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Chapter 2.5

THE OLDEST TERRESTRIAL MINERAL RECORD: A REVIEW OF 4400 TO 4000 MA DETRITAL ZIRCONS FROM JACK HILLS, WESTERN AUSTRALIA

AARON J. CAVOSIE[a], JOHN W. VALLEY[b], SIMON A. WILDE[c]

[a]*Department of Geology, University of Puerto Rico, PO Box 9017, Mayagüez, Puerto Rico, 00681, USA*
[b]*Department of Geology and Geophysics, University of Wisconsin, 1215 W. Dayton, Madison, WI 53706, USA*
[c]*Department of Applied Geology, Curtin University of Technology, Perth, WA 6102, Australia*

2.5-1. INTRODUCTION

Little is known of the Earth's earliest history due to the near absence of a rock record for the first several hundred million years after accretion. Earth's earliest history is commonly referred to as the Hadean Eon, and comprises the time following accretion at ca. 4560 Ma, when impacts and magma oceans maintained extreme surface temperatures at or above the temperatures where oceans are vaporized to a dense steam atmosphere. The existence of buoyant crust as early as 4400 Ma is indicated by the preservation of Hadean zircons. The Earth eventually cooled, quenching the high surface temperatures of the Hadean, and gave rise to oceans. This transition to a more familiar and clement Earth ushered in the beginning of the Archean Eon (Cavosie et al., 2005a; Valley, 2006). The timing of the transition from a Hadean to an Archean Earth is inferred to pre-date the oldest known rocks, ca. 4000 to 3800 Ma orthogneisses and metasedimentary rocks that are exposed in the Slave craton of northwest Canada (Bowring and Williams, 1999) and in the North Atlantic craton of southwest Greenland (Nutman et al., 2001).

The only identified materials on Earth potentially old enough to record the Hadean–Archean transition are ancient, ⩾4000 Ma zircons found in Archean metasedimentary rocks in Australia, China, and the USA. In Western Australia, variably metamorphosed metasedimentary rocks in several localities have yielded zircons older than 4000 Ma, older than the known rock record, including the Jack Hills (Table 2.5-1), Mount Narryer (Froude et al., 1983), and Maynard Hills (Wyche et al., 2004). Rare >4000 Ma zircons have also been reported as xenocrysts in younger Archean granitoids (Nelson et al., 2000).

The Jack Hills metasedimentary rocks have received the most investigation out of the above localities, primarily due to both the consistently higher concentration of ⩾4000 Ma zircon grains, as well as the presence of the oldest known detrital zircons. Given the unique

Table 2.5-1. Data for $\geqslant$3900 Ma zircons from Jack Hills[1]

Reference	U-Pb[2]	REE	CL	$\delta^{18}O$	ε_{Hf}	Ti	^{244}Pu	Methods
Group I: 1986 to 1992								
Compston and Pidgeon (1986)	17	–	–	–	–	–	–	SIMS
Kober et al. (1989)	5	–	–	–	–	–	–	TIMS
Maas and McCulloch (1991)	12	–	–	–	–	–	–	SIMS
Maas et al. (1992)	10	10	–	–	–	–	–	SIMS
Group II: 1998 to 2001								
Amelin (1998)	9	–	–	–	–	–	–	TIMS
Amelin et al. (1999)	(7)	–	–	–	7	–	–	TIMS
Nelson (2000)	2	–	–	–	-	–	–	SIMS
Wilde et al. (2001)	1	1	1	1	–	–	–	SIMS
Mojzsis et al. (2001)	7	–	–	7	–	–	–	SIMS
Peck et al. (2001)	4 (1)	4 (1)	(1)	4 (1)	–	–	–	SIMS
Group III: 2004 to 2006								
Cavosie et al. (2004)	48	–	24	–	–	–	–	SIMS
Turner et al. (2004)	–	–	–	–	–	–	7	LRI-MS
Cavosie et al. (2005)	–	–	24 (20)	44	–	–	–	SIMS
Dunn et al. (2005)	16	–	–	–	–	–	–	SIMS
Crowley et al. (2005)	38	36	21	–	–	–	–	LAICPMS
Watson and Harrison (2005)	–	–	1	–	–	54	–	SIMS
Harrison et al. (2005)	104	–	–	–	104	–	–	TIMS/LAICPMS
Nemchin et al. (2006)	8	–	8	8	–	–	–	SIMS
Pidgeon and Nemchin (2006)	11	–	11	–	–	–	–	SIMS
Valley et al. (2006)	–	–	(2)	–	–	36	–	SIMS
Cavosie et al. (2006)	–	42	(42)	–	–	–	–	SIMS
Fu et al. (2007)	–	–	–	–	–	(36)	–	SIMS
Total grains	292	93	90	64	111	90	7	

SIMS = secondary ionization mass spectrometry, TIMS = thermal ionization mass spectrometry. LRI-MS = Laser resonance ionization mass spectrometry. LAICPMS = laser ablation inductively coupled plasma mass spectrometry. REE = rare earth elements. CL = cathodoluminescence. $\delta^{18}O$ = oxygen isotope ratio. ε_{Hf} = epsilon hafnium.

[1] Values are number of new grains reported. Values in parentheses indicate additional grains described.

[2] Values are only listed for grains where analytical results were published.

window these grains offer on early Earth processes, this review focuses primarily on published reports that describe the population of $\geqslant$4000 Ma zircons from the Jack Hills.

2.5-2. THE JACK HILLS

The Jack Hills, located in the Narryer Terrane of the Yilgarn Craton in Western Australia (Fig. 2.5-1), comprise a ~90 km long northeast-trending belt of folded and weakly
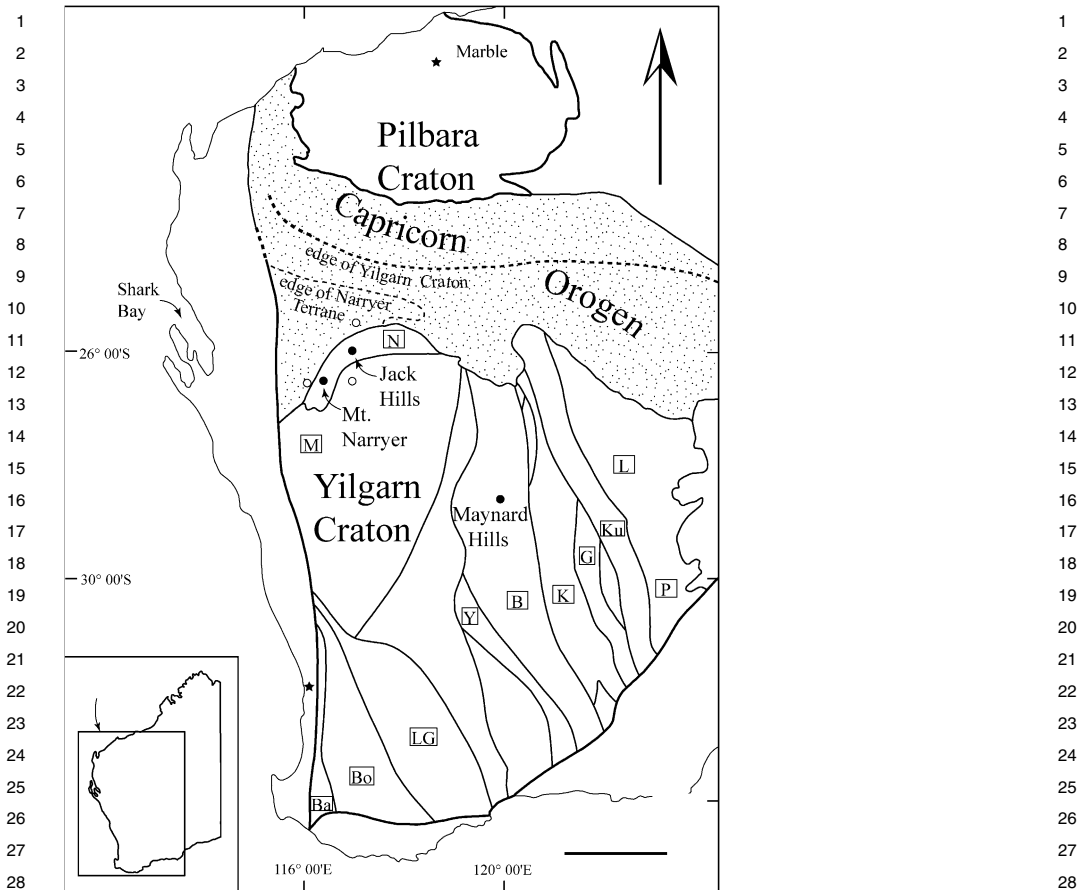
Fig. 2.5-1. Map of Archean cratons in Western Australia, after Wilde et al. (1996). Filled circles are known locations of >4000 Ma detrital zircons, open circles are locations of xenocrysts with similar ages (zircon locations referenced in text). Terranes of the Yilgarn Craton – B: Barlee, Ba: Balingup, Bo: Boddington, G: Gindalbie, K: Kalgoorlie, Ku: Kurnalpi, L: Laverton, LG: Lake Grace, M: Murchison, N: Narryer, P: Pinjin, Y: Yellowdine. Dashed lines are inferred boundaries in basement.

metamorphosed supracrustal rocks that are composed primarily of siliciclastic and chemical metasedimentary rocks, along with minor metamafic/ultramafic rocks (Fig. 2.5-2: see also Wilde and Spaggiari, this volume). Bedding strikes east-northeast and has a sub-vertical 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 a now famous site referred to as 'W74' (Fig. 2.5-2), the name originally assigned to a sample collected at this site by
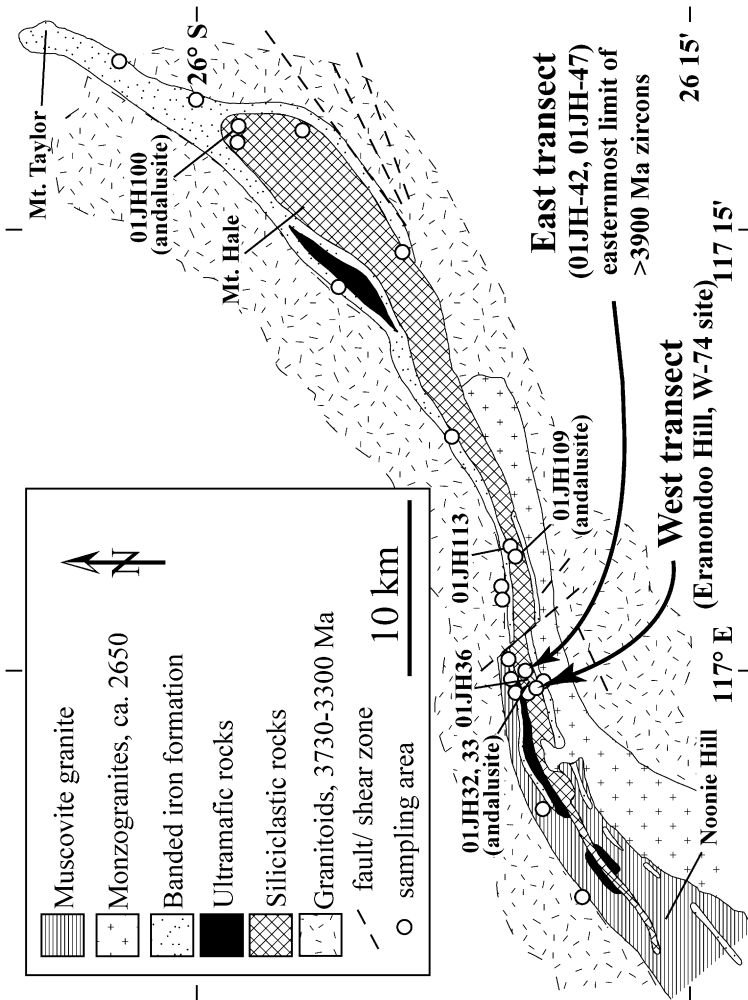
Fig. 2.5-2. Geologic map of the Jack Hills metasedimentary belt, modified from Wilde et al. (1996) and Cavosie et al. (2004). The 'West' and 'East' transects refer to the sampling transects described in Cavosie et al. (2004).

the Curtin University group. The W74 site contains a well-exposed, 2-meter thick quartz pebble metaconglomerate. This previously un-described unit was originally sampled by S. Wilde, R. Pidgeon and J. Baxter in 1984 during exploratory precious metal surveying, and was described by Compston and Pidgeon (1986) who reported the first $\geqslant$4000 Ma detrital zircons from the Jack Hills, including a grain with one spot as old as 4276 ± 6 Ma. Aliquots of zircons from the original W74 zircon concentrate, and additional samples from the same outcrop, have since been the subject of many studies (see below).

2.5-2.1. Age of Deposition

The age of deposition of the Jack Hills metasediments is somewhat controversial, as it appears to vary with location in the belt. The maximum age of the W74 metaconglomerate based on the youngest detrital zircon age has long been cited as ca. 3100 Ma (e.g., Compston and Pidgeon, 1986). However, the first precise age for a concordant 'young' zircon was a 3046 ± 9 Ma grain reported by Nelson (2000). A similar age of 3047 ± 21 Ma was later reported as the youngest zircon by Crowley et al. (2005); thus, it appears that ca. 3050 is the maximum age of deposition of the metaconglomerate at the W74 site.

To explore the distribution of detrital zircon ages away from the W74 site, Cavosie et al. (2004) analyzed zircons from several samples along two transects within the conglomerate-bearing section, including a 60 m section that contains the W74 site (Fig. 2.5-3), and a 20 m conglomerate-bearing section 1 km east of W74. Both transects are dominated by chemically mature clastic metasedimentary rocks (>95 wt% SiO_2), including metaconglomerate, quartzite, and metasandstone. In the west transect, 4 out of 5 samples of quartz pebble metaconglomerate and quartzite contain detrital zircons with ages $\geqslant$3100 Ma (Cavosie et al., 2004), consistent with previous results from sample W74. However, the stratigraphically highest quartzite in the west transect, sample 01JH-63, contains Proterozoic zircons with oscillatory zoning and ages as young as 1576 ± 22 Ma (Cavosie et al., 2004), and lacks zircons older than ca. 3750 Ma (see discussion by Wilde and Spaggiari, this volume). The presence of Proterozoic zircons in this unit was confirmed by Dunn et al. (2005). Thus, independent studies have demonstrated that the youngest metasedimentary rocks in the Jack Hills are Proterozoic in age. The origin of these metasedimentary rocks remains unknown (see discussion in Cavosie et al., 2004); however, recent field investigations by the current authors have identified layer-parallel faults in the west transect between samples 01JH-63 and the W74 metaconglomerate, which suggests tectonic juxtaposition of two different-age packages of metasedimentary units (see Wilde and Spaggiari, this volume). The minimum age of the Archean sediments in the Jack Hills is constrained by granitoid rocks which intruded the belt at ca. 2654 ± 7 Ma (Pidgeon and Wilde, 1998).

2.5-2.2. Metamorphism

The metamorphic history of the Jack Hills metasedimentary belt remains poorly documented. However, early workers described rare occurrences of andalusite, kyanite, and
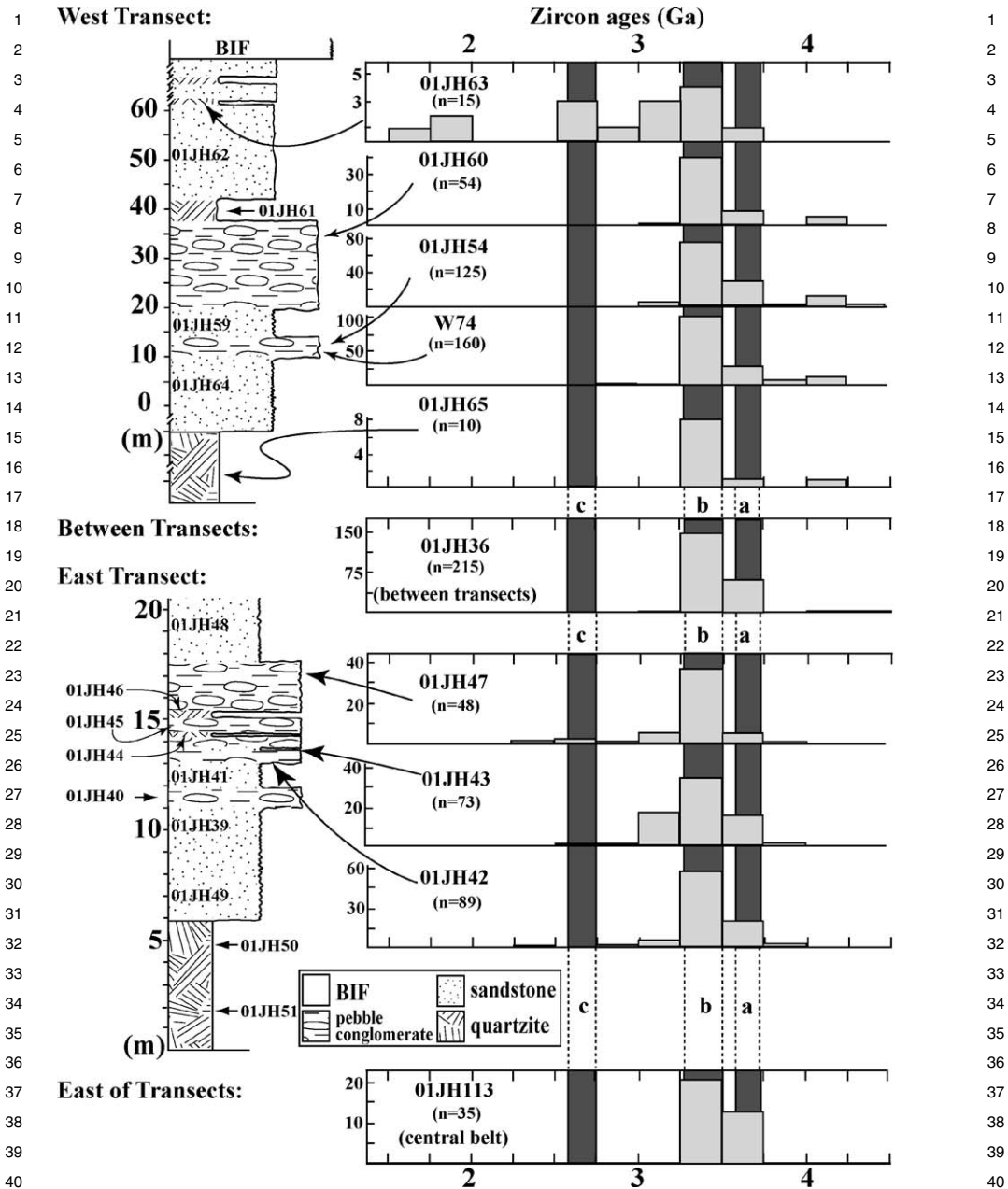
Fig. 2.5-3. Stratigraphic columns of the West and East sampling transects of Cavosie et al. (2004). Note the West transect includes two samples of the same metaconglomerate at the W74 site (samples 01JH-54 and W74).

chloritoid in the western part of the belt (Elias, 1982; Baxter et al., 1984). Recent pet-
rographic studies have expanded the known occurrences of andalusite to the central and
eastern parts of the belt (Cavosie et al., 2004), which suggests that the majority of the
metasedimentary rocks in the Jack Hills metasedimentary belt experienced a pervasive
greenschist to lower amphibolite facies metamorphism, despite the absence of index miner-
als in most units. The common association of metamorphic muscovite with quartz, and the
absence of K-feldspar indicates that the clastic metasediments did not reach granulite fa-
cies.

2.5-2.3. Geology of Adjacent Rocks

Near Jack Hills are outcrops of the Meeberrie Gneiss, a complex layered rock that yields
a range of igneous zircon ages from 3730 to 3600 Ma (Kinny and Nutman, 1996; Pid-
geon and Wilde, 1998), establishing it as the oldest identified rock in Australia (Myers
and Williams, 1985). Included within the Meeberrie Gneiss near both Jack Hills and Mt.
Narryer are cm- to km-scale blocks of a dismembered layered mafic intrusion that together
comprise the Manfred Complex (Myers, 1988b). Zircons from Manfred Complex samples
yield ages as old as 3730 ± 6 Ma, suggesting it formed contemporaneously with the oldest
components of the Meeberrie Gneiss (Kinny et al., 1988). Exposures of the 3490–3440 Ma
Eurada Gneiss occur 20 km west of Mt. Narryer, and contain a component of younger
ca. 3100 Ma zircons (Nutman et al., 1991). West of Jack Hills, the Meeberrie Gneiss was
intruded by the precursor rocks of the Dugel Gneiss, which contain 3380–3350 Ma zir-
cons (Kinny et al., 1988; Nutman et al., 1991), and, like the Meeberrie gneiss, contain
enclaves of the Manfred Complex (Myers, 1988b). Younger granitoids, from 2660 ± 20
to 2646 ± 6 Ma, intrude the older granitoids in the vicinity of Jack Hills and Mt. Narryer
(Kinny et al., 1990; Pidgeon, 1992; Pidgeon and Wilde, 1998). Contacts between the Jack
Hills metasedimentary rocks and the older granitoids are everywhere sheared, whereas the
ca. 2650 Ma granitoids appear to intrude the belt (Pidgeon and Wilde, 1998).

2.5-3. JACK HILLS ZIRCONS

Since their discovery two decades ago, compositional data and images of Jack Hills
zircons have been described in more than 20 peer-reviewed articles (Table 2.5-1). In an
attempt to acknowledge all those who have contributed to this research and to facilitate
discussion, we have classified the published articles into three main pulses of research:
articles published from 1986 to 1992 are Group I, articles published from 1998 to 2001
are Group II, and articles published from 2004 to the present are Group III. Data and
conclusions from these reports are reviewed below.

2.5-3.1. Ages of Jack Hills Zircons

Many thousands of detrital grains have now been analyzed for U-Pb age using several an-
alytical methods, including secondary ion mass spectrometry (SIMS), thermal ionization

mass spectrometry (TIMS), and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS). To date, analytical data of U-Pb analyses of $\geqslant$3900 Ma zircons have been reported for >300 detrital grains (Table 2.5-1).

2.5-3.1.1. Group I: 1986 to 1992

The first zircon U-Pb age study in the Jack Hills was made with SHRIMP I by Compston and Pidgeon (1986), who reported 17 zircons from W74 with ages in excess of 3900 Ma from a population of 140 grains, including one crystal that yielded four ages ranging from 4211 $\pm$ 6 to 4276 $\pm$ 6 Ma, the latter constituting the oldest concordant zircon spot analysis at that time. Subsequent U-Pb studies of zircons from the W74 site by Köber et al. (1989: TIMS), Maas and McCulloch (1991: SHRIMP), and Maas et al. (1992: SHRIMP) confirmed that $\geqslant$4000 Ma zircons make up anywhere from 8 to 12% of the analyzed populations, and resulted in published age data for 44 $\geqslant$3900 Ma zircons. Köber et al. (1989) used the direct Pb-evaporation TIMS method to identify >4000 Ma grains and concluded that they originated from a granitoid rock, based on similarity of ^{208}Pb/^{206}Pb ratios with known rocks. Also noted at the time were the generally low U abundances for Jack Hills zircons, including concentrations of 50–100 ppm (Compston and Pidgeon, 1986) and 60–413 ppm (Maas et al., 1992).

2.5-3.1.2. Group II: 1998 to 2001

The second wave of Jack Hills zircon research began near the end of the 1990s. New isotopic U-Pb ages for >4000 Ma grains were published in Amelin (1998: TIMS), Nelson (2000: SIMS), Wilde et al. (2001: SIMS), Mojzsis et al. (2001: SIMS), and Peck et al. (2001: SIMS). Amelin (1998) demonstrated high precision ^{207}Pb/^{206}Pb age analyses (<1% uncertainty) of whole grains and air abraded fragments, and again low U abundances (35–228 ppm). Similar low U abundances were found in two grains with ages of 4080 and 4126 Ma (54–236 ppm) by Nelson (2000), and also in four grains with ages of 4039 to 4163 Ma (41–307 ppm) by Peck et al. (2001).

Perhaps one of the most significant discoveries in U-Pb studies of Jack Hills zircons is a grain fragment that yielded a single concordant spot age of 4404 $\pm$ 8 Ma (Wilde et al., 2001). Five additional >95% concordant spot analyses yielded a weighted mean age of 4352 $\pm$ 10, confirming the great antiquity of the crystal (Wilde et al., 2001; Peck et al., 2001). The assignment of 4400 Ma as the crystallization age of the zircon followed the same methodology and rationale as that used by Compston and Pidgeon (1986) for the 4276 $\pm$ 6 Ma crystal; namely, with no analytical reason for exclusion (e.g., U-Pb concordance, ^{204}Pb, etc.), the oldest concordant spot analysis represents the minimum age of the crystal, and the younger population of ages represent areas of the crystal affected by Pb loss or younger overgrowths. Thus, the 4400 Ma zircon extends the known age population of zircons in Jack Hills by $\sim$125 Ma, and currently remains the oldest terrestrial zircon thus far identified.
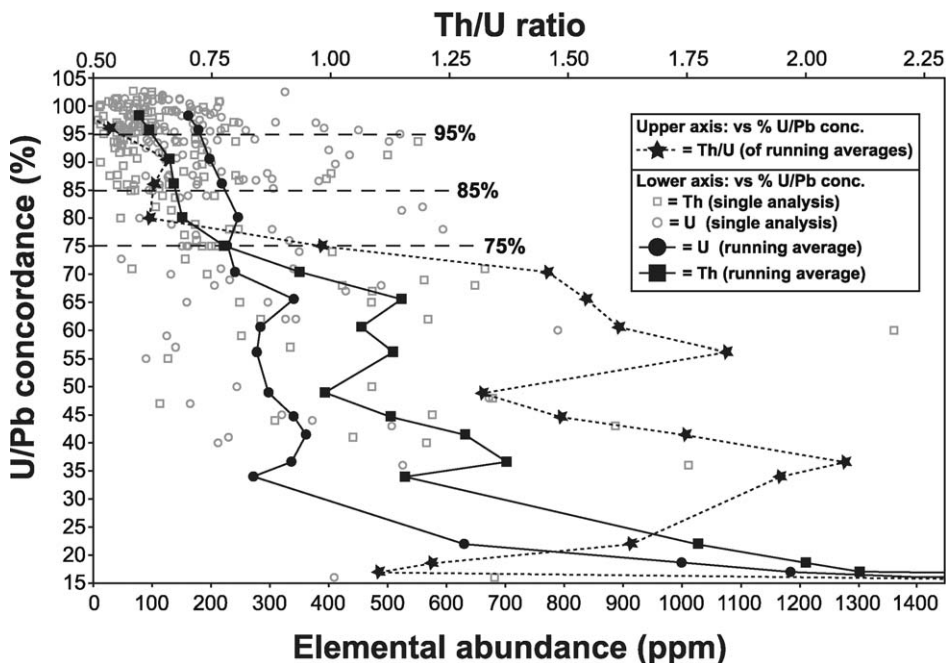
Fig. 2.5-4. Elemental Th and U abundances (lower *x*-axis) and Th/U ratio (upper *x*-axis) plotted against percentage of U-Pb concordance for 140 Jack Hills zircons. Averages of Th, U, and Th/U ratio were calculated as 10% running averages at 5% increments of concordance beginning with 100%. Each running average includes all data points in a bin that extends over ±5% concordance from the given increment (i.e., a running average calculated at 90% concordance averages all data points that are 85–95% concordant).

2.5-3.1.3. Group III: 2004 to the present

As of now, large numbers of ⩾4000 Ma zircon U-Pb ages are available from Jack Hills. Cavosie et al. (2004) reported ages for 42 grains ranging from 3900 to 4350 Ma, including U concentrations from 35–521 ppm. Harrison et al. (2005) reported U-Pb ages >4000 Ma for 104 Jack Hills zircons, with ages from 4371 to 4002 Ma. Additional ages and U concentrations within this range have also been reported by Dunn et al. (2005), Crowley et al. (2005), and Nemchin et al. (2006) (Table 2.5-1). In addition, Pidgeon and Nemchin (2006) identified a single, nearly concordant 4106 ± 22 Ma zircon with 21 ppm U, the lowest U concentration known for a >4000 Ma zircon from Jack Hills.

2.5-3.1.4. Pb-loss in Jack Hills zircons

Zircons that have experienced Pb-loss are ubiquitous in the Jack Hills metasedimentary rocks (e.g., Compston and Pidgeon, 1986; Maas et al., 1992; Cavosie et al., 2004; Nemchin et al., 2006). In an attempt to address the issue of Pb-loss, Cavosie et al. (2004) developed a method for evaluating the extent of U-Pb discordance a grain can exhibit while still

yielding reliable crystallization ages, instead of picking an arbitrary cut-off value. It was shown that a correlation exists between the Th/U ratio, abundances of U and Th, and U-Pb concordance, that suggests zircons >85% concordant in U/Pb age preserve reliable isotopic ages (Cavosie et al., 2004) (Fig. 2.5-4). The cause of the observed ancient Pb-loss is unknown. However, proposed explanations include otherwise unrecognized granulite facies thermal events that might have disturbed the U-Pb systems in the grains in question (e.g., Nelson, 2002, 2004; Nemchin et al., 2006).

2.5-3.1.5. Distribution of >4000 Ma zircons in Jack Hills metasedimentary rocks

Of the studies that analyzed detrital zircons in samples away from the W74 site, all found that the percentage of ⩾4000 Ma grains is highly variable, and moreover ⩾4000 Ma zircons are not present in many units (Cavosie et al., 2004; Dunn et al., 2005; Crowley et al., 2005). The high percentage of >4000 Ma grains in the W74 metaconglomerate (e.g., 10–14%: Compston and Pidgeon, 1986; Maas et al., 1992; Amelin, 1998; Cavosie et al., 2004) is unique among analyzed samples, given the demonstrated heterogeneous distribution of ⩾4000 Ma grains throughout the belt. The consistency of studies finding this high percentage, however, may not be surprising given that all of the studies listed in Table 2.5-1 contain analyses of zircons separated from the W74 site, and thus essentially analyzed similar populations, often from the same ∼2 m³ W74 outcrop on Eranondoo Hill.

2.5-3.2. Imaging Studies of Jack Hills Zircons

Physical grain aspects of Jack Hills zircons were first described by Compston and Pidgeon (1986), who commented that grains ranged from nearly colorless to deep purplish-brown, were mostly fragments, and were rounded and exhibited pitting, suggestive of sedimentary transport. Maas et al. (1992) reported similar features, and also the occurrence of euhedral crystal terminations. The first grain images of zircons published from the Jack Hills were transmitted light images of grains analyzed by Köber et al. (1989), which showed their rounded forms and pitted surfaces. The extreme rounding of grains and pitting of surfaces was also shown in a back-scattered electron image of a rounded Jack Hills zircon mounted on carbon tape (Valley, 2005). A color image of ∼40 Jack Hills zircons mounted on tape prior to casting in epoxy was published by Valley (2006), and shows a population of mostly intact grains and a few grain fragments. The color image illustrates the range of deep red colors that are characteristic of the Jack Hills zircons, as well as the morphological spectrum, from essentially euhedral to completely rounded grains.

The first cathodoluminescence (CL) image of a Jack Hills zircon was published in Wilde et al. (2001) and Peck et al. (2001), and shows a 4400 Ma zircon with oscillatory zoning (Table 2.5-1). Cavosie et al. (2004, 2005a) showed CL images and reported aspect ratios of 1.0 to 3.4 for an additional 48 zircon grains >3900 Ma from Jack Hills (Fig. 2.5-5), and interpreted that the majority of the 4400–3900 Ma population is of magmatic origin based on the common occurrence of oscillatory zoning. Crowley et al. (2005) examined 21 zircon grains >3900 Ma from Jack Hills, and also noted that oscillatory zoning was a common feature. They used the style of oscillatory and/or sector zoning to interpret that

4400 to 4200 Ma zircons

(a) W74/2-36: 4404±8

(b) 01JH54-D7: 4348±6

(c) 01JH54-77: 4324±12

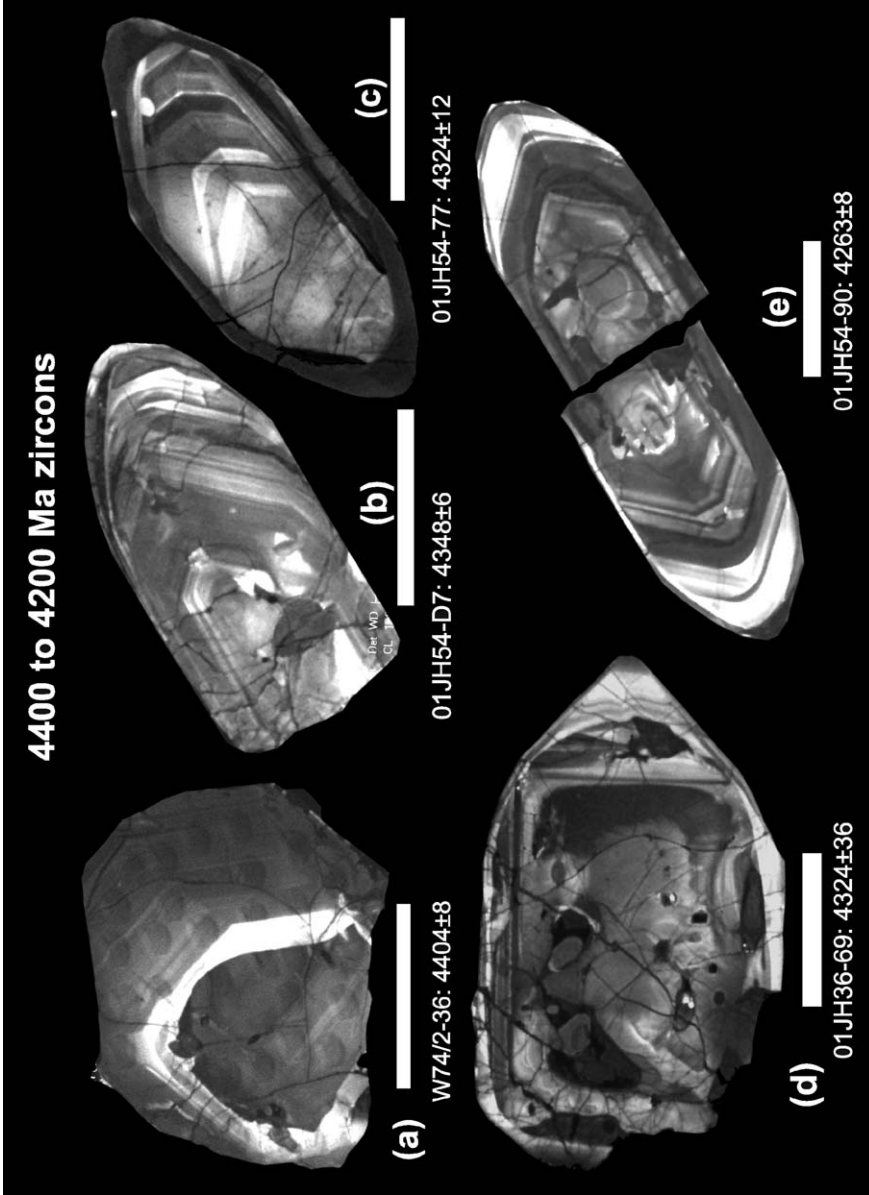(d) 01JH36-69: 4324±36

(e) 01JH54-90: 4263±8

Fig. 2.5-5. Cathodoluminescence images of five 4400–4200 Ma detrital zircons from Jack Hills. (Details of grains presented in Cavosie et al. (2004, 2005b, 2006).)

differences in CL zoning patterns between similar age zircons from Mt. Narryer implied that the source rocks of the two belts were of different composition. In contrast, Nemchin et al. (2006) noted disturbed margins in CL images of oscillatory-zoned >4000 Ma zircons, and interpreted that the eight grains in their study had experienced complex histories, and that all but one zircon likely did not preserve their magmatic compositions. Pidgeon and Nemchin (2006) presented CL images for 11 additional >3900 Ma grain fragments.

2.5-3.3. Oxygen Isotope Composition of Jack Hills Zircons

Due to the slow diffusivity of oxygen in zircon (e.g., Watson and Cherniak, 1997; Peck et al., 2003; Page et al., 2006), magmatic zircon can provide a robust record of the oxygen isotope composition (δ^{18}O) of host magmas during crystallization (Valley et al., 1994, 2005; Valley, 2003). Wilde et al. (2001) and Peck et al. (2001) reported δ^{18}O data, measured by SIMS for a population of five >4000 Ma Jack Hills zircons which ranged from 5.6 to 7.4‰; values elevated relative to mantle-equilibrated zircon (δ^{18}O $= 5.3 \pm 0.6$‰, 2σ). The results were interpreted to indicate that the protolith of the host magmas to the zircons had experienced a low-temperature history of alteration prior to melting, which required the presence of liquid surface waters (Valley et al., 2002). A subsequent study by Mojzsis et al. (2001) confirmed the presence of slightly elevated δ^{18}O by reporting the same range of values (5.4 to 7.6‰) for four zircons with concordant U-Pb ages from 4282 to 4042 Ma. However, three other zircons were reported by Mojzsis et al. (2001) to have δ^{18}O from 8 to 15‰ that were interpreted to be igneous and to represent "S-type" granites. Such high values have not been reported for any other igneous zircons of Archean age (Valley et al., 2005, 2006) (Fig. 2.5-6) and the values of 8–15‰ have alternatively been interpreted as due to radiation damage or metamorphic overgrowth (Peck et al., 2001; Cavosie et al., 2005a; Valley et al., 2006). In contrast, in a study of 44 >3900 Ma zircons by Cavosie et al. (2005a), the location of *in situ* δ^{18}O analyses was correlated with the location of U-Pb analysis sites. It was found that by applying a protocol of targeting concordant U-Pb domains and discarding analyses that produced anomalous sputter pits (as viewed by SEM), the range of δ^{18}O varied from 4.6 to 7.3‰, values that overlap, or are higher than, mantle equilibrated zircon (Fig. 2.5-7). More significantly, based on results from oscillatory zoned grains with concordant U-Pb ages, Cavosie et al. (2005a, 2005b) documented that the highest δ^{18}O relative to mantle oxygen (e.g., from 6.5 to 7.5‰) only occurred in zircons with U-Pb ages younger than 4200 Ma (Fig. 2.5-7), and interpreted this to indicate that the end of the Hadean, and the onset of crustal weathering and recycling began, at ca. 4200 Ma ago, or possibly even earlier. In a study of eight >4200 Ma Jack Hills zircons, Nemchin et al. (2006) also reported multiple δ^{18}O spot analyses for single grains, with grain averages ranging from 4.80 to 6.65‰, and interpreted that the δ^{18}O values represent low-temperature alteration of primary magmatic zircon. However, we note that the range of δ^{18}O values reported by Nemchin et al. (2006) lies entirely within the range of magmatic δ^{18}O values (4.6 to 7.3‰) reported by Cavosie et al. (2005a) for a larger population of >4000 Ma Jack Hills detrital zircons. No evidence for low-temperature oxygen isotope exchange has been documented thus far for any Jack Hills zircon.
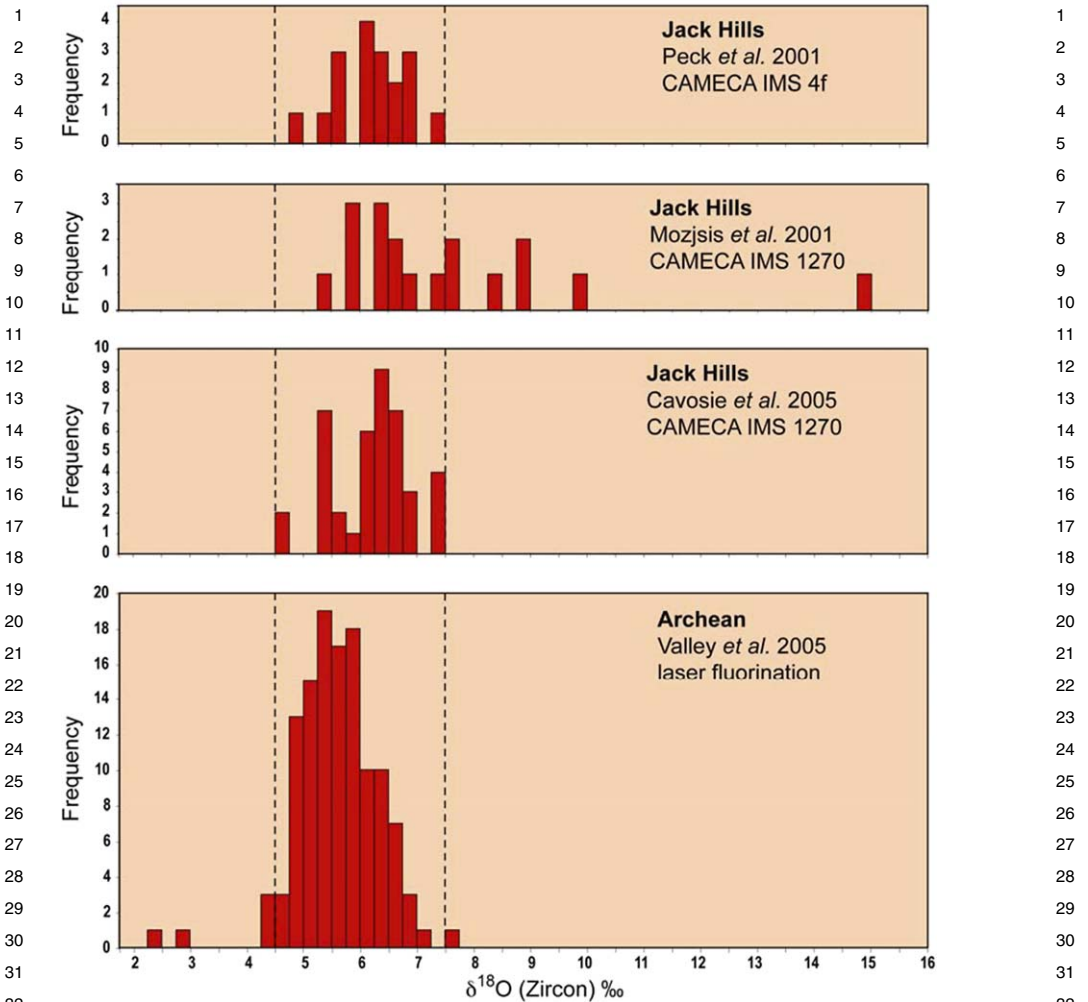
Fig. 2.5-6. Comparison of oxygen isotope ratio for Jack Hills >3900 Ma detrital zircons and Archean igneous zircons.

2.5-3.4. Trace Element Composition of Jack Hills Zircons

2.5-3.4.1. Rare earth elements

To date, four studies of rare earth elements (REE) have been conducted on >3900 Ma zircons from Jack Hills (Maas et al., 1992; Peck et al., 2001; Wilde et al., 2001; Crowley et al., 2005; Cavosie et al., 2006). All have shown that most grains have compositions that are typical of igneous zircon from crustal environments, as characterized by Hoskin and
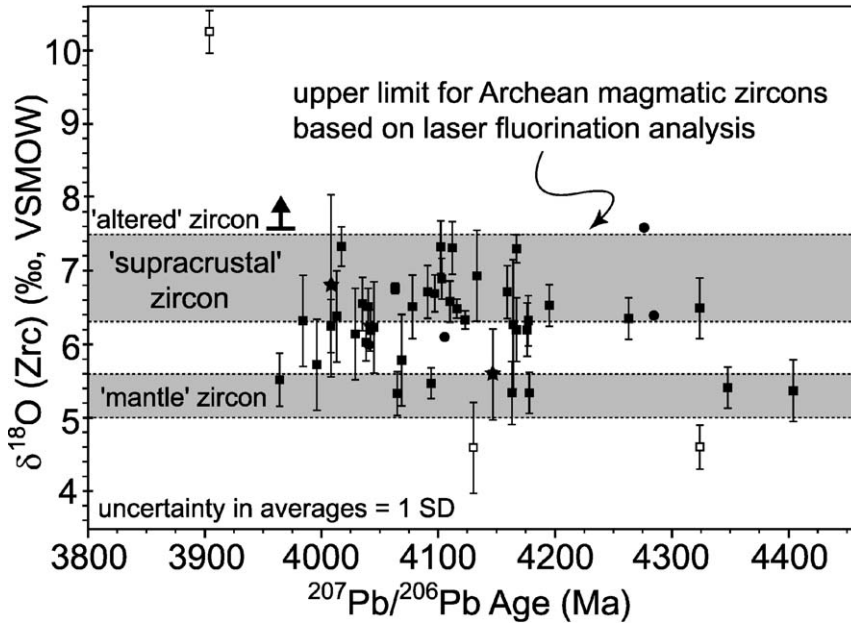
Fig. 2.5-7. Average $\delta^{18}O$ vs. age for Jack Hills zircons. Filled squares are zircons interpreted to pre-serve magmatic $\delta^{18}O$ (after Cavosie et al., 2005b). Open squares are zircons interpreted to be altered, with non-magmatic $\delta^{18}O$. Uncertainty in $\delta^{18}O$ = 1 S.D. The 'mantle' zircon field is $5.3 \pm 0.6‰$ (2 S.D.), as defined in Valley et al. (1994) and Valley (2003). The 'supracrustal' field indicates a range in magmatic $\delta^{18}O(\mathrm{Zrc})$ that is elevated relative to zircon in equilibrium with mantle melts. The identification of $\delta^{18}O(\mathrm{Zrc}) > 7.5‰$ in >2500 Ma zircons as 'altered zircon' is based on the obser-vation that analyses of zircon samples from >120 Archean igneous rocks by laser fluorination have not yielded $\delta^{18}O(\mathrm{Zrc}) > 7.5$, and that all previously reported >2500 Ma zircons above 7.5‰ are discordant in U/Pb age or have non-magmatic CL patterns.

Schaltegger (2003). General enrichments in the heavy REE (HREE) over the light REE (LREE) indicate that the Jack Hills zircons crystallized in fractionated melts, suggesting the existence of differentiated rocks on the early Earth (Maas et al., 1992; Peck et al., 2001; Wilde et al., 2001; Cavosie et al., 2006). Maas et al. (1992) first demonstrated the similarity of Jack Hills zircons to crustal zircons by showing that characteristics such as positive Ce anomalies and negative Eu anomalies occurred in a population of ten >3900 Ma grains, with total REE abundances from 93 to 563 ppm. Wilde et al. (2001) and Peck et al. (2001) reported similar results, and in addition documented unusual LREE enrichments in some grains, with abundances ranging from 10 to 100 times chondritic abundance, and a much larger range of abundance for total REEs, from 414 to 2431 ppm. Crowley et al. (2005) analyzed 36 grains for REEs, and concluded that Jack Hills zircons were not similar in composition to zircons from neighboring Paleoarchean gneisses.

Hoskin (2005) noted that the unusual LREE enrichments in some of the >4000 Ma grains reported by Wilde et al. (2001) and Peck et al. (2001) were similar to the LREE enrichment measured in hydrothermal zircons from southeast Australian granites, and speculated that some of the Jack Hills zircons might have been affected by hydrothermal processes. To test the 'hydrothermal' hypothesis, Cavosie et al. (2006) analyzed REE in 42 >3900 Ma grains and correlated the location of REE analyses with locations of prior $\delta^{18}O$ and U-Pb analyses (Fig. 2.5-8). Two compositional types of REE domains were identified based on chondrite normalized abundances of La and Pr (Fig. 2.5-9). Type 1
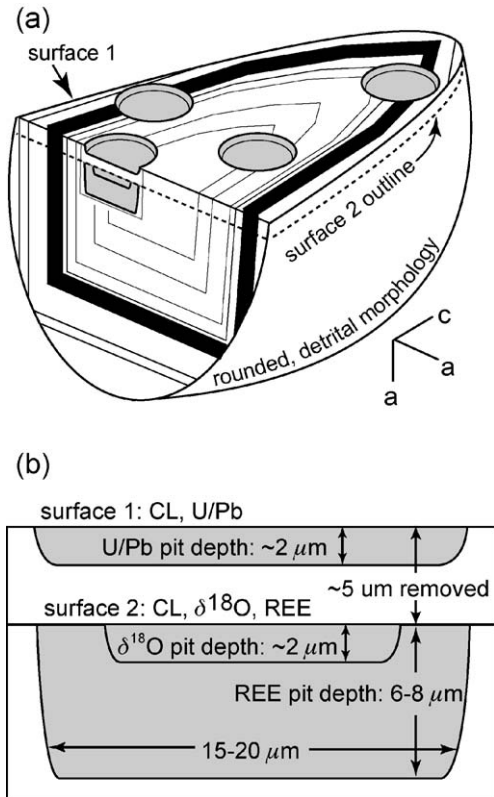

Fig. 2.5-8. Correlated microanalysis of zircon. (a) Schematic representation of a zoned detrital zircon with correlated analyses of U-Pb, $\delta^{18}O$, and REE (the orientation of crystallographic axes are indicated to the lower-right). The 'a–c plane' [(100), roughly horizontal] represents polished 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) Cross-section (001) of the volumes analyzed for U-Pb age, $\delta^{18}O$, and REE in (a). The dimension of the entire volume varies, but is on average 20 μm in diameter, and 10–15 μm deep.
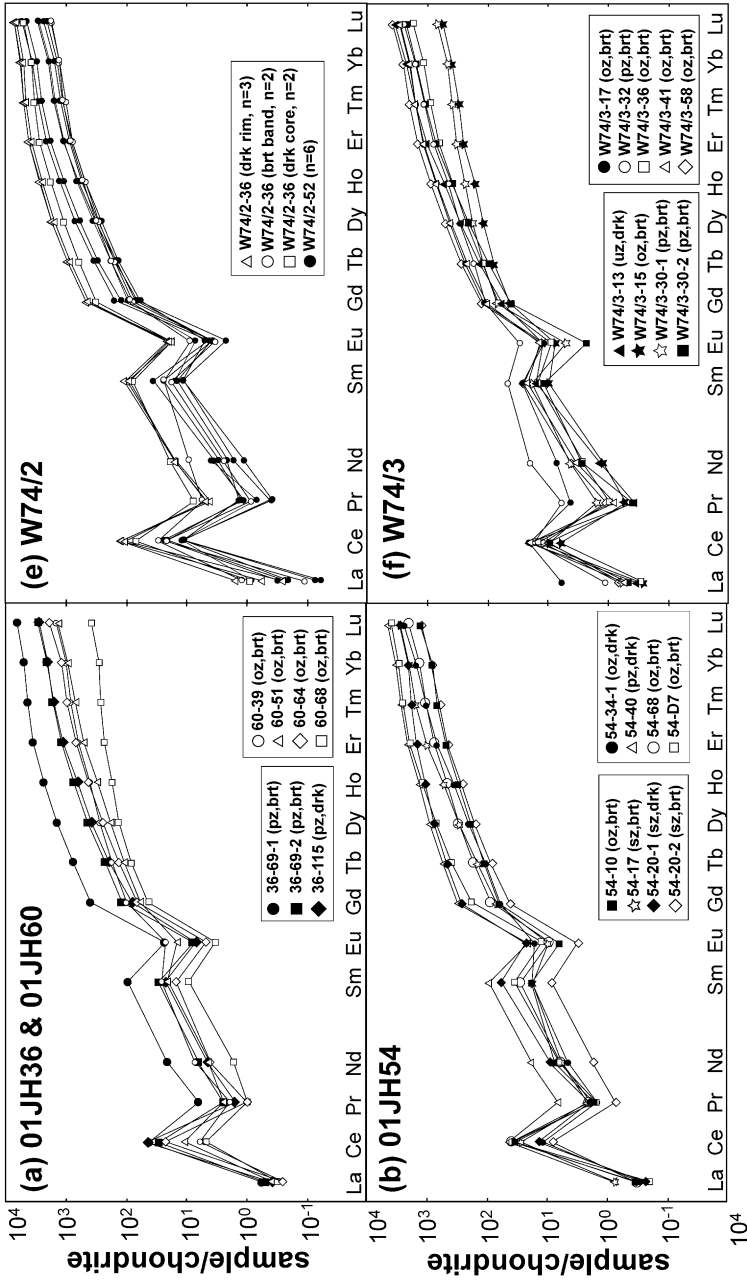
Fig. 2.5–9. Chondrite-normalized REE plots for 42 Jack Hills zircons (from Cavosie et al., 2006): (a) through (g) are 'Type 1' (magmatic); (h) is 'Type 2' (non-magmatic).
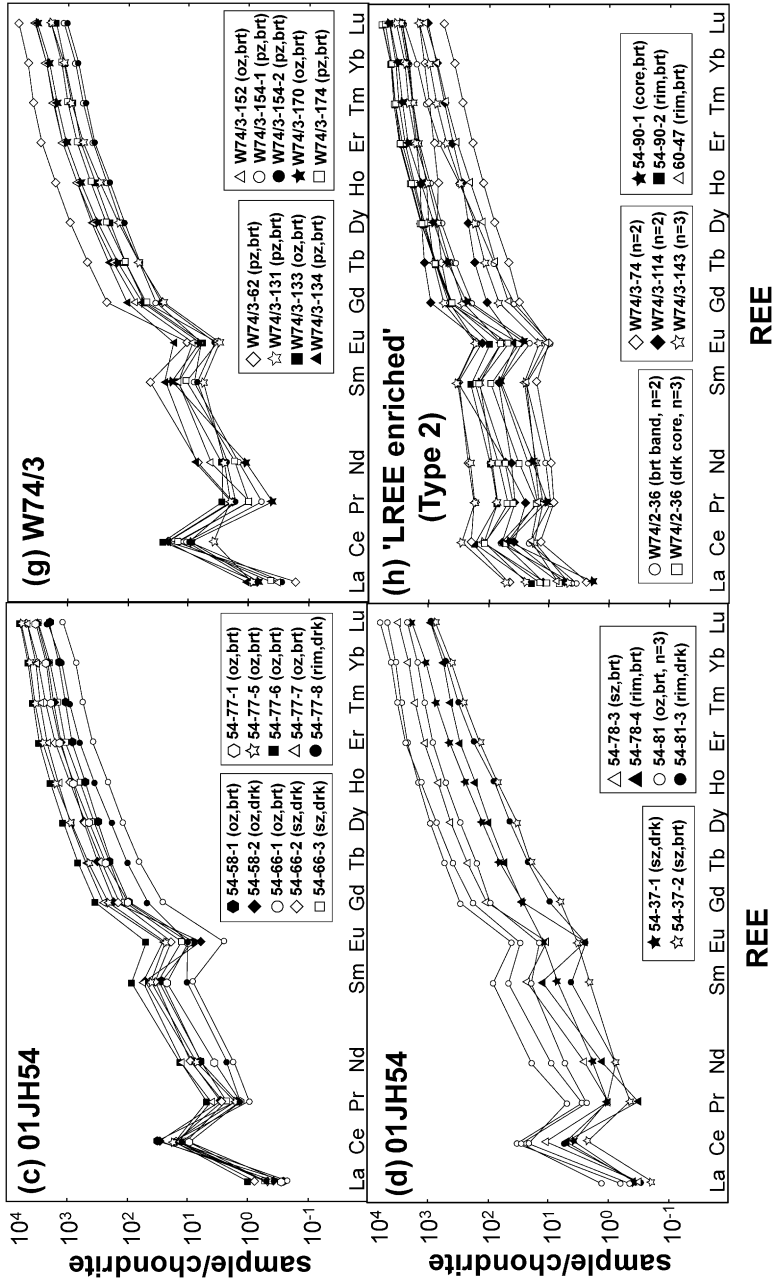
Fig. 2.5-9. (*Continued.*)

(magmatic, Fig. 2.5-9) compositions were preserved in 37 of 42 grains, and consisted of 'typical' crustal REE patterns for zircon (e.g., Hoskin and Schaltegger, 2003). Type 2 (non-magmatic, Fig. 2.5-9) compositions were found in some spots on six grains, and were defined based on the combination of $La_N > 1$ and $Pr_N > 10$. The observation that the Type 2 grain domains that yielded anomalous LREE enrichments also preserved magmatic $\delta^{18}O$ values was used to argue against a hydrothermal origin for the LREE enrichment. The Type 2 LREE enriched compositions were attributed to analysis of sub-surface mineral inclusions and/or radiation-damaged domains, and were not deemed representative of magmatic composition.

2.5-3.4.2. Ti thermometry of Jack Hills zircons

The Ti abundance of zircon (typically a few to tens of ppm) has recently been shown to be a function of melt chemistry and crystallization temperature (Watson and Harrison, 2005). Ti compositions were measured for 54 Jack Hills zircons that range in age from 4000 to 4350 Ma by Watson and Harrison (2005), who interpreted most of their Ti-in-zircon temperatures to average $696 \pm 33\,°C$ (15% of the samples yielded higher temperatures), and thus to provide evidence for minimum-melting, water-saturated granitic magmatism on Earth by 4350 Ma. Valley et al. (2006) questioned the uniqueness of this interpretation for wet-granite melting, citing new data that shows Ti-in-zircon temperatures determined for zircons from a wide range of rock types, including anorthosite, gabbro, and granitoid, overlap with compositions of Jack Hills zircons. The measured Ti abundances for 36 >3900 Ma zircons cited by Valley et al. (2006) were reported by Fu et al. (in press), and yielded an average temperature of $715 \pm 55\,°C$, slightly higher but in general agreement with the average temperature reported by Watson and Harrison (2005). While the range of applications of this relatively new thermometer is still being explored, the similarity of Ti abundance for zircon in a wide range of felsic and mafic rock types appears to limit the usefulness of Ti composition as a specific petrogenetic indicator for detrital zircons.

2.5-3.4.3. Other trace elements

In addition to the REE, other elements have provided information about the origin of >3900 Ma zircons from Jack Hills. Maas et al. (1992) analyzed Sc by electron microprobe analysis (EMPA) and found from <17 ppm (detection limit) to 59 ppm in 10 grains, and interpreted these low abundances as indicating an origin in felsic to intermediate rocks based on Sc partitioning behavior.

Turner et al. (2004) reported evidence that detectable quantities of the now extinct isotope ^{244}Pu had been incorporated in Jack Hills zircons by measuring anomalies in Xe isotopes in 4100 to 4200 Ma grains. The detection of fissiogenic Xe allows further constraints to be placed on the original Pu/U ratio of Earth.

2.5-3.5. Hf Isotope Composition of Jack Hills Zircons

Hf isotope composition in zircon is a sensitive chronometer for crust/mantle differentiation that can be coupled to U-Pb age. Amelin et al. (1999) reported ε_{Hf} composi-
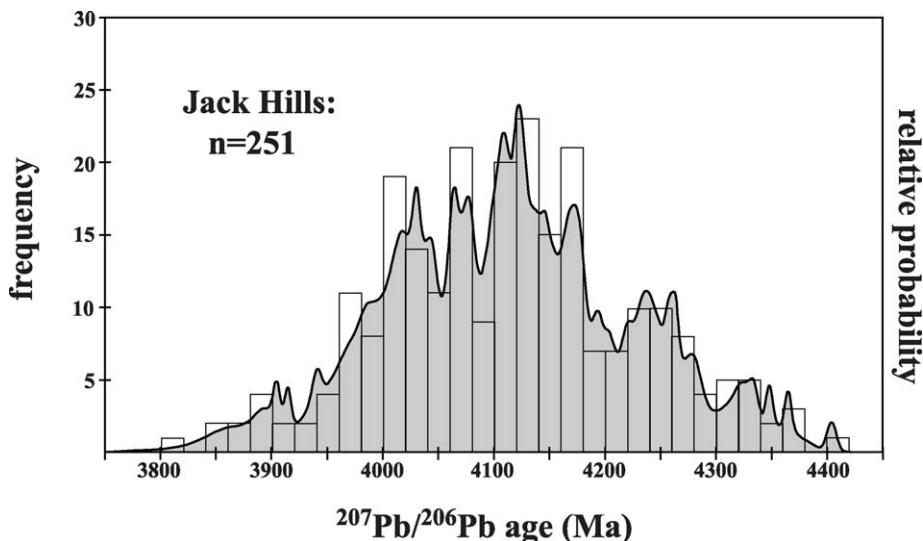
Fig. 2.5-10. Histogram and relative probability plot of 251 concordant ^{207}Pb/^{206}Pb ages for Jack Hills detrital zircons. Each datum is the oldest age assigned to a single zircon that is at least 85% concordant in the U-Pb system. Data sources are as follows: Compston and Pidgeon, 1986 ($n = 17$), Maas et al., 1992 ($n = 8$), Wilde et al., 2001 ($n = 1$), Peck et al., 2001 ($n = 3$), Mojzsis et al., 2001 ($n = 4$); Nelson, 2000 ($n = 2$); Cavosie et al. 2004 ($n = 40$), Crowley et al., 2005 ($n = 45$), Dunn et al., 2005 ($n = 16$), Harrison et al., 2005 ($= 98$), Nemchin et al., 2006 ($n = 8$), Pidgeon and Nemchin, 2006 ($n = 8$). Bin width = 20 My.

tions ranging from -2.5 to -6.0 (ε_{Hf} values re-calculated with λ^{176} value of Schärer et al., 2001) for Jack Hills zircons with ^{207}Pb/^{206}Pb ages from 4140 to 3974 Ma. The paucity of positive εHf composition was cited as evidence that none of the zircons originated from depleted mantle sources, while negative ε_{Hf} compositions indicated that significant crust had formed by ca. 4150 Ma (Amelin et al., 1999). A recent Hf isotope study by Harrison et al. (2005) analyzed even older grains from the Jack Hills, including grains from 4000 to 4370 Ma. Harrison et al. (2005) reported a remarkable range of ε_{Hf} compositions, including positive values to $+15$ and negative values to -7, and interpreted these results to show that continental crust formation and sediment recycling was initiated by ca. 4400 Ma. This interpretation was questioned by Valley et al. (2006) who suggested that such extreme values could be caused in complexly zoned zircons by measurements of Hf in domains (LA-ICP-MS) over 100 times larger than the SHRIMP U-Pb spots, which, moreover, did not always coincide. This suggestion is supported by more recent ε_{Hf} analyses reported by Harrison et al. (2006). In the newer dataset, ε_{Hf} and U-Pb were measured during the same LA-ICP-MS analysis, and by this method, no extreme compositions of ε_{Hf} were reported (Harrison et al., 2006).

2.5-4. EARLY EARTH PROCESSES RECORDED IN JACK HILLS ZIRCONS

2.5-4.1. *Existence of >4300 Ma Terranes*

The large number of reported concordant U-Pb ages from 4400 to 3900 Ma suggests the former existence of terranes comprised at least partially of zircon-bearing igneous rocks. The distribution of published ages for 251 detrital zircons shows that a peak of magmatic activity from 4200 to 4000 Ma dominates the detrital record of Jack Hills zircons (Fig. 2.5-10). In addition, an important population of 17 zircons older than 4300 Ma attests to an earlier period of magmatism that is not as well preserved in the detrital record. The identification of a growing number of >4300 Ma zircons suggests that pre-4300 Ma crust was present on the early Earth, and survived perhaps until the time of deposition of the Jack Hills metasedimentary rocks at ca. 3000 Ma. The location and size of this ancient crust is difficult to estimate. The fact that many of the known >4300 Ma zircons have been found in a single layer at the W74 site (Wilde et al., 2001; Cavosie et al., 2004; Harrison et al., 2005; Nemchin et al., 2006; Pidgeon and Nemchin, 2006) suggests that they were locally derived. However, one 4324 Ma grain found ~1 km east of the W74 site (Cavosie et al., 2004), and a 4352 Ma grain described by Wyche et al. (2004) from Maynard Hills (Fig. 2.5-1), over 300 km from Jack Hills, suggests that the area of >4300 Ma crust may have been either larger or more widespread, in order to contribute to Archean sediments in multiple locations. In addition, Cavosie et al. (2004) documented younger rims on two >4300 Ma zircons, interpreted as magmatic overgrowths, which yielded ages of ca. 3360 Ma and 3690 Ma. These ages match the ages of Archean granitoids in the Narryer Terrane, and suggest that ca. 4300 Ma crustal material may have been incorporated in younger Archean magmas.

2.5-4.2. *The Cooling of Earth's Surface*

Oxygen isotope ratios in zircon record the cooling of Earth's surface and the condensation of the first oceans before ca. 4200 Ma. The global transformation to cooler surface conditions and stable surface waters began the aqueous alteration of crustal rocks at low temperatures, a new process that would fundamentally influence the composition of igneous rocks. Magmatic recycling of this crust, altered at low-temperatures, produced igneous rocks with elevated $\delta^{18}O$ compositions, and was operative as a significant geologic process at ca. 4200 Ma, and possibly earlier. 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 from a Hadean Earth. We propose that this transition at ca. 4200 Ma is a global boundary condition that can be used to define the beginning of the Archean Eon on Earth (Cavosie et al., 2005b).