et al. 2014). The origin of the graphite was less certain but deemed also likely due to contamination. This left the true occurrence rate and nature of carbonaceous materials in the Jack Hills zircons uncertain.

Bell et al. (2015b) optically examined a large number of >3.8 Ga Jack Hills zircons and found ~25% contain opaque inclusions. Imaging these selected grains by Raman spectroscopy revealed two isolated carbonaceous inclusions in a concordant, 4.10 Ga zircon (RSES 61-18.8; Fig. 6). To ensure that these inclusions were never in contact with the laboratory environment prior to structural and isotopic analyses, Bell et al. (2015b) extracted a ~160 ng sliver of the zircon containing the two carbonaceous phases via focused ion beam milling and examined it using X-ray nanotomography (Fig. 6). The 40 nm spatial resolution of this imaging method revealed no cracks associated with the graphite inclusions. Their isolation within the zircon crystal and from cracks indicated a primary origin. Carbon isotopic measurements using SIMS yielded an average  $\delta^{13}\text{C}_{\text{PDB}}$  of  $-24 \pm 5\%$ . As carbon isotopic fractionation between gaseous and condensed species in magmas is expected to be relatively small (e.g.,  $\leq 4\%$ ; Javoy et al. 1978), such a low  $\delta^{13}\text{C}$  value is consistent with a biogenic origin. While there are possible inorganic mechanisms that could also produce such a signal, they require what we see as an unlikely chain of geologic events (Bell et al. 2015b). Alternatively, House (2015) offered the “wild” suggestion that a high carbon content in Earth’s core could have resulted in an initially highly  $^{13}\text{C}$ -depleted mantle. If the Bell et al. (2015b) result does indeed represent an isotopic signal of biologic activity, it would extend our knowledge of the timing of terrestrial life back to at least 4.1 Ga, or  $\geq 300$  Ma earlier than the previously suggested and coincident with estimates derived from molecular divergence among prokaryotes (Battistuzzi et al. 2004).





**Figure 6.** High resolution transmission X-ray image of RSES 61-18.8 with arrows pointing to the two graphite inclusions analyzed for carbon isotopes (Bell et al. 2015b).

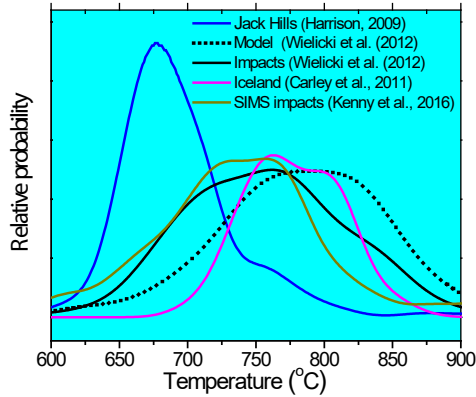
Reports of graphite in S-type granites are relatively rare but cases have been documented in which it was inherited from the source (Seifert et al. 2010; Zeng et al. 2001), incorporated via wallrock assimilation (Duke and Rumble 1986), or precipitated during subsolidus interactions with  $\text{CO}_2$  (Frezzotti et al. 1994; also see Carroll and Wyllie 1989). Graphite inclusions have been reported in metamorphic zircon (Song et al. 2005) but, to our knowledge, ours is the first documented case of primary graphite in magmatic zircon. Given the relative paucity of investigations of zircon inclusion populations, it is difficult to know whether this reflects their low abundance or simply the lack of a concerted search.

The oxygen fugacity over which graphite can be stable in a granitic magma depends on  $\text{H}_2\text{O}$  and  $\text{H}_2$  activities (Ohmoto and Kerrick 1977), but relatively reducing redox conditions (i.e., below FMQ) are implied.

### Zircon geochemistry

**Titanium.** Because the abundance of a trace element partitioned between mineral and melt is temperature dependent, crystallization temperatures can in principle be estimated from knowledge of the concentration of that element in the solid phase if the magma is appropriately buffered. The advent of the Ti-in-zircon thermometer permitted zircon crystallization temperatures to be assessed provided the activities of quartz and rutile can be estimated (Watson and Harrison 2005; Watson et al. 2006; Ferry and Watson 2007). The diffusion of Ti in zircon is vanishingly slow under crustal conditions (Cherniak and Watson 2007) and thus the potential for re-equilibration of the thermometer is very low. In the case in which zircon co-exists with both quartz and rutile (i.e.,  $a_{\text{SiO}_2} \approx a_{\text{TiO}_2} \approx 1$ ), an accurate and precise temperature (i.e.,  $\pm 15^\circ\text{C}$ ) can routinely be determined.

The first application of the Ti-in-zircon thermometer was to Hadean zircons from Jack Hills. Watson and Harrison (2005) measured Ti in zircons ranging from 3.91 to 4.35 Ga, and the vast majority of these plotting in a normal distribution. Excluding high temperature outliers yielded an average temperature of  $680 \pm 25^\circ\text{C}$  (data shown in Fig. 7). However, a limitation in applying this thermometer to detrital zircons is the unknown  $a_{\text{TiO}_2}$  of the parent magma. In the case of the zircon shown in Fig. 3, which contains both primary quartz and rutile, an accurate crystallization temperature is expected. However, unless co-crystallization with rutile is known, the calculated temperature it is a minimum estimate. In the absence of rutile inclusions, Watson and Harrison (2005) argued that  $a_{\text{TiO}_2}$  is largely restricted to between

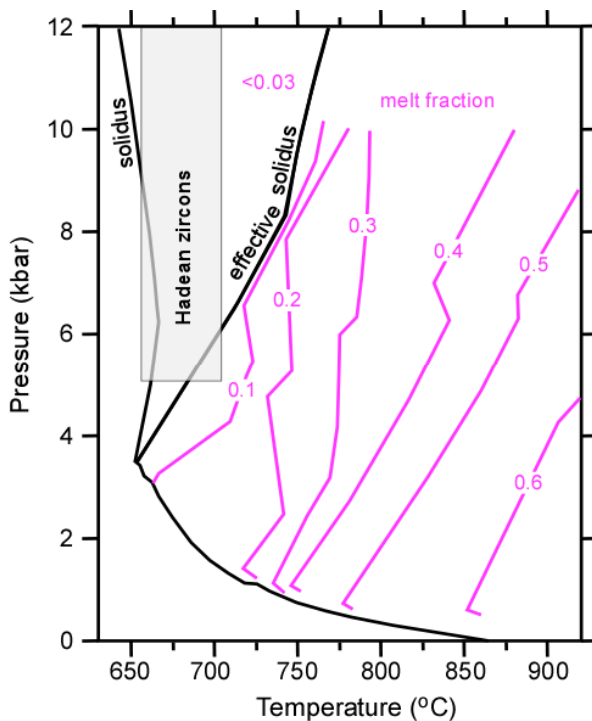


**Figure 7.** Probability plot of apparent zircon crystallization temperature comparing Hadean data (blue) with data for Icelandic (magenta) and impact formed (black) zircons. The dashed curve shows the distribution predicted by a model incorporating impact thermal effects, continental rock chemistry, and zircon saturation behavior (Modified from Wielicki et al. 2012).

~0.5 and 1 in continental igneous rocks as the general nature of evolving magmas leads to high  $a_{\text{TiO}_2}$  prior to zircon saturation. Thus for Hadean zircons of magmatic origin, it would be a rare case in which zircon formed in the absence of a Ti-rich phase (e.g., rutile, ilmenite, titanite), thus generally restricting  $a_{\text{TiO}_2}$  to  $\geq 0.5$ . In case of  $a_{\text{TiO}_2} \approx 0.5$ , calculated temperatures in the range 650–700°C would be underestimated by 40–50°C, although this is entirely compensated for if  $a_{\text{SiO}_2} = a_{\text{TiO}_2}$  (Ferry and Watson 2007). Hofmann et al. (2009) inferred that enhanced Ti contents could be incorporated during non-equilibrium crystallization resulting in higher than actual calculated temperatures. If this effect were significant in the generation of granitic Jack Hills zircons this would further support their low-temperature origin.

While it is widely acknowledged that water saturation in intracrustal magmas is rare and that the vast majority of intermediate to siliceous magmas form by dehydration melting under vapor absent conditions (Clemens 1984), Watson and Harrison (2005) concluded that the tight cluster of Hadean zircon crystallization temperatures at  $680 \pm 25$  °C (Fig. 7) reflects prograde melting under conditions at or near water saturation. They arrived at this interpretation because prograde, vapor-absent melting of metapelites and orthogneisses containing typical crustal Zr concentrations (i.e., 150–200 ppm; Harrison et al. 2007) at 5 to 10 kbar would be expected to record zircon crystallization temperature peaks corresponding to the relevant dehydration melting equilibria (e.g., muscovite at ca. 740 °C, biotite at ca. 770–800 °C, amphibole at  $\geq 800$  °C; Spear 1993). Thus, for example, Hamilton's (2007) assertion that Hadean zircons were derived solely through melting resulting from hornblende breakdown is fundamentally inconsistent with all thermometric results to date.

Rock porosities in the middle and deep crust are typically  $< 0.1\%$  (Ingebritsen and Manning 2002) and thus  $< 0.03$  wt.% free H<sub>2</sub>O is available to flux melting. During metamorphism, water is progressively lost from rocks via discontinuous, subsolidus dehydration reactions through the greenschist and amphibolite facies (Spear 1993). Structural water is stored in hydrous minerals (e.g., ~4% in muscovite, ~3% in biotite, ~2% in hornblende, ~2–4% in altered basalt at greenschist facies; Clemens and Vielzeuf 1987; Franzson et al. 2010). The correspondingly low water contents of pelitic (~1.2%) and quartzofeldspathic rocks (~0.6%) are expected to produce only small amounts of melt at temperatures close to 700 °C (Clemens and Vielzeuf 1987). Figure 8 (White et al. 2001) underscores the limited melting potential of a metapelite (represented by the Na+CaO–K<sub>2</sub>O–FeO–MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O system) for the temperature range (655–705 °C)



**Figure 8.**  $P$ - $T$  pseudosection for a model pelite in the NCKFMASH system containing added 20 mol% added  $H_2O$  (modified from White et al. 2001). Note that even in the presence of this free water, the  $P$ - $T$  region populated by Hadean zircons would result in essentially melt-free conditions indicating that very high water contents ( $>9$  wt%; Burnham 1975) would be required to create significant, mobile magmas.

and pressures ( $>6$  kbars) inferred for Hadean Jack Hills zircons which fall below the “effective solidus” melt fraction of 0.03 (even in the presence of 20 mol% added  $H_2O$ ). That is, under vapor absent conditions at the pressure–temperature range documented for Hadean zircons (Hopkins et al. 2010), both pelitic and quartzofeldspathic source rocks would be effectively melt free.

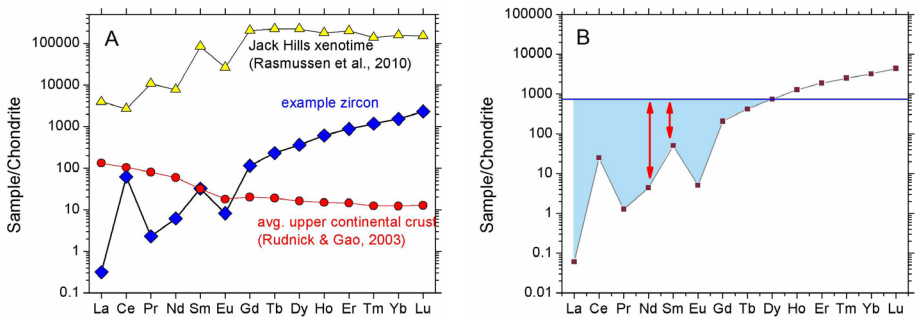
Concluding that Hadean Jack Hills zircons largely formed under water-saturated conditions sharply limits the possible tectonic settings in which they formed. The key issue is that silicate magmas at pressures above 6 kbar dissolve much more  $H_2O$  than is available in rocks (up to 70 mol% at 10 kbar; Burnham 1975; Clemens 1984) and thus requires an external (e.g., dehydrating underthrust sediments) source of water for saturation to be achieved.

**Rare earths.** As previously noted, the abundance ratio of Ce in zircon relative to that interpolated from the light rare earth pattern ( $Ce/Ce^*$ ) has been developed as a quantitative estimate for host magma  $f_{O_2}$  (Trail et al. 2011a). Most Hadean Jack Hills zircons are within error of FMQ (similar present-day upper mantle) but range as low as IW suggesting a diversity of source materials (Trail et al. 2011a). Another, qualitative estimate for magma  $f_{O_2}$  involves the mineralogy of Fe-Ti oxide phases. Ishihara (1977) observed that both oxidized and reduced series of granitoids occur in accretionary settings, with the oxide mineralogy of high  $f_{O_2}$  granites dominated by magnetite and that of the reduced granites dominated by ilmenite. Since oxide inclusions are often a minor constituent of igneous zircon inclusion suites (e.g., Rasmussen et al. 2011), the coupled investigation of oxide inclusion mineralogy with  $Ce/Ce^*$  in the host zircon provides the ability to check for internal consistency between these two estimates of Hadean magma redox conditions.

It will be helpful to establish both the characteristic ranges of zircon  $Ce/Ce^*$  for magnetite vs. ilmenite series granitoids and whether the oxide mineralogy of the whole rock is accurately reflected by the mineralogy included in zircons. Reconnaissance EDS analysis (Hopkins et al. 2010; reported by Bell et al. 2015a) suggests that the Hadean opaque inclusions are dominated by Fe oxides, potentially magnetite. Further investigation of the mineralogy of Hadean oxide inclusions, coupled with their host zircon  $Ce/Ce^*$ , may help to better classify the granitoids they derive from or potentially to diagnose alteration affecting the inclusions or host zircon. This coupled approach will better illuminate the redox conditions in the Hadean crust and any potential complexities that igneous zircon may record.

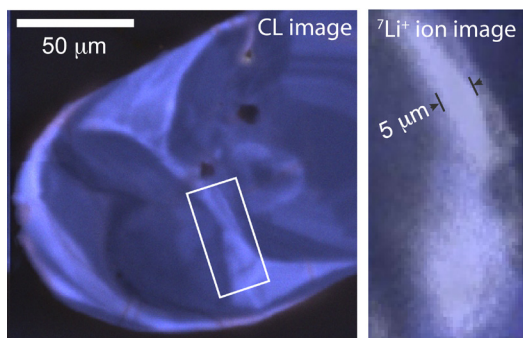
However, petrologically important trace element characteristics such as  $Ce/Ce^*$  and Ti content can be obscured by alteration or contamination (e.g., cracks, inclusions, etc.). Hydrothermal alteration of zircon is often diagnosed by a high, flat light rare earth element (LREE) pattern. Among Jack Hills zircons, such alteration is dominantly characterized by anomalously high Ti, Fe, P, U, and LREE contents (Bell et al. 2016). To remediate this issue, Bell et al. (2016) developed a trace element indicator (i.e., the LREE-Index; Fig. 9) which permits altered and hydrothermal zircons to be clearly identified.

**Lithium.** As noted earlier, Trail et al. (2016) proposed the use of Li zoning in zircon as a peak temperature indicator, particularly for use in ascertaining the retention of primary remanent magnetic signals. Figure 9 shows a direct ion image of  $^7Li^+$  of the surface of a sectioned 4.02 Ga Jack Hills zircon containing a  $\sim 5\text{-}\mu\text{m}$ -wide Li concentration band (Fig. 10). The general preservation of this band requires that peak heating temperature(s) for this detrital zircon did not exceed  $\sim 500^\circ\text{C}$  for million-year timescales. Thus this grain did not exceed the Curie temperature for magnetite of  $585^\circ\text{C}$  and would be a viable candidate for study of primary magnetism. Of course each detrital zircon in a population may have a different pre-depositional thermal history, but this result indicates that, post deposition, the metaconglomerates at Erawondoo Hill have not experienced temperatures greater than  $500^\circ\text{C}$ , consistent with other thermometric determinations (Rasmussen et al. 2010).



**Figure 9.** A) Typical zircon trace element pattern vs. that for metamorphic xenotime in Jack Hills discovery site quartzite and average upper continental crust. Most potential contaminating materials would have higher LREE and/or a higher LREE/HREE slope than primary magmatic zircon. B) Definition of the Light Rare Earth Element Index (LREE-I), based on the ratio of the LREE (represented by Nd and Sm) to the MREE (represented by Dy). Reprinted from Bell et al. (2016) Recovering the primary geochemistry of Jack Hills zircons through quantitative estimates of chemical alteration *Geochimica et Cosmochimica Acta* 191:287–292., with permission from Elsevier.

**Aluminum.** Trail et al. (2017) found that zircons from peraluminous granitoids contain average Al concentrations of  $\sim 10$  ppm (with a range from 0 to 23 ppm), in contrast to I- and A-type zircons, which average  $\sim 1.3$  ppm. Although alumina activity appears not to be



**Figure 10.** Li-in-zircon geospeedometry applied to a 4.03 Ga Jack Hills zircon. (Left) CL image showing growth zoning. (Right)  ${}^7\text{Li}^+$  image in boxed region at left. The 5  $\mu\text{m}$  scale of Li banding requires peak heating temperatures to have never exceed 500  $^\circ\text{C}$  for Ma-timescales. This constrains the Jack Hills Hadean zircons to have never been heated above the magnetite Curie point since 4.03 Ga. Reprinted from Trail (2016) Li zoning in zircon as a potential geospeedometer and peak temperature indicator. Contributions to Mineralogy and Petrology 171:1–15, with permission from Springer.

a simple function of the degree of the peraluminosity, zircon Al concentration could be calibrated as a proxy for melt  $\text{Al}_2\text{O}_3/(\text{CaO}+\text{Na}_2\text{O}+\text{K}_2\text{O})$  where molar values  $>1$  reflect an origin from recycled pelitic material (Trail et al. 2017). They applied this approach to Hadean Jack Hills zircons and found both metaluminous and peraluminous sources, albeit with the former apparently dominating the population. Although the scarcity of high Al contents from Hadean zircons suggests that metaluminous crustal rocks may have been more common than peraluminous rocks in the Hadean, the  $\sim 20\%$  overlap of low Al (i.e.,  $<5$  ppm) in S-type zircons somewhat obscures this inference.

**Carbon.** As carbon is long known to dissolve in silicates at trace levels (e.g., Freund et al. 1980; Oberheuser et al. 1983; Mathez et al. 1984; Tingle et al. 1988; Keppler et al. 2003; Rosenthal et al. 2015), the coexistence of zircon and graphite raises the possibility that C could be present at measurable levels in zircon. As SIMS has the potential for detection levels of C as low as  $\sim 1$  ppb, it is ideally suited for such a search.

The lack of dependency of carbon solubility in silicates on oxygen fugacity suggested to Shcheka et al. (2006) that  $\text{C}^{4+}$  substitutes for  $\text{Si}^{4+}$ , with increased levels as the volume of the  $\text{SiO}_4$  tetrahedron decreases. In this regard, they emphasized that the relatively small volume of the  $\text{SiO}_4$  tetrahedron in zircon should enhance carbon solubility. Alternatively, Sen et al. (2013) found evidence that C substitutes for nonbridging oxygen in synthesized silicate nanodomains. As such they hypothesized that trace carbon could be incorporated into silicates across a broader range of  $f_{\text{O}_2}$  than previously thought and speculated that this incorporation mechanism might have been preferentially important during the Hadean eon.

In the same way that a zircon co-crystallizing with rutile contains a predictable temperature-dependent Ti concentration, zircons growing in the presence of a carbonaceous species appear to partition C in a fashion that could be calibrated as a magma volatile probe. Having an approach with which to detect Hadean crustal C could potentially reconcile the disparate views regarding the magnitude of carbon in the crust during that eon. Some authors argued for a net increase in crustal carbon from essentially zero at 4 Ga (e.g., Hayes and Waldbauer 2006; Kelemen and Manning 2015) to its present day inventory in a broadly linear fashion. Marty et al. (2013) envisioned an essentially continuous transfer of carbon from undegassed mantle reservoirs implying a net increase to the crust over time. In contrast, Dasgupta (2013) advocated for higher than present day concentration on early Earth. The development of a proxy to detect the presence of carbon in Hadean (and younger) melts may eventually permit selection among these models.



**OTHER WESTERN AUSTRALIAN HADEAN ZIRCON OCCURRENCES****Mt. Narryer**

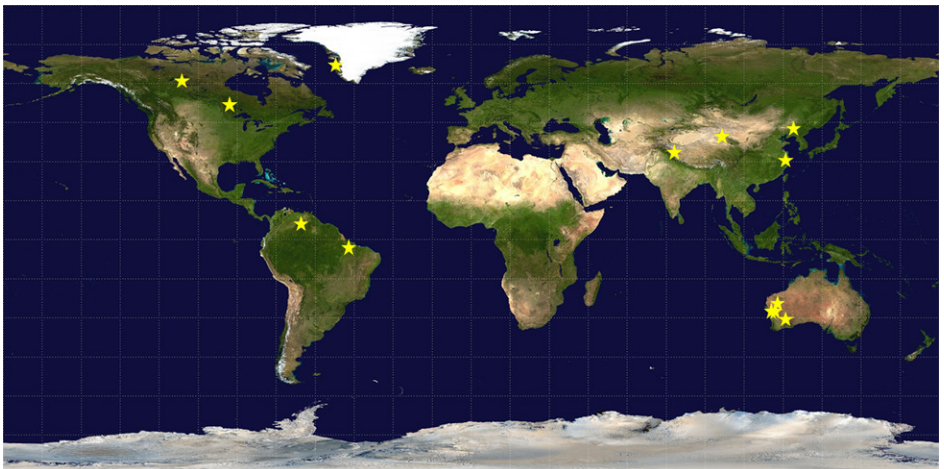
Ion microprobe dating of detrital zircons from several quartzites at Mt. Narryer in Western Australia (Fig. 11) have revealed a minor Hadean component ranging from 2% (Froude et al. 1983) to 12% grains  $>4.0$  Ga (Pidgeon and Nemchin 2006), with younger zircons ranging to ca. 3 Ga. A LA-ICP-MS study of Mt. Narryer zircons of all ages suggested that they generally display higher U contents and lower Ce/Ce\* than Jack Hills zircons (Crowley et al. 2005). Our preliminary ion microprobe data for 80 zircons between ca. 3 and 3.75 Ga in age from two Mt. Narryer quartzites suggests that zircons with unaltered magmatic chemistry (i.e., via the LREE-Index) do indeed show slightly higher U contents and lower Ce/Ce\* than Jack Hills zircons of similar age, although there is significant overlap between the populations. However, crystallization temperatures for these zircons is higher than at Jack Hills, averaging  $\sim 750 \pm 50^\circ\text{C}$ . All but one of our studied zircons has Th/U  $> 0.2$ , indicative of magmatic origins. Calculated  $f_{\text{O}}$  for these zircons suggests values on average several log units below the FMQ buffer, which overlaps the range of many less-oxidized Hadean Jack Hills zircons. Although we have not yet identified  $>4$  Ga zircons from Mt. Narryer in our preliminary survey, these differences in chemistry likely point to a diversity of Eoarchean-Hadean source rocks represented in Western Australia, as also suggested by Crowley et al. (2005) and by Hf isotopic compositions (Nebel-Jacobsen et al. 2010).

**Churla Wells**

Ion microprobe dating of a zircon from an orthogneiss from near Churla Well,  $\sim 25$  km west of the Mt. Narryer site (Fig. 11), yielded grains with  $^{207}\text{Pb}/^{206}\text{Pb}$  ages of 4.14 to 4.18 Ga (Nelson et al. 2000). Electron microprobe traverses show that the core containing the oldest ages has much lower Hf, REE, U and Th than the outer regions. Nonetheless, several observations—U contents in the core ranging up to 666 ppm, Th/U as high as 0.6, and trace element concentrations and ratios—strongly suggest its origin in a granitic magma.

**Maynard Hills**

In the Southern Cross Granite–Greenstone Terrane, Western Australia (Fig. 11), ion microprobe dating of a single zircon from a quartzite within the Maynard Hills greenstone belt (Wyche 2007) yielded a mean  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $4.35 \pm 0.01$  Ga.



**Figure 11.** Location map of the 13 sites from which  $>4$  Ga zircons have been documented.

## Mt Alfred

At the Mt. Alfred locality of the Illaara Greenstone Belt further along strike, Nelson (2005) documented a concordant zircon with an age of  $4.17 \pm 0.01$  Ga. Thern and Nelson (2012) reported three additional Hadean zircon ages from this sample ranging from 4.23 to 4.34 Ga. To our knowledge, no geochemistry for Hadean zircons from this sample have been published.

## NORTH AMERICAN HADEAN ZIRCON OCCURRENCES

### Northwest Territory, Canada

The Acasta tonalite orthogneiss from the Western Slave craton (Fig. 11) yields a range of U–Pb zircon ages interpreted to date protolith crystallization at 3.96 Ga (Bowring and Williams 1999; Stern and Bleeker 1998; Mojzsis et al. 2014). However, Iizuka et al. (2006) documented a  $4.20 \pm 0.06$  Ga zircon grain using LA-ICP-MS. This apparent xenocryst has a LREE pattern (Bell et al. 2016) within the field associated with unaltered zircon. Its Th/U suggests a magmatic origin and, along with other trace element concentrations and ratios, derivation from a felsic melt by a process other than differentiation of a mafic magma. Pronounced Ce and Eu anomalies correspond, respectively, to an  $f_{O_2}$  close to the FMQ buffer (assuming a crystallization temperature of 750 °C) and a crustal, as opposed to mantle, origin.

### Greenland

Detailed ion microprobe dating of a tonalitic orthogneiss from Akilia Island, West Greenland (Fig. 11), that crosscuts the oldest known marine sediment (Manning et al. 2006) established a crystallization age of  $3.83 \pm 0.01$  Ga (Mojzsis and Harrison 2002). A U–Pb survey of zircons identified in thin section documented a single zircon, concordant within uncertainty, with an age of  $4.08 \pm 0.02$  Ga.

## ASIAN HADEAN ZIRCON OCCURRENCES

### Tibet

Duo et al. (2007) report a 4.1 Ga ion microprobe age for a zircon from a quartzite in Buring County, western Tibet (Fig. 11). Th/U ratios greater than 0.7 suggest a magmatic origin for this detrital grain.

### North Qinling

Wang et al. (2007) reported a LA-ICP-MS age of  $4.08 \pm 0.01$  Ga for a xenocrystic zircon from Ordovician volcanics of the Caotangou Group, North Qinling Orogenic Belt (Fig. 11). Subsequent ion microprobe and LA-ICP-MS analyses identified additional Hadean grains with ages ranging from 4.03 to 4.08 Ga (Diwu et al. 2010, 2013). Hafnium isotope analyses of these grains are consistent with origin in crust extracted between 4.0 to 4.4 Ga (Diwu et al. 2013).

### North China Craton

Cui et al. (2013) reported a LA-ICP-MS U–Pb date of  $4.17 \pm 0.05$  Ga, concordant within uncertainty, for a xenocrystic zircon from the Anshan–Benxi Archaean supracrustal greenstone belt (Fig. 11). Correction of common Pb was made using  $^{208}\text{Pb}$  and assumed concordancy between the U–Pb and Th–Pb systems. The zircon was separated from fine-grained amphibolites intruded into banded iron formation and bedded coarse-grained amphibolites. Its Th/U of 0.46 suggests a magmatic origin.

### Southern China

Using ion microprobe U–Pb dating, two Hadean detrital zircons were documented from a quartzite within Neoproterozoic metasediments from the Cathaysia Block in southwestern

Zhejiang (Fig. 11; Xing et al. 2014). One zircon core yielded a  $^{207}\text{Pb}/^{206}\text{Pb}$  age of  $4.13 \pm 0.01$  Ga with a  $\delta^{18}\text{O} = 5.9 \pm 0.1\%$ . The other zircon grain has a  $4.12 \pm 0.01$  Ga magmatic core, a  $\delta^{18}\text{O}$  of  $7.2 \pm 0.2\%$ , a positive Ce anomaly indicative of highly oxidizing conditions, and a high apparent Ti-in-zircon crystallization temperature of  $910^\circ\text{C}$ . While the authors interpreted these results to suggest the zircons originated via dry melting of oxidized and hydrothermally altered supracrustal rocks, closer examination of the high apparent Ti content may be warranted due to Ti contamination effects (Harrison and Schmitt 2007). Trace element discrimination diagrams and REE patterns place the zircon core within the continentally-derived field.

## SOUTH AMERICAN HADEAN ZIRCON OCCURRENCES

### Southern Guyana

A xenocrystic zircon from a felsic volcanic unit of the Iwokrama Formation, Guyana Shield (Fig. 11), yielded a concordant LA-ICP-MS U–Pb age of  $4.22 \pm 0.02$  (Nadeau et al. 2013). No other geochemical analyses of this zircon have been reported.

### Eastern Brazil

The Archean core of the São Francisco Craton, northeastern Brazil (Fig. 11), contains meta-volcanosedimentary supracrustal rocks including the Ibitira–Ubirac greenstone belt. Paquette et al. (2015) analyzed a zircon from an amphibolite facies pelite from this belt by LA-ICP-MS yielding a distribution of U–Pb ages that intersected concordia at  $4.22 \pm 0.02$  Ga (four  $^{207}\text{Pb}/^{206}\text{Pb}$  ages  $> 4.01$  Ga). The core Th/U ratios of 0.8 and high U contents (up to 1400 ppm) suggest a felsic magmatic origin of this probably detrital grain.

The above discussion is complicated by limitations comparing data generated by different analytical methodologies. For example, the LA-ICP-MS approach lacks the capacity to measure common  $^{204}\text{Pb}$  and thus the possibility exists that single zircon occurrences with apparent ages of  $> 4$  Ga could be due to inclusion of non-radiogenic Pb.

## OTHER PROPOSED MECHANISMS FOR FORMING HADEAN JACK HILLS ZIRCONS

The collective data obtained over the last 15 years broadly support an origin of many Hadean zircons as crystallizing from relatively cool, relatively wet felsic melts sourced at least in part from sedimentary protoliths at a plate boundary. Nonetheless, numerous other models have been proposed, and we evaluate the consistency of the data with these hypotheses.

### Icelandic rhyolites

Iceland's unusual geochemical character and thick basaltic crust couple to produce an unusually high proportion (~10%) of silicic magmatism. These rocks in turn host abundant zircon making Iceland a seemingly attractive model to explain the production of Hadean zircons (Taylor and McLennan 1985; Galer and Goldstein 1991; Valley et al. 2002). However, comprehensive investigations of the trace element and oxygen isotope composition of Icelandic zircons show that the two populations to be distinctively different (Carley et al. 2011, 2014; cf. Reimink et al. 2014). In contrast to the elevated  $^{18}\text{O}$  signature in some Hadean zircons, Icelandic zircons are characterized by  $^{18}\text{O}$ -depleted values, likely the result of recycling of altered basaltic crust rather than direct melting of sedimentary rocks (Bindeman et al. 2012). Zircon crystallization temperatures are similarly different, with Icelandic zircons yielding an average of  $780^\circ\text{C}$  compared to the  $680^\circ\text{C}$  average of Jack Hills Hadean zircons.

As noted in the previous section, higher temperature data from the Mt. Narryer and southwestern Zhejiang sites may indicate their formation in different environments relative to the Jack Hills population, possibly similar to an Iceland-like source.

### **Intermediate igneous rocks**

Several authors have argued that the low temperature Hadean peak could reflect zircon saturation at low temperatures in rocks of the tonalite-trondhjemite-granodiorite (TTG) suite (Glikson 2006; Nutman 2006). Glikson (2006) proposed that Hadean zircons could have originated in TTG's that formed at high-temperatures but did not crystallize zircon until near eutectic temperatures were reached. Similarly, Nutman (2006) argued on the basis of calculated saturation temperatures (Watson and Harrison 1983) for TTG's that high-temperature melts do not crystallize zircon until they cool to temperatures near that of minimum melting (i.e., zircons from both wet tonalite and minimum melts yield similarly low crystallization temperatures). However, Harrison et al. (2007) showed bulk rock saturation thermometry to be inapplicable to zircons crystallizing from TTGs. Rather, a cooling magma system first crystallizes modally abundant phases, increasing the Zr concentration in the residual melt while moving the melt towards compositions with much lower capacities to dissolve zircon. Thus temperatures calculated from bulk rock chemistry significantly underestimate the onset temperature of zircon crystallization in TTGs. The expected and observed result is that zircons crystallized from TTG melts (as documented by electron imaging studies) yield significantly higher temperatures than seen in the Hadean Jack Hills population (e.g., Harrison et al. 2007).

### **Mafic igneous rocks**

A variety of authors have suggested that the > 4 Ga zircon temperature distribution could be derived from zircons originating in mafic magmas (Coogan and Hinton 2006; Valley et al. 2006; Rollinson 2008). However, zircon formation temperatures in these environments are significantly higher (>750 °C) than the Hadean peak (e.g., Harrison et al. 2007; Hellebrand et al. 2007). As a case in point, Rollinson (2008) argued that the  $\delta^{18}\text{O}$  and trace element signatures in Hadean Jack Hills zircons were consistent with an origin in ophiolitic trondhjemites rather than continental crust. The author pointed to water-saturated, low pressure melting experiments on oceanic gabbros at > 900 °C that yielded trondhemitic melts. While the origin of the excess water is potentially explicable in this scenario, the origin of muscovite, a mineral uncharacteristic of trondhjemite but the most common inclusion in Jack Hills Hadean zircons (Hopkins et al. 2008), was not addressed. Although we noted earlier the clear separation between Hadean and MORB zircons on a plot of U/Yb vs. Y plot (Grimes et al. 2007), Rollinson (2008) argued that data on such discrimination diagrams showed a ~20% overlap and were thus permissive of such an origin. While this is true when plotting present U concentrations, the separation becomes essentially complete once an appropriate correction for U decay has been made (e.g., a 4.3 Ga zircon presently containing 100 ppm U originally crystallized with 244 ppm U).

As noted earlier, zircons derived from a wide range of mafic rocks yield much higher average temperatures (~770 °C; Valley et al. 2006; Fu et al. 2008) than the Hadean population (Harrison et al. 2007). In the absence of a natural selection mechanism that preferentially excludes zircons formed at high temperature (the opposite of what is expected from preservation effects on high radioactivity zircons), intermediate to mafic sources are unlikely to have contributed significantly to the Hadean Jack Hills population. However, sparse, higher temperature zircons from the Mt. Narryer and southwestern Zhejiang locations may well be consistent with such an origin and could be tested by studies of their inclusion populations.

## Sagduction

A feature of modern plate tectonics is that oceanic lithosphere older than about 20 Ma is negatively buoyant and thus can be underthrust beneath adjacent plates. At 80–120 km depths, the basaltic crust undergoes a transformation to much denser eclogite and the resulting pull on the downgoing slab provides a first-order contribution to the global plate tectonic energy budget. In the hotter mantle of early Earth, it is assumed that oceanic lithosphere would have been thicker and thus may not have been able to achieve the neutral buoyancy required for subduction making plate tectonic-type behavior uncertain (Davies 1992; cf., Korenaga 2013). Under such conditions, a low apparent geotherm could be achieved locally where thermally and/or compositionally dense crust sinks into the mantle as downward moving drips (sagduction; Macgregor 1951). While this can insulate the descending mass from reaching melting temperature until high pressures are attained (e.g., Davies 1992), more nuanced scenarios are also possible (e.g., François et al. 2014). Such a mechanism was invoked by several authors (Williams 2007; Nemchin et al. 2008) to explain the anomalously low ( $<10^{\circ}\text{C}/\text{km}$ ) geotherms required by the apparent occurrence of diamond in Hadean Jack Hills zircons, although recognition that the diamonds were contamination (Dobrzhinetskaya et al. 2014) obviated the need for such models.

The sagduction model shares similar limitations to those discussed above, the source of the needed water and, in the case of blocks delaminated into the mantle, the lack of a mechanism to return zircons formed by this mechanism to the surface. Consider the case of a sagducting block of mafic eclogite. As noted earlier, below the brittle-ductile transition rock porosities are typically  $<0.1\%$  (Ingebritsen and Manning 2002). Structural water stored in hydrous minerals is limited to  $\leq 2\%$  of virtually all rock types and is lost progressively via discontinuous, subsolidus dehydration reactions through the greenschist and amphibolite facies (Spear 1993).

Any water liberated by dehydration is likely to ascend from the sagducting drip into colder, overlying rocks. Thus fusion is likely to be forestalled until temperatures greatly exceeding that of minimum melting are reached. In the case of complete devolatilization, temperatures of  $>900^{\circ}\text{C}$  would be required for melting of dry rock. As noted earlier, the absence of peaks in the Hadean zircon crystallization spectrum corresponding to dehydration melting does not support such a mechanism and such melts are unlikely to be characterized by quartz and muscovite inclusions. Even the most appealing scenario involving eclogitized pelite containing a 50:50 mixture of muscovite and quartz contains only  $\sim 2$  wt.% water and vapour absent melting of such a protolith produces highly water-undersaturated melts (e.g., Patiño Douce and Harris 1998).

Sagduction models lack a mechanism to introduce water-rich fluids into fertile source rocks capable of yielding both peraluminous and metaluminous magmas at temperatures close to minimum melting (as required by Ti thermometry) and then sustain the supply of water until the rock's melt fertility is essentially exhausted (thus resulting in the single Hadean zircon peak at ca.  $680^{\circ}\text{C}$ ). The twofold appeal of a plate boundary environment is the continuous source of water available in the hangingwall of a submarine underthrust and the potential for long-term (i.e.,  $>4$  Ga) preservation of any zircons created by water-fluxed melting. In contrast, how zircons formed during dehydration melting in a block sagducting into the mantle will reappear to be preserved at the Earth's surface is unclear.

## Impact melts

Given the likelihood of high bolide fluxes to early Earth, the potential for impact melts to be a source of Hadean zircons requires investigation. Studies of neo-formed zircon in preserved terrestrial basins large enough to have created melt sheets (e.g., Sudbury, Morokweng, Manicouagan, Vredefort) show that their crystallization temperatures average more than  $100^{\circ}\text{C}$  greater than that of  $>4$  Ga Jack Hills zircons and thus impacts do not represent a dominant source for that Hadean population (Darling et al. 2009; Wielicki et al. 2012). This observation is supported by models that relate expected impact thermal anomalies with early crustal rock



chemistry (Wielicki et al. 2012; Fig. 7), which confirm that observations from the handful of known impact melt sheets is indeed globally representative. Recently, Kenny et al. (2016) argued that zircon crystallization temperatures for the granophyre layer at the Sudbury impact crater had been underemphasized and proposed this rock type as a source of at least a portion of Hadean Jack Hills zircons (Fig. 7). They raised the prospect of an unspecified selection process that had preferentially destroyed high temperature Hadean zircons and thus biased the detrital record to low temperatures. Nature does tend to bias the detrital zircon record but that mechanism operates in exactly the opposite sense. Late crystallizing, thus low temperature, granitoid zircons are known to contain elevated U and Th concentrations which lead to metamictization (Claiborne et al. 2010) and thus they are more likely lost from the detrital record, resulting in preferential preservation of higher temperature zircons (Harrison and Schmitt 2007). Wielicki et al. (2016) tested the Kenny et al. (2016) hypothesis statistically and showed that the probability of extracting the Hadean Jack Hills Ti-in-zircon temperature distribution from their data, or any permutation of the published dataset of impact-produced zircons, is vanishingly small.

Marchi et al. (2014) proposed that an intense bombardment event at ~4.1 Ga covered the planet with ca. 20 km of flood basalt in which the Hadean Jack Hills zircons were formed. In brief, this model is fundamentally incompatible with virtually every geochemical record obtained from that population (i.e., hydrous melting conditions, low geotherm, peraluminous compositions, etc.).

The above statements are specifically relevant to the Hadean Jack Hills zircons and conclusions should be tempered by the reconnaissance-scale data obtained for samples from Mt. Narryer and southwestern Zhejiang, which yield apparent zircon crystallization temperatures of 750 and 910 °C, respectively. While both results are subject to potential Ti contamination effects, developing a strong geochemical database from the dozen or so locations for which >4 Ga zircons have been documented should be a research priority.

### Heat pipe tectonics

Moore and Webb (2013) investigated the thermal effects of “heat-pipe” magmatism in which volcanism dominates the near surface thermal structure early in planetary evolution. Their simulations showed that low geotherms could develop in response to frequent volcanic eruptions that advect surface material downwards. They argued that Hadean zircons arose in ascending TTG plutons within the diamond stability field produced at the intersection of the wet basalt solidus and their exceedingly low calculated geotherms. Unfortunately, this constraint was predicated on a report that diamonds had been included in these grains during formation (Menneken et al. 2007). This was subsequently shown to be due to contamination during sample preparation (Dobrzhinetskaya et al. 2014). Even putting this issue aside, left unaddressed is the source of sufficient water to saturate an intermediate melt (>25 wt.%; Mysen and Wheeler 2000) at depths of >100 km. As noted earlier, the geochemistry of Hadean Jack Hills zircons is inconsistent with low water activity melting and the inclusion assemblage is unlikely to arise from a basaltic source.

### Terrestrial KREEP

KREEP is an acronym reflecting K-, REE- and P-enriched materials on Earth’s moon, which are thought to reflect progressive crystallization of a magma ocean (Warren and Wasson 1979). As noted earlier, initial  $^{176}\text{Hf}/^{177}\text{Hf}$  of Jack Hills zircons show large deviations in  $\epsilon_{\text{Hf}(T)}$  from bulk silicate Earth (see summary in Bell et al. 2014). The initial report of Harrison et al. (2005) of positive  $\epsilon_{\text{Hf}}$  results utilizing ion microprobe U–Pb age spots with LA-ICP-MS Lu–Hf results on differing portions of the analyzed zircon were not reproduced in a follow-up study (Harrison et al. 2008) in which age and Hf isotopes were measured on the same volume. This was ascribed to non-linear mixing effects between zircon rims and cores (see Harrison et al. 2005) that almost certainly also affected the bulk results of Blichert-Toft and Albarède (2008).

Kemp et al. (2010) chose a small subset of the Jack Hills  $\epsilon_{\text{HF}}$  data that aligned along a subchondritic array extrapolating back to 4.4–4.5 Ga. They interpreted the coherence of this limited dataset to reflect formation of an incompatible element enriched reservoir during solidification of a magma ocean—in effect, a terrestrial KREEP layer. In their model, ~400 Ma of subsequent intra-crustal melting of basalt hydrated by interaction with an early atmosphere/hydrosphere produced the Hadean Jack Hills zircons including those with high  $^{18}\text{O}$ . They interpreted the results of an experimental study of the simple system  $\text{CaO}+\text{MgO}+\text{Al}_2\text{O}_3+\text{SiO}_2+\text{H}_2\text{O}$  (Ellis and Thompson 1986), which produced peraluminous melts at  $\geq 800^\circ\text{C}$  under water-saturation, as explaining the presence of muscovite inclusions in Jack Hills zircons and thus obviating the requirement for a metasedimentary source. While true that corundum-normative melts are produced under these conditions, muscovite was of course not present in the K-free experimental system and would have been an unlikely modal phase to form from a basaltic protolith. As with most of the above hypotheses, the principal problem with the Kemp et al. (2010) model is the lack of a source for the copious amounts of water required to saturate melts at high pressure and the implied high zircon formation temperatures. As described in the Sagduction and Heat pipe sections, carrying water from surface through a continuous series of dehydration reactions during burial would result in production of inextractable amounts of melt below  $750^\circ\text{C}$ .

### Multi-stage scenarios

Shirey et al. (2008) interpreted the origin of Hadean zircons through a multi-part model that included: 1) global separation of an early ( $>4.4$  Ga) enriched reservoir, 2) deep mantle fractionation of Ca-silicate and Mg-silicate perovskite from a terrestrial magma ocean following lunar formation, 3) formation of a mafic to ultramafic crust, and 4) repeated cycles of remelting of that crust under “wet” conditions to produce progressively more silica-oversaturated TTGs. Their arguments against Hadean Jack Hills zircons forming in a dominantly granitic crust are the occurrence of zircons in MORB and Icelandic settings (see *Icelandic rhyolites* and *Mafic igneous rocks* sections as well as the requirement of water-saturated melting for counter arguments). Shirey et al. (2008) note that an Iceland-like environment would permit hydrothermally altered basalt to be buried to the depths of wet melting to produce zircons of similar character to the Jack Hills zircons. However, no such population has been documented in extensive studies of Icelandic zircons (Carley et al. 2011, 2014).

### Summary

Although considered separately above, most of the alternative explanations for the geochemical characteristics of the Jack Hills zircons share the assumption that melting occurred intracrustally in the absence of an external source of water (i.e., sagduction, Davies 1992; burial beneath impact melts, Marchi et al. 2014; heat pipe burial, Moore and Webb 2013; terrestrial KREEP, Kemp et al. 2010). As noted previously (see Fig. 8), the  $P$ – $T$  conditions indicated by these zircons puts them outside conditions that would produce extractable melts fractions thus requiring addition of significant water from an exotic source, such as dehydration of a downgoing slab. Despite the attractions of a plate boundary-type model, as noted at the outset, it is not possible to ascribe unique conditions to Hadean Earth from geochemical records preserved in  $>4$  Ga zircons. Rather, our goal should be to identify a parsimonious, internally-consistent model of Earth evolution that explains robust aspects of the zircon record. We acknowledge that our perspective is strongly biased towards Jack Hills zircons because the vast majority of information about Hadean conditions has been derived from them. Increasingly comprehensive studies of other zircon populations, e.g., from Narryer Hills, might reveal other aspects of Hadean geology. Nonetheless, given data available to date, plate boundary interactions not only provide a setting that explains the nature of Hadean zircon geochemistry and the inclusions they host, but also invoke the simplest dynamical mode that

is clearly plausible for this planet. Granted, internal consistency is not smoking gun proof and most accumulated evidence is indirect and open to alternate interpretations. Overly elaborate scenarios, especially those that stand in contradiction to important aspects of the geochemical evidence, do not help advance our understanding of the first five hundred million years of Earth history. Rather, they muddle a discussion that is generally poorly understood by those outside this somewhat narrow field. Furthermore, although it should go without saying, mantle-derived rocks do not possess a record that rocks of continental affinity do not exist elsewhere on the planet (e.g., Kamber et al. 2005; Kemp et al. 2015; Reimink et al. 2016). This is the equivalent of concluding that no cratons exist on the planet today from analysis of a rock from Samoa.

Even if we ultimately conclude that plate boundary interactions were the dominant source of the Hadean zircon geochemical signals, numerous questions remain unanswered. Was the process continuous throughout the Hadean or did it repeatedly start and stop? Is the inferred convergent boundary an island arc, a continent-continent collision, a mixture of the two, or an entirely different kind of setting unique to early Earth?

### A LINK TO THE LATE HEAVY BOMBARDMENT?

As noted previously, Jack Hills detrital zircons show a characteristic bimodal age distribution with peaks at about 3.4 and 4.1 Ga, and ages as old as 4.38 Ga (Holden et al. 2009). A curious feature of this distribution is the relative rarity of zircons between 3.9 and 3.6 Ga (Bell and Harrison 2013), a period which includes a hypothesized spike in impacts to the Earth-Moon system (termed the Late Heavy Bombardment; LHB). Evidence of such an event was first seen in ca. 3.9 Ga isotopic disturbances of lunar samples (Tera et al. 1974), although others (e.g., Hartmann 1975) interpreted this as the tail of a decreasing bolide flux. The lack of an identifiable signature in the fragmentary terrestrial rock record from the LHB era (ca. 3.9 Ga) 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 gravitational cross section and surface area, the Earth likely experienced ~20 times the impact flux to the Moon causing a widespread crustal thermal disturbance. Thus it is somewhat surprising that the Jack Hills zircon population does not contain a significant proportion grown in impact melt sheets (Wielicki et al. 2012, 2016). Because of their crustal origin, all Hadean Jack Hills zircons share one feature in common—they all must have resided within 10s of km of the Earth surface during the LHB era. Thermal perturbations in the crust during this time, perhaps due to impacts, could mobilize Zr to form epitaxial growths on Hadean-age zircons. Trail et al. (2007) U–Pb depth profiled four Hadean zircons and found that they preserved 3.94–3.97 Ga rims. While they could not rule out endogenic processes as the precipitating event, they speculated that this common trait might be the terrestrial evidence of the LHB. Abbott et al. (2012) followed up this study by simultaneously depth profiling U–Pb age and crystallization temperature of overgrowths on Hadean zircons. Of the eight grains examined, four had 3.85–3.95 Ga rims that yield significantly higher formation temperatures (>840 °C) than either younger rims or older cores. This was again seen as suggestive of an LHB link.

Bell and Harrison (2013) undertook an intensive age survey to archive a large number (>100) of Jack Hills zircons formed in the age range 3.9 to 3.6 Ga. Geochemical analyses on this population showed surprising differences. Specifically, zircons between ca. 3.91 and 3.84 Ga were found to be unique in the >3.6 Ga Jack Hills zircon record in having two distinct trace element groupings. The existence of a distinct high-U (and Hf), low-Ti (and Ce, P, Th/U) zircon provenance (they termed “Group II”) is specific to this ca. 70 million year period. The remaining 3.91–3.84 Ga zircons (termed “Group I”) resemble the majority of Hadean zircons both in apparent crystallization temperature and numerous other trace elements. 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, were interpreted to result from thermally-driven, transgressive recrystallization (Hoskin and Schaltegger 2003) at 3.91–3.84 Ga. The persistent coincidence of an apparent thermal event within the period postulated for the LHB suggests that the terrestrial archive of Hadean material may potentially be a superior to lunar samples for establishing the timing, and even existence (Boehnke and Harrison 2016), of a Late Heavy Bombardment.

## BROADER IMPACTS OF HADEAN ZIRCONS

### The role of Hadean zircons in geochemical innovation

Geochemical studies of Hadean zircons have collectively led to a paradigm shift in our concept of early Earth—there is general agreement that evidence derived from these zircons implies abundant water at or near Earth’s surface during the Hadean. Almost as interesting as the paradigm shift itself is the manner by which it occurred and what that says about the role of early Earth research in driving geochemical innovation. As previously noted, it was the need to date large ( $> 10^5$ ) numbers of zircons to create an archive of  $> 10^3$  Hadean grains that drove development of the first automated ion microprobe stage.

Zircon has long been appreciated as the leading crustal geochronometer for its robust U–Pb system and resistance to physical and chemical alteration in most geologic environments. Thus knowing the temperature at which magmatic zircon crystallizes sharpens both interpretations of U–Pb dates and permits a range of new petrochronologic investigations. Although this appeal has existed since at least the 1970s, it was through the challenge of the unknown provenance of Hadean zircons that the Ti-in-zircon thermometer was realized (Watson and Harrison 2005; Watson et al. 2006; Ferry and Watson 2007). This application subsequently erupted across geochemistry and petrology (as attested by the over 1,700 citations these three papers have attracted since 2005; Google Scholar). Subsequent developments, including terrestrial Pu/U tracing (Turner et al. 2007), zircon  $f_{O_2}$  barometry (Trail et al. 2011a), and a magma aluminosity proxy (Trail et al. 2016), underscore the degree to which a vanishingly small lithic record has inspired innovation.

### The role of Hadean zircons in scientific thought

Perhaps the most remarkable feature of inferences drawn from  $> 4$  Ga zircons is that none were gleaned from theory. Rather, generations of models innocent of observational constraints fed a paradigm of a hellish, desiccated, uninhabitable Earth (e.g., Cloud 1976; Smith 1981; Sleep et al. 1989; Collerson and Kamber 1999; Ward and Brownlee 2000; O’Neill and Debaille 2014) for which there is no empirical evidence. What compelled the scientific community to create an origin myth in the absence of direct evidence? While science is distinguished from mythology by its emphasis on verification, its practitioners may be as subject to the same existential need for explanations as any primitive society. In context with high expected Hadean heat production and impact flux, it proved irresistible to explain the lack of ancient continental crust by its non-existence rather than the equally or more plausible notion that it has been largely consumed by the same processes we see operating on the planet today.

Whether or not this episode represents a scientific anomaly is, to us, a matter of debate. It is at least arguable that such behavior has been a feature of geophysical modelers approach to Earth evolution since Kelvin’s “certain truth” that the planet was less than 2% of its actual age (Thompson 1897) or Jeffreys’ denial of the fit between South America and Africa (Jeffreys 1924). For reasons that remain obscure, calculations carried out in the absence of observational constraints can take on an edifice-like character in the geo- and planetary sciences that slows progress and distracts the community from fresh, and possibly better, ideas. Perhaps David Stevenson (1983) said it best when referring to speculations of Hadean dynamics: “Basic physical principles need to be understood but detailed scenarios or predictions based upon them are best regarded as ‘convenient fictions’ worthy of discussion but not enshrinement”.

## SUMMARY

Advances in geochemical microanalysis and innovative applications of zircon geochemistry have made this mineral perhaps the only currently known probe of the time predating Earth's known rock record. Zircon's resistance to mechanical breakup and chemical weathering allow it to preserve chemical, isotopic, and mineral inclusion information with an associated U–Pb timestamp through later metamorphism and sedimentary cycling. Although the Jack Hills locality in Western Australia is the best known and most highly studied source of Hadean zircons, worldwide twelve additional localities are known to have yielded at least one zircon older than 4 Ga. Geochemical investigations carried out on Jack Hills zircons have yielded a view of Hadean Earth fundamentally at odds with traditional notions of a dry, impact-disrupted, certainly uninhabitable environment, and these lines of investigation can serve as a useful guide as attention turns to these additional Hadean zircon-bearing localities. Isotopic investigations reveal the likelihood of a surface or near-surface hydrosphere as early as 4.3 Ga ( $\delta^{18}\text{O}$ ; e.g., Peck et al. 2001; Mojzsis et al. 2001) and of felsic crust as early as 4.5 Ga (Lu–Hf system; e.g., Harrison et al. 2008). Magmatic Th/U ratios (e.g., Cavosie et al. 2006; Bell and Harrison 2013; Bell et al. 2014), dominantly granitic mineral inclusions (Hopkins et al. 2008, 2010; Bell et al. 2015a), and innovations such as the Ti-in-zircon thermometer (Watson and Harrison 2005) and Ce/Ce\* as  $f_{\text{O}_2}$  barometer (Trail et al. 2011a) further suggest minimum melt conditions and redox conditions near the present-day upper mantle for the Hadean magmas that produced the Jack Hills zircons. One zircon containing primary graphite with a light isotopic value reminiscent of biologic carbon fixation may point to a terrestrial biosphere as early as 4.1 Ga (Bell et al. 2015b). Preliminary geochemical investigation of zircons from the other localities suggest higher-temperature origins, and further study of these materials will doubtless shed light on the diversity of preserved Hadean magmatic environments. Epitaxial rims on Hadean zircon cores tend toward ca. 3.9 Ga ages and their anomalously high formation temperatures have led some workers to speculate that this could be a terrestrial signal of the Late Heavy Bombardment.

Although a complete picture of Hadean Earth will likely not be possible from detrital zircon alone, they have thus far provided the only known empirical data on pre-4 Ga Earth. Models for this period must consider all of the data from the various isotopic, trace chemical, and mineral inclusion lines of evidence in the zircons. Increasing the geographic (and possibly petrogenetic) diversity of Hadean samples available for study will undoubtedly continue to drive geochemical innovation and new insights into this obscure yet important period of our planet's history.

## ACKNOWLEDGMENTS

We thank Dustin Trail, an anonymous reviewer, and editor Matt Kohn for helpful reviews, and we thank Matthew Wielicki, Ellen Alexander, Bruce Watson, Stephen Mojzsis, and Ben Weiss for discussions that helped refine many of the arguments made in this paper. This work was supported by NSF grant EAR-1551437. The ion microprobe facility at the University of California, Los Angeles, is partly supported by a grant from the Instrumentation and Facilities Program, Division of Earth Sciences, National Science Foundation.

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