Chapter 12

The Oldest Terrestrial Mineral Record: Thirty Years of Research on Hadean Zircon From Jack Hills, Western Australia

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Chapter Outline

1. INTRODUCTION

Little is known of the early Earth because of the absence of a rock record for the first 500 million years after accretion. Earth's earliest history is assigned to the Hadean eon, which began at the onset of accretion at c.4560 Ma, when meteorite impacts and magma oceans maintained extreme surface temperatures at or above the temperatures where surface water vaporized to a dense steam atmosphere. The existence of buoyant crust as early as 4400 Ma is indicated by preservation of magmatic zircon. The Earth eventually cooled, quenching the high surface temperatures and allowing H_2O to condense as oceans. The transition to a more familiar and clement Earth was a global process and may be viewed to represent the end of Hadean conditions (Valley, 2005, 2006). Establishing the timing of the Hadean—Archean transition is challenging based on the fragmentary rock record, yet it is critically important for both defining the early Earth geological timescale and also constraining when Earth became habitable (Valley, 2008; Cavosie, 2014). The present definition of the Hadean—Archean transition at 4000 Ma (e.g., Cohen et al., 2013) is near the limit of the oldest recognized rock record (Reimink et al., 2016), including c.4030—3800 Ma orthogneisses and metasedimentary rocks in the Northwest Territory of Canada (e.g., Bowring and Williams, 1999; Chapter 15), similar-aged supracrustal rocks in the Nuvvuagittuq Greenstone Belt (Cates and Mojzsis, 2007) and Saglek Block (Komiya et al., 2015) in northeast Canada, and c.3900—3800 Ma orthogneisses in the Isua supracrustal belt of southwest Greenland (e.g., Nutman et al., 2001; Chapter 17). Older Hadean ages have been reported for

Earth's Oldest Rocks. https://doi.org/10.1016/B978-0-444-63901-1.00012-5

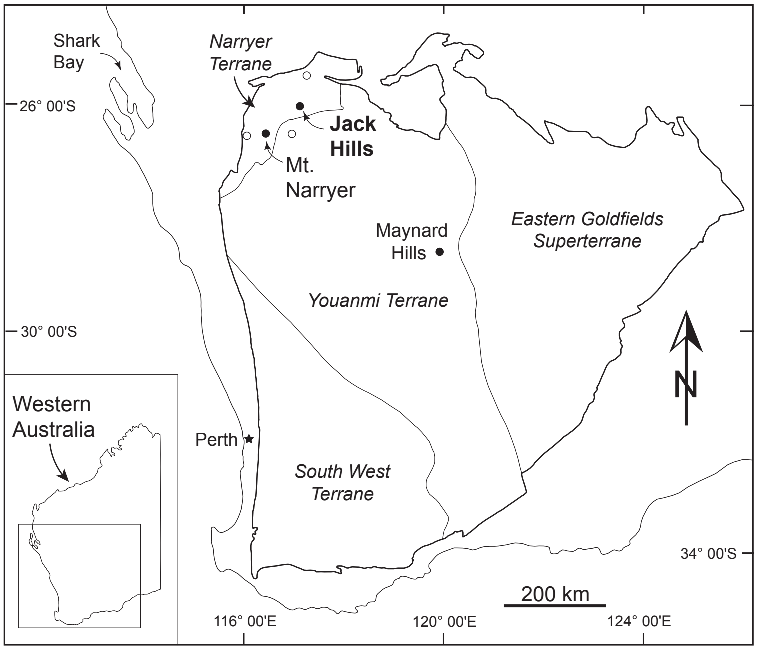

FIGURE 12.1 Map of the Yilgarn Craton in Western Australia, showing Hadean zircon localities (after Wilde et al., 1996; Wyche et al., 2012). *Filled circles* are known locations of >4000 Ma detrital zircon and *open circles* are locations of xenocrysts with similar ages (see text for references).

mafic volcanic rocks from Nuvvuagittuq (e.g., O'Neil et al., 2016; Chapter 16), however, the interpretation of these ages as dating the timing of crystallization of these rocks remains a topic of debate.

The only identified materials on the Earth with unequivocal U–Pb ages extending into the Hadean are ancient >4000 Ma zircon grains that are dominantly found as detrital grains in Archean rocks in the ancient crustal nuclei of Western Australia and are only rarely found elsewhere. In Western Australia, variably metamorphosed metasedimentary rocks from several localities in the Yilgarn Craton have yielded zircon older than 4000 Ma. These include sites at Mount Narryer and the Jack Hills (Froude et al., 1983; Compston and Pidgeon, 1986; Cavosie et al., 2004; Wang and Wilde, 2018) and Maynard Hills and Mount Alfred (Wyche et al., 2004; Thern and Nelson, 2012; Chapter 13) (Fig. 12.1). Rare >4000 Ma grains have also been reported as xenocrysts in younger Archean granitoids close to Mount Narryer (Nelson et al., 2000).

Metasedimentary rocks in the Jack Hills have received the most attention of the above localities, primarily because of both the consistently high concentration (up to 12%, Compston and Pidgeon, 1986) of Hadean zircon grains and the presence of the oldest known detrital grains. Given the unique window these grains offer on early Earth processes, this review focuses primarily on published reports that describe the population of Hadean zircon grains from the Jack Hills.

2. JACK HILLS METASEDIMENTARY ROCKS

The Jack Hills, located in the Narryer Terrane of the Yilgarn Craton in Western Australia (Fig. 12.1), comprise a ~90 km-long northeast-trending belt of folded and weakly metamorphosed supracrustal rocks that are composed primarily of siliciclastic and chemical metasedimentary rocks, along with minor felsic and mafic volcanic rocks and also ultramafic rocks (Fig. 12.2; Wilde and Spaggiari, 2007; Chapter 18). Bedding strikes east-northeast and has a subvertical dip. The siliciclastic portion of the belt has been interpreted as alluvial fan-delta deposits, based on repeating fining upward sequences consisting of basal conglomerate, medium-grained sandstone, and fine-grained sandstone (Wilde and Pidgeon, 1990). Located on Eranondoo Hill in the central part of the belt is now a famous site referred to as "W74" (Fig. 12.3), the number originally assigned to a sample collected from conglomerate at this spot by the Curtin University group. The W74 site contains a well-exposed, 2-m thick quartz pebble metaconglomerate. The previously undescribed unit was originally sampled by S. Wilde, R. Pidgeon, and J. Baxter in 1984 during mapping for an Australian Research Council project and was later described by Compston and Pidgeon (1986), who reported the first U–Pb ages for detrital zircon grains from the Jack Hills, including one grain with a spot as old as 4276 ± 6 Ma. Aliquots of zircon from the original W74 zircon concentrate, as well as additional samples from the same outcrop, have subsequently been the subject of many studies.

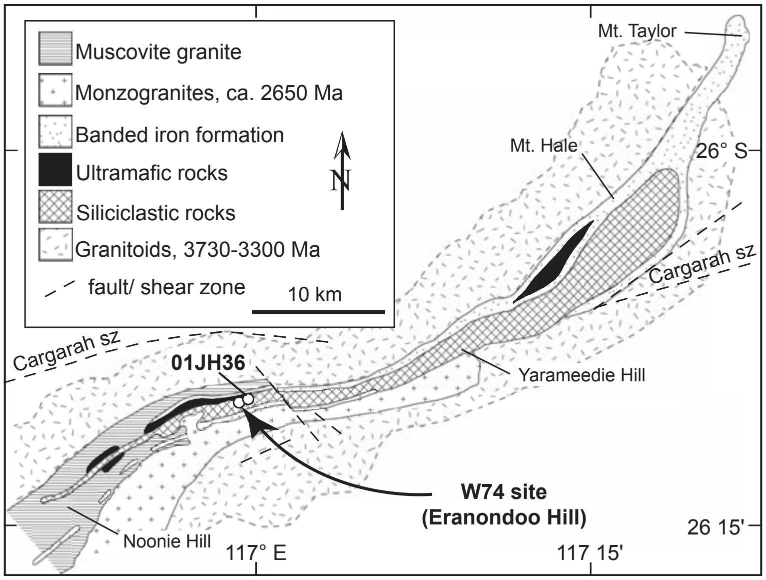

FIGURE 12.2 Geologic map of the Jack Hills metasedimentary belt (after Cavosie et al., 2004). Two localities where Hadean zircon grains with concordant U-Pb ages >4350 Ma have been reported, W74 and 01JH36, are shown. *The trace of the Cargarah shear zone (sz) is from Spaggiari (2007).*

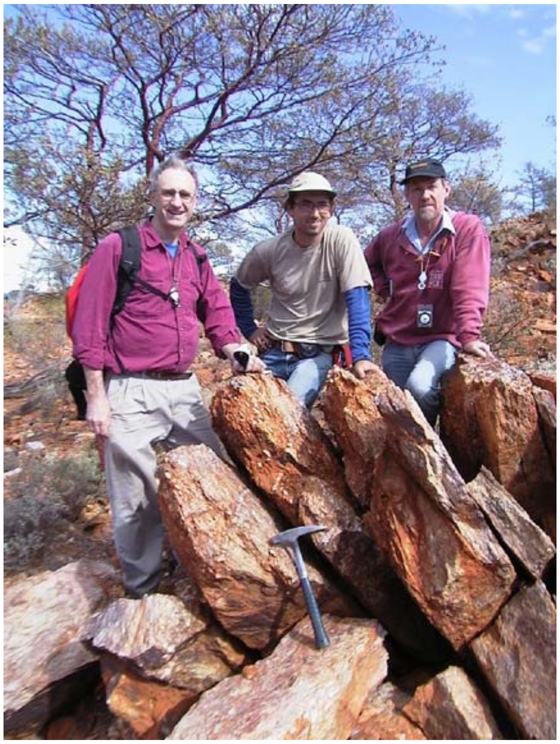

FIGURE 12.3 Photo of the authors at the W74 site in the Jack Hills in July 2001. Shown are J.W. Valley (left), A.J. Cavosie (middle), and S.A. Wilde (right). *Photo by D. Valley.*

2.1 Age of Deposition

The deposition age of metasedimentary rocks in Jack Hills is somewhat controversial, as it appears to vary with location. The maximum age of the W74 metaconglomerate was originally cited as c.3100 Ma based on the youngest detrital zircon age (Compston and Pidgeon, 1986). However, numerous studies have produced concordant zircon U−Pb ages that are younger, including grains with ages of 3046 ± 9 Ma (Nelson, 2000) and 3047 ± 21 Ma (Crowley et al., 2005). Thus, it appears that the maximum age of deposition of the W74 metaconglomerate may be c.3050 Ma. An Archean deposition age is consistent with the observation that metamorphic monazite with an age of 2653 ± 5 Ma was identified in the matrix of the conglomerate at the W74 site (Rasmussen et al., 2010). Furthermore, some of the metasedimentary rocks are intruded by granitoids that yield zircon U–Pb ages of c.2650 Ma (Pidgeon and Wilde, 1998; Spaggiari et al., 2007).

Studies of the distribution of detrital zircon ages away from the W74 site show that not all of the Jack Hills metasedimentary rocks were deposited in the Archean. Detrital grains with Proterozoic ages have been reported, including a 1576 ± 22 Ma grain from a 60-m section that contains the W74 site (Fig. 12.2) and <3000 Ma grains from a 20-m conglomerate-bearing section 1 km east of W74 (Cavosie et al., 2004). All of the rocks sampled along these two sections are dominated by chemically mature clastic metasedimentary rocks (>95 wt.% SiO_2) and include metaconglomerate, quartzite, and metasandstone. The presence of detrital Proterozoic zircon grains in these sections and elsewhere in the Jack Hills metasedimentary sequence has been confirmed by other studies. Dunn et al. (2005) reported c.1800 Ma detrital grains, and Grange et al. (2010) reported concordant detrital grains from a site ~1 km west of W74 with ages as young as 1220 Ma. In addition to detrital grains, zircon from felsic volcanic rocks with crystallization ages from 1970 to 1775 Ma has been reported in Jack Hills (Wilde, 2010). In a recent study (Wang, 2015; Wang and Wilde, 2018) based on a north–south traverse through the entire belt immediately east of the W74 site, at least 12% of the Jack Hills belt is composed of Proterozoic metasedimentary rocks, with the possibility that up to ~30% of the rocks could potentially contain Proterozoic zircon. Thus, multiple studies have demonstrated the widespread presence of Proterozoic sedimentary and volcanic rocks, which calls into question how much of the belt has an Archean ancestry. The origin of Mesoproterozoic metasedimentary rocks in Jack Hills remains unknown; however, field investigations by the authors have identified layer-parallel faults in the sections described by Cavosie et al. (2004), which suggests tectonic juxtaposition of two different age packages of metasedimentary units (see also Wilde and Spaggiari, 2007; Spaggiari et al., 2007; Grange et al., 2010).

Significant interest has arisen in obtaining a more complete understanding of the geological history of the Jack Hills metasedimentary rocks (e.g., Spaggiari et al., 2007), and several studies have focused on zircon younger than c.3800 Ma. It is beyond the scope of this paper to review these studies in detail; however, interested readers are encouraged to consult studies that report data for zircon with U–Pb ages that are younger than the deposition age of c.3050 Ma (e.g., Cavosie et al., 2004; Dunn et al., 2005; Grange et al., 2010; Wilde, 2010; Bell et al., 2011; Wang, 2015; Wang and Wilde, 2018).

2.2 Metamorphism

The metamorphic history of the Jack Hills metasedimentary belt remains poorly documented, primarily because of the absence of metamorphic index minerals in most units. Early workers described rare occurrences of andalusite, kyanite, and chloritoid in the western part of the belt (Elias, 1982; Baxter et al., 1984), and later petrographic studies expanded the occurrence of andalusite to the central and eastern parts of the belt (Cavosie et al., 2004; Spaggiari et al., 2007). The distribution of andalusite suggests that the majority of metasedimentary rocks in Jack Hills experienced pervasive low-pressure greenschist to lower amphibolite facies metamorphism. The common association of metamorphic muscovite with quartz and the absence of alkali feldspar with aluminosilicate indicate that the siliciclastic metasedimentary rocks did not reach granulite facies. The presence of grunerite in banded iron formation and hornblende in amphibolite indicate that the chemical sedimentary and mafic rock association reached higher metamorphic grade (amphibolite facies) consistent with evidence that it forms an earlier succession than the clastic sedimentary association (Wilde and Pidgeon, 1990; Rasmussen et al., 2010). The structural relation of the higher-grade rocks relative to the W74 site has not been well established.

2.3 Geology of Adjacent Rocks

Adjacent to Jack Hills, the Meeberrie Gneiss (Myers, 1988) is a complex banded unit that crops out across the Narryer Terrane. The gneisses are deformed tonalite–trondhjemite–granodiorite (TTG) granitoids that yield a range of igneous zircon ages from 3730 to 3600 Ma (Kinny and Nutman, 1996; Pidgeon and Wilde, 1998), establishing it as the oldest rock unit in Australia (Myers and Williams, 1985). Included within the Meeberrie Gneiss near both Jack Hills and Mount Narryer are cm- to km-scale blocks of a dismembered layered mafic intrusion that together comprises the Manfred Complex (Myers, 1988). Zircon from Manfred Complex samples also yield ages as old as 3730 Ma, suggesting it formed contemporaneously with the oldest components of the Meeberrie Gneiss (Kinny et al., 1988). Exposures of the 3490 to 3440 Ma Eurada Gneiss occur 20 km west of Mount Narryer and contain a component of younger c.3100 Ma zircon (Nutman et al., 1991). West of Jack Hills, the Meeberrie Gneiss was intruded by the precursor rocks of the Dugel Gneiss, which contains 3380 to 3350 Ma zircon (Kinny et al., 1988; Nutman et al., 1991) and the Meeberrie gneiss contains enclaves of the Manfred Complex (Myers, 1988). Younger granitoids, from 2660 to 2646 Ma, intrude older granitoids in the vicinity of Jack Hills and Mount Narryer (Pidgeon and Wilde, 1998; Kinny, 1990; Pidgeon, 1992). Contacts between the Jack Hills metasedimentary rocks and the older granitoids are everywhere sheared, whereas the c.2650 Ma granitoids locally intrude the belt (Pidgeon and Wilde, 1998).

3. STUDIES OF JACK HILLS ZIRCON

Since their discovery over three decades ago, data and images for thousands of Jack Hills zircon grains have been described in nearly 100 peer-reviewed articles (Fig. 12.4). Although it is beyond available space to summarize every published article on Jack Hills, it is clear that interest in this topic continues to increase with time. There was an early pulse of publications from 1986 to 1992 and again from 1998 to 2001; however, since 2004 there has been a steady stream of multiple publications per year on Jack Hills, with most focused on zircon (Fig. 12.4). Interested readers can also consult previous review articles (Cavosie et al., 2007; Peck and Valley, 2009; Harrison, 2009; Wilde, 2011; Arndt, 2013; Trail et al., 2013; Nebel et al., 2014; Harrison et al., 2017).

3.1 Images of Jack Hills Zircon

Physical aspects of Jack Hills zircon grains include early descriptions of mostly deep purplish-brown grains and fragments, some rounded and others with pyramids, with many exhibiting pitting suggestive of sedimentary transport (e.g., Compston and Pidgeon, 1986; Maas et al., 1992). A variety of shapes are visible in grains mounted on tape prior to casting in epoxy. Color images of unmounted grains reveal a range of dark red colors that are characteristic of Jack Hills zircon, as well as their morphological spectrum, from essentially euhedral to completely rounded grains (Fig. 12.5A). The rounded forms and pitted surfaces are visible in transmitted light images of polished grains (Köber et al., 1989, Fig. 12.5B).

Cathodoluminescence (CL) images of populations of Jack Hills zircon appear in many publications (e.g., Cavosie et al., 2004; Dunn et al., 2005; Crowley et al., 2005; Nemchin et al., 2006; Pidgeon and Nemchin, 2006; Trail et al., 2007a, 2017; Ushikubo et al., 2008; Grange et al., 2010). Most CL images show grains with oscillatory or sector zoning; however, there is evidence for disturbance of growth zoning in many grains that may result from either magmatic modification, such as growth of younger rims, or modification from solid-state processes such as metamorphism (Cavosie et al., 2005a; Nemchin et al., 2006; Trail et al., 2007b) or radiation damage (Valley et al., 2014a, 2015).

3.2 Age of the Hadean Zircon Population

3.2.1 The U–Pb Story

The initial focus of most studies on Jack Hills zircon has been on U–Pb geochronology, as it is the only way to identify which grains in the population are Hadean. However, investigations vary in scope; typical approaches involve detailed study of 10s–100s of grains, whereas larger surveys have involved rapid screening of >10,000 grains. Approaches to U–Pb geochronology have involved various analytical methods, each with inherent strengths and limitations. Studies

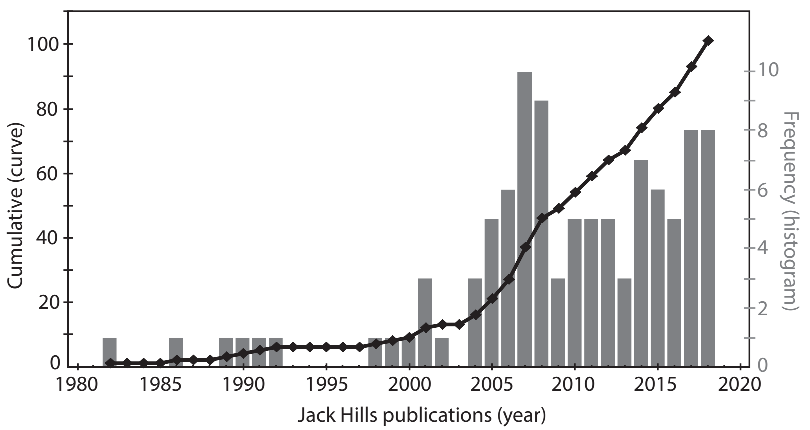

FIGURE 12.4 Publication history of the Jack Hills, Western Australia, as of mid-2018. The 101 publications shown are peer-reviewed studies of the geology of the Jack Hills, with most (85) focused on different aspects of zircon. No conference abstracts are included in this compilation.

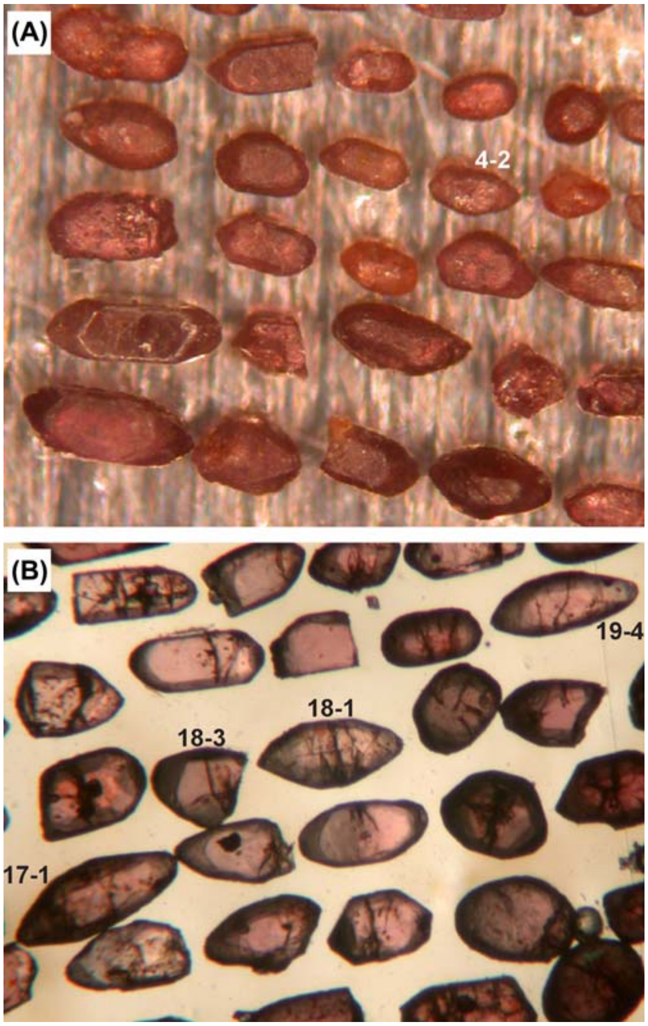

FIGURE 12.5 Images of Jack Hills detrital zircon grains. (A) Images of unpolished grains from sample 01JH13b_5M. The grains are sitting on mounting tape prior to casting in epoxy. The grain labeled 4.2 yielded a SIMS $^{207}Pb/^{206}Pb$ age of 3904 ± 6 Ma (94% concordant). (B) Transmitted light image of polished zircon grains from sample 01JH13b_2.5NM. Four >3900 Ma grains are labeled: 17-1 ($^{207}Pb/^{206}Pb$ age = 4010 ± 10 Ma, 102% concordant); 18-1 ($^{207}Pb/^{206}Pb$ age = 3925 ± 18 Ma, 99% concordant); 18-3 ($^{207}Pb/^{206}Pb$ age = 4126 ± 18 Ma, 99% concordant); and 19-4 ($^{207}Pb/^{206}Pb$ age = 4090 ± 6 Ma, 100% concordant). Uncertainties on age are cited at 2σ. *SIMS*, secondary ion mass spectrometry. *Images are from Cavosie, 2005.*

requiring the highest precision U/Pb ages (<1%) use thermal ionization mass spectrometry (TIMS), isotope dilution TIMS (ID-TIMS), and/or isotope dilution inductively coupled plasma mass spectrometry (ID-ICPMS), although these methods have low spatial resolution as they involve dissolving whole grains or fragments of grains. Studies that survey large numbers of grains typically use laser ablation ICPMS (LA-ICPMS), a method that can make in situ spot analyses on ~500 to 1000 grains per day, albeit at lower analytical precision (~3−5%). Historically, the most widely applied method for Jack Hills zircon U−Pb geochronology has been secondary ion mass spectrometry (SIMS), a method capable of intermediate analytical precision (~1%), high spatial resolution (~20 μm spot), and that in routine operation is capable of analyzing ~50 to 100 grains per day. A "large survey" approach to U−Pb geochronology of Jack Hills zircon was introduced by a group at the Australian National University (ANU), who used automated SIMS analysis with modified protocols ("fast scan") to analyze epoxy mounts containing 225−400 grains; many such mounts were analyzed over nearly a decade. The ANU group provided periodic updates in conference abstracts of their "running grain tally," starting with 15,000 in 2003 (Harrison et al., 2003), which increased to 60,000 (Holden et al., 2006), then up to 80,000 (Harrison and Project MtREE, 2007), and finally culminated with a report of 103,000 grains surveyed for U−Pb age (Holden et al., 2009). More recently, next-generation automated "large survey" approaches to U−Pb geochronology have incorporated functions that allow automated grain picking, coupled with automated LA-ICPMS analysis of unmounted grains, as described in a study of 3800 grains by Isozaki et al. (2017).

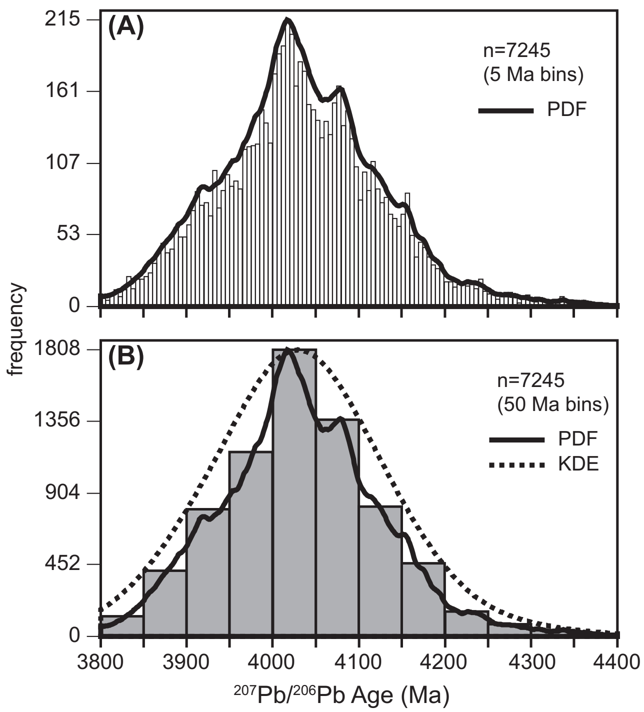

FIGURE 12.6 Age spectra of Jack Hills detrital zircon grains. (A) Age spectrum that includes all 7245 analyses listed in the data Appendix of Holden et al. (2009). A histogram bin size of 5 Ma was used in an attempt to reproduce the original data plot of Holden et al. (their Fig. 10A). The *solid line curve* is a probability density function (PDF). (B) Same data as shown in A (n = 7245), plotted using a histogram bin size of 50 Ma, may more closely approximate uncertainties of secondary ion mass spectrometry analysis. The *solid curve* is the same PDF as show in (A). The *dashed line* is a kernel density estimate (KDE), plotted using a bandwidth of 50 Ma. Both spectra were plotted using the program DensityPlotter (Vermeesch, 2012).

The first wave of zircon U–Pb studies in Jack Hills was made using SIMS and TIMS. Compston and Pidgeon (1986) reported that 17 of 140 grains (12%) from sample W74 were older than 3900 Ma. This population included one zircon that yielded four spots between 4211 ± 6 and 4276 ± 6 Ma, the latter constituting the oldest concordant U–Pb analysis at that time. Subsequent U–Pb studies of zircon from the W74 site by Köber et al. (1989: TIMS), Maas and McCulloch (1991: SHRIMP), and Maas et al. (1992: SHRIMP) published data for 44 ≥3900 Ma grains and confirmed that Hadean grains comprise from 8% to 12% of the analyzed population. A second wave of zircon research began near the end of the 1990s and included the first application of ICPMS to Jack Hills. New Hadean zircon U–Pb ages were published by Amelin (1998: ID-ICPMS), Nelson (2000: SIMS), Wilde et al. (2001: SIMS), Mojzsis et al. (2001: SIMS), and Peck et al. (2001: SIMS). Amelin (1998) demonstrated the ability to obtain high-precision $^{207}Pb/^{206}Pb$ ages (<1% uncertainty) of whole grains and abraded fragments. Since 2004, many additional U–Pb data sets for Jack Hills detrital zircon have been published, which include several thousand Hadean grains (Cavosie et al., 2004; Crowley et al., 2005; Dunn et al., 2005; Nemchin et al., 2006; Pidgeon and Nemchin, 2006; Trail et al., 2007a,b; Ushikubo et al., 2008; Holden et al., 2009; Grange et al., 2010; Kemp et al., 2010; Bell et al., 2011; Abbott et al., 2012; Valley et al., 2014a; Isozaki et al., 2017; Wang and Wilde, 2018). Common trends in U–Pb ages have emerged from the above studies. The main peak in the Hadean Jack Hills age distribution is from 4000 to 4100 Ma, with the distribution "tailing off" toward both younger (~3800 Ma) and older (~4375 Ma) grains (e.g., Holden et al., 2009) (Fig. 12.6). In the recent study by Wang (2015), over 6300 grains were dated by SIMS and ICPMS, with the concordant grains (n = 2819) extending from 1618 to 4381 Ma, with a major peak at 3383 Ma; the main age peak for Hadean grains is at 4019 Ma.

3.2.2 U Abundance, Radiation Damage, and Pb Loss

The ancient crystallization ages of Jack Hills Hadean zircon predict that these grains should have accumulated radiation damage over time. While Hadean zircon with, notably, low U concentration (e.g., 20–60 ppm) has been reported (e.g., Compston and Pidgeon, 1986; Maas et al., 1992; Amelin, 1998; Nelson, 2000; Peck et al., 2001; Cavosie et al., 2004; Pidgeon and Nemchin, 2006), many grains in Jack Hills metasedimentary rocks (e.g., Compston and Pidgeon, 1986) and surrounding granitoids (Utsunomiya et al., 2007) have conspicuous radiation damage and demonstrable Pb loss.

However, some Jack Hills grains do not preserve as much radiation damage as is predicted by their calculated "alpha dose" (Palenik et al., 2003); some of the "missing" radiation damage appears to have been annealed. Quantification of the difference between measured versus predicted radiation damage, as determined by laser Raman spectroscopy, has given rise to so-called radiation damage ages, which, though based on untested assumptions, are interpreted to date when annealing ceased; grains from the Jack Hills yield a Mesoproterozoic radiation damage age of 1120 ± 130 Ma (Pidgeon, 2014), which agrees with Ar/Ar dates obtained from mica by Spaggiari et al. (2008).

Many Jack Hills zircon grains indeed demonstrate discordance in U–Pb age, which is likely a consequence of radiation damage–facilitated open-system behavior, resulting in localized loss of radiogenic Pb from originally high U areas of some grains. For the reason mentioned earlier, in situ methods for U–Pb analysis are often preferred over methods that dissolve grains. However, even with in situ U–Pb methods, it is critically important to characterize grains using various imaging methods prior to analysis to avoid suspect areas in individual crystals (i.e., cracks, younger rims, mineral inclusions, radiation damage). With careful targeting protocols aimed at analysis of crystalline zircon domains, meaningful geochronological data can be extracted from grains that otherwise have pervasive radiation damage or other defects.

Although Pb loss in most grains is demonstrably young, as evidenced by Phanerozoic or "zero age" lower intercepts on discordia regressions (e.g., Wilde et al., 2001; Grange et al., 2010), potential Pb loss that occurred in the Hadean (e.g., >4000 Ma) can either be speculated on (e.g., Nelson, 2002, 2004; Nemchin et al., 2006) or modeled (Guitreau and Blichert-Toft, 2014). The effects of U–Pb discordance on isotopic systematics of Jack Hills zircon have long been discussed (e.g., Amelin, 1998; Valley et al., 2006; Valley et al., 2015). To qualify as "acceptable" U–Pb analyses, some studies select an arbitrary threshold value for U–Pb concordance (typically 90%) for assigning age significance to a given analysis. Other studies have attempted to develop empirical metrics to evaluate the reliability of U–Pb ages in Hadean grains with demonstrable Pb loss by correlating the Th/U ratio, U, Th, Ca concentration, or Sm/La with U/Pb concordance (Cavosie et al., 2004; Bouvier et al., 2012).

3.2.3 The Oldest Grains in the Jack Hills

One of the most significant discoveries in Jack Hills zircon research is a grain that yielded a concordant $^{207}Pb/^{206}Pb$ age of 4404 ± 8 Ma (Wilde et al., 2001; Peck et al., 2001). These data remain the oldest concordant analysis of any terrestrial zircon. Five additional spot analyses, all >95% concordant, yielded a somewhat younger weighted mean age of 4352 ± 10 Ma, which, although younger than the oldest spot, confirmed the great antiquity of the crystal. Interpreting the 4400 Ma age as the crystallization age of the zircon generated lively discussion at conferences and in subsequent literature for years. However, the approach followed for the 4400 Ma grain was the same methodology and rationale as that used by Compston and Pidgeon (1986) for a 4276 ± 6 Ma crystal and that is also routinely applied in U–Pb studies of Archean and Hadean zircon. If the analysis that yields the oldest age is not associated with any sample- or instrument-related aspects to justify its exclusion (e.g., U–Pb concordance, presence of ^{204}Pb, textural considerations, etc.), it is interpreted as the minimum age of the crystal, whereas younger ages are interpreted as having experienced Pb loss. The 4400 Ma grain dramatically pushed back the maximum age of zircon in Jack Hills by ~125 Ma and simultaneously extended the terrestrial geologic record further back in time.

The observation of Pb loss for many subdomains and inferred radiation damage in the 4400 Ma zircon (and other grains) has been used to question whether or not primary crystallization ages are preserved in the Jack Hills zircon suite. A solution ID-ICPMS study of 63 Jack Hills zircon grains did not reproduce >4300 Ma ages measured in some of the grains by SIMS, which led to the suggestion that Jack Hills Hadean zircon formed in one event at c.4100 Ma and that the older ~4300 Ma SIMS ages resulted from incorporation of inherited cores and/or common Pb (^{204}Pb) in the analysis (Blichert-Toft and Albarède, 2008). However, ID-ICPMS analysis involves dissolving entire grains, and thus a bulk analysis of a single complex grain cannot resolve ages of disparate domains in grains that contain older cores with younger rims, as is common in the Jack Hills zircon suite (e.g., Cavosie et al., 2004; Valley et al., 2014a).

Grains older than 4300 Ma are uncommon, and grains with ages >4350 Ma are even rarer. Grains older than c.4350 Ma typically only yield such ages from one or a few concordant spots; other areas in these grains generally yield younger ages, which can be either concordant or discordant (e.g., Wilde et al., 2001; Wyche et al., 2004; Cavosie et al., 2004; Nemchin et al., 2006; Harrison and Schmitt, 2007; Harrison et al., 2008). At present, we are aware of only four documented Hadean grains where ages >4350 Ma were reproduced in three or more spot analyses that are concordant (Wilde et al., 2001; Wyche et al., 2004; Nemchin et al., 2006; Valley et al., 2014a). A histogram of concordant analyses made on six grains >4350 Ma is shown in Fig. 12.7. Grains older than c.4350 Ma typically show textural and isotopic evidence of disturbance and/or open-system behavior in some parts of the crystal, which is not surprising given their history, but other domains in the same grain can be perfectly preserved. Such zonation complicates correct interpretation of primary crystallization age.

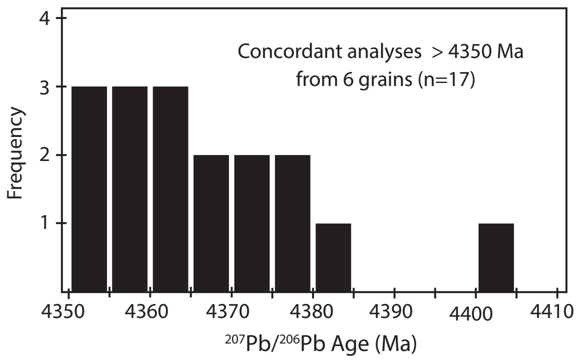

FIGURE 12.7 Histogram showing concordant $^{207}Pb/^{206}Pb$ ages from six grains >4350 Ma. *Data sources include Wilde et al. (2001); Wyche et al. (2004); Nemchin et al. (2006); Harrison and Schmitt (2007); Harrison et al. (2008); Valley et al. (2014a).*

Detailed investigations of the mobility of radiogenic Pb at the nanoscale in Jack Hills zircon by transmission electron microscopy (TEM) have led to direct imaging of mobilized Pb (Utsunomiya et al., 2004). However, the ability to characterize Pb isotopes (^{206}Pb and ^{207}Pb) at the nanometer scale was not available until the application of atom probe tomography (APT) to zircon (Valley et al. 2014a, 2015). APT allows the 3D spatial reconstruction of atoms with nm-scale precision and thus can determine Pb isotope behavior in a volume of zircon $\sim 10^6$ smaller than that analyzed by a $\sim$20 μm diameter SIMS spot. Atom probe analysis was conducted on zircon 01JH36-69, one of the rare >4350 Ma (4374 ± 6 Ma) grains mentioned earlier, which yielded three concordant overlapping SIMS analyses, each located in core domains that preserve oscillatory growth zoning (Fig. 12.8). Grain 01JH36-69 also contained a pronounced symmetric overgrowth that yielded three U/Pb ages of c.3400 Ma, revealing that the Hadean core had been magmatically recycled during the Archean.

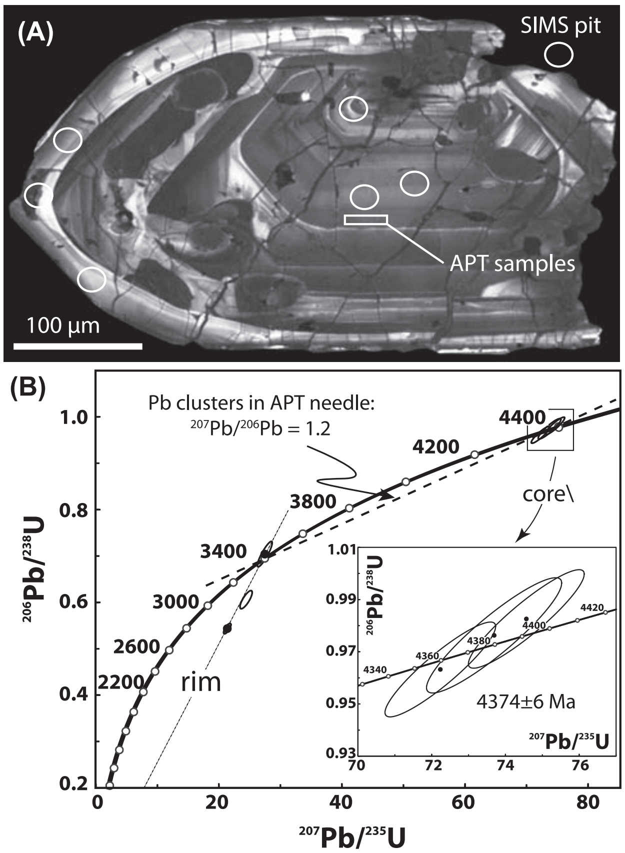

FIGURE 12.8 U–Pb concordia diagram showing secondary ion mass spectrometry (SIMS) analyses of the 4374 Ma zircon analyzed by atom probe tomography (APT) (after Valley et al., 2014a). (A) Cathodoluminescence (CL) image of grain 01JH36-69, showing preserved igneous growth zoning in the core, and a wide truncating rim that is also zoned. The locations of SIMS pits and the APT needle sampling site are indicated. (B) Concordia curve showing the six SIMS analysis for U-Pb (3 in core, 3 on rim). Also shown is a dashed line (long dash) connecting points on the Concordia curve at 4400 Ma and $\sim$3400 Ma that corresponds to the $^{207}Pb/^{206}Pb$ ratio of 1.2 measured for Pb clusters in the atom probe needles.

Atom probe analysis of two 100 × 1000 nm needlelike tips extracted adjacent to a 4382 Ma SIMS spot in the core of the zircon (Fig. 12.8) revealed that the needles contain ~10 nm diameter clusters surrounded by homogenous zircon. The clusters contain enrichments of Pb and other trace elements, including Y and rare earth elements (REEs) but not U (Valley et al., 2014a, 2015). The two needles yielded $\sim 6 \times 10^8$ atoms and a bulk $^{207}Pb/^{206}Pb$ ratio of 0.52 ± 0.04, which overlaps the more precise value of 0.548 ± 0.002 measured by SIMS. However, the Pb isotope ratio of the two domains differs significantly; the Pb in clusters yields a $^{207}Pb/^{206}Pb$ ratio of 1.2 ± 0.05, whereas the homogenous zircon surrounding the clusters yields a $^{207}Pb/^{206}Pb$ ratio of 0.30 ± 0.05. The $^{207}Pb/^{206}Pb$ ratio of ~1.2 in clusters represents the early history of this zircon, when ^{235}U was relatively more plentiful. However, this ratio is impossible to preserve in even the oldest zircon grains, as continued ingrowth of ^{206}Pb decreases the ratio over time. The Pb clusters analyzed by atom probe are nearly U-free (measurements of U were below the detection limit of 10 ppm), and thus the clusters record a "snapshot" of the $^{207}Pb/^{206}Pb$ in the bulk zircon during a Pb mobility event after the zircon crystallized. Preserved in a U-free environment (i.e., the clusters), the $^{207}Pb/^{206}Pb$ ratio of 1.2 did not evolve over time; anchored at 4374 Ma, a line with slope 1.2 intersects the concordia curve at c.3400 Ma, thus dating the thermal event when Pb was concentrated into clusters (Fig. 12.8). The c.3400 Ma "cluster formation age" is indistinguishable from the magmatic rim age measured by SIMS, providing further confirmation of the reliability of Pb data from the clusters. Taken together, the atom probe results document that Pb mobility occurred but that average migration distances were ~25 nm, the average distance between clusters. This observation validates the interpretation that the oldest U–Pb ages preserved in Jack Hills zircon record primary crystallization from magma and that Pb mobility at the <50 nm scale was homogenized over the much larger ($\sim 10^6$ times) volume analyzed by SIMS (Valley et al., 2014a).

3.2.4 Distribution of Hadean Grains

Studies that have analyzed detrital zircon in samples away from the W74 site have found that the percentage of Hadean grains is highly variable across the belt and, moreover, that Hadean grains are not present in all units (Cavosie et al., 2004; Dunn et al., 2005; Crowley et al., 2005). The high percentage of Hadean grains among those analyzed in the W74 metaconglomerate (up to 12%) appears to be unique in the Jack Hills, given the heterogeneous distribution of ≥4000 Ma grains throughout the belt. However, in the recent study of Wang (2015), a sample of quartzite from the northern part of the belt contained 20% Hadean grains; importantly, it also contained a Proterozoic grain with an age of 1642 ± 25 Ma (Wang and Wilde, 2018).

3.3 Oxygen Isotopes

Because of the slow diffusivity of oxygen in zircon (e.g., Valley et al., 1994; Watson and Cherniak, 1997; Peck et al., 2003; Page et al., 2007; Bowman et al., 2011; Bindeman et al., 2018), nonmetamict magmatic zircon can provide a robust record of the oxygen isotope composition ($\delta^{18}O$) of host magmas during crystallization (Valley et al., 1994, 2005; Valley, 2003). The composition of zircon in equilibrium with mantle-derived melt has been well established and falls within a narrow range of $\delta^{18}O = 4.7$ to 5.9 (5.3 ± 0.6‰, 2SD) (Valley et al., 1998, 2005; Cavosie et al., 2009). The first oxygen isotope studies of Jack Hills zircon were published in 2001. Wilde et al. (2001), Peck et al. (2001), and Mojzsis et al. (2001) reported SIMS $\delta^{18}O$ data for grains >4000 Ma from Jack Hills that ranged from 5.4 to 7.6‰, which includes values elevated relative to mantle-equilibrated zircon. The results were interpreted to indicate that the protolith of the host magmas to the zircon grains had experienced a low-temperature history of alteration prior to melting, which required the presence of liquid surface water (Valley et al., 2002). Other grains reported by Mojzsis et al. (2001) with anomalously high $\delta^{18}O$, up to 15‰, were interpreted to originate from Hadean "S-type" granite. However, the U–Pb ages for the high $\delta^{18}O$ grains were highly discordant (Trail et al., 2007a). Such high $\delta^{18}O$ values have not been reported for any concordant igneous zircon older than 2500 Ma (Valley et al., 2005; Spencer et al., 2017) but might occur in a metamorphic zircon (Cavosie et al., 2011) or from exchange facilitated by radiation damage above the first percolation point, when amorphous domains form continuous pathways throughout the crystal (see Ewing et al., 2003; Valley et al., 2015; Pidgeon et al., 2017).

Oxygen isotope data have since been published for many Hadean grains from Jack Hills (e.g., Cavosie et al., 2005a; Nemchin et al., 2006; Trail et al., 2007a; Ushikubo et al., 2008; Harrison et al., 2008; Bell et al., 2011; Bouvier et al., 2012; Bell and Harrison, 2013). Typical approaches for measuring $\delta^{18}O$ by SIMS involve correlating the location of in situ $\delta^{18}O$ analyses with the location of U–Pb analysis sites (Fig. 12.9). By targeting concordant U–Pb domains and discarding analyses that produced anomalous sputter pits (as viewed postanalysis by scanning electron microscopy [SEM]), the range of $\delta^{18}O$ in Jack Hills varies over a narrow interval from 4.6 to 7.3‰, values that overlap or are mildly elevated above

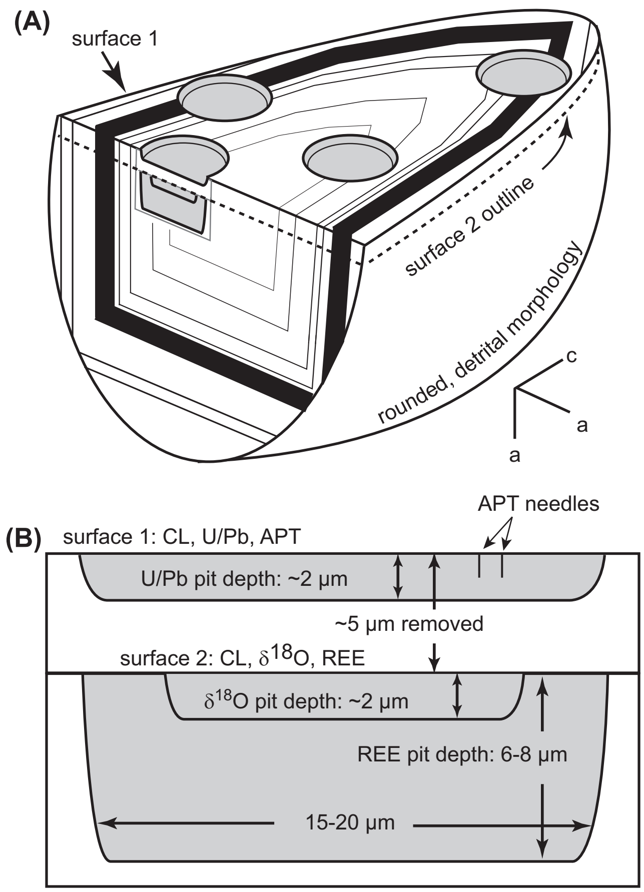

FIGURE 12.9 Cartoon illustrating the concept of spatially correlating in situ analyses of zircon (after Cavosie et al., 2006). (A) Schematic representation of a zoned detrital zircon with correlated analyses of U–Pb, $\delta^{18}O$, atom probe tomography (APT), and rare earth elements (REEs) (the orientation of crystallographic axes is indicated to the lower right). The "a–c plane" [(100), roughly horizontal] represents polished surfaces 1 and 2. Surface 1 was analyzed for U–Pb (*shaded ovals*). The *dashed line* indicates the plane of surface 2, analyzed for $\delta^{18}O$ and REE. The "a–a plane" [(001), roughly vertical] shows a hypothetical cross section through the grain and the volumes analyzed for U/Pb, $\delta^{18}O$, and REE. (B) A cross section (001) of the volumes analyzed for U–Pb age, $\delta^{18}O$, APT, and REE in (A). The dimension of the entire volume varies but is on average 20 μm in diameter and 10–15 μm deep. This volume will likely decrease over time as spot sizes for individual analyses become smaller. *APT*, atom probe tomography; *CL*, cathodoluminescence.

mantle-equilibrated zircon. When only analyses from oscillatory zoned grains with concordant U–Pb ages are considered, elevated $\delta^{18}O$ values relative to mantle oxygen (e.g., >6.5‰) only occur in zircon with ages younger than 4300–4200 Ma. This transition has been interpreted to record low-temperature alteration of crust by liquid water and magmatic recycling of the altered crust before c.4200 Ma or possibly earlier (e.g., Wilde et al., 2001; Peck et al., 2001; Valley et al., 2002; Cavosie et al., 2005a).

Oxygen 3-isotopes have been measured in a subset of Hadean zircon grains from the Jack Hills to test for evidence of crustal evolution or meteoritic input. A total of 44 grains were analyzed in situ for $\delta^{18}O$ and $\delta^{17}O$ by SIMS (CAMECA ims-1280) with a 15-nm spot and $\Delta^{17}O$ was calculated (Valley et al., 2007; Valley and Kita, 2009). Values were standardized against the zircon oxygen isotope standard KIM-5, which is a mantle megacryst from kimberlite (Valley, 2003). Thus $d^{18}O$ is reported relative to ocean water (VSMOW) and $\Delta^{17}O$ is relative to bulk silicate Earth, which differs from VSMOW by ~0.1‰, which is less than the analytical precision for SIMS. Values of $\Delta^{17}O$ are -0.05 ± 0.24‰ (2se = 0.04‰) for 44 Jack Hills zircon grains with ages from 4.0 to 4.35 Ga. The values of $\Delta^{17}O$ are 0‰ (by definition) for KIM-5 (± 0.22‰ 2sd, N = 28, 2se = 0.04‰). There is no significant difference in $\Delta^{17}O$ between KIM-5, which represents oxygen from the Earth's mantle at ~0.1Ga, and the $\Delta^{17}O$ of Jack Hills detrital zircon grains, which preserve values of oxygen isotope ratio from magmas that were contaminated by supracrustal oxygen at > 4 Ga in the Hadean. Thus, the Jack Hills grains are demonstrably terrestrial in origin, and there is no evidence in these data for a secular trend in $\Delta^{17}O$ on Earth for the mantle, crust, or hydrosphere.

3.4 Trace Elements

3.4.1 Lithium

Measurement of Li concentration [Li] and isotope ratio (δ^7Li) in zircon is a relatively new technique by SIMS (Ushikubo et al., 2008). The Li abundance of zircon from primitive rocks (kimberlite megacrysts and ocean crust) is <0.1 ppm, whereas zircon from evolved crust (e.g., granitoid) typically has 10s−100s of ppm Li (Ushikubo et al., 2008; Bouvier et al., 2012). These compositions are predicted to be preserved in ancient zircon because Li^+ is charged balanced by trivalent cations such as REEs and Y, which diffuse slowly in zircon; however Li^+ exchange with H^+ may be faster. Measurements of Li abundance and δ^7Li in Jack Hills zircon were reported by Ushikubo et al. (2008) and Bouvier et al. (2012), with values from 1 to 70 ppm and with δ^7Li from -18.5 to 11.8‰. The high concentrations of Li are indicative of evolved crust, and the fractionated isotopic values overlap with δ^7Li of altered rocks (Bouvier et al., 2012). Isotope exchange rates for Li in zircon are relatively fast (Cherniak and Watson, 2010), and preserved growth zoning defined by narrow bands of Li have been interpreted from a speedometry perspective and cited as evidence that Hadean grains from Jack Hills did not experience temperatures >500 °C (Trail et al., 2016).

3.4.2 Ti Thermometry

The Ti abundance of zircon (typically a few to tens of ppm) has been experimentally shown to be a function of melt composition and crystallization temperature; Ti abundance can thus yield crystallization temperature if a_{SiO2}, a_{TiO2}, and pressure are either empirically constrained or estimated (Watson and Harrison, 2005). Ti abundance data have been reported for hundreds of Jack Hills Hadean grains (Watson and Harrison, 2005; Harrison and Schmitt, 2007; Trail et al. 2007a, 2011; Fu et al., 2008; Harrison et al., 2008; Bell et al. 2011, 2014; Abbott et al., 2012; Bell and Harrison, 2013), and compilations indicate that average [Ti] concentrations correspond to estimated temperatures of 680 ± 25°C (e.g., Harrison, 2009). Such low magmatic temperatures were interpreted by Watson and Harrison (2005) to provide evidence for minimum-melt, water-saturated granitic magmatism on the Earth by c.4350 Ma. However, nano-SIMS mapping shows fine zonation of [Ti] consistent with nonequilibrium partitioning of Ti (Hofmann et al., 2009). Furthermore, other studies have questioned the uniqueness of the interpretation for wet granite melting, citing data that show Ti-in-zircon temperatures determined for zircon from a wide compositional range of rock types, including anorthosite, gabbro, and granitoid, overlap with Ti compositions of Jack Hills zircon (Valley et al., 2006; Fu et al., 2008). It is likely that many zircon grains hosted by mafic igneous rocks have crystallized at lower temperature in small fractions of late-evolved residual melt, and thus their temperatures of crystallization are not indicative of the bulk rock. The similarity of Ti abundance for zircon from a wide range of felsic and mafic igneous rock types highlights that caution should be applied when applying the Ti-in-zircon thermometer to detrital grain populations for the purpose of inferring host rock composition.

3.4.3 Rare Earth Elements, Yttrium and Phosphorous

REEs record information about the petrogenesis of zircon and have been used to place constraints on host rock composition for detrital grains (e.g., Hoskin and Schaltegger, 2003). Many REE data sets have been published for Hadean zircon from Jack Hills as measured by both SIMS and LA-ICPMS (e.g., Maas et al., 1992; Peck et al., 2001; Wilde et al., 2001; Crowley et al., 2005; Cavosie et al., 2006; Trail et al., 2007a; Hofmann et al., 2009; Grimes et al., 2011; Bouvier et al., 2012; Bell and Harrison, 2013; Bell et al., 2016; Burnham and Berry, 2017). Most studies show that Hadean grains from Jack Hills have compositions typical of igneous zircon from crustal environments (Hoskin and Schaltegger, 2003). Characteristics such as enrichment in heavy REE over light REE (LREE) indicate that Jack Hills zircon crystallized in fractionated melts. Positive Ce anomalies and negative Eu anomalies are further evidence of oxidized melts with a history of plagioclase fractionation. The elements Ce and Eu have also been used to infer redox conditions of magmas parental to Hadean grains (Trail et al., 2011).

Anomalous LREE enrichment in some grains, including abundances ranging from 10 to 100 times chondritic values, has generally been interpreted as *not* representative of primary igneous zircon (Wilde et al., 2001; Peck et al., 2001; Cavosie et al., 2006; Bell et al., 2016) and instead is described as "hydrothermal" zircon (Hoskin, 2005). However, many zircon grains with anomalous LREE (and other geochemical variations) are altered as a result of radiation damage and are not precipitated from hydrothermal solutions (Valley et al., 2015). Differences between primary and altered REE compositions have been characterized in several studies (Cavosie et al., 2006; Bell et al., 2016); analyses from altered domains can generally be identified by anomalously high values for La ($La_N > 1$) and Pr ($Pr_N > 10$). Careful targeting protocols that correlate in situ spot analyses for REE with areas that yield magmatic $\delta^{18}O$ and concordant U−Pb ages (Fig. 12.9) can increase the likelihood of retrieving primary (igneous) REE values (e.g., Cavosie et al., 2006).

Analysis of the ratio of the molar abundance of Y + REE to P in zircon, also known as "xenotime substitution" (Hanchar et al., 2001), has been applied in several studies of Jack Hills zircon where P was typically measured by SIMS, as measurement of P by LA-ICPMS is difficult. Incorporation of REE in zircon via xenotime substitution is predicted to produce a 1:1 ratio of Y + REE to P; measured values for Jack Hills zircon typically deviate from unit values. Cavosie et al. (2006) noted the presence of phosphate inclusions in many grains where Y + REE:P deviated from unity; Bell et al. (2016) reported similar behavior. Substitution of Li^{+} or H^{+} in an interstitial site has also been shown to charge balance $(Y + REE)^{3+}$ substitution for Zr^{4+} in Jack Hills zircon (Ushikubo et al., 2008; Bouvier et al., 2012). A recent study by Burnham and Berry (2017) compared previously published Y + REE:*P* values in Jack Hills zircon with grains from peraluminous and metaluminous granites from the Lachlan Fold Belt and found that the majority of Hadean zircon grains from Jack Hills have values consistent with an origin in metaluminous granitoid.

3.4.4 Other Trace Elements (Al, Sc, Sm/Nd, Xe)

Other trace elements in Hadean zircon have been used to infer information on host rocks, and in one case, aspects of the primordial composition of the Earth. Maas et al. (1992) analyzed Sc in Hadean grains by electron microprobe analyzer (EMPA) and found concentrations from <17 ppm (detection limit) to 59 ppm. These values were used to interpret an origin for the grains in intermediate rocks based on Sc partitioning behavior, based on the assumption that mafic rocks with higher whole-rock Sc values would crystallize zircon with higher Sc abundance.

A recent study reported Al abundance in Hadean zircon as measured by 35 μm spot analysis using LA-ICPMS (Trail et al., 2017). The Hadean Jack Hills grains uniformly contained <5 ppm Al, which was interpreted as a primary compositional feature of the zircon, rather than resulting from alteration (e.g., Utsunomiya et al., 2007). The Al abundances were cited to interpret an origin for the Hadean grains in metaluminous granitoid, as zircon from metaluminous granitoids from the Lachlan Fold belt in Australia contains <4 ppm Al, whereas the peraluminous granitoids contain >4 ppm Al. In addition to Al, other "nonformula" elements in Jack Hills zircon (e.g., Ca, Fe) have been cited as evidence of element mobility in subdomains of some grains (Bouvier et al., 2012; Valley et al., 2015).

An attempt to detect the former presence of ^{146}Sm, an extinct isotope, in Hadean zircon involved dissolution of a composite aliquot consisting of 790 Hadean grains (4190−3950 Ma) for Sm−Nd by ID-ICPMS (Caro et al., 2008). The measurement was designed to detect evidence for a ^{142}Nd anomaly that would record the former presence of ^{146}Sm, which may be detectable in zircon as young as ~4200 Ma. However, the results were inconclusive and indicated disturbance had occurred in the Sm−Nd of the composite sample; information on the composition of the early crust was not retrievable in this case. Turner et al. (2004, 2007) reported evidence that ^{244}Pu, another extinct isotope, had been incorporated in Jack Hills Hadean grains by detection of isotopic anomalies in Xe isotopes. The detection of fissiogenic Xe was interpreted to provide further constraints on the original Pu/U ratio of the Earth.

3.5 Hafnium Isotopic Compositions

The $^{176}Hf/^{177}Hf$ isotope ratio in zircon is a sensitive chronometer that can provide a "model age" for when parental magmas that crystallized zircon and/or their protoliths were originally extracted from the mantle and thus provides insights into crustal growth events. A key aspect of using $^{176}Hf/^{177}Hf$ isotopic compositions to "date" crustal extraction events is that the initial isotopic composition is determined using the measured U−Pb age from the same zircon. A model age is then calculated by projecting from this composition to the intersection with the model mantle Hf isotopic evolution curve. As zircon has low $^{176}Lu/^{177}Hf$, corrections for in situ decay are minimal. Analysis of zircon with a single-stage crystallization history is relatively straightforward; grains with long and complicated histories, metamorphic and/or magmatic overgrowths, and radiation damage or other defects, such as is common in the Jack Hills zircon population, represent challenges for assigning a correct Hf model age (Valley et al., 2006; Harrison et al., 2006; Vervoort and Kemp, 2016). This is because projection to mantle Hf evolution curves for the period before the crystallization age of the zircon requires estimating the $^{176}Lu/^{177}Hf$ of the source material prior to zircon formation. The detrital nature of the grains means that the $^{176}Lu/^{177}Hf$ ratio of the source material is unknown, making it uncertain as to what ratio should be used to obtain a meaningful "model age," with the choice of ratio having a large effect on calculated ages.

Two general methods have been applied to measure Lu−Hf isotopic compositions in Hadean zircon, including dissolution and the addition of calibrated enriched isotope solutions for precise concentration measurements (ID-TIMS, ID-ICPMS), and in situ (LA-ICPMS) analysis (e.g., Amelin et al., 1999; Harrison et al., 2005; Blichert-Toft and Albarède, 2008;

Kemp et al., 2010; Bell et al., 2011; Bell et al., 2014). Studies of Hadean zircon suites using these methods have produced data sets that generally show most grains have unradiogenic $^{176}Hf/^{177}Hf$ (negative εHf values) relative to the chondritic uniform reservoir, indicating extraction of parental magmas from a crustal reservoir at c.4400 Ma (e.g., Amelin et al., 1999; Harrison et al., 2005; Kemp et al., 2010). However, some LA-ICPMS studies produced positive zircon εHf values, which have been interpreted as evidence for the existence of an early depleted mantle reservoir requiring massive early continental crust formation (Harrison et al., 2005; Blichert-Toft and Albarède, 2008). This interpretation was questioned by Valley et al. (2006) who suggested that calculation of such extreme initial εHf values could be caused by a mis-assignment of U−Pb age and Hf isotopic composition; in complexly zoned zircon, measurement of Hf by LA-ICPMS required (in 2006) analysis of domains over 100 times larger than 20 μm SHRIMP U−Pb spots. The general protocol of U−Pb age determination by SHRIMP using a 20 × 1 μm sampling domain, followed by laser analysis of a much larger (>35 × 30 μm), means that the Hf and U−Pb isotopic data did not originate from the same volume of the grain. In other words, making separate spot analyses for both Hf and U−Pb creates a scenario where each data set may not originate from the same age domain within the grain. This was confirmed by later Hf studies that used methods to simultaneously measure Hf and Pb isotopes to more closely correlate isotopic data to age volumes analyzed (Harrison et al., 2008; Kemp et al., 2010) and which did not reproduce the extreme positive εHf values. Negative εHf values, which form the bulk of the data in all published studies on Jack Hills zircon, have been widely cited as evidence for derivation of parental magmas of Jack Hills Hadean zircon from mafic crust as old as 4400−4500 Ma (e.g., Kemp et al., 2010).

3.6 Mineral Inclusion Studies

A wide range of mineral inclusions have been reported in Hadean zircon from Jack Hills, including silicates, such as quartz, alkali feldspar, plagioclase, muscovite, biotite/chlorite, amphibole, and phosphates, including apatite, monazite, and xenotime (e.g., Maas et al., 1992; Cavosie et al., 2004; Hopkins et al., 2008; Hopkins et al., 2010; Ortiz-Cordero, 2010; Rasmussen et al., 2010, 2011). Large survey approaches have also been applied to mineral inclusion studies, with, for example, Hopkins et al. (2010) describing inclusions in ∼1500 Hadean grains. Cameron et al. (2016) surveyed populations of Jack Hills grains and compared inclusion mineral assemblages with similar assemblages in >4000 crystals of zircon from a wide range of rock types (granite to gabbro) and concluded that Jack Hills mineral inclusions are most similar to those in voluminous Archean TTG plutons.

A major consideration in all mineral inclusion studies of Jack Hills zircon is determining if they are primary inclusions that were incorporated as the zircon grew or are secondary inclusions that were either incorporated into the grain or altered by subsolidus processes after igneous crystallization. Few high-resolution images of inclusions exposed on polished surfaces have been published, and it is clear that although some appear to be primary, many are texturally associated with cracks, veins, and other features (e.g., Rasmussen et al., 2011, 2012). The importance of open cracks that may be recent is not clear, but some inclusions are also cut by healed cracks where zircon has recrystallized.

Furthermore, inclusions exposed on a polished surface, which are not associated with visible cracks, may be connected to cracks in the subsurface. An example that reveals such "hidden cracks" associated with a quartz + muscovite + monazite inclusion in a c.4200 Ma grain is featured in Fig. 12.10A and B, where "hidden cracks" are shown to be part of a vein network connected to the exterior of the zircon. In the same 4200 Ma zircon, muscovite grains that occur as apparently isolated inclusions (Fig. 12.10C) are texturally indistinguishable from muscovite grains that precipitated in cross-cutting veins that are clearly secondary (Fig. 12.10D). Despite their apparently "pristine" appearance on the initial polished surface (Fig. 12.10A, B and C), none of the mineral inclusions in this Hadean zircon can be considered as primary magmatic inclusions.

Recently, Cameron et al. (2016) analyzed $\delta^{18}O$ in quartz inclusions from Hadean zircon grains and showed that 40% of the inclusions preserve pristine high-temperature isotopic compositions but that the rest appear to be altered. Given the inherent uncertainty of their origin and the paucity of accompanying images at sufficient resolution to evaluate textural relations (e.g., Fig. 12.10), data from mineral inclusions in Jack Hills zircon grains should be judged individually, and overall remain controversial.

Studies of the Si content of muscovite inclusions by Hopkins et al. (2008, 2010) show a high phengite component and were used to argue for magmatic growth of muscovite at relatively high pressures, and hence the host zircon, in thermal conditions consistent with generation of the inferred peraluminous host granitoids in a subduction environment. This interpretation was questioned by Valley et al. (2010) who show that secondary fluorescence can erroneously elevate [Si] by EMPA for inclusions in Jack Hills zircon grains that are typically less than 5 μm in short dimension (e.g., Fig. 12.10C) and sometimes are adjacent to quartz (e.g., Fig. 12.10B). A later study of phosphate inclusions associated with muscovite in a suite of Jack Hills zircon questioned the veracity of interpreting muscovite as a primary mineral inclusion. Inclusions of

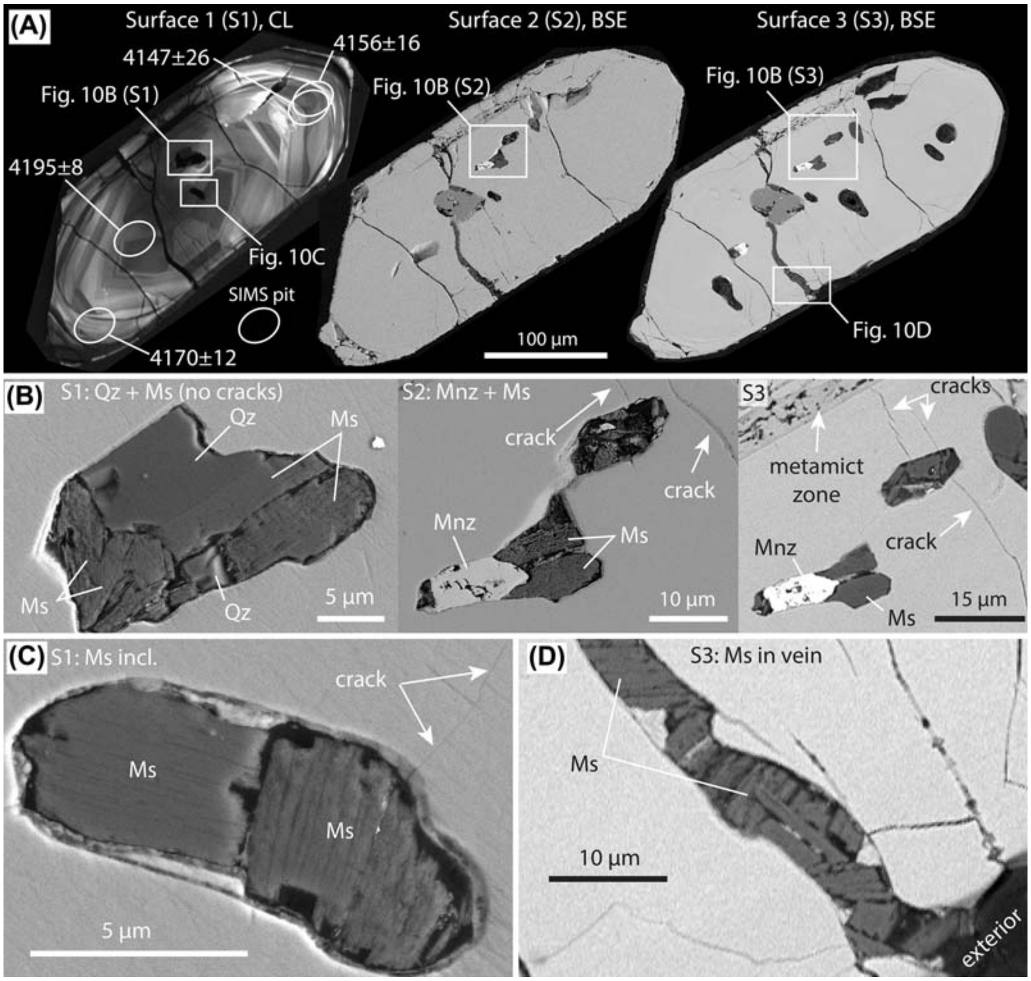

FIGURE 12.10 Mineral inclusions with "hidden cracks" in a c.4200 Ma detrital zircon from Jack Hills (Cavosie et al., 2004, grain 01JH54-66). (A) Images of three polished surfaces of the same grain (S1, S2, and S3). The cathodoluminescence (CL) images (S1) show igneous growth zoning and location of secondary ion mass spectrometry (SIMS) age analyses. Two muscovite-bearing inclusions were exposed on S1 (shown in panels B and C), including one that contained the assemblage muscovite + quartz. Subsequent surfaces (BSE images of S2, S3) reveal both the presence of monazite and hidden cracks that are not visible on S1. (B) BSE images showing the same Qz + Ms + Mnz inclusion on three polished surfaces (S1, S2, and S3). Note the change in morphology of the inclusion and the appearance of monazite. Note also that no cracks are visible in the image of S1; however, hidden cracks are visible in images of S2 and S3. These cracks connect to a metamict zone (S3 image), which further connects to the exterior of the zircon. (C) BSE image of an apparently pristine muscovite inclusion exposed on S1 with one small crack. (D) BSE image of muscovite grains in a secondary vein exposed on S3. Note the textural similarity of muscovite in the vein with muscovite in the isolated inclusion (panel C). None of the inclusions in this grain are interpreted as primary magmatic inclusions. *BSE*, backscattered electron; *CL*, cathodoluminescence; *Mnz*, monazite; *Ms*, muscovite; *Qz*, quartz.

monazite and xenotime yielded in situ U−Pb ages (SIMS) that were younger than both the host zircon crystallization age and the age of deposition, even though no textural evidence (cracks, veins) to support a secondary origin was visible (Rasmussen et al., 2010; see also Rasmussen et al., 2011, 2012; Hopkins et al., 2012; Bell et al., 2015a). The U−Pb geochronology of phosphate inclusions demonstrate convincingly that the REE-bearing accessory phases that have been cited as evidence for peraluminous host rocks do not preserve primary compositions.

More surprising were reports of diamond and graphite inclusions in Hadean zircon. Menneken et al. (2007) analyzed 1000 Jack Hills grains by laser Raman spectroscopy and reported the presence of diamond inclusions in 45 grains. A follow-up SIMS study by the same authors reported light and highly variable carbon isotope ($\delta^{13}C = -5$ to $-55‰$) values for diamond and graphite in 18 of the grains; these data were cited to infer new insights into lithospheric dynamics on the early Earth, as well as the existence of isotopically light carbon reservoirs (Nemchin et al., 2008). However, a subsequent TEM study on the same grains later revealed that the diamond inclusions were not indigenous to the zircon grains and instead resulted from contamination during sample preparation (Dobrzhinetskaya et al., 2014). The presence of graphite inclusions with light $\delta^{13}C$ values in a Hadean zircon was reported in a later study by Bell et al. (2015b). In this case, the authors attempted to demonstrate a primary origin for the graphite inclusions through use of TEM sectioning. Low $\delta^{13}C$ values measured by SIMS were interpreted as potentially recording biologic activity on the early Earth (Bell et al., 2015b). However, the significance of $\delta^{13}C$ values in graphite inclusions within accessory minerals from igneous or high-grade metamorphic rocks has long been questioned (e.g., Fedo and Whitehouse, 2002; Peck and Tumpane, 2007). The significance of the $\delta^{13}C$ values from graphite inclusions in Hadean zircon from Jack Hills will likely remain a controversial subject. Recently, CO_2 inclusions have been identified by confocal micro−Raman spectroscopy in zircon grains with an age range from 3.36 to 4.13 Ga, some of which are accompanied by graphitic carbon (Menneken et al., 2017). Utilizing CO_2 inclusion density data and Ti-in-zircon thermometry, the conditions of formation are consistent with high-grade, midcrustal regional metamorphism. The authors interpret the graphitic carbon to have been precipitated from a CO_2-rich fluid, casting further doubt on the biogenic origin of the carbon in Jack Hills zircon (Menneken et al., 2017).

4. EARLY EARTH PROCESSES RECORDED BY JACK HILLS ZIRCON

4.1 Derivation of Jack Hills Zircon From Early Mafic Crust (εHf)

The origin, age, and composition of the earliest crust remains a focus of debate (see discussion in Harrison, 2009). Analysis of Lu−Hf isotopes in Hadean zircon provides unique insight into the composition of the early crust. Nearly all Hadean detrital zircon from Jack Hills have negative εHf values, as low as $\sim \varepsilon Hf = -10$, which record parental magmas originating from preexisting crust, rather than a depleted mantle reservoir (Harrison et al., 2008; Kemp et al., 2010). Data arrays in εHf versus $^{207}Pb/^{206}Pb$ diagrams record derivation of the parental magmas to Hadean zircon as early as 4400−4500 Ma, predominantly from a chondritic or mafic crustal reservoir characterized by a $^{176}Lu/^{177}Hf$ value of ~ 0.02 (Harrison et al., 2008; Kemp et al., 2010). Generation of Jack Hills zircon in this environment has been envisioned as resulting from progressive partial melting of thickened mafic Hadean crust, possibly resulting from consolidation of a magma ocean, generating reservoirs of intermediate composition granitoid at a range of scales (Kemp et al., 2010). Although the early mafic crust would most likely have been primitive in composition, overlying volcanic rocks would have been susceptible to alteration and when magmatically recycled could crystallize Hadean zircon with the diverse (nonprimitive) isotopic compositions of Hf, O, and other elements.

4.2 Existence of >4300 Ma Granitoid

Jack Hills zircon grains with concordant U−Pb ages up to 4400 Ma record the former existence of terranes comprised at least partially of zircon-bearing igneous rocks. The size of the terranes and volume of individual plutons or flows cannot be constrained by data from Jack Hills zircon, as it is not known if they originated from cm-scale melt segregations (e.g., Kemp et al., 2010) or km-scale plutons (e.g., Harrison, 2009). The near-continuous spectra of U−Pb ages from oscillatory zoned grains indicate protracted magmatism throughout the Hadean. Debate over the composition of Hadean zircon host rocks for grains from Jack Hills has existed since their discovery, with various lines of evidence cited to infer mafic (Compston and Pidgeon, 1986), intermediate granitoid (Köber et al., 1989), or peraluminous granite (e.g., Mojzsis et al., 2001; Hopkins et al., 2008) as the parent. However, the $\delta^{18}O$ and mineral inclusion data on which some of these interpretations were made have since been questioned (e.g., Valley et al., 2006; Rasmussen et al., 2011), and thus the use of mineral inclusion data in constraining host rock composition remains controversial. Other geochemical indicators discussed here (U/Pb, εHf, $\delta^{18}O$, Ti) provide a wealth of information on petrogenesis of Hadean zircon but do not provide precise constraints on the host rock composition for an individual detrital grain. The Lu−Hf data of Wang (2015), obtained from >1000 analyses of <5% discordant zircon, require a range of rock types to produce the Jack Hills detrital zircon population and are most consistent with generation of the earliest crust from a depleted mantle, followed by subsequent multiple reworking into the Neoarchean (Wang and Wilde, 2018). The recent trace element studies of Al (if igneous) and Y + REE:P from large grain populations present what may be the strongest lines of evidence thus far published that argue for the dominance of metaluminous granitoid as the host rock to most Hadean grains (e.g., Burnham and Berry, 2017; Trail et al., 2017).

An outstanding question is whether intact Hadean rocks were present on the Earth's surface during deposition of the Jack Hills sedimentary rocks in the Archean, as no rock fragments of Hadean granitoid have thus far been described in the Jack Hills metaconglomerate. It therefore remains an open question as to whether or not remnants of the original c.4300 Ma granitoids (or other rocks) survived until deposition of Jack Hills metasedimentary rocks at c.3000 Ma or whether the Hadean detrital grains had previously been eroded from their source rocks and were recycled at this time. Many Hadean grains from Jack Hills contain younger rims interpreted as magmatic overgrowths, which yield ages younger than Hadean, from c.3360 to 3690 Ma (e.g., Cavosie et al., 2004; Valley et al., 2014a). Some rim ages match ages of Archean granitoids in the Narryer Terrane, which suggests that c.4300 Ma crustal materials were magmatically recycled into younger Archean magmas.

4.3 Significance of Surface Alteration on the Early Earth

Magmatic oxygen isotope ratios preserved in Hadean zircon from Jack Hills have been interpreted as a record of the cooling of Earth's surface, as global condensation of surface water (oceans) is required to pervasively alter rocks by aqueous processes at low temperature. Thermal constraints show that cooling of Earth's surface could have happened in less than 5 myr (Sleep et al., 2001; Elkins-Tanton, 2008), but the importance of greenhouse gases is not known. The zircon record indicates mildly elevated $\delta^{18}O$ values (6.3–7.5‰) relative to mantle-equilibrated zircon as far back as 4300 Ma and that by 4200 Ma many igneous grains had crystallized in magmas sourced by recycling of altered rock (Peck et al., 2001; Cavosie et al., 2005a; Trail et al., 2007a; Bell and Harrison, 2013; Valley et al., 2015). The cooling of Earth's surface, the stabilization and availability of surface water, and its influence on melting and magma generation all represent fundamental changes in the early Earth (Valley et al., 2002). The global scale of this transition has also been proposed as a boundary condition that could be used to define the end of the Hadean and the beginning of the Archean (Cavosie et al., 2005b). Documenting the presence and timing of surface water is likewise important for constraining when surface conditions became habitable (Valley et al., 2002; Valley, 2008; Cavosie, 2014).

4.4 Impact Events Recorded in Jack Hills Zircon?

Given the presence of zircon as old as 4400 Ma in the Jack Hills (e.g., Valley et al., 2014a, Figs. 12.7 and 12.8) and the discovery of shock deformation in >4000 Ma grains from the Moon (e.g., Timms et al., 2012), it is sensible to consider if shocked zircons, resulting from impacts during the early terrestrial meteorite bombardment (Marchi et al., 2014), are present in the Jack Hills suite. Zircon is one of the best records of shock deformation from meteorite impact (Timms et al., 2017), as diagnostic microstructural evidence of shock, such as {112} deformation twins (Moser et al., 2011; Cavosie et al., 2015a), reidite (Cavosie et al., 2015b; Erickson et al., 2017), and granular zircon (Cavosie et al., 2016), has been found in diverse geological environments and materials. Studies at the largest and oldest impact structures on Earth have demonstrated that shocked zircon in bedrock survives the processes of post-impact thermal conditions and erosion (Cavosie et al., 2010; Erickson et al., 2013a,b; Thomson et al., 2014), including sedimentary transport as detrital grains to locations that are thousands of km distal from the source crater (Montalvo et al., 2017).

Investigations to search for evidence of impact processes in Jack Hills zircon have focused on both chemical effects and microstructural indicators of shock. Approaches that involve searching for chemical evidence of impact include U–Pb age, $\delta^{18}O$, and Ti abundance. Depth profiling studies of Hadean Jack Hills grains for U–Pb age have found evidence for discrete, μm-scale overgrowths with ages from 3969 to 2684 Ma, which were interpreted as recording thermal events, potentially related to impact-generated heating (Trail et al., 2007b; Abbott et al., 2012). While overgrowths attest to thermal events that caused zircon growth and/or modification, it is not possible to quantitatively distinguish these features from growth events caused by endogenic magmatism; thus their connection to impact processes is speculative. Variability in $\delta^{18}O$ values in Hadean zircon from 4000 to 3800 Ma has also been cited as evidence for a transition that may relate to impact processes (Bell and Harrison, 2013), although no relation of $\delta^{18}O$ and shock textures is seen for > 4000 Ma zircon grains from the Moon (Valley et al., 2014b). Such excursions in zircon $\delta^{18}O$, if magmatic, could also result from incorporation of variable volumes of altered crust into endogenic magmas and thus are not diagnostic of impact processes.

The Ti abundance in Hadean zircon has been compared with neoblastic zircon crystallized in terrestrial impact melt (Darling et al., 2009; Wielicki et al., 2012). As noted earlier, Ti abundance and the calculated temperature of crystallization for Jack Hills zircon of $680 \pm 25°C$ are uniformly lower when compared with zircon from impact melt (Darling et al., 2009; Wielicki et al., 2012). One exception where overlapping Ti values were discovered is zircon from Sudbury granophyre, a minor component of the Sudbury Igneous Complex (Kenny et al., 2016). However, an origin of Jack Hills zircon from a comparable impact environment would require selective preservation of the volumetrically smallest component of early impact melt sheets and the preferential destruction of all shocked and unshocked higher Ti grains, which seems unlikely.

Approaches that involve searching for microstructural evidence of impact processes in the Jack Hills have primarily focused on using optical imaging and SEM to search for diagnostic evidence of shock deformation; results have thus far only been reported in three conference abstracts. A study of 1400 undated zircon grains (presumably 4400–3000 Ma) from the W74 site (sample 01JH13) by Montalvo et al. (2014) used backscattered electron (BSE) to image exterior surfaces of grains to search for planar microstructures indicative of shock. No grains with planar microstructures were reported in that

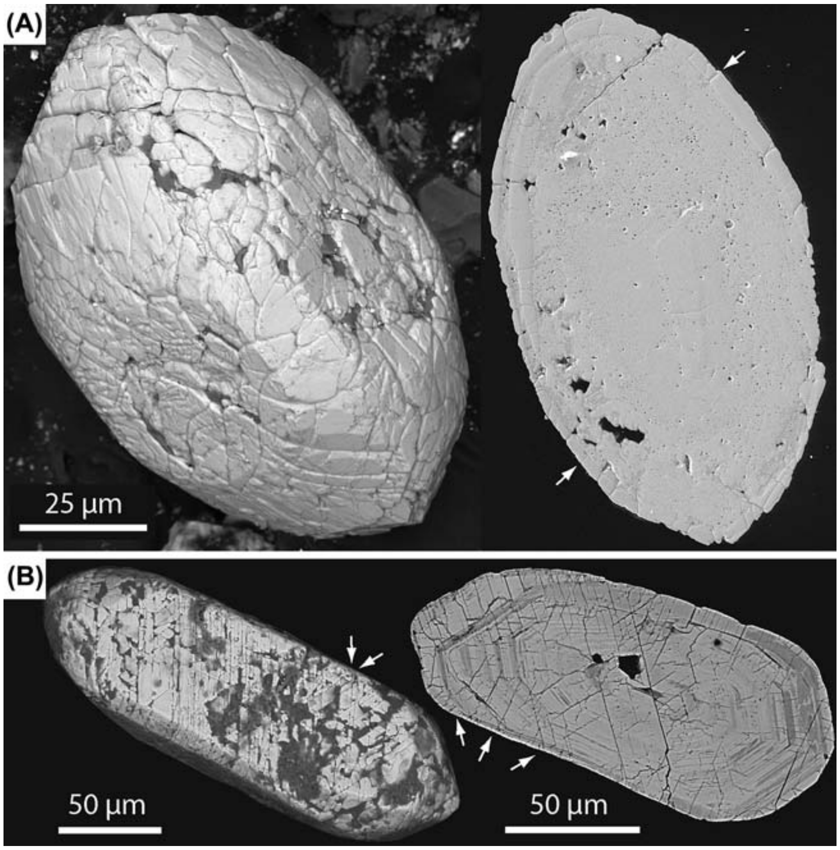

FIGURE 12.11 Images of zircon grains with subplanar and planar microstructures. (A) Backscattered electron (BSE) image of a Jack Hills detrital zircon grain from the W74 site (sample 01JH13). An extensive network of subplanar fractures is visible on the exterior surface, which looks superficially similar to features found in shocked zircon grains. However, on the polished surface, the fractures are shown to be limited to the near surface of the grain (*arrows*) and are interpreted to result from differential lattice expansion of metamict domains. The interior is porous and vuggy, consistent with metamict zircon; these features are not caused by shock deformation (after Cox et al., 2017). (B) BSE image of detrital shocked zircon grains from modern alluvium in the Vaal River, South Africa. Microstructural and isotopic data were used to show that these grains originated from the Vredefort Dome impact structure (Erickson et al., 2013b). Detrital shocked zircon grains typically exhibit multiple orientations of pervasive planar fractures that are visible on exterior surfaces (left, *arrows*) and also in polished section (right, *arrows*).

study, from which the authors inferred that the abundance of detrital shocked zircon, if present, would be <0.07% (1/1400) or <0.7% (1/140) for Hadean grains, assumed to comprise ~10% of the population. A second study of 14,000 undated Jack Hills detrital zircon grains reported the presence of "shock features" in some grains based on optical and electron imaging methods, including planar and subplanar microstructures, as well as partial to completely granular grains (Yamamoto et al., 2016). However, these results have yet to be substantiated, as microstructures similar to those found in shocked zircon can form as a result of other processes. Planar microstructures in zircon are only diagnostic of shock if the presence of {112} deformation twin lamellae are documented (e.g., Erickson et al., 2013a), as subplanar fractures in zircon can result from nonimpact processes (e.g., Schaltegger et al., 2015). Granular zircon with neoblast orientations that record the former presence of the high-pressure phase reidite have been documented to occur in impact melts (e.g., Cavosie et al., 2016; Timms et al., 2017) and ejecta (e.g., Cavosie et al., 2018). However, similar appearing granular grains have also been shown to occur in non-impact environments (Cavosie et al., 2015a; Montalvo et al., 2018) and thus, in the absence of critical orientation data, granular zircon is not diagnostic of shock deformation in detrital grains that have no petrographic context in the absence of other supporting evidence of shock-related processes. A third BSE external imaging study of 21,000 undated zircon grains from the W74 site (again from sample 01JH13) also did not yield any grains with planar microstructures (Cox et al., 2017); these results were combined with those of Montalvo et al. (2014) to further refine the maximum abundance of shocked zircon at the W74 site to <0.005% (1/22,400) or <0.05% (1/2240) for the Hadean population. The study by Cox et al. (2017) did, however, document images of subparallel planar fractures on the surfaces of a few Jack Hills zircon grains (Fig. 12.11A); the critical observation is that these features were not observed on polished surfaces (Fig. 12.11A) and were instead interpreted to result from differential lattice expansion caused by metamict domains.

This contrasts with the majority of detrital shocked zircon grains described from sites such as the Vredefort Dome, which show sets of planar microstructures that are readily visible as penetrative features on grain surfaces and also in polished sections (Fig. 12.11B). The three studies described earlier surveyed >36,000 detrital zircon grains, and at present, no definitive evidence of shock metamorphism or impact processes has been confirmed in the Jack Hills population.

Finally, in a study of Hadean and Archean zircon grains extracted from quartz pebbles enclosed in conglomerate ~1 km west of the W74 site at Jack Hills, Tarduno et al. (2015) found evidence of a geomagnetic field as early as 4224 Ma, thus predating the Late Heavy Bombardment (Chapter 2) on Earth. This finding was further interpreted as evidence for the presence of a core dynamo in the Hadean. However, subsequent studies reported evidence for pervasive remagnetization of the host rocks to the Jack Hills zircon population (Weiss et al., 2015), and also evidence that magnetic fields measured in individual zircon grains may originate from secondary ferromagnetic mineral inclusions (Weiss et al., 2018). Establishing unequivocal evidence for a Hadean geodynamo thus remains an ongoing debate.

ACKNOWLEDGMENTS

The authors thank many people who have contributed to our studies of Jack Hills zircon over the years: Anne-Sophie Bouvier, Emma Cameron, Morgan Cox, John Craven, Liu Dunyi, John Fournelle, Brian Hess, Noriko Kita, Pedro Montalvo, Dayanidi Ortiz, William Peck, Chris Spencer, Mike Spicuzza, Takayuki Ushikubo, Mary and Matcham Walsh, and Qian Wang. Work cited in the text by the authors was supported by grants from the ARC, DOE, the NASA Astrobiology Institute (NNAI3AA94A), and the US National Science Foundation (EAR1524336).

REFERENCES

Abbott, S.S., Harrison, T.M., Schmitt, A.K., Mojzsis, S.J., 2012. A search for thermal excursions from ancient extraterrestrial impacts using Hadean zircon Ti-U-Th-Pb depth profiles. Proceedings of the National Academy of Sciences 109 (34), 13486–13492.

Amelin, Y.V., 1998. Geochronology of the Jack Hills detrital zircons by precise U–Pb isotope dilution analysis of crystal fragments. Chemical Geology 146, 25–38.

Amelin, Y., Lee, D.-C., Halliday, A.N., Pidgeon, R.T., 1999. Nature of the Earth's earliest crust from hafnium isotopes in single detrital zircons. Nature 399, 252–255.

Arndt, N.T., 2013. Formation and evolution of the continental crust. Geochem Perspectives 2, 405–533.

Baxter, J.L., Wilde, S.A., Pidgeon, R.T., Fletcher, I.R., 1984. The Jack Hills metasedimentary belt: an extension of the early Archaean Terrain in the Yilgarn block, Western Australia. In: Seventh Australian geological Convention - Geoscience in the Development of Natural Resources, 12. Geological Society of Australia, pp. 56–57. Abstracts.

Bell, E.A., Harrison, T.M., McCulloch, M.T., Young, E.D., 2011. Early Archean crustal evolution of the Narryer gneiss complex inferred from Lu-Hf systematics of Jack Hills zircons. Geochimica et Cosmochimica Acta 75, 4816–4829.

Bell, E.A., Harrison, T.M., 2013. Post-hadean transitions in Jack Hills zircon provenance: a signal of the late heavy bombardment? Earth and Planetary Science Letters 364, 1–11.

Bell, E.A., Harrison, T.M., Kohl, I.E., Young, E.D., 2014. Eoarchean crustal evolution of the Jack Hills zircon source and loss of Hadean crust. Geochimica et Cosmochimica Acta 146, 27–42.

Bell, E.A., Boehnke, P., Hopkins-Wielicki, M.D., Harrison, T.M., 2015a. Distinguishing primary and secondary inclusion assemblages in Jack Hills zircons. Lithos 234–235, 15–26.

Bell, E.A., Boehnke, P., Harrison, T.M., Mao, W.L., 2015b. Potentially biogenic carbon preserved in a 4.1 Ga zircon. Proceedings of the National Academy of Sciences 112, 14518–14521.

Bell, E.A., Boehnke, P., Harrison, T.M., 2016. Recovering the primary geochemistry of Jack Hills zircons through quantitative estimates of chemical alteration. Geochimica et Cosmochimica Acta 191, 187–202.

Bindeman, I., Schmidt, A., Lundstrom, C., Hervig, R., 2018. Stability of zircon and its isotopic ratios in high-temperature fluids: Long-term (4 months) isotope exchange experiment at 850 °C and 50 MPa. Frontiers in Earth Science 6.

Blichert-Toft, J., Albarède, F., 2008. Hafnium isotopes in Jack Hills zircons and the formation of the Hadean crust. Earth and Planetary Science Letters 265, 686–702.

Bouvier, A.-S., Ushikubo, T., Kita, N.T., Cavosie, A.J., Kozdon, R., Valley, J.W., 2012. Li isotopes and trace elements as a petrogenetic tracer in zircon: insights from Archean TTG's and sanukitoids. Contributions to Mineralogy and Petrology 163, 745–768.

Bowman, J.R., Moser, D.E., Valley, J.W., Wooden, J.L., Kita, N.T., Mazdab, F., 2011. Zircon U- Pb isotope, $\delta^{18}O$ and trace element response to 80 m.y. of high temperature formation. American Journal of Science 311, 719–772. https://doi.org/10.2475/04.2011.00.

Bowring, S.A., Williams, I.S., 1999. Priscoan (4.00–4.03 Ga) orthogneisses from northwestern Canada. Contributions to Mineralogy and Petrology 134, 3–16.

Burnham, A.D., Berry, A.J., 2017. Formation of Hadean granites by melting of igneous crust. Nature Geoscience 10, 457–462.

Cameron, E., Valley, J., Ortiz-Cordero, D., Kitajima, K., Cavosie, A., 2016. Detrital Jack Hills zircon-quartz $\delta^{18}O$ analysis tests alteration of zircon and zircon inclusions. In: Goldschmidt Conference, 349, Yokohama, Japan.

Caro, G., Bennett, V.C., Bourdon, B., Harrison, T.M., Mojzsis, S.J., Harris, J.W., 2008. Precise analysis of 142Nd/144Nd in small samples: application to Hadean zircons from Jack Hills (W. Australia) and diamond inclusions from Finsch (S. Africa). Chemical Geology 247, 253–265.

Cates, N.L., Mojzsis, S.J., 2007. Pre-3750 Ma supracrustal rocks from the Nuvvuagittuq supracrustal belt, northern Quebec. Earth and Planetary Science Letters 255, 9–21.

Cavosie, A.J., 2005. Geochemistry of >3900 Ma Detrital Zircons from Jack Hills [PhD Thesis]. University of Wisconsin-Madison, Western Australia, p. 389.

Cavosie, A.J., 2014. Reconciling early impacts and the rise of life. Geology 42, 463–464.

Cavosie, A.J., Wilde, S.A., Liu, D., Weiblen, P.W., Valley, J.W., 2004. Internal zoning and U–Th–Pb chemistry of Jack Hills detrital zircons: a mineral record of early Archean to Mesoproterozoic (4348–1576 Ma) magmatism. Precambrian Research 135, 251–279.

Cavosie, A.J., Valley, J.W., Wilde, S.A., EIMF, 2005a. Magmatic $\delta^{18}O$ in 4400–3900 Ma detrital zircons: a record of the alteration and recycling of crust in the Early Archean. Earth and Planetary Science Letters 235, 663–681.

Cavosie, A.J., Wilde, S.A., Valley, J.W., 2005b. A lower age limit for the Archean based on $\delta^{18}O$ of detrital zircons. Geochimica et Cosmochimica Acta 69, A391.

Cavosie, A.J., Valley, J.W., Wilde, S.A., EIMF, 2006. Correlated microanalysis of zircon: trace element, $\delta^{18}O$, and U–Th–Pb isotopic constraints on the igneous origin of complex >3900 Ma detrital grains. Geochimica et Cosmochimica Acta 70 (22), 5601–5616.

Cavosie, A.J., Valley, J.W., Wilde, S.A., 2007. The oldest terrestrial mineral record: a review of 4400 to 3900 Ma detrital zircons from Jack Hills, Western Australia. In: van Kranendonk, M.J., Smithies, R.H., Bennett, V.C. (Eds.), World's Oldest Rocks. Elsevier Science, Amsterdam, pp. 91–111.

Cavosie, A.J., Kita, N.T., Valley, J.W., 2009. Primitive oxygen-isotope ratio recorded in magmatic zircon from the Mid-Atlantic Ridge. American Mineralogist 94, 926–934.

Cavosie, A.J., Quintero, R.R., Radovan, H.A., Moser, D.E., 2010. A record of ancient cataclysm in modern sand: shock microstructures in detrital minerals from the Vaal River, Vredefort Dome, South Africa. Geological Society of America Bulletin 122, 1968–1980.

Cavosie, A.J., Valley, J.W., Kita, N.T., Spicuzza, M.J., Ushikubo, T., Wilde, S.A., 2011. The origin of high $\delta^{18}O$ zircons: marbles, megacrysts and metamorphism. Contributions to Mineralogy and Petrology 162, 961–974.

Cavosie, A.C., Erickson, T.M., Timms, N.E., Reddy, S.M., Talavera, C., Montalvo, S.D., Pincus, M.R., Gibbon, R.J., Moser, D., 2015a. A terrestrial perspective on using ex situ shocked zircons to date lunar impact. Geology 43, 999–1002.

Cavosie, A.J., Erickson, T.M., Timms, N.E., 2015b. Nanoscale record of ancient shock deformation: reidite ($ZrSiO_4$) in sandstone at the Ordovician Rock Elm impact crater. Geology 43, 315–318.

Cavosie, A.J., Timms, N.E., Erickson, T.M., Koeberl, C., 2018. New clues from Earth's most elusive impact crater: Evidence of reidite in Australasian tektites from Thailand. Geology 46, 203–206.

Cavosie, A.J., Timms, N.E., Erickson, T.M., Hagerty, J.J., Hörz, F., 2016. Transformations to granular zircon revealed: twinning, reidite, and ZrO_2 in shocked zircon from Meteor Crater (Arizona, USA). Geology 44 (9), 703–706.

Cherniak, D.J., Watson, E.B., 2010. Li diffusion in zircon. Contributions to Mineralogy and Petrology 160, 383–390.

Cohen, K.M., Finney, S.C., Gibbard, P.L., Fan, J.-X., 2013. The ICS International Chronostratigraphic Chart. Episodes 36, 199–204.

Compston, W., Pidgeon, R.T., 1986. Jack Hills, evidence of more very old detrital zircons in Western Australia. Nature 321, 766–769.

Cox, M.A., Cavosie, A.J., Reddy, S.M., Bland, P.A., Valley, J.W., 2017. The hunt for shocked zircon in the Jack Hills: 21,000 and counting…. In: Lunar and Planetary Science Conference, Abstr. 1402.

Crowley, J.L., Myers, J.S., Sylvester, P.J., Cox, R.A., 2005. Detrital zircon from the Jack Hills and Mount Narryer, Western Australia: evidence for diverse >4.0 Ga source rocks. Journal of Geology 113, 239–263.

Darling, J., Storey, C., Hawkesworth, C., 2009. Impact melt sheet zircons and their implications for the Hadean crust. Geology 37, 927–930.

Dobrzhinetskaya, L., Wirth, R., Green, H., 2014. Diamonds in Earth's oldest zircons from Jack Hill conglomerate, Australia, are contamination. Earth and Planetary Science Letters 387, 212–218.

Dunn, S.J., Nemchin, A.A., Cawood, P.A., Pidgeon, R.T., 2005. Provenance record of the Jack Hills metasedimentary belt: source of the Earth's oldest zircons. Precambrian Research 138, 235–254.

Elias, M., 1982. Explanatory Notes of the Belele Geological Sheet. Geological Survey of Western Australia, Perth, WA, pp. 1–22.

Elkins-Tanton, L.T., 2008. Linked magma ocean solidification and atmospheric growth for Earth and Mars. Earth and Planetary Science Letters 271 (1), 181–191.

Erickson, T.M., Cavosie, A.J., Moser, D.E., Barker, I.R., Radovan, H.A., 2013a. Correlating planar microstructures in shocked zircon from the Vredefort Dome at multiple scales: crystallographic modeling, external and internal imaging, and EBSD structural analysis. American Mineralogist 98, 53–65.

Erickson, T.M., Cavosie, A.J., Moser, D.E., Barker, I.R., Radovan, H.A., Wooden, J., 2013b. Identification and provenance determination of distally transported, Vredefort-derived shocked minerals in the Vaal River, South Africa using SEM and SHRIMP-RG techniques. Geochimica et Cosmochimica Acta 107, 170–188.

Erickson, T.M., Pearce, M.A., Reddy, S.M., Timms, N.E., Cavosie, A.J., Bourdet, J., Rickard, W.D.A., Nemchin, A.A., 2017. Microstructural constraints on the mechanisms of the transformation to reidite in naturally shocked zircon. Contributions to Mineralogy and Petrology 172, 6.

Ewing, R.C., Meldrum, A., Wang, L., Weber, W.J., Corrales, L.R., 2003. Radiation effects in zircon. Reviews in Mineralogy and Geochemistry 53, 387–425.

Fedo, C.M., Whitehouse, M.J., 2002. Metasomatic origin of quartz-pyroxene rock, Akilia, Greenland, and implications for Earth's earliest life. Science 296, 1448–1452.

Froude, D.O., Ireland, T.R., Kinny, P.D., Williams, I.S., Compston, W., Williams, I.R., Myers, J.S., 1983. Ion microprobe identification of 4100−4200 Myr-old terrestrial zircons. Nature 304, 616−618.

Fu, B., Page, F.Z., Cavosie, A.J., Fournelle, J., Kita, N.T., Lackey, J.S., Wilde, S.A., Valley, J.W., 2008. Ti-in-zircon thermometry: applications and limitations. Contributions to Mineralogy and Petrology 156, 197−215.

Grange, M.L., Wilde, S.A., Nemchin, A.A., Pidgeon, R.T., 2010. Proterozoic events recorded in quartzite cobbles at Jack Hills, Western Australia: new constraints on sedimentation and source of >4 Ga zircons. Earth and Planetary Science Letters 292, 158−169.

Grimes, C.B., Ushikubo, T., John, B.E., Valley, J.W., 2011. Uniformly mantle-like $\delta^{18}O$ in zircons from oceanic plagiogranites and gabbros. Contributions to Mineralogy and Petrology 161, 13−33. https://doi.org/10.1007/s00410-010-0519-x.

Guitreau, M., Blichert-Toft, J., 2014. Implications of discordant U-Pb ages on Hf isotope studies of detrital zircons. Chemical Geology 385, 17−25.

Hanchar, J.M., Finch, R.J., Hoskin, P.W., Watson, E.B., Cherniak, D.J., Mariano, A.N., 2001. Rare earth elements in synthetic zircon: part 1. Synthesis, and rare earth element and phosphorus doping. American Mineralogist 86 (5−6), 667−680.

Harrison, T.M., Blichert-Toft, J., Müller, W., Albarède, F., Holden, P., Mojzsis, S.J., 2006. Response to comment on "Heterogeneous Hadean hafnium: evidence of continental crust at 4.4 to 4.5 Ga". Science 312 (5777), 1139b.

Harrison, T.M., 2009. The Hadean crust: evidence from >4 Ga zircons. Annual reviews of earth and planetary. Science 37, 479−505.

Harrison, T.M., Project MtREE, 2007. The Hadean earth. In: Lunar and Planetary Science Conference, Abstract. 2033.

Harrison, T.M., Schmitt, A.K., 2007. High sensitivity mapping of Ti distributions in Hadean zircons. Earth and Planetary Science Letters 261, 9−19.

Harrison, T.M., Mojzsis, S.J., the MtREE TEAM, 2003. Initial results from the mission to really early Earth. In: European Geophysical Union Conference, Abstract 08060.

Harrison, T.M., Blichert-Toft, J., Muller, W., Albarede, F., Holden, P., Mojzsis, S.J., 2005. Heterogeneous Hadean hafnium: evidence of continental crust at 4.4 to 4.5 Ga. Science 310, 1947−1950.

Harrison, T.M., Schmitt, A.K., McCulloch, M.T., Lovera, O.M., 2008. Early (≥4.5 Ga) formation of terrestrial crust: Lu-Hf, $\delta^{18}O$, and Ti thermometry results for Hadean zircons. Earth and Planetary Science Letters 268, 476−486.

Harrison, T.M., Bell, E.A., Boehnke, P., 2017. Hadean zircon petrochronology. Reviews in Mineralogy and Geochemistry 83 (1), 329−363.

Hofmann, A.E., Valley, J.W., Watson, E.B., Cavosie, A.J., Eiler, J.M., 2009. Sub-micron scale distributions of trace elements in zircon. Contributions to Mineralogy and Petrology 158, 317−335.

Holden, P., Ireland, T.R., Bruce, Z., Harrison, T.M., 2006. Automated mining of detrital Hadean zircons from Jack Hills, Western Australia: flash geochronology with SHRIMP II. In: Goldschmidt Geochemistry Conference, Abstract. A259.

Holden, P., Lanc, P., Ireland, T.R., Harrison, T.M., Foster, J.J., Bruce, Z., 2009. Mass-spectrometric mining of Hadean zircons by automated SHRIMP multi-collector and single-collector U/Pb zircon age dating: the first 100,000 grains. International Journal of Mass Spectrometry 286, 53−63.

Hopkins, M., Harrison, T.M., Manning, C.E., 2008. Low heat flow inferred from >4 Gyr zircons suggests Hadean plate boundary interactions. Nature 456, 493−496.

Hopkins, M.D., Harrison, T.M., Manning, C.E., 2010. Constraints on Hadean geodynamics from mineral inclusions in >4 Ga zircons. Earth and Planetary Science Letters 298, 367−376.

Hopkins, M.D., Harrison, T.M., Manning, C.E., 2012. Metamorphic replacement of mineral inclusions in detrital zircon from Jack Hills, Australia: implications for the Hadean earth: comment. Geology 40, 281.

Hoskin, P.W.O., Schaltegger, U., 2003. The composition of zircon and igneous and metamorphic petrogenesis. In: Hanchar, J.M., Hoskin, P.W.O. (Eds.), Zircon. Reviews in Mineralogy and Geochemistry, 53, pp. 27−55.

Hoskin, P.W., 2005. Trace-element composition of hydrothermal zircon and the alteration of Hadean zircon from the Jack Hills, Australia. Geochimica et Cosmochimica Acta 69 (3), 637−648.

Isozaki, Y., Yamamoto, S., Sakata, S., Obayashi, H., Hirata, T., Obori, K., Maebayashi, T., Takeshima, S., Ebisuzaki, T., Maruyama, S., 2017. High-reliability zircon separation for hunting the oldest material on Earth: an automatic zircon separator with image-processing/microtweezers-manipulation system and double-step dating (in press). Geoscience Frontiers. https://doi.org/10.1016/j.gsf.2017.04.010.

Kemp, A.I.S., Wilde, S.A., Hawkesworth, C.J., Coath, C.D., Nemchin, A., Pidgeon, R.T., Vervoort, J.D., DuFrane, S.A., 2010. Hadean crustal evolution revisited: new constraints from Pb−Hf isotope systematics of the Jack Hills zircons. Earth and Planetary Science Letters 296, 45−56.

Kenny, G.G., Whitehouse, M.H., Kamber, B.S., 2016. Differentiated impact melt sheets may be a potential source of Hadean detrital zircon. Geology 44, 435−438.

Kinny, P.D., Nutman, A.P., 1996. Zirconology of the Meeberrie gneiss, Yilgarn craton, Western Australia: an early Archaean migmatite. Precambrian Research 78, 165−178.

Kinny, P.D., Williams, I.S., Froude, D.O., Ireland, T.R., Compston, W., 1988. Early Archaean zircon ages from orthogneisses and anorthosites at Mount Narryer, Western Australia. Precambrian Research 38, 325−341.

Kinny, P.D., 1990. Age spectrum of detrital zircons in the Windmill Hill quartzite. In: Ho, S.E., Glover, J.E., Myers, J.S., Muhling, J.R. (Eds.), Proceedings of the 3rd International Archaean Symposium, Perth, Excursion Guidebook. Geology Department and University Extension, University of Western Australia Publication no. 21, University of Western Australia, Western Australia, pp. 116−117.

Köber, B., Pidgeon, R.T., Lippolt, H.J., 1989. Single-zircon dating by stepwise Pb-evaporation constrains the Archean history of detrital zircons from the Jack Hills, Western Australia. Earth and Planetary Science Letters 91, 286−296.

Komiya, T., Yamamoto, S., Aoki, S., Sawaki, Y., Ishikawa, A., Tashiro, T., Koshida, K., Shimojo, M., Aoki, K., Collerson, K.D., 2015. Geology of the Eoarchean, >3.95 Ga, Nulliak supracrustal rocks in the Saglek Block, northern Labrador, Canada: The oldest geological evidence for plate tectonics. Tectonophysics 662, 40−66.

Maas, R., McCulloch, M.T., 1991. The Provenance of Archean clastic metasediments in the Narryer Gneiss Complex, Western Australia: trace element geochemistry, Nd isotopes, and U-Pb ages for detrital zircons. Geochimica et Cosmochimica Acta 55, 1915−1932.

Maas, R., Kinny, P.D., Williams, I.S., Froude, D.O., Compston, W., 1992. The Earth's oldest known crust: a geochronological and geochemical study of 3900−4200 Ma old detrital zircons from Mt. Narryer and Jack Hills, Western Australia. Geochimica et Cosmochimica Acta 56, 1281−1300.

Marchi, S., Bottke, W.F., Elkins-Tanton, L.T., Bierhaus, M., Wuennemann, K., Morbidelli, A., Kring, D.A., 2014. Widespread mixing and burial of Earth's Hadean crust by asteroid impacts. Nature 511, 578−582.

Menneken, M., Nemchin, A.A., Geisler, T., Pidgeon, R.T., Wilde, S.A., 2007. Hadean diamonds in zircon from Jack Hills, Western Australia. Nature 448, 917−920.

Menneken, M., Geisler, T., Nemchin, A.A., Whitehouse, M.J., Wilde, S.A., Gasharova, B., Pidgeon, R.T., 2017. CO_2 fluid inclusions in Jack Hills zircons. Contributions to Mineralogy and Petrology 172, 66. https://doi.org/10.1007/s00410-017-1382-9.

Mojzsis, S.J., Harrison, T.M., Pidgeon, R.T., 2001. Oxygen isotope evidence from ancient zircons for liquid water at the Earth's surface 4300 Myr ago. Nature 409, 178−181.

Montalvo, P.E., Cavosie, A.J., Valley, J.W., 2014. A constraint on shocked mineral abundance in the Jack Hills zircon suite. In: Lunar and Planetary Science Conference, Abstr. 2338.

Montalvo, P.E., Cavosie, A.J., Erickson, T.M., Kirkland, C.L., Evans, N., McDonald, B., Talavera, C., Lugo-Centeno, C., 2018. Detrital shocked zircon provides new constraints on the age and size of the Santa Fe impact structure, New Mexico (USA) (in revision). Geological Society of America Bulletin (in press).

Montalvo, S.D., Cavosie, A.J., Erickson, T., Talavera, C., 2017. Fluvial transport of impact evidence from cratonic interior to passive margin: Vredefort-derived shocked zircon on the Atlantic coast of South Africa. American Mineralogist 102, 813−823.

Moser, D.E., Cupelli, C.L., Barker, I.R., Flowers, R.M., Bowman, J.R., Wooden, J., Hart, J.R., 2011. New zircon shock phenomena and their use for dating and reconstruction of large impact structures revealed by electron nanobeam (EBSD, CL, EDS) and isotopic U-Pb and (U-Th)/He analysis of the Vredefort dome. Canadian Journal of Earth Sciences 48, 117−139.

Myers, J.S., 1988. Oldest known terrestrial anorthosite at Mount Narryer, Western Australia. Precambrian Research 38, 309−323.

Myers, J.S., Williams, I.R., 1985. Early precambrian crustal evolution at Mount Narryer, Western Australia. Precambrian Research 27, 153−163.

Nebel, O., Rapp, R.P., Yaxley, G.M., 2014. The role of detrital zircons in Hadean crustal research. Lithos 190−191, 313−327.

Nelson, D.R., 2000. Compilation of geochronology data, 1999. In: Geological Survey of Western Australia Record 2000/2, 62−65.

Nelson, D.R., 2002. Hadean Earth crust: microanalytical investigation of 4.4 to 4.0 Ga zircons from Western Australia. Geochimica et Cosmochimica Acta 66, A549.

Nelson, D.R., Robinson, B.W., Myers, J.S., 2000. Complex geological histories extending for ≥4.0 Ga deciphered from xenocryst zircon microstructures. Earth and Planetary Science Letters 181, 89−102.

Nelson, D.R., 2004. The early Earth, Earth's formation and first billion years. In: Eriksson, P.G., et al. (Eds.), The Precambrian Earth: Tempo and Events. Elsevier, Amsterdam, pp. 3−27.

Nemchin, A.A., Pidgeon, R.T., Whitehouse, M.J., 2006. Re-evaluation of the origin and evolution of >4.2 Ga zircons from the Jack Hills metasedimentary rocks. Earth and Planetary Science Letters 244, 218−233.

Nemchin, A.A., Whitehouse, M.J., Menneken, M., Geisler, Th., Pidgeon, R.T., Wilde, S., 2008. A light carbon reservoir recorded in zircon-hosted diamond from the Jack Hills. Nature 454, 92−95.

Nutman, A.P., Kinny, P.D., Compston, W., Williams, I.S., 1991. SHRIMP U−Pb zircon geochronology of the Narryer gneiss complex, Western Australia. Precambrian Research 52, 275−300.

Nutman, A.P., Friend, C.R.L., Bennett, V.C., 2001. Review of the oldest (4400-3600 Ma) geological and mineralogical record: Glimpses of the beginning. Episodes 24 (2), 93−101.

O'Neil, J., Rizo, H., Boyet, M., Carlson, R.W., Rosing, M.T., 2016. Geochemistry and Nd isotopic characteristics of Earth's Hadean mantle and primitive crust. Earth and Planetary Science Letters 442, 194−205.

Ortiz-Cordero, D.M., 2010. Mineral Inclusions in Zircons: A Tool for Provenance Analysis of Sedimentary Rocks [MS Thesis]. University of Wisconsin-Madison, p. 44.

Page, F.Z., Ushikubo, T., Kita, N.T., Riciputi, L.R., Valley, J.W., 2007. High precision oxygen isotope analysis of picogram samples reveals 2-μm gradients and slow diffusion in zircon. American Mineralogist 92, 1772−1775.

Palenik, C.S., Nasdala, L., Ewing, R.C., 2003. Radiation damage in zircon. American Mineralogist 88, 770−781.

Peck, W.H., Tumpane, K.P., 2007. Low carbon isotope ratios in apatite: an unreliable biomarker in igneous and metamorphic rocks. Chemical Geology 245, 305−314.

Peck, W.H., Valley, J.W., 2009. Archean environments. In: Gornitz, V. (Ed.), Encyclopedia of Paleoclimatology and Ancient Environments. Springer, Dordrecht, The Netherlands, pp. 34−38.

Peck, W.H., Valley, J.W., Wilde, S.A., Graham, C.M., 2001. Oxygen isotope ratios and rare earth elements in 3.3 to 4.4 Ga zircons: ion microprobe evidence for high $\delta^{18}O$ continental crust and oceans in the Early Archean. Geochimica et Cosmochimica Acta 65, 4215−4229.

Peck, W.H., Valley, J.W., Graham, C.M., 2003. Slow oxygen diffusion rates in igneous zircons from metamorphic rocks. American Mineralogist 88, 1003−1014.

Pidgeon, R.T., 1992. Recrystallisation of oscillatory zoned zircon: some geochronological and petrological implications. Contributions to Mineralogy and Petrology 110, 463−472.

Pidgeon, R.T., 2014. Zircon radiation damage ages. Chemical Geology 367, 13−22.

Pidgeon, R.T., Wilde, S.A., 1998. The interpretation of complex zircon U−Pb systems in Archaean granitoids and gneisses from the Jack Hills, Narryer gneiss terrane, Western Australia. Precambrian Research 91, 309−332.

Pidgeon, R.T., Nemchin, A.A., 2006. High abundance of early Archaean grains and the age distribution of detrital zircons in a sillimanite-bearing quartzite from Mt. Narryer, Western Australia. Precambrian Research 150, 201−220.

Pidgeon, R.T., Nemchin, A.A., Whitehouse, M.J., 2017. The effect of weathering on U−Th−Pb and oxygen isotope systems of ancient zircons from the Jack Hills, Western Australia. Geochimica et Cosmochimica Acta 197, 142−166.

Rasmussen, B., Fletcher, I.R., Muhling, J.R., Wilde, S.A., 2010. In situ U−Th−Pb geochronology of monazite and xenotime from the Jack Hills belt: implications for the age of deposition and metamorphism of Hadean zircons. Precambrian Research 180 (1), 26−46.

Rasmussen, B., Fletcher, I.R., Muhling, J.R., Gregory, C.J., Wilde, S.A., 2011. Metamorphic replacement of mineral inclusions in detrital zircon from Jack Hills, Australia: implications for the Hadean earth. Geology 39, 1143−1146.

Rasmussen, B., Fletcher, I.R., Muhling, J.R., Gregory, C.J., Wilde, S.A., 2012. Metamorphic replacement of mineral inclusions in detrital zircon from Jack Hills, Australia: implications for the Hadean earth: REPLY. Geology 40, e282−e283.

Reimink, J.R., et al., 2016. No evidence for Hadean continental crust within Earth's oldest evolved rock unit. Nature Geoscience 9 (10), 777−780.

Schaltegger, U., Ulianov, A., Muntener, O., Ovtcharova, M., Peytcheva, I., Vonlanthen, P., Vennemann, T., Antognini, M., Girlanda, F., 2015. Megacrystic zircon with planar fractures in miaskite-type nepheline pegmatites formed at high pressures in the lower crust (Ivrea Zone, southern Alps, Switzerland). American Mineralogist 100, 83−94.

Sleep, N.H., Zahnle, K., Neuhoff, P.S., 2001. Initiation of clement surface conditions on the earliest Earth. Proceedings of the National Academy of Sciences 98 (7), 3666−3672.

Spaggiari, C.V., 2007. Structural and lithological evolution of the Jack Hills Greenstone belt, Narryer terrane, Yilgarn craton, Western Australia. Geological Survey of Western Australia Record 49.

Spaggiari, C.V., Pidgeon, R.T., Wilde, S.A., 2007. The Jack Hills greenstone belt, Western Australia Part 2: lithological relationships and implications for the deposition of ≥4.0 Ga detrital zircons. Precambrian Research 155, 261−286.

Spaggiari, C.V., Wartho, J.A., Wilde, S.A., 2008. Proterozoic deformation in the Northwest of the Archean Yilgarn craton, Western Australia. Precambrian Research 162 (3), 354−384.

Spencer, C.J., Cavosie, A.J., Raub, T.D., Rollinson, H., Searle, M.P., Miller, J.A., Jeon, H., 2017. Evidence for melting mud in Earth's mantle from extreme oxygen isotope signatures in zircon. Geology 45 (11), 975−978.

Tarduno, J.A., Cottrell, R.D., Davis, W.J., Nimmo, F., Bono, R.K., 2015. A Hadean to Paleoarchean geodynamo recorded by single zircon crystals. Science 349, 521−524.

Thern, E.R., Nelson, D.R., 2012. Detrital zircon age structure within ca. 3 Ga metasedimentary rocks, Yilgarn Craton: elucidation of Hadean source terranes by principal component analysis. Precambrian Research 214−215, 28−43.

Thomson, O.A., Cavosie, A.J., Moser, D.E., Barker, I., Radovan, H.A., French, B.M., 2014. Preservation of detrital shocked minerals derived from the 1.85 Ga Sudbury impact structure in modern alluvium and Holocene glacial deposits. Geological Society of America Bulletin 126, 720−737.

Timms, N.E., Reddy, S.M., Healy, D., Nemchin, A.A., Grange, M.L., Pidgeon, R.T., Hart, R., 2012. Resolution of impact-related microstructures in lunar zircon: a shock-deformation mechanism map. Meteoritics and Planetary Science 47, 120−141.

Timms, N.E., Erickson, T.M., Pearce, M.A., Cavosie, A.J., Schmieder, M., Tohver, E., Reddy, S.M., Zanetti, M., Nemchin, A., Wittmann, A., 2017. A pressure-temperature phase diagram for zircon at extreme conditions. Earth-Science Reviews 165, 185−202.

Trail, D., Mojzsis, S.J., Harrison, T.M., Schmitt, A.K., Watson, E.B., Young, E.D., 2007a. Constraints on Hadean zircon protoliths from oxygen isotopes, REEs and Ti-thermometry. Geochemistry, Geophysics, Geosystems (G3) 8, Q06014. https://doi.org/10.1029/2006GC001449.

Trail, D., Mojzsis, S.J., Harrison, T.M., 2007b. Thermal events documented in Hadean zircons by ion microprobe depth profiles. Geochimica et Cosmochimica Acta 71, 4044−4065.

Trail, D., Watson, E.B., Tailby, N.D., 2011. The oxidation state of Hadean magmas and implications for early Earth's atmosphere. Nature 480, 79−82.

Trail, D., Watson, E.B., Tailby, N.D., 2013. Insights into the Hadean Earth from experimental studies of zircon. Journal of the Geological Society of India 81, 605−636.

Trail, D., Cherniak, D.J., Watson, E.B., Harrison, T.M., Weiss, B.P., Szumila, I., 2016. Li zoning in zircon as a potential geospeedometer and peak temperature indicator. Contributions to Mineralogy and Petrology 171:25.

Trail, D., Tailby, N., Wang, Y., Harrison, T.M., Boehnke, P., 2017. Aluminum in zircon as evidence for peraluminous and metaluminous melts from Hadean to present. Geochemistry Geophysics Geosystems 18, 1580−1593.

Turner, G., Harrison, T.M., Holland, G., Mojzsis, S.J., Gilmour, J., 2004. Extinct ^{244}Pu in ancient zircons. Science 306, 89−91.

Turner, G., Busfield, A., Crowther, S., Mojzsis, S.J., Harrison, T.M., Gilmour, J., 2007. Pu-Xe, U-Xe, U-Pb chronology and isotope systematics of ancient zircons from Western Australia. Earth and Planetary Science Letters 261, 491−499.

Ushikubo, T., Kita, N.T., Cavosie, A.J., Wilde, S.A., Rudnick, R.L., Valley, J.W., 2008. Lithium in Jack Hills zircons: evidence for extensive weathering of Earth's earliest crust. Earth and Planetary Science Letters 272, 666−676. https://doi.org/10.1016/j.epsl.2008.05.032.

Utsunomiya, S., Palenik, C.S., Valley, J.W., Cavosie, A.J., Wilde, S.A., Ewing, R.C., 2004. Nanoscale occurrence of Pb in an Archean zircon. Geochimica et Cosmochimica Acta 68, 4679−4686.

Utsunomiya, S., Valley, J.W., Cavosie, A.J., Wilde, S.A., Ewing, R.C., 2007. Radiation damage and alteration of zircon from a 3.3 Ga porphyritic granite from the Jack Hills, Western Australia. Chemical Geology 236, 92−111.

Valley, J.W., 2003. Oxygen isotopes in zircon. In: Hanchar, J.M., Hoskin, P.W.O. (Eds.), Zircon. Reviews in Mineralogy and Geochemistry, 53, pp. 343−386.

Valley, J.W., October 2005. A Cool Early Earth? Scientific American, pp. 58−65.
Valley, J.W., 2006. Early Earth. Elements 2, 201−204.
Valley, J.W., 2008. The origin of habitats. Geology 36, 911−912.
Valley, J.W., Kita, N.T., 2009. In situ Oxygen Isotope Geochemistry by Ion Microprobe. In: Fayek, M. (Ed.), MAC Short Course: Secondary Ion Mass Spectrometry in the Earth Sciences, 41, pp. 19−63.
Valley, J.W., Chiarenzelli, J.R., McLelland, J.M., 1994. Oxygen isotope geochemistry of zircon. Earth and Planetary Science Letters 126, 187−206.
Valley, J.W., Ushikubo, T., Kita, N.T., 2007. In Situ Analysis of Three Oxygen Isotopes and OH in ALH 84001: Further Evidence of Two Generations of Carbonates. Lunar Planet. Sci. Conf 38 abstr. #1147.
Valley, J.W., Kinny, P.D., Schulze, D.J., Spicuzza, M.J., 1998. Zircon megacrysts from kimberlite: oxygen isotope variability among mantle melts. Contributions to Mineralogy and Petrology 133, 1−11.
Valley, J.W., Peck, W.H., King, E.M., Wilde, S.A., 2002. A cool early Earth. Geology 30, 351−354.
Valley, J.W., Lackey, J.S., Cavosie, A.J., Clechenko, C.C., Spicuzza, M.J., Basei, M.A.S., Bindeman, I.N., Ferreira, V.P., Sial, A.N., King, E.M., Peck, W.H., Sinha, A.K., Wei, C.S., 2005. 4.4 billion years of crustal maturation: oxygen isotope ratios of magmatic zircon. Contributions to Mineralogy and Petrology 150, 561−580.
Valley, J.W., Cavosie, A.J., Fu, B., Peck, W.H., Wilde, S.A., 2006. Comment on "Heterogeneous Hadean hafnium: evidence of continental crust at 4.4 to 4.5 Ga". Science 312, 1139a.
Valley, J.W., Grimes, C.B., Bouvier, A.-S., Ushikubo, T., Ortiz, D.M., Cavosie, A.J., Wilde, S.A., 2010. What can we agree on before 4 Ga? In: Tyler, I.M., Knox-Robinson, C.M. (Eds.), 5th International Archean Symposium. Australia, Perth, pp. 5−7.
Valley, J.W., Cavosie, A.J., Ushikubo, T., Reinhard, D.A., Lawrence, D.F., Larson, D.J., Clifton, P.H., Kelly, T.F., Wilde, S.A., Moser, D.E., Spicuzza, M.J., 2014a. Hadean age for a post-magma-ocean zircon confirmed by atom-probe tomography. Nature Geoscience 7, 219−223.
Valley, J.W., Spicuzza, M.J., Ushikubo, T., 2014b. Correlated $\delta^{18}O$ and [Ti] in lunar zircons: a terrestrial perspective for magma temperatures and water content on the Moon. Contributions to Mineralogy and Petrology 167 (1), 1−15. https://doi.org/10.1007/s00410-013-0956-4.
Valley, J.W., Reinhard, D.A., Cavosie, A.J., Ushikubo, T., Lawrence, D.F., Larson, D.J., Kelly, T.F., Snoeyenbos, D.R., Strickland, A., 2015. Nano- and micro-geochronology in Hadean and Archean zircons by atom-probe tomography and SIMS: new tools for old minerals. American Mineralogist 100, 1355−1377.
Vermeesch, P., 2012. On the visualisation of detrital age distributions. Chemical Geology 312−213, 190−194.
Vervoort, J.D., Kemp, A.I.S., 2016. Clarifying the zircon Hf isotope record of crust-mantle evolution. Chemical Geology 425, 65−75.
Wang, Q., 2015. A Geological Traverse across the Jack Hills Metasedimentary Belt, Western Australia: Isotopic Constraints on the Distribution of Proterozoic Rocks and the Evolution of Hadean Crust. Curtin University Doctoral Thesis, p. 338 (unpublished).
Wang, Q., Wilde, S.A., 2018. New constraints on the Hadean to proterozoic history of the Jack Hills belt, Western Australia. Gondwana Research 55, 74−91.
Watson, E.B., Cherniak, D.J., 1997. Oxygen diffusion in zircon. Earth and Planetary Science Letters 148, 527−544.
Watson, E.B., Harrison, T.M., 2005. Zircon thermometer reveals minimum melting conditions on earliest Earth. Science 308, 841−844.
Weiss, B.P., Fu, R.R., Einsle, J.F., Glenn, D.R., Kehayias, P., Bell, E.A., Gelb, J., Araujo, J.F.D.F., Lima, E.A., Borlina, C.S., Boehnke, P., Johnstone, D.N., Harrison, T.M., Harrison, R.J., Walsworth, R.L., 2018. Secondary magnetic inclusions in detrital zircons from the Jack Hills, Western Australia, and implications for the origin of the geodynamo. Geology 46, 427−430.
Weiss, B.P., Maloof, A.C., Tailby, N., Ramezani, J., Fu, R.R., Hanus, V., Trail, D., Watson, E.B., Harrison, T.M., Bowring, S.A., Kirschvink, J.L., Swanson-Hysell, N.L., Coe, R.S., 2015. Pervasive remagnetization of detrital zircon host rocks in the Jack Hills, Western Australia and implications for records on the early geodynamo. Earth and Planetary Science Letters 430, 115−128.
Wielicki, M.M., Harrison, T.M., Schmitt, A.K., 2012. Geochemical signatures and magmatic stability of terrestrial impact produced zircon. Earth and Planetary Science Letters 321, 20−31. https://doi.org/10.1016/j.epsl.2012.01.009.
Wilde, S.A., 2010. Proterozoic volcanism in the Jack Hills Belt, Western Australia: some implications and consequences for the World's oldest zircon population. Precambrian Research 183, 9−24.
Wilde, S.A., 2011. Jack Hills. In: Gargaud, M. (Ed.), Encyclopedia of Astrobiology, pp. 875−878. https://doi.org/10.1007/978-3-642-11274-4.
Wilde, S.A., Middleton, M.F., Evans, B.J., 1996. Terrane accretion in the southwestern Yilgarn Craton: evidence from a deep seismic crustal profile. Precambrian Research 78, 179−196.
Wilde, S.A., Pidgeon, R.T., 1990. Geology of the Jack Hills metasedimentary rocks. In: Ho, S.E., Glover, J.E., Myers, J.S., Muhling, J.R. (Eds.), Proceedings of the Third International Archaean Symposium on Excursion Guidebook. University of Western Australia, Perth, WA, pp. 82−89.
Wilde, S.A., Spaggiari, C., 2007. The Narryer terrane, Western Australia: a review. In: van Kranendonk, M.J., Smithies, R.H., Bennett, V.C. (Eds.), World's Oldest Rocks. Elsevier Science, Amsterdam, pp. 275−304.
Wilde, S.A., Valley, J.W., Peck, W.H., Graham, C.M., 2001. Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago. Nature 409, 175−178.
Wyche, S., Kirkland, C.L., Riganti, A., Pawley, M.J., Belousova, E., Wingate, M.T.D., 2012. Isotopic constraints on stratigraphy in the central and eastern Yilgarn Craton, Western Australia. Australian Journal of Earth Science 59, 657−670.
Wyche, S., Nelson, D.R., Riganti, A., 2004. 4350−3130 Ma detrital zircons in the southern cross granite-greenstone terrane, Western Australia: implications for the early evolution of the Yilgarn craton. Australian Journal of Earth Sciences 51, 31−45.
Yamamoto, S., Komiya, T., Iizuka, T., Shibuya, T., Collerson, K.D., 2016. Shock-metamorphosed zircons discovered in Jack Hills metaconglomerate from the Narryer gneiss complex, Western Australia. In: Goldschmidt Geochemistry Conference, Abstr. 3531.