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Hadean crustal evolution revisited: New constraints from Pb–Hf isotope systematics of the Jack Hills zircons

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ABSTRACT

Detrital zircon crystals from the Jack Hills metasedimentary belt, Western Australia, are the only surviving vestiges of Hadean crust and represent an extraordinary archive into the nature of the early Earth. We report the results of an in situ isotopic study of 68 Jack Hills zircons in which the Hf and Pb isotope ratios were measured concurrently, allowing a better integration of isotope tracer information ($^{176}Hf/^{177}Hf$) with crystallization age ($^{207}Pb/^{206}Pb$). These data are augmented by Hf isotope data from zircons of the surrounding Narryer gneisses (3.65–3.30 Ga) and from Neoarchaean granites that intrude the Jack Hills belt. The detrital zircons define a subchondritic ε_{Hf}–time array that attests to a far simpler evolution for the Hadean Earth than claimed by recent studies. This evolution is consistent with the protracted intra-crustal reworking of an enriched, dominantly mafic protolith that was extracted from primordial mantle at 4.4–4.5 Ga, perhaps during the solidification of a terrestrial magma ocean. There is no evidence for the existence of strongly depleted Hadean mantle, or for juvenile input into the parental magmas to the Jack Hills zircons. This simple Hf isotope evolution is difficult to reconcile with modern plate tectonic processes. Strongly unradiogenic Hf isotope compositions of zircons from several Archaean gneiss terranes, including the Narryer and Acasta gneisses, suggest that Hadean source reservoirs were tapped by granitic magmas throughout the Archaean. This supports the notion of a long-lived and globally extensive Hadean protocrust that may have comprised the nuclei of some Archaean cratons.

1. Introduction

There is mounting evidence for extensive differentiation of the terrestrial planets within the first few million years of their accretion. This process generated crustal material as seen in some meteorite suites (Tera et al., 1997), on the moon (Norman et al. 2003; Nemchin et al., 2008; Edmunson, et al. 2009), and on Mars (Borg et al., 1997). Evidence for early differentiation of the silicate Earth is largely in the form of elevated $^{142}Nd/^{144}Nd$ ratios detected in a range of crustal and mantle-derived rocks (Caro et al., 2003; Boyet and Carlson, 2005; Bennett et al., 2007). These ^{142}Nd anomalies may signal the formation of an incompatible element depleted mantle with superchondritic Sm/Nd within the first 30–75 million years of Earth history (Boyet and Carlson, 2005; Bennett et al., 2007), which predates the extant rock record by 500 million years. The generally unradiogenic hafnium isotope composition of the oldest terrestrial minerals, detrital zircon crystals from the Jack Hills of Western Australia (Froude et al. 1983; Compston and Pidgeon, 1986; Wilde et al., 2001), point to the existence of a complementary 'enriched' reservoir by 4.3 Ga (Amelin et al., 1999) or even earlier (Harrison et al., 2005, 2008; Blichert-Toft and Albarède, 2008). An ancient 'protocrust' formed at or before 4.3 Ga has also been invoked to explain the Pb isotope variability of Archaean cratons (Kamber et al., 2003). Yet, the volume and composition of the Hadean crust, how long it persisted, and under what geodynamic conditions it formed, all remain enigmatic and contentious issues. Scenarios range from a voluminous granitic continental crust shaped by plate tectonics (Armstrong, 1981; Bowring and Housh, 1995; Harrison et al., 2005, 2008), to a single-plate basaltic 'protocrust' (Kamber et al., 2005; Nemchin et al., 2006) that accumulated after solidification of a global magma ocean (Kramers, 2007). Hafnium isotope systematics of the Hadean zircons can help constrain the composition of their protoliths (e.g. Amelin et al., 1999), but this approach is clouded by complex age distributions in the grains and the difficulty of reliably associating Hf isotope ratios with the time of zircon crystallisation. Debate continues

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Table 1
A summary of the concurrent Pb–Hf isotope data for the Jack Hills detrital zircons analysed during this study (OZ, oscillatory zoning; SZ, sector zoning). Analyses with asterisks were used for the regression in Fig. 6. Analytical uncertainties for $\varepsilon_{Hf}(t)$ combine the within-run errors in interference-corrected $^{176}Hf/^{177}Hf$ and $^{176}Lu/^{177}Hf$ and uncertainties in $\lambda^{176}Lu$ and $^{207}Pb/^{206}Pb$ age, the latter also incorporating the reproducibility of bracketing NIST610 analyses and the uncertainty in the Pb isotope composition of this material. No common lead corrections were made. Epsilon Hf values are calculated using the 176Lu decay constant of Söderlund et al. (2004) and relative to the chondritic parameters of Bouvier et al. (2008); these yield ε_{Hf} values for the oldest Jack Hills zircons that are 0.7 units higher than those derived with the CHUR values of Blichert-Toft and Albarède (1997). Full analyses are listed in supplementary Table 2.

Grain/spot	CL zoning	Age (Ma)	±2σ	$\varepsilon_{Hf(t)}$	±2σ
JH17					
1.1	Planar, contorted	4112	8	−3.8	0.9
1.2	Dk, contorted	4078	13	−3.9	1.1
2.1	Dk, vague OZ	4102	21	−1.6	1.1
3.1	Light, OZ**	4101	2	−4.3	0.9
5.1	Contorted	3926	10	−7.2	0.9
6.1	OZ core**	4090	5	−3.8	0.8
6.2	OZ core**	4084	2	−4.1	0.8
6.3	OZ overgrowth**	4090	8	−3.8	0.7
7.1	Light, contorted	3931	23	−7.7	0.9
7.2	Unzoned	3991	17	−7.0	0.7
7.3	Unzoned	4067	3	−4.3	0.7
8.1	Dk, contorted	3967	26	−6.5	0.8
8.2	Dk, contorted	3889	30	−9.1	1.1
9.1	Vague fir−tree	4090	3	−1.9	0.8
9.2	Vague fir-tree	4068	3	−3.2	1.0
10.1	Irreg., contortion	3944	9	−7.6	1.1
10.2	Irregular planar	3873	20	−10.4	0.8
11.1	OZ, SZ**	4073	5	−4.7	0.9
11.2	OZ, SZ**	4061	4	−5.3	0.7
13.1	Dk, contorted	4134	2	−4.5	0.7
13.2	Broad irregular	4129	3	−3.6	0.9
14.1	Dk banded core	4106	1	−2.9	0.6
14.2	Rim, broad zoning	4065	7	−3.9	0.8
15.1	Dk, broad banding	4089	1	−4.0	0.8
16.1	Dk, irreg. banding	3932	6	−5.6	0.8
17.1	Dk, patchy	3869	1	−4.3	0.8
17.2	Dk, patchy	3838	6	−5.4	0.9
18.1	OZ core**	4296	35	−1.4	2.0
18.2	OZ core**	4236	5	−3.0	1.7
19.1	Dk OZ core**	4063	2	−3.8	0.9
19.2	Broad banding	3989	16	−4.0	1.6
20.1	Irreg dk banding	4083	2	−2.0	0.9
20.2	Irreg dk banding	4082	4	−2.7	0.6
21.1	Faint OZ	3957	6	−5.9	0.7
21.2	Unzoned	3910	10	−7.8	1.1
22.1	OZ**	4021	2	−2.8	0.7
23.1	OZ**	4018	8	−3.2	0.8
24.1	Dk, contorted	4102	4	−3.5	0.7
24.2	Contorted zoning	4063	9	−4.3	0.6
25.1	Vague, irreg OZ	3934	9	−7.3	0.7
26.1	Irreg. OZ rim	4015	45	−6.2	0.9
26.2	Dk core, contorted	3841	7	−9.9	0.9
28-1	OZ core**	4139	9	−3.2	0.6
30	Dk, OZ tip**	3886	7	−4.6	0.7
32.1	Dk, OZ fragment**	4153	6	−3.2	1.1
33.1	Irreg OZ rim	4011	4	−3.4	0.6
35.1	OZ core, contorted	4013	9	−5.8	0.6
35.2	Unzoned rim	3982	6	−4.1	1.0
36.1	Dk, relict OZ	4021	3	−3.9	0.9
37.1	Irreg. broad banding	3950	6	−8.1	0.8
38.1	Dk, faint relict OZ	4064	10	−5.7	1.3
39.1	Unzoned	4002	8	−7.4	1.2
40.1	Sharp OZ**	4263	6	−3.6	0.7
40.2	Sharp OZ**	4240	7	−3.8	0.9
40.3	Sharp OZ**	4277	1	−3.0	0.7
41	OZ core, some irreg.**	3910	25	−6.7	0.7
42	Unzoned	3965	32	−7.8	0.9
43	Unzoned	4039	8	−1.8	0.9
44.1	Dark, irregular	4019	3	−1.3	0.7
44.2	OZ rim, patchy	4042	3	−2.2	0.9
JH14					
190.1	Dk core, planar	4295	12	−3.8	1.6

Table 1 (*continued*)

Grain/spot	CL zoning	Age (Ma)	±2σ	$\varepsilon_{Hf(t)}$	±2σ
JH14					
190.2	Unzoned overgrowth	4171	5	−4.1	0.8
159.1	Dk OZ core	4174	21	−3.9	2.2
159.2	OZ rim	3414	9	−10.8	0.5
175.1	Sharp OZ, core**	4098	12	−4.0	1.1
155.1	Broad OZ core**	4015	4	−2.9	1.1
94.1	Dk core, convolute	3938	25	−5.3	1.2
91.1	Faint OZ	4071	11	−3.2	0.9
84.1	Broad banding	4122	7	−3.8	2.7
82.1	Broad banding	3929	24	−5.9	0.4
102.1	Dk, irreg zoned	4138	11	−3.4	0.8
117.1	Remant OZ core	4255	11	−2.8	1.8
117.2	Dk overgrowth	3930	45	−4.6	0.7
117.3	Tip, irregular zoning	4010	20	−5.9	0.7
118.1	Bright, irreg. zoning	3986	4	−4.3	1.1
149.1	Broad banding	4065	4	−2.5	1.3
113	Broad, irreg. banding	4004	4	−4.2	0.8
8	Irreg. OZ	4100	30	−6.4	1.0
33	Remnant, irreg. OZ	4225	4	−3.2	0.5
206.2	Broadly OZ rim	3369	51	−9.1	2.0
292.1	Dark, OZ**	4053	6	−2.3	1.3
128	Broad banding	3744	19	−6.8	2.3
148	Broad irreg banding	3989	19	−4.2	0.7
79	Irreg broad banding	4094	4	−3.7	0.7
32	Unzoned	3960	3	−7.8	0.6
68	Broad, irreg banding	3998	13	−6.0	1.0
218	Dark, OZ**	4017	1	−4.2	1.2
216	Bright, core	4017	1	−5.3	0.8
310	Dark core, contorted	4004	4	−5.0	0.8
309	Core, remant OZ	3801	50	−5.7	0.8
206	OZ core	3750	93	−10.3	2.3
234	Dark, fine OZ**	3903	11	−5.9	0.9
247	Faint, fine OZ	3981	3	−2.9	0.8
305	Irreg. planar zoning	3866	23	−5.1	1.3
276-1	OZ core**	4069	3	−2.3	0.9
276-2	OZ core**	4026	5	−4.5	0.9

on whether the extreme Hf isotope heterogeneity reported for the Jack Hills zircons reflects complex crust–mantle interaction and recycling processes consistent with plate tectonics (Harrison et al., 2005, 2008) or is simply an artefact of incorrect age assignment (Valley et al., 2006).

Here, we report the results of an isotopic study of the Jack Hills detrital zircons where the Pb and Hf isotope ratios are measured by laser ablation MC-ICP-MS concurrently with high spatial resolution (40–50 µm spots), allowing a more robust integration of age and isotope tracer information (Woodhead et al., 2004; Kemp et al., 2009a). These data are augmented by the first Hf isotope data, obtained by both laser ablation and on purified solutions, from zircons of meta-igneous rocks (3.65–2.65 Ga) that surround the Jack Hills belt. The goal is to evaluate the degree of Hf isotope heterogeneity in the Hadean Earth, constrain the timing of crust formation and the composition of this crust, and to test whether Hadean crustal sources were sampled by younger magmas. The new data define a much simpler Hf isotope evolution than seen in previous studies of the Jack Hills zircons. These data attest to the formation of a dominantly mafic protocrust at 4.4–4.5 Ga that underwent repeated remelting during the Hadean period.

2. Sample details

The ~70 km-long Jack Hills metasedimentary belt lies within the Narryer terrane near the northern periphery of the Archaean Yilgarn Craton, Western Australia (Wilde and Spaggiari, 2007). The belt comprises a multiply deformed succession of clastic metasedimentary rocks, chert and banded iron formations and mafic–ultramafic lenses overprinted by greenschist to low amphibolite facies metamorphism (Spaggiari et al., 2007). These units are in tectonic contact with Eo- to Mesoarchaean granitic gneisses (the Narryer Gneiss Complex, Kinny et al., 1988; Pidgeon and Wilde, 1998), and are intruded to the south

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Table 2
Summary of the Hf isotope composition of zircons from the Jack Hills meta-igneous rocks. Epsilon Hf values are computed at the igneous crystallisation ages inferred by Pidgeon and Wilde (1998). Analytical uncertainties were calculated as for Table 1. Laser ablation data are restricted to grains with concordant to near-concordant (U–Th)–Pb isotope systems, and to those with SHRIMP analyses that plot along chords with well-constrained concordia intercepts. Full analyses are given in Supplementary Table 4.

Grain	Mode	Age (Ma)	±2σ	$\varepsilon_{Hf(t)}$	±2σ
W63 trondjemite					
1.1	LA	3282	8	−6.7	0.5
2.1	LA	3269	12	−6.4	0.5
3.1	LA	3500	6	−3.4	0.6
3.1r	LA	3500	6	−3.9	0.5
4.1	LA	3645	8	−5.8	0.8
5.1	LA	3652	12	−6.1	0.5
5.1b	LA	3652	12	−5.3	0.5
5.5	LA	3309	4	−8.5	0.8
6.2	LA	3027	20	−12.3	0.5
7.1	LA	3756	20	−2.4	0.8
7.2	LA	3756	14	−1.9	1.1
9.1	LA	3278	8	−6.3	0.5
10.1	LA	3602	4	−2.5	0.6
12.1	LA	3433	30	−11.0	0.4
14.1	LA	3266	8	−6.2	0.4
15.1	LA	3504	6	−1.4	0.6
15.4	LA	3474	6	−2.4	0.6
16.1	LA	3355	4	−4.4	0.8
16.3	LA	3244	4	−6.5	0.7
W29 tonalite					
1.1	LA	3500	39	−5.3	1.9
2.1	LA	3500	29	−4.6	2.2
2.3	LA	3523	19	−3.3	1.7
3.1	LA	3621	13	−2.6	0.8
6.1	LA	3608	13	−2.1	0.5
7.2	LA	3586	7	−2.6	0.4
9.1	LA	3617	20	−1.4	0.5
9.1b	LA	3617	20	−1.5	0.7
W65 porphyritic granodiorite					
3.1	LA	3408	12	−5.3	0.9
4.1	LA	3454	16	−4.9	0.5
11.1	LA	3574	14	−3.3	0.6
W35 granodiorite					
1.1	LA	3516	32	−4.3	0.7
3.1	LA	3516	32	−1.7	0.8
6.1	LA	3516	32	−2.1	0.7
7.1	LA	3516	32	−2.5	0.6
8.1	LA	3516	32	−1.7	0.9
W61 porphyritic granite					
1.1	LA	3290	20	−5.8	0.5
6.1	LA	3290	20	−6.7	0.8
W61 porphyritic granite					
50.1	LA	3290	20	−6.4	0.9
3.1	LA	3290	20	−6.2	0.9
51.1	LA	3290	20	−5.8	0.9
52.1	LA	3290	20	−6.5	0.5
g2	SOLN	3290	20	−4.8	0.1
g3	SOLN	3290	20	−5.7	0.1
g4	SOLN	3290	20	−4.7	0.1
W62 monzogranite					
1.2	LA	3611	4	−2.7	0.5
3.1	LA	2654	14	−8.2	0.5
4.1	LA	2654	14	−8.5	0.6
5.1	LA	2654	14	−8.4	0.7
6.1	LA	2654	14	−8.5	0.5
6.2	LA	2654	14	−7.9	0.5
10.1	LA	2654	14	−7.9	0.5
12.1	LA	2654	14	−8.8	0.6
13.1	LA	2654	14	−8.1	0.7
14.1	LA	2654	14	−8.2	0.5
14.3	LA	2654	14	−7.8	0.4
18.1	LA	2654	14	−8.4	0.8

Table 2 (*continued*)

Grain	Mode	Age (Ma)	±2σ	$\varepsilon_{Hf(t)}$	±2σ
W62 monzogranite					
19.1	LA	2654	14	−8.3	0.5
21.1	LA	2654	14	−8.3	0.7
12.2	LA	2654	14	−8.8	0.4
13.2	LA	2654	14	−8.5	0.4
14.2	LA	2654	14	−8.3	0.6
50.1	LA	2654	14	−8.2	0.6
g7	SOLN	2654	14	−8.1	0.2
g8	SOLN	2654	14	−7.1	0.1
g9	SOLN	2654	14	−7.9	0.3
g9r	SOLN	2654	14	−8.1	0.2
W34 monzogranite					
1.1	LA	2643	14	−11.1	1.1
2.2	LA	2643	14	−13.9	0.7
2.2	LA	2643	14	−14.2	0.8
3.1	LA	2643	14	−8.9	1.0
4.1	LA	2643	14	−12.5	0.7
6.2	LA	2643	14	−14.9	0.6
8.1	LA	2643	14	−10.4	1.2
10.1	LA	2643	14	−13.9	1.3
g2	SOLN	2643	14	−14.8	0.3
g3	SOLN	2643	14	−12.7	0.2
g4	SOLN	2643	14	−13.1	0.3

by less deformed Neoarchaean granites. The detrital zircons analysed in this study are from meta-conglomerate samples JH14 and JH17 obtained from the same outcrop identified by Compston and Pidgeon (1986) that yielded zircons with $^{207}Pb/^{206}Pb$ ages up to ~4.4 Ga (Wilde et al., 2001). The depositional age of these conglomerates is constrained by a metamorphic monazite age of ~2.65 Ga and the age of the youngest dated detrital zircon at ~3.05 Ga (Rasmussen et al., 2010). Detrital zircons from this locality (the 'discovery site', Wilde and Spaggiari, 2007) have also been studied by Amelin et al. (1999), Harrison et al. (2005, 2008), Cavosie et al. (2004, 2005) and Crowley et al. (2005). Zircon crystals from JH14 and JH17 were previously analysed for (U–Th)–Pb isotopes by SHRIMP II (Curtin University, Perth) and O isotopes by Cameca ims 1270 (Stockholm). A subset of these data were published by Nemchin et al. (2006). SHRIMP $^{207}Pb/^{206}Pb$ ages range from 4.35 Ga to 3.38 Ga (Supplementary Table 1). Most zircons have concordant U–Pb ages, with only 10 analyses >10% discordant. The $\delta^{18}O$ values for individual spots vary from 3.8 ‰ to 7.7 ‰ (average 6.1 ± 0.7‰, 1 SD), overlapping the range reported by Cavosie et al. (2005), Trail et al. (2007) and Harrison et al. (2008).

The zircon geochronology of the Narryer gneisses has been investigated by a number of workers (e.g. Kinny et al., 1988; Kinny and Nutman, 1996; Pidgeon and Wilde, 1998). We have analysed Hf isotopes in zircons from the samples of Pidgeon and Wilde (1998), which were collected from outcrops adjacent to the Jack Hills belt. These rocks include tonalite–trondhjemite–granodiorite (TTG) gneisses (W29, W63, and W65), porphyritic meta-granite (W61), meta-granodiorite (W35), and 'post-tectonic' monzogranites (W34 and W62). Zircons of the TTG gneisses yield complicated (U–Th)–Pb age spectra spanning 3.75–3.30 Ga that attest to a protracted thermal evolution for the host rocks (Pidgeon and Wilde, 1998). Other samples have simpler zircon age distributions. Granodiorite W35 is dominated by zircons with $^{207}Pb/^{206}Pb$ ages near 3.5 Ga, considered to date magmatic crystallisation. Ion microprobe data for porphyritic meta-granite W61 and the monzogranites are dispersed along discordia arrays with upper intercept ages of ~3.30 Ga and 2.65 Ga, respectively, also taken to reflect igneous emplacement (Pidgeon and Wilde, 1998).

3. Analytical techniques

The isotope ratio measurements reported here were undertaken on polished, sectioned zircon crystals in the original epoxy mounts of

Nemchin et al. (2006) (Jack Hills meta-conglomerate) and Pidgeon and Wilde (1998) (Jack Hills meta-igneous rocks), as guided by cathodoluminescence images and ion microprobe age data.

The concurrent Pb–Hf isotope data (Table 1) were acquired with a Thermo-Scientific Neptune multi-collector ICP-MS attached to a New Wave 193 nm ArF laser at the University of Bristol, targeting the same area of the zircons that were previously dated by SHRIMP and analysed for oxygen isotopes. The analytical protocols are outlined in Kemp et al. (2009a). In brief, analysis involved 18 measurement cycles alternating between Lu–Yb–Hf (2 second integration time) and Pb isotopes (1 second integration time), with 1.5 seconds settling time between magnet jumps. Either 40 µm or 50 µm laser beam diameters were employed at a 4 Hz laser repetition rate. These conditions thus differ from those of Harrison et al. (2008), who used larger spot sizes (62–82 µm beam diameter) and a less rapid alternation between Hf and Pb isotope measurements (10 s Hf, 3 s delay, 3 s Pb, 3 s delay). Corrections for instrumental mass fractionation of the Pb isotopes (<0.5%) were derived by periodic analysis of the silicate glass NIST610 (^{207}Pb/^{206}Pb = 0.90986 ± 5, Baker et al., 2004). This procedure is justified by agreement between the accepted ^{207}Pb/^{206}Pb ages of zircon standards and those determined by concurrent Pb–Hf isotope analysis (Woodhead et al., 2004; Kemp et al., 2009a). Pb–Hf isotope data quality was monitored by the frequent analysis of reference zircons 91500 (1065 Ma), FC1 (1099 Ma) and QGNG (1852 Ma) during each analytical session (Supplementary Table 3). FC1 has the highest ^{176}Yb/^{177}Hf ratios and thus provides the best indication of the veracity of ^{176}Yb and ^{176}Lu interference corrections on ^{176}Hf; these ^{176}Yb/^{177}Hf values exceed those measured from 88% of the Jack Hills detrital zircons in our dataset. The mean ^{176}Hf/^{177}Hf ratios (±2 SD) determined from the standard zircons was 0.282305 ± 20 (n = 24) for 91500, 0.281608 ± 20 (n = 9) for QGNG and 0.282180 ± 26 (n = 28) for FC1, indistinguishable from the solution values (Woodhead and Hergt, 2005). Accurate ^{176}Lu/^{177}Hf ratios are important for calculation of the correct initial ^{176}Hf/^{177}Hf given the antiquity of the Jack Hills zircons. The ^{176}Lu/^{177}Hf ratios measured from 91500 (0.00029 ± 3), QGNG (0.00074 ± 9) and FC1 (0.00123 ± 21) agree with the solution values (0.00031, 0.00073 and 0.00126, respectively) for these zircons (Woodhead and Hergt, 2005).

The Hf isotope compositions of zircons from the Jack Hills meta-igneous rocks were acquired by both laser ablation and on purified solutions (Table 2). The laser data were obtained with a Thermo-Scientific Neptune and Coherent GeoLas 193 nm ArF laser at James Cook University. Standard zircons analysed during the study yielded mean ^{176}Hf/^{177}Hf values (±2 SD) of 0.282504 ± 16 for Mud Tank (n = 19), 0.282685 ± 22 (n = 42) for Temora 2 and 0.282175 ± 19 for FC1 (n = 61) (Supplementary Table 5). Sample zircons were analysed directly over the SHRIMP pits, or (in the case of repolishing) in the same CL-defined growth domain where the age data were previously acquired.

The solution Lu–Hf isotope data were obtained by dissolution of single zircon crystals from samples that showed the simplest zircon age distributions. Optically clear grains as free as possible from cracks and inclusions were loaded into individual mini capsules for acid digestion according to the procedure of Parrish (1987). Solutions were spiked with a mixed ^{176}Lu–^{180}Hf tracer and purified for Hf and HREE by single-stage column chemistry (Dowex AG50W-X12 resin) prior to analysis with a Thermo-Scientific Neptune at Washington State University (details in Goodge and Vervoort 2006). Small chips of Temora 2 and 91500 digested for quality control yielded ^{176}Hf/^{177}Hf ratios of 0.282691 ± 8 and 0.282303 ± 2 (2 SE), respectively, identical to accepted values (Woodhead and Hergt, 2005).

4. Results

4.1. Jack Hills detrital zircons

Ninety-six Pb–Hf isotope analyses were obtained from 68 zircons in August 2007. Multiple analyses were conducted on the largest grains, or those for which SHRIMP analysis revealed significant age variation. In the case of within-run age or Hf isotope zoning the initial Hf isotope compositions were calculated using the ^{207}Pb/^{206}Pb age isolated from the same part of the signal.

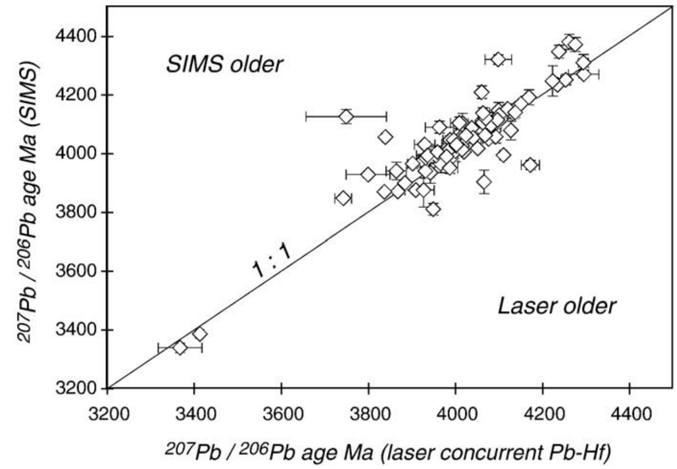

Fig. 1. Comparison between ^{207}Pb/^{206}Pb ages measured by ion microprobe (SHRIMP II) and those determined from the same part of the zircon by concurrent Pb–Hf isotope analysis (laser ablation multi-collector ICPMS). Error bars on this and subsequent figures are at 2σ. SHRIMP (U–Th)–Pb isotope analyses for all grains are provided in Supplementary Table 1.

4.1.1. Intra-grain Pb and Hf isotope variations

Overall, the ^{207}Pb/^{206}Pb ages measured by laser ablation agree reasonably well with those determined by SHRIMP (Fig. 1). The ICP-MS ages tend to be younger, however, as also reported by Harrison et al. (2008) and Blichert-Toft and Albarède (2008). One possible explanation is that the greater volume of material excavated by the laser increases the likelihood of sampling younger zircon overgrowths or modified domains that have lost radiogenic lead. Evidence for this can be found in time-resolved ^{207}Pb/^{206}Pb variations, where a systematic decrease in apparent age with depth in the crystal is sometimes observed (Fig. 2). In extreme cases this age shift exceeds 400 Ma. Pronounced core-rim decreases in ^{207}Pb/^{206}Pb ages in Jack Hills zircons over <15 µm have been detected by ion microprobe depth profiling, and attributed to Pb loss during ancient thermal events (Trail et al., 2007).

Within-run decreases in ^{207}Pb/^{206}Pb ages are generally not accompanied by changes in ^{176}Hf/^{177}Hf (Fig. 2), consistent with the younger apparent ages being due to ancient Pb loss. However, large excursions in ^{176}Hf/^{177}Hf do occur in some grains. For example, ^{176}Hf/^{177}Hf ratios in grain JH14-102 increase markedly from ~0.2801 to 0.2805, as ^{207}Pb/^{206}Pb ages fall from 4139 Ma in the core to 3700 Ma towards the rim (Fig. 2A). This corresponds to a shift of 15 ε_{Hf} units at the same crystallisation age. These Pb–Hf isotope profiles reflect the sampling of relatively radiogenic Hf from younger zircon overgrowths.

The Hf isotope heterogeneity of individual zircons can also be assessed through multiple spot analyses. Fig. 3 shows that the ^{176}Hf/^{177}Hf ratio obtained from different parts of the same grain are usually equivalent within analytical uncertainty, where the age difference between spots is small. This implies closed system behaviour for the Hf isotopes during crystallisation of the Jack Hills zircons. Four examples to the contrary have younger overgrowths with much higher ^{176}Hf/^{177}Hf. These data, together with the within-run evidence from JH14-102, indicate that some younger age zones in the Jack Hills detrital zircons incorporated relatively radiogenic Hf, either from new magmatic additions or remobilized from the corresponding rock prior to removal from the protolith. This underlines the potential for obtaining mixed (geologically meaningless) ages and/or Hf isotope

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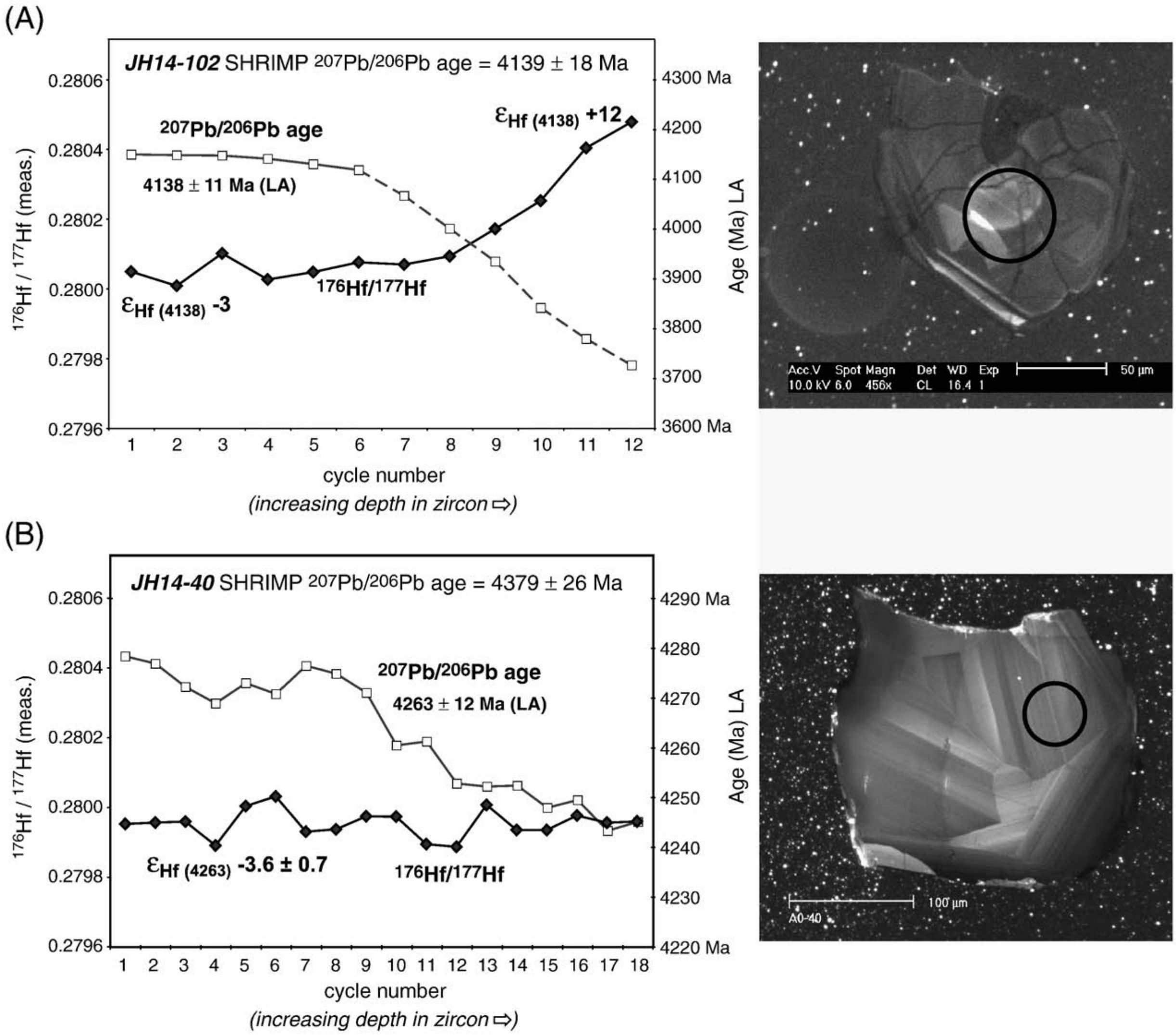

Fig. 2. Time-resolved isotope ratio signals shown by two Jack Hills detrital zircons of this study that exhibit contrasting Pb–Hf isotope zoning. The analysis sites are indicated on the corresponding CL images. See text for explanation (LA = laser ablation).

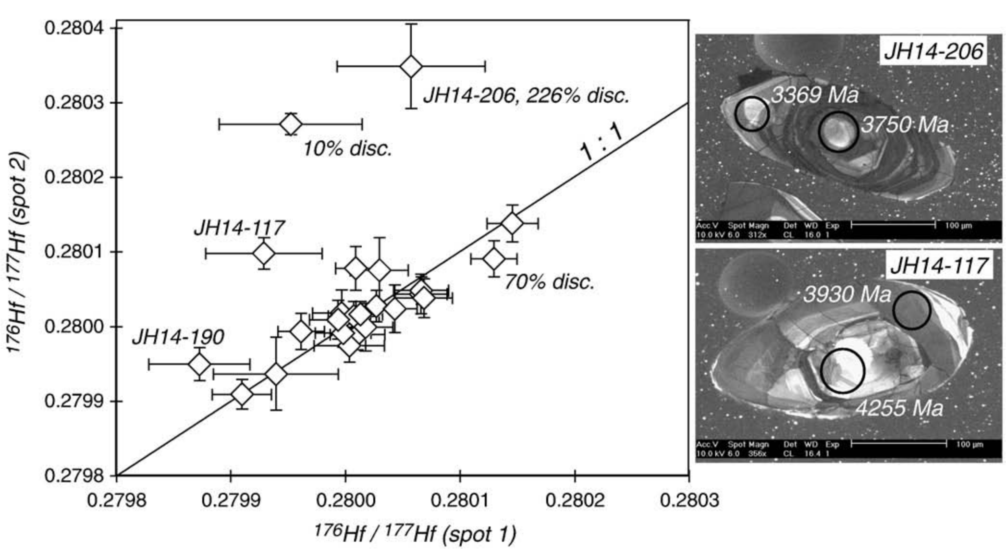

Fig. 3. Comparison of the Hf isotope ratios obtained by multiple spot analysis of the same zircon grain (corrected for radiogenic ingrowth using the concurrently measured $^{207}Pb/^{206}Pb$ ages). The percentage of age discordance (% disc.) is calculated from the SHRIMP U–Pb data as: 100 x [($^{207}Pb/^{206}Pb$ age/$^{206}Pb/^{238}U$ age) − 1]. The relatively radiogenic data from the second analytical site in four grains are from younger, transgressive overgrowths. The CL images are labelled with $^{207}Pb/^{206}Pb$ ages determined by concurrent Pb–Hf isotope analysis.

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compositions by both laser ablation and solution analysis in complex zircons where the age of the analysed volume is poorly constrained.

4.1.2. Hf isotope-time variations

Fig. 4B summarises the Pb–Hf isotope data obtained from the Jack Hills detrital zircons during this study, in which initial Hf isotope compositions are computed at the concurrently measured $^{207}Pb/^{206}Pb$ age. All data points have subchondritic initial $^{176}Hf/^{177}Hf$ and collectively define a sloping, wedge-shaped ε_{Hf}–time array that originates from near CHUR at 4.4–4.5 Ga and widens with decreasing age. This array is bracketed between the evolution lines defined by a putative upper crustal 'granitic' reservoir, and a reservoir with a higher $^{176}Lu/^{177}Hf$ similar to that of mafic crust, both extracted from a chondritic source at 4.5 Ga. The ε_{Hf} values from zircons with discordant U–Pb ages fall within the main array (Supplementary Fig. 1), as might be expected if discordance was due to recent Pb loss, whereby the $^{207}Pb/^{206}Pb$ age is a reasonable proxy for the time of zircon formation. The position of data points in the ε_{Hf}–time diagram is independent of their Yb/Hf ratios, and thus of the magnitude of the isobaric Lu–Yb interference correction (Supplementary Fig. 2).

We observe no systematic correlation between ε_{Hf} and oxygen isotope composition (Supplementary Fig. 3), as previously noted by Harrison et al. (2008). This could reflect the reworking of a diverse assemblage of crustal rocks with different $\delta^{18}O$ values, reflecting variable exchange of oxygen with liquid water (Peck et al., 2001; Wilde et al. 2001; Mojzsis et al., 2001; Valley et al. 2002; Cavosie et al. 2005; Harrison et al. 2008). Alternatively, some of the $\delta^{18}O$ variation may be due to subsolidus alteration (Hoskin, 2005; Nemchin et al. 2006), obscuring any primary relationship between ε_{Hf} and $\delta^{18}O$.

The Hf isotope compositions of the Jack Hills zircons measured during this study show excellent agreement with the whole-grain solution data of Amelin et al. (1999) (Fig. 4). Our dataset is also broadly consistent with those published by Harrison et al. (2005, 2008) and Blichert-Toft and Albarède (2008), but differs in two important respects — (1) none of our Hf isotope compositions are sufficiently unradiogenic as to plot close to the 'forbidden region' that would require formation from CHUR of a terrestrial reservoir with Lu/Hf approaching zero by 4.5 Ga (cf. Harrison et al., 2008); and (2) there are no positive ε_{Hf} values in our dataset, whereas these comprise ~35% and ~20% of the data reported by Harrison et al. (2005) and Blichert-Toft and Albarède (2008), respectively. The latter observation is particularly significant because positive ε_{Hf} deviations in Hadean zircons have been used to argue for the existence of depleted mantle domains that comprised a 'substantial fraction of the silicate Earth' (Harrison et al., 2005) and which formed in response to the extraction of a voluminous primordial crust. The Hf isotope compositions in these previous studies were, however, obtained either by laser ablation using large beam sizes (62–81 μm; Harrison et al., 2005), or by whole grain dissolution (Harrison et al., 2005; Blichert-Toft and Albarède, 2008). Both approaches, when applied to complexly zoned zircons, are susceptible to mixed sampling of domains with disparate age and $^{176}Hf/^{177}Hf$, which can produce spurious positive ε_{Hf} values, as we have demonstrated above.

One relatively subtle feature of Fig. 4B that is also discernable within the datasets of Harrison et al. (2008) and Blichert-Toft and Albarède (2008) concerns a bulging of the ε_{Hf}–time array towards slightly more radiogenic values between 4.1 and 4.0 Ga. The significance of this feature is explored below.

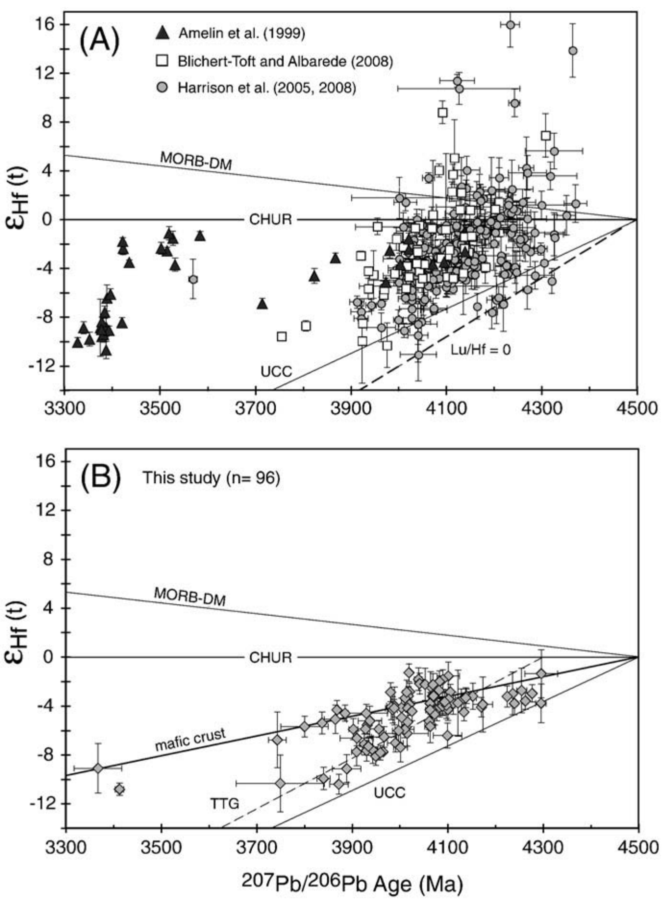

Fig. 4. Hf isotope evolution plots for the Jack Hills detrital zircons comparing (A) previously published datasets (Amelin et al. 1999; Harrison et al. 2005, 2008; Blichert-Toft and Albarède 2008) with (B) data obtained during this study by concurrent Pb–Hf isotope analysis (ε_{Hf} values on both panels were computed with the CHUR parameters of Bouvier et al. 2008). Plots are shown at the same scale to facilitate comparison. The isotope trajectories of putative upper continental crust ($^{176}Lu/^{177}Hf = 0.008$; Rudnick and Gao, 2003), mafic crust ($^{176}Lu/^{177}Hf = 0.022$) and TTG reservoirs (formed at 4.3 Ga with $^{176}Lu/^{177}Hf = 0.005$, Blichert-Toft and Albarède, 2008) are shown for reference, assuming silicate Earth differentiation at ~4.5 Ga (Bennett et al., 2007). The dashed line plots the Hf ratios of a reservoir formed from CHUR at 4.5 Ga with Lu/Hf~0. The model depleted mantle curve (MORB-DM), similar to that of Vervoort and Blichert-Toft (1999), was derived by back calculating the isotope composition of mean modern MORB and taking $\varepsilon_{Hf} = 0$ at 4.5 Ga. Note that Fig. 4B includes data from 10 zircon analyses with >10% U–Pb discordance.

4.2. Jack Hills meta-igneous zircons

The Hf isotope compositions of zircons from the meta-igneous rocks are plotted on Fig. 5 as a function of SHRIMP $^{207}Pb/^{206}Pb$ age. Despite wholly negative ε_{Hf} values (−1.4 to −14.9), most analyses have more radiogenic $^{176}Hf/^{177}Hf$ compared to Jack Hills detrital zircons of similar age, and define a broad band that plots above the detrital zircon data array. The evolution line of 4.5 Ga mafic crust demarcates the lower limit of this band. Several data clusters are also present. A group of points around 3.62–3.59 Ga with ε_{Hf} −2 to −3 correspond to older cores in zircons of the TTG gneisses, and an inherited core in monzogranite W61. A 3.5 Ga age population in zircons from the gneisses has ε_{Hf} −2 to −5. Laser ablation data for the 3.29 Ga zircon in porphyritic granite W61 yields ε_{Hf} -6.2 ± 0.8 (average, 2 SD), within error of solution data from these zircons ($\varepsilon_{Hf} = -5.1 \pm 0.9$). Monzogranite W62 appears to have homogenous zircon ε_{Hf} at the crystallisation age of 2.65 Ga (laser ablation: -8.3 ± 0.6, $n = 17$; solution: -7.8 ± 0.8, $n = 4$). Zircons of the other Neoarchaean monzogranite (W34) have more variable Hf isotope compositions (ε_{Hf} = − 9 to −15), where the solution data occupies the lower end of this range (ε_{Hf} = −12.7 to −14.8). These are amongst the least radiogenic Hf isotope compositions reported for zircons of this age.

Two key points emerge from Fig. 5. First, the negative to strongly negative ε_{Hf} values of the Narryer gneiss zircons suggest formation

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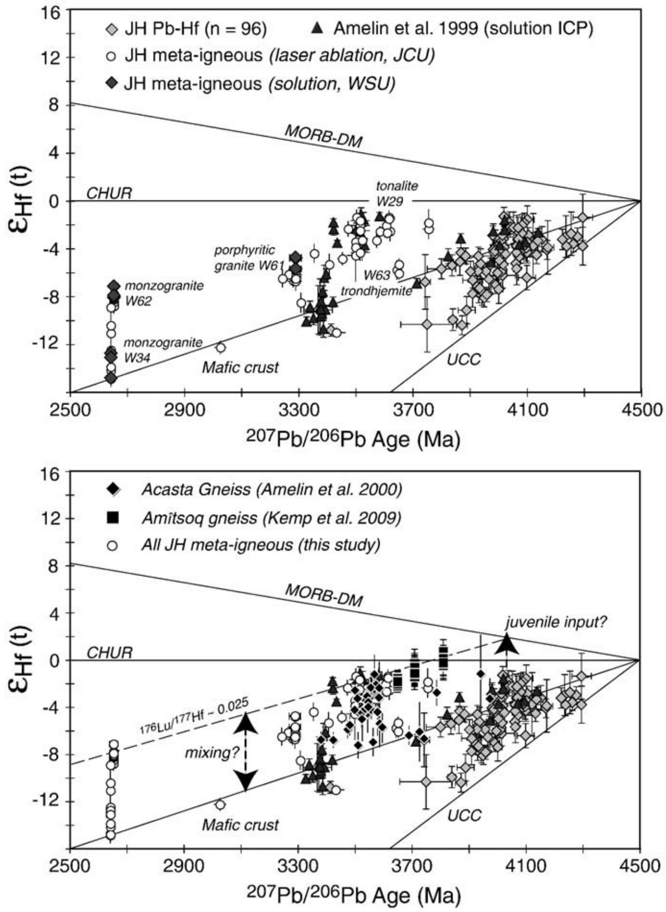

Fig. 5. (A) Hf isotope composition of zircons from the Jack Hills meta-igneous rocks in comparison to data from the Jack Hills detrital zircons (this study and Amelin et al. 1999). (B) the same plot but including Hf isotope data from Greenland (laser ablation data of Kemp et al., 2009a,b) and the Acasta Gneisses (data from Amelin et al. 1999, 2000).

of the igneous protoliths by remelting older crustal rocks, rather than by differentiation from juvenile magmas. These source reservoirs were, however, heterogeneous in age and Hf isotope composition. For example, trondhjemite W63 contains 3.6 Ga zircon cores with ε_{Hf} near −2, but also has 3.65 Ga cores with distinctly less radiogenic Hf (ε_{Hf} −5 to −6). The spread of ε_{Hf} values shown by the 3.5 Ga zircons (4 ε_{Hf} units) and zircons of monzogranite W34 (6 ε_{Hf} units) exceeds the ^{176}Hf/^{177}Hf reproducibility of the zircon standards (~2 ε_{Hf} units in Temora 2) and may suggest heterogeneous magma sources. The strikingly unradiogenic ^{176}Hf/^{177}Hf of zircons in monzogranite W34, confirmed by solution analysis, requires an ancient (Mesoarchaean or older) mantle extraction age for one of the source components.

Second, although the Jack Hills meta-igneous zircons generally plot above the Hf evolutionary trend defined by the Hadean detrital zircons, they do overlap the Hf isotope fields of the younger (<3.7 Ga) detrital zircon populations documented by Amelin et al. (1999) (Fig. 5). This is permissive evidence for the Mesoarchaean detrital populations in the Jack Hills conglomerate having been eroded from the surrounding Narryer gneisses (see Cavosie et al., 2004). This could imply that the source of the Hadean zircons was exposed at Earth's surface along with the Mesoarchaean gneisses during deposition of the Jack Hills conglomerate, although this material may have been sedimentary detritus derived from Hadean rocks, rather than the crystalline Hadean rocks themselves.

5. Discussion

5.1. Composition of early Earth reservoirs

The data in Fig. 4B are consistent with crystallisation of the Jack Hills detrital zircons from melts derived from older material with subchondritic Lu/Hf (i.e. ^{176}Lu/^{177}Hf<0.0336). This, coupled with the antiquity of the grains, their felsic mineral inclusion assemblages and elevated ^{18}O/^{16}O, testifies to the existence of Hadean crust by at least 4.3 Ga (Wilde et al., 2001; Harrison et al., 2005, 2008). Moreover, the unradiogenic ^{176}Hf/^{177}Hf values of the oldest zircons, and the convergence of the ε_{Hf}–time array towards CHUR at 4.4–4.5 Ga (Fig. 4B), suggests that this source reservoir separated from a chondritic mantle very soon (perhaps <100 Ma) after planetary accretion (e.g. Harrison et al., 2005, 2008).

Establishing the bulk composition of the Hadean crust is critical for geodynamic models of early Earth differentiation. For example, a voluminous continental-type crust at 4.4–4.5 Ga as proposed by Harrison et al. (2005) might imply the operation of plate subduction processes. In contrast, a long-lived and dominantly mafic to ultramafic protocrust (e.g. Galer and Goldstein, 1991; Kamber et al. 2005) could only endure on the Earth's surface in the absence of subduction, thus militating against Hadean plate tectonics. Notably, the most recent candidate for extant Hadean crust, an amphibolite from the Nuvvuagittuq greenstone belt in northern Québec (O'Neil et al. 2008), is of basaltic affinity.

Well-defined arrays on Hf evolution diagrams, such as shown by data of this study, offer an empirical means to constrain the average composition of the source to the melts from which the Jack Hills zircons crystallised, and the time that this source separated from the mantle. These ε_{Hf}–time arrays indicate that the parental magmas formed by the repeated reworking of a source reservoir with broadly similar ^{176}Lu/^{177}Hf. The approximate ^{176}Lu/^{177}Hf value of this reservoir can be determined from the slope of the ε_{Hf}–time array. Amelin et al. (1999) used this approach to derive a ^{176}Lu/^{177}Hf value of ~0.022 from their Jack Hills zircon dataset, and suggested that this typifies a mafic source.

Regressing all data points (weighted by analytical error) on Fig. 4B yields a slope (0.011 ± 0.002) corresponding to an average ^{176}Lu/^{177}Hf of 0.018 ± 0.003 that intersects CHUR at 4.47 ± 0.09 Ga (95% confidence, MSWD = 11.7; calculated using *Isoplot*, Ludwig, 2001). The large MSWD, however, suggests that the assumption of a single source extracted from the mantle at one time is not tenable. The scatter within the array could be reconciled by the melting of mixed sources with the same mantle extraction age but with different ^{176}Lu/^{177}Hf ratios. Mafic crust and a differentiated progenitor with lower ^{176}Lu/^{177}Hf similar to that of granitic crust are plausible end-member source components, given that the evolutionary lines of these reservoirs bracket the Jack Hills zircon ε_{Hf}–time array. In a mixing scenario the dispersion in the Jack Hills array reflects the divergent trajectories of the source reservoirs, thus increasing the isotope heterogeneity within the derivative melts with time.

An important consideration in this interpretation is whether the low ε_{Hf} points that plot near the UCC line on Fig. 4B are artefacts of underestimation of the crystallisation age. This is particularly pertinent as many zircons in the dataset have variable intracrystalline ^{207}Pb/^{206}Pb ages and show evidence for recrystallisation accompanied by obliteration of igneous oscillatory zoning, features that are consistent with ancient Pb loss (Nemchin et al., 2006). Using ages that are too young results in lower calculated ε_{Hf} values, producing a steeper, spurious crustal evolutionary trend on an ε_{Hf}–time diagram (see Kemp et al., 2009a).

This ambiguity can be minimised by focussing on data from zircons with unmodified igneous microstructures and that show the least evidence for isotope disturbance. Rigorous application of the criteria of Nemchin et al. (2006) identifies only 1 grain in our dataset that can be confidently ascribed a wholly igneous origin, JH17-40, with an average SHRIMP $^{207}Pb/^{206}Pb$ age of 4.36 ± 0.02 Ga (Nemchin et al. 2006). Three Pb–Hf isotope analyses of this zircon yielded identical $\varepsilon_{Hf\,(4.36\,Ga)}$ values of −1.3 ± 0.7, −1.0 ± 0.9 and −1.0 ± 0.7 (average −1.1 ± 0.4 at 2 SD). The permissible CHUR extraction ages for the sources of this zircon fall between 4.41 ±0.02 Ga (for $^{176}Lu/^{177}Hf = 0$) and the time of initial silicate Earth differentiation, taken as ~4.5 Ga (Bennett et al., 2007). The latter yields a source $^{176}Lu/^{177}Hf$ of ~0.025, similar to that of modern MORB. These calculations require that the protolith to the magma from which JH17-40 crystallised be generated by at least 4.41 Ga.

Seventeen other zircons in our study preserve CL-zoning characteristics broadly consistent with growth from melt with minimal post-crystallisation disturbance. The ε_{Hf} values for these grains were calculated using the oldest $^{207}Pb/^{206}Pb$ age determined for each spot by either SHRIMP or laser ablation, assuming that this is the closest estimate of the true crystallisation age. Collectively, these data define a tighter array than shown by the unfiltered dataset (slope = 0.009 ± 0.003) that is consistent with the evolution of a reservoir with an average $^{176}Lu/^{177}Hf$ of 0.020 ± 0.004 and a CHUR extraction age of 4.46 ± 0.12 Ga (95% confidence, MSWD = 4.1) (Fig. 6). The existence of Hadean crust with $^{176}Lu/^{177}Hf$ of ~0.02 is strengthened by the Hf isotope characteristics of Archaean zircons (Section 5.5).

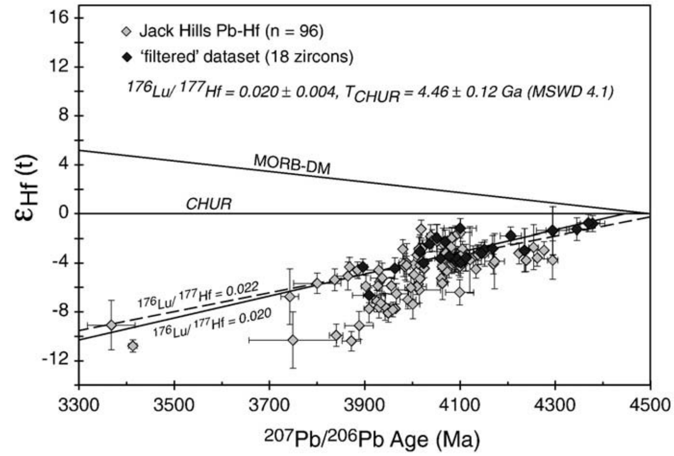

Fig. 6. Hf isotope data for a subset of the Jack Hills zircons (solid symbols) where the analysed growth domains retain well-preserved oscillatory zoning, yield concordant Pb/U isotope ages (with the exception of JH17 18.1) and have Th/U ≥ 0.3 and $\delta^{18}O > 4.5‰$. The $^{207}Pb/^{206}Pb$ ages determined by laser ablation and SHRIMP do not differ by more than 3%, and most ages agree to better than 1%. The solid regression line is weighted according to analytical errors, whereas the dashed line is derived by robust (non-parametric) regression (calculated from *Isoplot*, Ludwig, 2001). The MSWD of 4 suggests a source of scatter not accounted for by the assigned analytical errors, which could reflect minor Hf isotope heterogeneity and/or ancient lead loss, or an unidentified systematic error in the laser ablation analyses.

5.2. Source rocks of the Hadean zircons

The $^{176}Lu/^{177}Hf$ value inferred above imposes general constraints on the bulk composition of the chemical reservoir from which the parental magmas to the Hadean Jack Hills zircons were derived; we emphasise that a unique solution is precluded by the natural variability in this ratio shown by common rock types, even from the same tectonic setting (see Fig. 7 in Blichert-Toft and Albarède, 2008). An average source $^{176}Lu/^{177}Hf$ of 0.020 is much higher than that of time-integrated upper continental crust (0.008, Rudnick and Gao, 2003), ruling out most strongly differentiated igneous rocks and clastic metasedimentary rocks as exclusive magma sources. This value also exceeds that of bulk (andesitic) continental crust ($^{176}Lu/^{177}Hf = 0.012$; Rudnick and Gao, 2003) and isotopically juvenile crust (average $^{176}Lu/^{177}Hf \sim 0.014$; Vervoort and Blichert-Toft, 1999). Blichert-Toft and Albarède (2008) suggested that the Jack Hills zircons formed from partial melts of '4.3 Ga old felsic crust dominated by TTG' suites with very low $^{176}Lu/^{177}Hf$ (<0.01). TTG crust, however, evolves to Hf isotope ratios that are clearly too unradiogenic for most Jack Hills zircons in our dataset (Fig. 4B). Moreover, as discussed above, the 4.3 Ga zircons have distinctly unradiogenic $^{176}Hf/^{177}Hf$, requiring an older source component.

Using the Lu/Hf versus silica distribution of Archaean volcanic rocks as a guide (Supplementary Fig. 4), an average $^{176}Lu/^{177}Hf$ of ~0.02 is most typical of mafic to intermediate crust with ~45–55% SiO_2. This value falls towards the lower end of maxima on histograms of $^{176}Lu/^{177}Hf$ defined by modern MORB and some oceanic plateau basalts (Blichert-Toft and Albarède, 2008), but is higher than that of ocean island basalts (average 0.012). We note that the inferred mafic protoliths to the Eoarchaean TTG plutons of the Pilbara craton, Western Australia (Coonterunah F2 basalts) also have a mean $^{176}Lu/^{177}Hf$ of ~0.02 (Smithies et al. 2009). If the magma sources of the Jack Hills zircons were mafic, the marginally lower average $^{176}Lu/^{177}Hf$ compared to some oceanic basalts could reflect derivation from less depleted Hadean mantle, lower degrees of mantle melting, and/or melting or crystallisation in the garnet stability field. For example, melts with $^{176}Lu/^{177}Hf \sim 0.02$ can be derived by ~23% non-modal equilibrium melting or ~27% fractional melting of fertile garnet peridotite (calculated using the parameters in Table 3 of Chauvel and Blichert-Toft, 2001). The same $^{176}Lu/^{177}Hf$ ratio could also result from 40% crystallisation of mantle magma

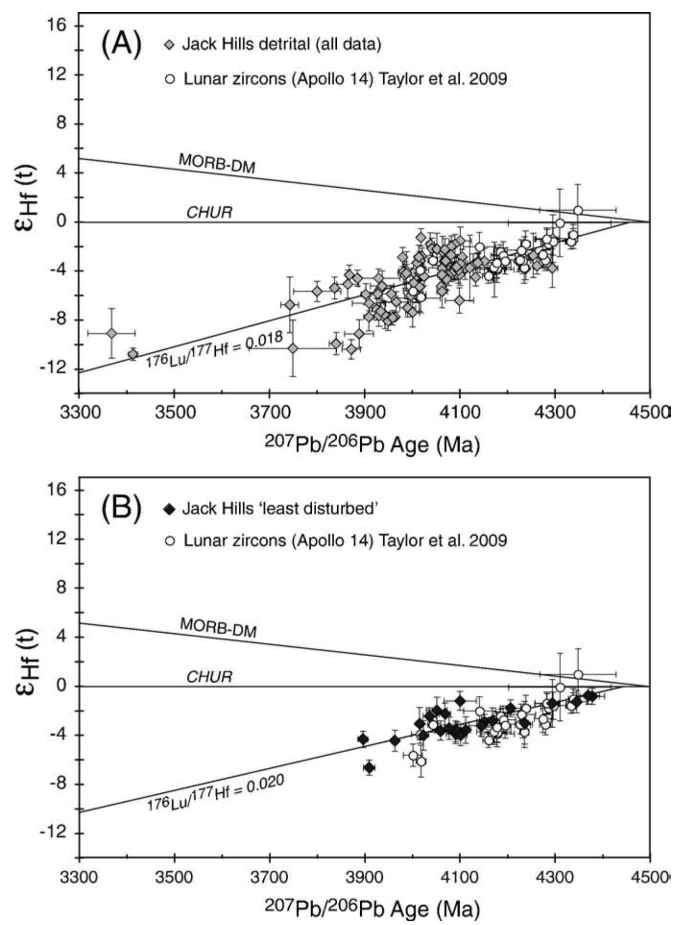

Fig. 7. Hf isotope-time systematics of the Jack Hills detrital zircons (this study) compared to those of lunar zircons separated from Apollo 14 breccias (data from Taylor et al. 2009). The top panel (A) shows a regression of all Jack Hills data, yielding $^{176}Lu/^{177}Hf = 0.018$, whereas the bottom panel (B) plots (and regresses) only those analyses from oscillatory-zoned grains.

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with chondritic Lu/Hf leaving a cumulate with 25% garnet, or 72% crystallisation of a cumulate with 10% garnet (Blichert-Toft and Albarède, 2008).

5.3. A KREEP connection?

Fig. 7 compares the Hf isotope compositions of Jack Hills detrital zircons with those of lunar zircons from Apollo 14 breccias (data from Taylor et al 2009). The lunar zircons are believed to have crystallised from melts of an incompatible element rich source component referred to as 'KREEP' (elevated potassium, rare earth element and phosphorous contents), which formed from residual liquid produced during solidification of a lunar magma ocean. The lunar zircons show striking chemical differences from their terrestrial Hadean counterparts, reflecting growth under contrasting conditions. For example, high Ti contents (up to 260 ppm) and the absence of Ce enrichment relative to La and Pr (e.g. Taylor et al. 2009) may denote crystallisation of the lunar zircons from hot, dry and low f_{O2} magmas, compared to the cooler, hydrous and relatively oxidised parental melts hypothesised for the Jack Hills zircons (Watson and Harrison, 2005; Fu et al. 2008). Despite these differences, the lunar zircons define a simple Hf isotope evolution that is indistinguishable from that of the Jack Hills zircons. This indicates that the >4 Ga lunar and terrestrial zircons formed by the repeated sampling of a chemical reservoir that had similar average Lu/Hf and was extracted from a broadly chondritic mantle source at the same time. If a chondritic heritage is valid, lunar KREEP segregated by ~4.48 Ga (from Hf in zircon: Taylor et al. 2009) or 4.49 Ga (from Sm–Nd isotopes: Edmunson et al. 2009), synchronous with initial crust formation on Earth deduced from our Jack Hills zircon dataset. Lunar KREEP has an average ^{176}Lu/^{177}Hf of 0.019 (Warren, 1989), a value shared by 'pristine' olivine-rich KREEP basalts (e.g. Neal and Kramer, 2003) and indistinguishable to that inferred above for the Jack Hills zircon magma source. These observations suggest that the mafic crustal protolith to the Jack Hills magmas may have formed during crystallisation of a terrestrial magma ocean, in a similar manner to lunar KREEP.

5.4. Implications for Hadean Earth evolution

The ε_{Hf}–time array in Fig. 4B portrays a far simpler evolution for the Hadean Earth than advocated by Harrison et al. (2005, 2008). In particular, the data indicate much less Hf isotope heterogeneity in the sources to the magmas from which the Jack Hills detrital zircons crystallised. Hadean source reservoirs that evolved with anomalously high or low Lu/Hf are not required. The Hf isotope data do not favour the existence of strongly depleted Hadean mantle, effectively refuting a key piece of evidence for a voluminous complementary crustal reservoir in the early Earth (e.g. Harrison et al., 2005). We also find no evidence for continuous crustal growth (mantle input) throughout the Hadean period, as would be manifest by a smearing of zircon Hf isotope data along CHUR or depleted mantle curves. This does not preclude mantle-derived magmatism during this time, but indicates that any subsequent juvenile components escaped reworking by the parental magmas to the Jack Hills zircons.

The approximately linear Hf isotope evolution in Fig. 4B requires an essentially closed system differentiation of the same, broadly mafic bulk source composition. This places tight constraints on geodynamic models for the Hadean Earth. For example, the Jack Hills ε_{Hf}–time array contrasts strongly with the complex isotope-time patterns defined by magmas generated at convergent plate margins, which record variable interactions between juvenile magmas and older crust over 400 Ma timescales (e.g. DeCelles et al. 2009; Kemp et al. 2009b). A simple Hf isotope evolution could theoretically arise by subduction of hydrated oceanic crust, provided that the slab angle was sufficiently shallow that the derivative melts did not pass through, and interact with, the mantle wedge (e.g., Smithies et al. 2003). The age range of the Jack Hills zircons, however, requires a protracted (>400 Ma) residence for the basaltic protolith on Earth's surface. This seems unlikely since the envisaged hotter Hadean mantle temperatures would promote plate velocities of up to six times more rapid than at present (Abbott and Hoffmann, 1984; Davies, 2006). Rollinson (2008) emphasises that the trace element and oxygen isotope geochemistry of the Jack Hills zircons resembles that of zircons from trondhjemites produced by shallow fusion of seawater-altered mafic rock at oceanic spreading ridges. Remelting of the same altered basaltic unit over 400 Ma is, however, implausible in an active spreading system where newly emplaced basaltic crust is continually hydrated as older crust migrates away from the hot ridge axis.

The Hf isotope data from the Apollo 14 zircons clearly demonstrate that a simple Hf isotope evolution like that defined by the Jack Hills detrital zircons can be generated without recourse to plate tectonics, continental crust or liquid water. Protracted magmatism and zircon crystallisation on the moon over 400 Ma is believed to reflect the periodic segregation of melts from a KREEP source reservoir, perhaps in response to major bolide impacts (Nemchin et al., 2008). An analogous situation may be applicable to the Hadean Earth (Fig. 8). The major difference, assuming that the high δ^{18}O of the Jack Hills zircons truly reflects the host magma, is that the enriched mafic crust formed by terrestrial magma ocean solidification interacted with a nascent hydrosphere at low temperature, forming a crustal reservoir with heavy δ^{18}O (Wilde et al., 2001; Valley et al., 2002). Such a layer would be predisposed to melt by virtue of its hydrous and incompatible element rich composition. Following Kamber et al. (2005), we speculate that foundering of this hydrated basaltic shell to deeper crustal levels in locally thickened eruptive centres, possibly facilitated by volcanic resurfacing, led to the intermittent generation of melts with mildly elevated δ^{18}O that crystallised the Jack Hills zircons. Resurfacing by voluminous basaltic or komatiitic lavas is especially favoured in the absence of plate tectonics as a mechanism to remove radiogenic heat from the Hadean mantle. Fusion within the buried basaltic source layer may have been promoted by heat advection from ongoing basaltic magmatism or by internal radiogenic heat production (Kamber et al., 2005), forming dispersed melt pockets (Nemchin et al., 2006) that were repeatedly rejuvenated as the protolith remained hot and near its solidus for long periods (Fig. 8). These melts thus remained essentially isolated from juvenile input. Experimental evidence demonstrates that minimum temperature melts derived by fluid-rich anatexis of basalt will be corundum-normative (Ellis and Thompson 1986), explaining the muscovite inclusions in the Jack Hills zircons (e.g. Hopkins et al., 2008), if indeed these have an igneous origin; this obviates the need for a metasedimentary source for the Jack Hills magmas (c.f. Mojzsis et al. 2001). The chemical differences between the Jack Hills zircons and lunar zircons reflects crystallisation of the former from hydrous anatectic melts (Watson and Harrison 2005), rather than from hot, dry liquids, although the parental melts in both cases were sourced from a reservoir of similar Lu/Hf. We also note that KREEP-rich lunar breccias have high Li contents (to 50 ppm, Seitz et al., 2006), and a similar crustal source (with Li further enhanced by weathering) could contribute towards the anomalously enriched Li contents of the Jack Hills zircons reported by Ushikubo et al. (2008).

5.5. Linking Hadean and Archaean crustal evolution

There are divergent views as to the longevity of Hadean crust, and the extent to which this material influenced crust–mantle differentiation processes in the Archaean. Reiterating the model of Armstrong (1981), Harrison et al. (2005) speculated that silicate Earth differentiation in the Hadean generated a 'continental crust with a volume similar in magnitude to the present day', but that this was 'largely recycled back into the mantle by the onset of the Archaean'. However, if the high μ (^{238}U/^{204}Pb) signature of some Archaean rocks was

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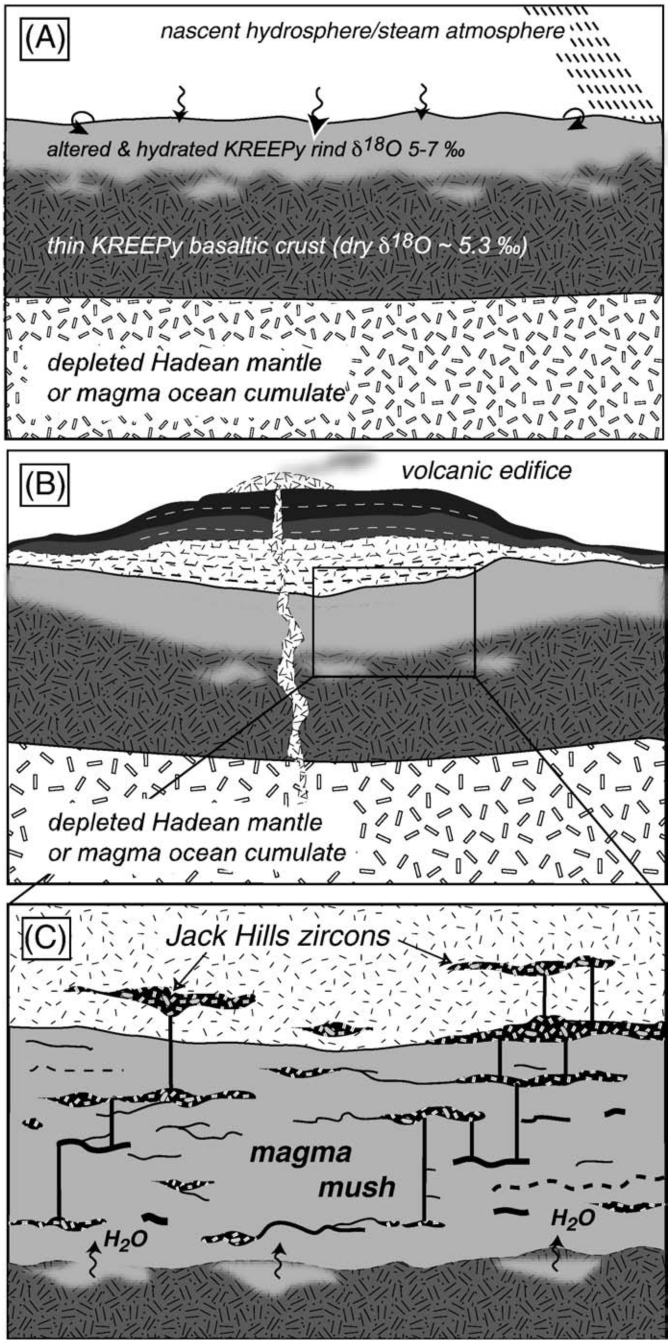

Fig. 8. Model for the evolution of Hadean crust and formation of the Jack Hills zircons. (A) Accumulation of a thin, trace-element rich KREEPy crustal layer at ~4.5 Ga following magma ocean crystallisation, and the interaction between this crust and the hydrosphere; (B) burial of the altered KREEPy rind beneath thick basaltic–komatiitic flows in locally thickened eruptive centres; and (C) remelting of the hydrated, chemically-fertile portion of the KREEPy source layer due to radioactive self-heating and the insulating effect of the overlying volcanic pile, generating small volume silicic melts from which the Jack Hills zircons crystallised. The age range of the zircons implies that partial melting was sustained over ~400 Ma.

inherited from enriched Hadean mafic crust (Kamber et al. 2003, 2005), then some of this material must have survived as the nucleus of the oldest Archaean cratons. Indeed, the Hf isotope–time array defined by the Jack Hills zircon dataset of Amelin et al. (1999) continues across the Hadean–Archaean boundary, suggesting that Hadean crust did persist into the Archaean and was reworked by younger magmas. Similar inferences have been drawn from the unradiogenic Hf isotope composition of Eoarchaean zircons from the Slave Craton, Canada (Amelin et al., 1999, 2000; Pietranik et al., 2008; Iizuka et al. 2009).

The Hf isotope data reported here from zircons of the Jack Hills meta-igneous rocks support the notion of long-lived Hadean crust. The least radiogenic of these data plot near the extension of the ε_{Hf} – time array defined by the filtered Hadean detrital zircon dataset and the evolutionary trend of 4.5 Ga mafic crust (Fig. 5). Hadean crust may therefore have contributed substantially to these Archaean magmas, and was potentially the dominant source in the 2.65 Ga monzogranites.

Most zircons from the Jack Hills meta-igneous rocks have Hf isotope compositions that plot above the detrital zircon array, however, indicating another, relatively juvenile, source component for the parental magmas. The absence of vertical mixing arrays towards high ε_{Hf} argues against substantial mantle inputs. Instead, we suggest that the juvenile source was crustal material whose mantle extraction age is constrained by the upper (radiogenic) limit of the meta-igneous zircon ε_{Hf}–time envelope. This bounding curve, which has a basalt-like $^{176}Lu/^{177}Hf$, also passes through Hf isotope data for the Greenland Amîtsoq gneisses and intersects CHUR near 3.85 Ga, and 'model' depleted mantle curves at 4.0–4.1 Ga (Fig. 5). The latter period coincides with a subtle shift to less negative ε_{Hf} values shown by the Hadean Jack Hills detrital zircons. This suggests that there may have been a crust generation episode at 4.0–4.1 Ga, contributing juvenile input into the magmas that crystallised the 4.0–4.1 Ga Jack Hills zircons and forming a source reservoir for younger Archaean magmas. Mixed sampling of 4.0–4.1 and 4.5 Ga crust during subsequent melting events can explain the Hf isotope diversity of the Archaean Jack Hills zircons. A similar scenario is applicable for the Slave craton, the oldest zircons of which have ε_{Hf} values that fall between the evolutionary trajectories of 4.0 and 4.5 Ga crust (Fig. 5).

The Hf isotope data are consistent with an enduring and perhaps widespread Hadean protocrust (Kamber et al., 2005), a portion of which was reworked into magmas throughout the Archaean. This is despite perceived difficulties with the preservation of basaltic crust in a hotter Hadean Earth (Kramers, 2007). The scarcity of markedly unradiogenic isotope ratios in Archaean rocks suggests either that the surviving volume of enriched Hadean protocrust was small, perhaps due to rapid crustal recycling or that the Hadean isotope signature was swamped by the progressive addition of juvenile magmas sourced from incompatible element depleted mantle.

6. Conclusions

We have determined the Hf isotope composition and concurrently measured $^{207}Pb/^{206}Pb$ ages of 68 Jack Hills detrital zircons by laser ablation MC-ICP-MS analysis. All data have subchondritic $^{176}Hf/^{177}Hf$, supporting the contention of previous workers (Harrison et al., 2005, 2008; Blichert-Toft and Albarède, 2008) that separation of a crustal reservoir from chondritic mantle occurred at or before 4.4 Ga. This finding further corroborates Nd isotope evidence for early differentiation of the silicate Earth (e.g. Bowring and Housh, 1995; Boyet and Carlson, 2005; Bennett et al., 2007). The simpler, broadly linear Hf isotope evolution defined by our dataset imposes additional constraints on models of Hadean crust–mantle differentiation. This evolution reflects the protracted intra-crustal reworking of a long-lived source with a narrow compositional range, whose average inferred $^{176}Lu/^{177}Hf$ value is consistent with intermediate to mafic igneous rock. We suggest that such a crustal protolith formed during the solidification of a terrestrial magma ocean, in analogous fashion to lunar KREEP. Boyet and Carlson (2005) have also postulated an enriched Hadean reservoir on Earth with chemical affinity to KREEP. There is no Hf isotope evidence for the existence of anomalously unradiogenic magma sources, or for the formation of depleted mantle

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domains whose formation might signal the extraction of large volumes of Hadean crust.

The Hf isotope data do not require a plate tectonic regime for the Hadean Earth similar to that operating today. The data are instead consistent with generation of the parental magmas to the Jack Hills zircons by remelting of an enriched basaltic protolith within a thickened volcanic pile. The total volume of resulting felsic material is not constrained by the Hf isotope data. This scenario has parallels with that proposed for the formation of some Eoarchaean TTG (e.g. Smithies et al., 2003) except that a mantle plume heat source is not required, given the enhanced radiogenic heat production predicted for (K–Th–U)-rich Hadean crust (Kamber et al. 2005), and the evidence that the Jack Hills zircons crystallised at temperatures near the wet granite solidus (Watson and Harrison 2005).

The strikingly unradiogenic Hf isotope composition of zircons from meta-igneous rocks that surround the Jack Hills belt, and those from other Archaean cratons, support the view (e.g. Kamber et al., 2005) that Hadean protocrust survived the postulated late heavy meteorite bombardment of the terrestrial planets at ~3.9 Ga (Ryder, 2002). Remarkably, this ancient crustal reservoir appears to have been sampled by magmas throughout the Archaean. Irrespective of the volume of continental crust in the infant Earth, the data reported here suggest that the Hf isotope legacy of a nascent Hadean crust endures within the present day continental mass, as it may also in the contemporary mantle (Boyet and Carlson, 2005).

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Appendix A. Supplementary data

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References

Abbott, D.H., Hoffmann, S.E., 1984. Archaean plate tectonics revisited: 1. Heat Flow, spreading rate, and the age of subducting oceanic lithosphere and their effects on the origin and evolution of continents. Tectonics 3, 429–448.

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.

Amelin, Y., Lee, D.-C., Halliday, A.N., 2000. Early–middle Archaean crustal evolution deduced from Lu–Hf and U–Pb isotopic studies of single zircon grains. Geochim. Cosmochim. Acta 64, 4205–4225.

Armstrong, R.L., 1981. Radiogenic isotopes: the case for crustal recycling on a near-steady-state no-continental-growth Earth. Phil. Trans. Roy. Soc. London A301, 443–472.

Baker, J., Peate, D., Waight, T., Meyzen, C., 2004. Pb isotopic analysis of standards and samples using a ^{207}Pb–^{204}Pb double spike and thallium to correct for mass bias with a double-focusing MC-ICP-MS. Chem. Geol. 211, 275–303.

Bennett, V.C., Brandon, A.D., Nutman, A.P., 2007. Coupled ^{142}Nd–^{143}Nd isotopic evidence for Hadean mantle dynamics. Science 318, 1907–1910.

Blichert-Toft, J., Albarède, F., 1997. The Lu–Hf isotope geochemistry of chondrites and the evolution of the mantle–crust system. Earth Planet. Sci. Lett. 148, 243–258.

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

Bouvier, A., Vervoort, J.D., Patchett, P.J., 2008. The Lu–Hf and Sm–Nd isotopic composition of CHUR: constraints from unequilibrated chondrites and implication for the bulk composition of terrestrial planets. Earth Planet. Sci. Lett. 273, 48–57.

Borg, L.E., Nyquist, L.E., Wiesmann, H., Shih, C.-Y., 1997. Constraints on Martian differentiation processes from Rb–Sr and Sm–Nd isotopic analysis of the basaltic shergottite QUE94201. Geochim. Cosmochim. Acta 61, 4915–4931.

Bowring, S.A., Housh, T., 1995. The Earth's early evolution. Science 269, 1535–1540.

Boyet, M., Carlson, R.W., 2005. ^{142}Nd evidence for Early (>4.53 Ga) global differentiation of the silicate Earth. Science 309, 576–581.

Caro, G., Bourdon, B., Birck, J.L., 2003. ^{146}Sm–^{142}Nd evidence from Isua metamorphosed sediments for early differentiation of the Earth's mantle. Nature 423, 428–431.

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 Archaean to Mesoproterozoic (4348–1576 Ma) magmatism. Precambrian Res. 135, 251–279.

Cavosie, A.J., Valley, J.W., Wilde, S.A., 2005. Magmatic δ^{18}O in 4400–3900 Ma detrital zircons: a record of the alteration and recycling of crust in the Early Archean. Earth Planet. Sci. Lett. 235, 663–681.

Chauvel, C., Blichert-Toft, J., 2001. A hafnium isotope and trace element perspective on melting of the depleted mantle. Earth Planet. Sci. Lett. 190, 137–151.

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

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. J. Geol. 113, 239–263.

Davies, G., 2006. Gravitational depletion of the early Earth's upper mantle and the viability of early plate tectonics. Earth Planet. Sci. Lett. 243, 376–382.

DeCelles, P.G., Ducea, M.N., Kapp, P., Zandt, G., 2009. Cyclicity in Cordilleran orogenic systems. Nat. Geosci. 2, 251–257.

Edmunson, J., Borg, L.E., Nyquist, L.E., Asmerom, Y., 2009. A combined Sm–Nd, Rb–Sr and U–Pb isotopic study of Mg-suite norite 78238: further evidence for early differentiation of the moon. Geochim. Cosmochim. Acta 73, 514–527.

Ellis, D.J., Thompson, A.B., 1986. Subsolidus and partial melting reactions in the quartz-excess $CaO + MgO + Al_2O_3 + SiO_2 + H_2O$ system under water-excess and water-deficient conditions to 10 kb: some implications for the origin of peraluminous melts from mafic rocks. J. Petrol. 27, 91–121.

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. Contrib. Mineral. Petrol. 156, 197–215.

Galer, S.J.G., Goldstein, S.L., 1991. Early mantle differentiation and its thermal consequences. Geochim. Cosmochim. Acta 55, 227–239.

Goodge, J.W., Vervoort, J.D., 2006. Origin of Mesoproterozoic A-type granites in Laurentia: Hf isotope evidence. Earth Planet. Sci. Lett. 243, 711–731.

Harrison, T.M., Blichert-Toft, J., Muller, W., Albarède, F., Holden, P., Mojzsis, S.J., 2005. Heterogeneous Hadean Hafnium: evidence for continental crust at 4.4 to 4.5 Ga. Science 310, 1947.

Harrison, T.M., Schmitt, A.K., McCulloch, M.T., Lovera, O.M., 2008. Early (4.5 Ga) formation of terrestrial crust: Lu–Hf, δ^{18}O, and Ti thermometry results for Hadean zircons. Earth Planet. Sci. Lett. 268, 476–486.

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

Hoskin, P.W.O., 2005. Trace-element composition of hydrothermal zircon and the alteration of Hadean zircon from the Jack Hills, Australia. Geochim. Cosmochim. Acta 69, 637–648.

Iizuka, T., Komiya, T., Johnson, S.P., Kon, Y., Maruyama, S., Hirata, T., 2009. Reworking of Hadean crust in the Acasta gneisses, northwestern Canada: evidence from in situ Lu–Hf isotope analysis of zircon. Chem. Geol. 259, 230–239.

Kamber, B.S., Collerson, K.D., Moorbath, S., Whitehouse, M.J., 2003. Inheritance of Early Archaean Pb-isotope variability from long-lived Hadean protocrust. Contrib. Mineral. Petrol. 145, 25–46.

Kamber, B.S., Whitehouse, M.J., Bolhar, R., Moorbath, S., 2005. Volcanic resurfacing and the early terrestrial crust: zircon U–Pb and REE constraints from the Isua Greenstone Belt, southern West Greenland. Earth Planet. Sci. Lett. 240, 276–290.

Kemp, A.I.S., Foster, G.L., Schersten, A., et al., 2009a. Concurrent Pb–Hf isotope analysis of zircon by laser ablation multi-collector ICP-MS, with implications for the crustal evolution of Greenland and the Himalayas. Chem. Geol. 261, 244–260.

Kemp, A.I.S., Hawkesworth, C.J., Collins, W.J., Gray, C.M., EIMF, 2009b. Isotopic evidence for rapid continental growth in an extensional accretionary orogen: The Tasmanides, eastern Australia. Earth Planet. Sci. Lett. 284, 455–466.

Kinny, P.D., Nutman, A.P., 1996. Zirconology of the Meeberrie gneiss, Yilgarn Craton, Western Australia: an early Archaean migmatite. Precambrian Res. 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 Res. 38, 325–341.

Kramers, J.D., 2007. Hierarchical Earth accretion and the Hadean Eon. J. Geol. Soc. London 164, 3–17.

Ludwig, K.R., 2001. Isoplot/Ex rev. 2.49. Berkeley Geochronology Centre. Special Publication 1a.

Mojzsis, S.J., Harrison, T.M., Pidgeon, R.T., 2001. Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4, 300 Myr ago. Nature 409, 178–181.

Neal, C.R., Kramer, G., 2003. The composition of KREEP: a detailed study of KREEP basalt 15386. Lunar Planet. Sci. XXXIV, 2023–2024.

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 Planet. Sci. Lett. 244, 218–233.

Nemchin, A.A., Pidgeon, R.T., Whitehouse, M.J., Vaughan, J.P., Meyer, C., 2008. SIMS U–Pb study of zircon from Apollo 14 and 17 breccias: implications for the evolution of lunar KREEP. Geochim. Cosmochim. Acta 72, 668–689.

Norman, M.D., Borg, L.E., Nyquist, L.E., Bogard, D.D., 2003. Chronology, geochemistry, and petrology of a ferroan noritic anorthosite clast from Descartes breccia 67215: clues to the age, origin, structure, and impact history of the lunar crust. Meteorit. Planet. Sci. 38, 645–661.

O'Neil, J., Carlson, R.W., Francis, D., Stevenson, R.K., 2008. Neodymium-142 evidence for Hadean mafic crust. Science 321, 1828–1831.

Parrish, R.R., 1987. An improved micro-capsule for zircon dissolution in U–Pb geochronology. Chem. Geol. 66, 99–102.

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 δ18O continental crust and oceans in the Early Archaean. Geochimica et Cosmochimica Acta 65, 4215–4229.

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 Res. 91, 309–332.

Pietranik, A.B., Hawkesworth, C.J., Storey, C.D., Kemp, A.I.S., Sircombe, K.N., Whitehouse, M.J., Bleeker, W., 2008. Episodic, mafic crust formation from 4.5 to 2.8 Ga. New evidence from detrital zircons, Slave craton, Canada. Geology 36, 875–878.

Rasmussen, R., 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, 26–46.

Rollinson, H., 2008. Ophiolitic trondhjemites: a possible analogue for Hadean felsic 'crust'. Terra Nova 20, 364–369.

Rudnick, R.L., Gao, S., 2003. Composition of the continental crust. In: Rudnick, R.L. (Ed.), The Crust. : Treatise on Geochemistry, vol. 3. Elsevier, Amsterdam, pp. 1–64.

Ryder, G., 2001. Mass flux in the ancient Earth-moon system and benign implications for the origin of life on Earth. Journal of Geophysical Research 107 6-1-6-13.

Seitz, H.-M., Brey, G.P., Weyer, S., Durall, S., Ott, U., Munker, C., Mezger, K., 2006. Lithium isotope compositions of Martian and lunar reservoirs. Earth Planet. Sci. Lett. 245, 6–18.

Smithies, R.H., Champion, D.C., Cassidy, K.F., 2003. Formation of Earth's early Archaean continental crust. Precambrian Res. 127, 89–101.

Smithies, R.H., Champion, D.C., Van Kranendonk, M.J., 2009. Formation of Paleoarchaean continental crust through infracrustal melting of enriched basalt. Earth Planet. Sci. Lett. 281, 298–306.

Söderlund, U., Patchett, P.J., Vervoort, J.D., Isachsen, C.E., 2004. The ^{176}Lu decay constant determined by Lu–Hf and U–Pb isotope systematics of Precambrian mafic intrusions. Earth Planet. Sci. Lett. 219, 311–324.

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 Res. 155, 261–286.

Taylor, D.J., McKeegan, K.D., Harrison, T.M., 2009. Lu–Hf zircon evidence for rapid lunar differentiation. Earth Planet. Sci. Lett. 279, 157–164.

Tera, F., Carlson, R.W., Boctor, N.B., 1997. Radiometric ages of basaltic achondrites and their relation to the early history of the solar system. Geochim. Cosmochim. Acta 61, 1713–1731.

Trail, D., Mojzsis, S.J., Harrison, T.M., 2007. Thermal events documented in Hadean zircons by ion microprobe depth profiles. Geochim. Cosmochim. Acta 71, 4044–4065.

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 Planet. Sci. Lett. 272, 666–676.

Valley, J.W., Peck, W.H., King, E.M., Wilde, S.A., 2002. A cool early Earth. Geology 30, 351–354.

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.

Vervoort, J.D., Blichert-Toft, J., 1999. Evolution of the depleted mantle: Hf isotope evidence from juvenile rocks through time. Geochim. Cosmochim. Acta 63, 533–556.

Warren, P.H., 1989. KREEP: major-element diversity, trace-element uniformity (almost). Workshop on Moon in Transition: Apollo 14, KREEP, and Evolved Lunar Rocks, pp. 149–153.

Watson, E.B., Harrison, T.M., 2005. Zircon thermometer reveals minimum melting conditions on earliest Earth. Science 308, 841–844.

Wilde, S.A., Spaggiari, C.V., 2007. The Narryer Terrane, Western Australia: a review. In: van Kranendonk, M.J., Smithies, R.H., Bennett, V.C. (Eds.), Earth's Oldest Rocks. : Developments in Precambrian Geology, vol. 15. Elsevier B.V, The Netherlands, 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 Ga ago. Nature 409, 175–178.

Woodhead, J.D., Hergt, J.M., Shelley, M., Eggins, S., Kemp, R., 2004. Zircon Hf-isotope analysis with an excimer laser, depth profiling, ablation of complex geometries, and concomitant age estimation. Chem. Geol. 209, 121–135.

Woodhead, J.D., Hergt, J.M., 2005. A preliminary appraisal of seven natural zircon reference materials for in situ Hf isotope determination. Geostand. Geoanal. Res. 29, 183–195.