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Early (≥4.5 Ga) formation of terrestrial crust: Lu–Hf, $\delta^{18}O$, and Ti thermometry results for Hadean zircons

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Abstract

Large deviations in $\varepsilon_{\mathrm{Hf}(T)}$ from bulk silicate Earth seen in >4 Ga detrital zircons from Jack Hills, Western Australia, have been interpreted as reflecting a major differentiation of the silicate Earth at 4.4 to 4.5 Ga. We have expanded the characterization of ^{176}Hf/^{177}Hf initial ratios (*Hf*) in Hadean zircons by acquiring a further 116 laser ablation Lu–Hf measurements on 87 grains with ion microprobe ^{207}Pb/^{206}Pb ages up to 4.36 Ga. Most measurements employed concurrent Lu–Hf and ^{207}Pb/^{206}Pb analyses, permitting assessment of the age of the volumetrically larger domain sampled by laser drilling against the spatially more restricted ion microprobe ages. Our new results confirm and extend the earlier observation of significant negative deviations in $\varepsilon_{\mathrm{Hf}(T)}$ throughout the Hadean, although no positive $\varepsilon_{\mathrm{Hf}(T)}$ values were documented in this study. Monte Carlo modelling of these data yields an essentially uniform spectrum of model ages between 4.56 and 4.20 Ga for extraction of the zircons' protoliths from a chondritic reservoir. To assess whether the five data plotting close to solar system initial *Hf* (Hf_o) are statistically robust, we derived the error propagation equation for a parameter, ε_o, which measures the difference of a sample from Hf_o. Our analysis suggests that this limited data is indicative of source sequestration in a crustal-type Lu/Hf environment prior to 4.5 Ga. Oxygen isotope data and Ti thermometry from Hadean zircons show little obvious correlation with *Hf*, consistent with their derivation through fusion of a broad suite of crustal rock types under water-saturated conditions. Together with other isotopic and trace element data obtained from these ancient zircons, our results indicate essentially continuous derivation of crust from the mantle from 4.5 to 4.2 Ga with concurrent recycling into the mantle and internal crustal re-working. These results represent further evidence that by 4.35 Ga, portions of the crust had taken on continental characteristics.

Keywords: zircon; U–Pb; Lu–Hf; Hadean

1. Introduction

The Hadean Eon (4.5–4.0 Ga) has long been considered the dark age of Earth history; there is no known rock record from this period. Although >4 Ga detrital zircons have been recovered from Western Australian sediments for over 20 years (Froude et al., 1983; Compston and Pidgeon, 1986), they were largely seen as curiosities that provided little in the way of constraints on early Earth processes (e.g., Taylor and McLennan, 1985; Galer and Goldstein, 1991). With the advent of refined analytical methodologies that permit precise isotopic measurements on ultra-small samples (e.g., Mahon et al., 1998; Gilmour et al., 1994; Caro et al., 2003; Woodhead et al., 2004), large numbers of >4 Ga zircons have been acquired to investigate trace element and isotopic signals that bear on the early evolution of the Earth.

The inclusion mineralogy of these ancient zircons (e.g., Maas et al., 1992) points towards their origin from diverse, but seemingly familiar, petrogenetic settings (meta- and peraluminous, SiO_2-saturated, hydrous, granitoid magmas; Mojzsis et al., 2001). The presence of microdiamonds (Menneken et al., 2007) suggest relatively cool conditions at ultrahigh-

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pressure during the Hadean. Single crystal Xe isotopic results yield Pu/U values ranging from chondritic to zero (Turner et al., 2004, 2007) implying limits on the capacity of mantle-derived Xe isotopes to be interpreted in terms of the age of the atmosphere. The heavy oxygen isotope signature in some Hadean zircons suggest that the magma protolith contained ^{18}O-enriched clay minerals which in turn implies that liquid water was present at or near the Earth's surface by ca. 4.3 Ga (e.g., Mojzsis et al., 2001; Cavosie et al., 2005). Using a new thermometer, Watson and Harrison (2005, 2006), found that crystallization temperatures of Hadean Jack Hills zircons cluster at 680±25 °C, substantiating the existence of wet, prograde melting conditions (Luth et al., 1964) relatively close to the Earth's surface throughout the Hadean. $^{142,143}Nd$ data reveal that the Nd budget in the Jack Hills zircons is dominated by exogenous radiogenic Nd, thus precluding a reliable evaluation of $^{146}Sm–^{142}Nd$ systematics in Jack Hills zircons (Amelin, 2004; Caro et al., in press).

Zircons have very low Lu/Hf and thus record initial $^{176}Hf/^{177}Hf$ (*Hf*) at the time given by the U–Pb age (Amelin et al., 1999) with high fidelity (Cherniak et al., 1997). $^{176}Hf/^{177}Hf$ reported for Hadean Jack Hills zircons show a surprisingly large range of ε_{Hf} values, from −9 to +15 (Harrison et al., 2005), which were interpreted as supporting a major differentiation of the silicate Earth at ~4.5 Ga (Caro et al., 2003; Boyet and Carlson, 2005). However, mixing of zircon cores and rims of contrasting age can lead to substantial errors in calculation of $\varepsilon_{Hf(T)}$. Harrison et al. (2005) identified >4 Ga grains by ion microprobe (crater size ~100 μm^3) and assumed that this age corresponded to the domain sampled either by laser ablation multi-collector inductively-coupled mass spectrometry (MC-ICPMS; ~20,000 μm^3) or the bulk zircon analysed by solution MC-ICPMS (~500,000 μm^3). Thus, in these previous studies, *Hf* was obtained on domains that varied from 200 to 5000 times larger than the U–Pb ion microprobe pits.

We have followed up the original study of Harrison et al. (2005) with additional analyses of Hadean detrital zircons characterized for Ti abundances, and many for $\delta^{18}O$. The majority of these results are based on a modified analytical approach in which coupled measurements of Lu–Hf and Pb isotopes are made during laser ablation drilling (Woodhead et al., 2004). The results of this study confirm the existence of large negative $\varepsilon_{Hf(T)}$ deviations from CHUR that require almost immediate creation of a low Lu/Hf reservoir upon formation of the Earth.

2. Sample details and U–Pb dating

The zircon-bearing rocks in the Jack Hills form part of a thick (>2 km) series of fan delta sequences deposited in a fault-bounded cratonic margin that were subsequently metamorphosed to upper greenschist facies at ca. 3.1 Ga (Maas et al., 1992; Spaggiari et al., 2007). Numerous U–Pb age studies of Jack Hills detrital zircons (Compston and Pidgeon, 1986; Maas et al., 1992; Amelin et al., 1999; Mojzsis et al., 2001; Cavosie et al., 2004; Trail et al., 2007) show a characteristic bimodal distribution with peaks close to 3.4 and 4.1 Ga. We have collected multiple samples of quartz-pebble conglomerates rich in heavy mineral indicators (e.g., fuchsite) from a 30×10 m locality in the Erawondoo region of the Jack Hills where the ancient zircons were first documented (Compston and Pidgeon, 1986). Separated zircons are hand picked and mounted in 15×15 (ANU mounts) or 20×20 (RSES mounts) rows and columns on adhesive tape together with standard zircon AS-3 (Paces and Miller, 1993). The 1" diameter epoxy mount is then ground and polished to reveal zircon internal surfaces. Using the SHRIMP I and II ion microprobes, $^{207}Pb/^{206}Pb$ was rapidly surveyed (Harrison et al., 2005) for each zircon (~10 s) in an automated fashion to identify those grains with $^{207}Pb/^{206}Pb$ ratios ≥0.4 (i.e., >3.9 Ga). The small fraction of grains that met this criterion (~3%) were then analysed for U–Pb age.

Zircon grains for Lu–Hf analysis were selected from the pool of dated grains on the basis of providing a range in age from 3.91–4.36 Ga with a generally high degree of U–Pb concordancy. Sixty-seven grains were analyzed for both Lu–Hf and $^{207}Pb/^{206}Pb$ by MC-ICPMS and 48 for Lu–Hf alone.

3. Analytical methods

3.1. Lu–Hf±Pb

Spatially-resolved laser ablation MC-ICPMS Lu–Hf isotopic measurements were undertaken with a Lambda Physik Compex 193 nm excimer laser coupled to a ThermoFinnigan Neptune MC-ICPMS. Zircons were directly analyzed in their 1" mounts with laser spot diameters of either 62 or 82 μm. Details of the laser system, isotopic analyses, including the schemes for correcting interferences of Yb and Lu on Hf isotopes, are given in Harrison et al. (2005). Briefly, two interference-free Yb isotopes, ^{171}Yb and ^{173}Yb, were measured to constrain Yb (and Lu) mass bias and mass 174 was monitored to determine the efficacy of the ^{174}Yb interference correction at mass 174. Since the ^{174}Yb interference is typically 90% of the signal at mass 174, the $^{174}Hf/^{177}Hf$ ratio is highly sensitive to inaccuracies in the correction procedure. We also report interference free, stable $^{178}Hf/^{177}Hf$ ratios as an independent measure of the effectiveness of the Hf isotope fractionation correction.

Two zircon standards (Mud Tank and Temora; Woodhead et al., 2004) were used throughout these analyses (Supplementary data Table 1). Mud Tank was analyzed as cm-sized, gem-quality fragments which permit high precision measurements, but the $^{176}Lu/^{177}Hf$ of ~0.00005 is significantly lower than the unknowns. Temora ($^{176}Lu/^{177}Hf \approx 0.001$) was measured to assess the effectiveness of the correction schemes on zircons with REE similar to the unknowns, but its smaller size (≤100 μm) resulted in shorter analysis times (<1 min) and thus lower precision than for Mud Tank.

In the Hf–Lu–Yb–Pb measurements of unknowns, we alternated between the mass range 171–181 and 204–206–207 or 206–207–208 by a combination of magnet switching and application of a ~95 V potential to the dispersion lens whereby mass 206 was focused on the axial detector. In this latter mode, we counted for 10 s at mass 171–181 followed by a 3 s delay, then 3 s on either 204–207 or 206–208 followed by a 3 s delay. For the

Hf–Lu–Yb only data acquisition, we continuously monitored the mass range 171–181. Typically analyses comprise 50–80 cycles of 1 s integrations (i.e., total time ~1 min). Peak intensities were corrected online for baseline contributions, exported, and further data reduction was done offline. All isotopic results are given in Supplementary data Table 2.

Typically, multiple standards were run every 5 to 6 unknowns. About half of the 70 standard analyses were performed on Mud Tank which yielded an average variation of $^{176}Hf/^{177}Hf$ from the published value (Woodhead et al., 2004) of 0.4±0.5 ε (Supplementary data Table 1). Thus instrumental discrimination within or between analysis sessions was not observed and we have not applied a correction to our unknowns with respect to the standards. A similar, but less precise result was obtained for Temora (0.8±0.8 ε) giving confidence that accurate corrections were applied for the range in $^{176}Lu/^{177}Hf$ seen in the unknown zircons of 0.0025–0.0001. This is consistent with the report (Taylor et al., 2008) that $^{176}Hf/^{177}Hf$ data accurate to 0.46 ε (2σ) are routinely obtained from laser ablation analysis of synthetic zircon doped with 800 ppm Yb (i.e., 20% ^{176}Yb at mass 176) using the NEPTUNE MC-ICPMS. We quote 2σ internal errors only in Supplementary data Table 2 so as not to convolve systematic errors into our later data analysis, which includes quadratic addition of ±0.46 ε to the $^{176}Hf/^{177}Hf$ uncertainty to account for errors introduced by peak stripping. Full error propagation for calculation of $\varepsilon_{Hf(T)}$ is described in Supplementary file B.

Naturally-invariant $^{174}Hf/^{177}Hf$ and $^{178}Hf/^{177}Hf$ ratios were used to evaluate the MC-ICPMS data (Supplementary data Table 2). Average $^{174}Hf/^{177}Hf$ and $^{178}Hf/^{177}Hf$ values of 0.00865±0.00009 and 1.46726±9, respectively (2σ), are within uncertainty of accepted values (Thirlwall and Anczkiewicz, 2004). No $^{178}Hf/^{177}Hf$ ratio exceeded 3σ from the accepted value (Thirlwall and Anczkiewicz, 2004). Two $^{174}Hf/^{177}Hf$ ratios (ANU111_2.6_2, Temora-14) exceeded 3σ, which is within expectation for a population of ~300 total analyses. The standard datum was omitted but as analysis ANU111_2.6_2 was a second measurement on the same grain and both yield the same overall result (i.e., $\varepsilon_{Hf(T)}=-10$), the datum was retained.

The average measured $^{176}Lu/^{177}Hf$ ratio of Temora of 0.00104±0.00032 (2σ) compares well with the value of 0.00109 reported by solution MC-ICPMS (Woodhead et al., 2004). During the Hf–Pb analyses, we monitored $^{207}Pb/^{206}Pb$ of the standard minerals which were typically reproducible and accurate to ±2% without a mass discrimination correction.

Ages and $\varepsilon_{Hf(T)}$ are calculated using a ^{176}Lu decay constant of $1.867\pm0.008\times10^{-11}$/a (Scherer et al., 2004; Soderlund et al., 2004; Amelin, 2005) and the chondritic parameters of Blichert-Toft and Albarède (1997) (see Supplementary file A).

3.2. Oxygen isotope measurements

Following polishing to remove prior analysis pits, $\delta^{18}O_{VSMOW}$ determinations of ~20 μm spots (~5 nA primary Cs^+ beam) of zircons in their epoxy mounts were made using a CAMECA *ims* 1270 ion microprobe in Faraday multicollection mode (see Trail et al., 2007). After recording the Faraday backgrounds during a 150 s pre-sputter, secondary ions passing a 30 eV energy slit (no energy offset) were admitted to the detector (mass resolving power ~2500). Under these conditions, average count rates for $^{16}O^-$ and $^{18}O^-$ were ~2×10^9 and ~4×10^6 cps, respectively. A liquid N_2 cold finger removed trace residual water from the sample chamber. The total integration time per analysis was 150 s and errors based on counting statistics are typically ±0.1‰ or less. Instrumental mass fractionation was monitored on the sample mount using zircon AS-3 as the primary standard ($\delta^{18}O=5.34\pm0.06$‰; Trail et al., 2007). A separate mount containing 91500 ($\delta^{18}O=+9.86$‰; Wiedenbeck et al., 2004) and Pacoima ($\delta^{18}O=+5.7$‰; Booth et al., 2005) zircons was used to monitor possible matrix effects. Internal and external errors are reported for unknowns, the latter propagating the variability of the AS-3 standard measurements for each mount. The final $\delta^{18}O_{unknown}$ was calculated and reported with respect to VSMOW ($^{18}O/^{16}O_{AS\text{-}3}=0.0020159$; $^{18}O/^{16}O_{VSMOW}=0.0020052$) in Table 1.

3.3. Ti thermometry

Analytical procedures and results for Ti-in-zircon thermometry for samples analysed for Lu–Hf in the February 2007 session (i.e., also analysed for $\delta^{18}O$; Table 1) are presented in Harrison and Schmitt (2007) and shown in Supplementary data Table 2 as equivalent temperature using the Watson and Harrison (2005) calibration. All other data were obtained using SHRIMP ion microprobes in which $^{49}Ti^+$ is ratioed to SiO^+ to determine absolute Ti concentrations. Analytical methods for those results are described in detail in Aikman (2007).

4. Results

One hundred and sixteen laser ablation Lu–Hf measurements were made on 87 zircons with $^{207}Pb/^{206}Pb$ ion microprobe ages between 3.57 and 4.36 Ga (Supplementary data Table 2). Forty-eight measurements were Lu–Hf alone and 68 used the combined Lu–Hf and Pb–Pb approach. For the former, $\varepsilon_{Hf(T)}$ is assigned on the basis of the $^{207}Pb/^{206}Pb$ ion microprobe age (see Harrison et al., 2005). As described below, our coupled Lu–Hf+Pb measurements permit us to assess the validity of our earlier assumption that the ion microprobe age appropriately characterizes the crystallization age of the domain analysed for Hf isotopes.

4.1. Analysis session 1 (March 2006)

Thirty-eight coupled Hf–Pb measurements on zircons with apparent ages from 3.6 and 4.2 Ga were undertaken in March 2006 and 29 mostly >4.2 Ga zircons were analyzed in February 2007. As the >4.2 Ga Jack Hills zircons are typically smaller than the younger grains, the latter group was exclusively measured using a 62 μm beam and the former with an 82 μm beam.

We initially explored simultaneous Hf and Pb isotope measurements during the March 2006 session by measuring masses 204, 206 and 207 with the goal of applying a ^{204}Pb correction for common Pb. However, in virtually all cases, the raw $^{207}Pb/^{206}Pb$

yielded far more coherent results than when corrected in this fashion indicating, as previously recognized, an extraneous signal at mass 204 (probably ^{204}Hg). This proved not to be particularly deleterious as the >4 Ga zircons are often close to 100% radiogenic (assessed using the measured Th/U and assuming concordancy in the ^{206}Pb/^{238}U and ^{208}Pb/^{232}Th systems). In the majority of cases, the ^{207}Pb/^{206}Pb ratio remained constant during laser ablation and corresponded reasonably well with the U–Pb date obtained by ion microprobe (Supplementary data Table 2). The average difference in age between the two approaches was 0.04 Ga, which is not substantially greater than the average ion microprobe age error of ±0.024 Ga and translates into a misestimation of $\varepsilon_{Hf(T)}$ of only ~1 ε unit. The variability of ^{207}Pb/^{206}Pb ratios during the multiple cycled measurements of mass 204–207 in an individual laser excavation is reflected in the age uncertainty, but dispersion was generally low. The average σ of ^{207}Pb/^{206}Pb ratios among the 38 measurements corresponds to an age variation of only ±3 Ma, although 11 of the 38 results yielded standard deviations in age between 5 and 11 Ma (Supplementary data Table 2). While these variations are still relatively small, they likely represent the effects of Pb loss, uncorrected common Pb, or analysis of multiple age domains.

In many cases, ion microprobe and laser ablation ^{207}Pb/^{206}Pb ages are indistinguishable. For example, RSES44-12.9, which shows an oscillatory CL zoning pattern indicative of a magmatic origin (Fig. 1A), exhibits essentially ideal behaviour. In this case, the ion microprobe age of 4.09±0.05 Ga was obtained near the laser ablation pit which yielded a uniform ^{207}Pb/^{206}Pb age of 4.095±0.002 Ga (MSWD=2.7) (Fig. 2). The simple zoning pattern and the concordant ages are clear evidence of a single age domain and we confidently ascribe Hf=0.280090±0.000012 to $\varepsilon_{Hf(T)}=-3.2\pm0.4$. RSES44-17.9 exhibits patchy zoning and a core/rim relationship visible in the CL image (Fig. 1B). The laser ablation ^{207}Pb/^{206}Pb yields an age of 4.03±0.02 Ga from a more variable signal but is consistent with the ion microprobe age of 4.08±0.04 Ga. Using the laser ablation age, the Hf=0.280048± 0.000016 corresponds to $\varepsilon_{Hf(T)}=-9.8\pm0.6$. In these examples, note that the sample with the higher negative $\varepsilon_{Hf(T)}$ also contains three times higher ^{176}Lu/^{177}Hf and thus requires a much larger correction for radiogenic ^{176}Hf ingrowth. Overall, however, we see no correlation between $\varepsilon_{Hf(T)}$ and ^{176}Lu/^{177}Hf (Fig. 3).

In those instances where multiple analyses were undertaken on the same zircon and yielded similar ages (RSES44-10.14, RSES44-16.6, RSES44-14.6, RSES42-17.19, RSES42-19.5), calculated $\varepsilon_{Hf(T)}$ were remarkably similar. In the one case where the two ages are clearly different (RSES44-12.1) and represent two separate age domains, the Hf was also distinctive and yielded $\varepsilon_{Hf(T)}$ values different by 2 ε units.

From the results of the first analysis session, we infer that characterizing the crystallization age of a domain sampled by an

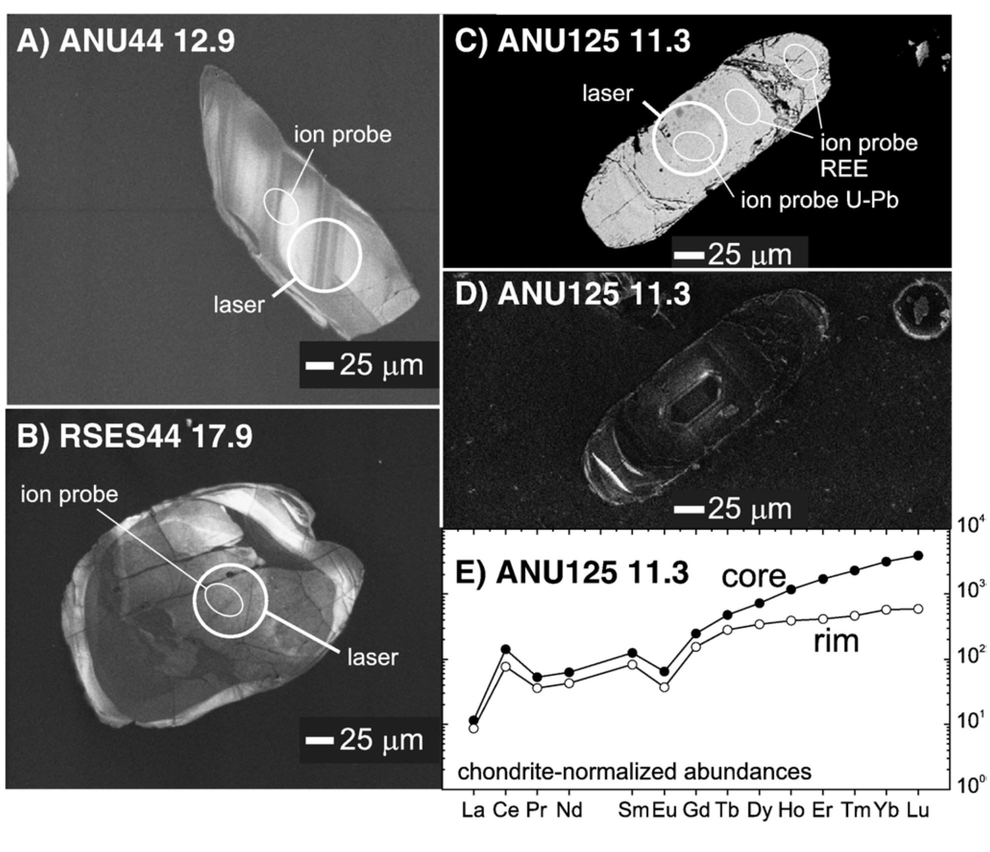

Fig. 1. A) Cathololuminescence (CL) image of RSES44-12.9 zircon exhibiting magmatic zoning showing locations of ion microprobe U–Pb and laser ablation Lu–Hf analyses. B) CL image of RSES44-17.9 zircon exhibiting patchy zoning showing locations of ion microprobe U–Pb and laser ablation Lu–Hf analyses. C) Backscattered image of ANU125_11.3 showing locations of ion microprobe U–Pb and laser ablation Lu–Hf analyses. D) CL images of ANU125_11.3. E) Chondrite normalized REE plots for core and rim analyses of ANU125_11.3 zircon.

82 μm laser spot using the ion microprobe U–Pb date is a reasonable approximation for 4.2 to 4.0 Ga Jack Hills zircons. That is, $\varepsilon_{Hf(T)}$ values calculated in this way will be typically accurate to better than 1 ε unit. Although multiple U–Pb analyses of Hadean zircons can yield highly variable ages, this largely reflects variable Pb loss rather than each date corresponding to a separate age domain as individual zircons rarely exhibit more than two generations of crystallization (cf. Valley et al., 2006).

We therefore treat the Lu–Hf data obtained without concurrent $^{207}Pb/^{206}Pb$ analysis (all obtained using an 82 μm spot) in the same fashion as in our earlier investigation (Harrison et al., 2005); i.e., by associating Hf with the ion microprobe age. For those analyses with both laser ablation MC-ICPMS and ion microprobe $^{207}Pb/^{206}Pb$ ages, the MC-ICPMS age is used for calculation of $\varepsilon_{Hf(T)}$. In the latter case, we have confidence that calculation artifacts produced by incorrect assignment of age to Hf in heterogeneous zircons (see Harrison et al., 2005) do not apply.

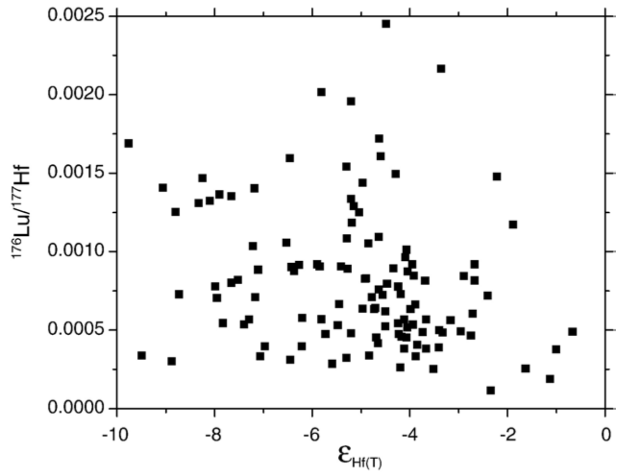

Fig. 3. Plot of ε_{Hf} vs. $^{176}Lu/^{177}Hf$ showing little obvious correlation indicating that samples with high Lu/Hf, and thus high corrections for mass 176 interferences, are indistinguishable.

4.2. Analysis session 2 (February 2007)

Given the interference at mass 204 seen in the March 2006 analyses, we abandoned monitoring of that mass and added 208 in addition to 206 and 207 in the February 2007 session as an alternative method to correct for common Pb and assess Th/U. During this interregnum, 22 zircons with $^{207}Pb/^{206}Pb$ ages from 4.22 to 4.36 Ga were identified and characterized for oxygen isotopes and Ti concentration in preparation for Lu–Hf analysis. As noted earlier, >4.2 Ga zircons are typically smaller than the younger grains and thus all Lu–Hf measurements in this session used a 62 μm laser beam diameter.

Analysis of these smaller, older grains resulted in nearly double the difference between the $^{207}Pb/^{206}Pb$ age determined by laser ablation and ion microprobe (Supplementary data Table 2). The average difference between the two ages was 0.08 Ga, and, again, the tendency was for the MC-ICPMS age to be younger. We observed more structure in $^{207}Pb/^{206}Pb$ ratios during analysis that, in several cases, correlated with *Hf* suggesting the presence of multiple isotopic domains. In those instances, we deconvolved these results by separating the time-domain signal into independent components within which apparent age is associated with the Hf isotopic composition (see Harrison et al., 2005).

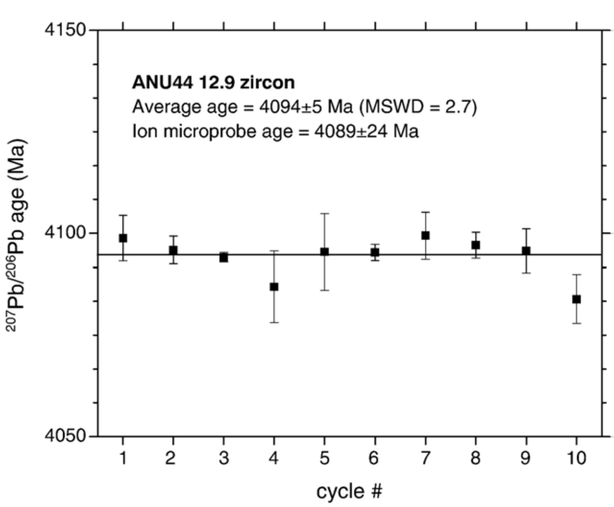

Fig. 2. $^{207}Pb/^{206}Pb$ profile during laser drilling of RSES44-12.9 zircon.

4.3. Hf results

All Lu–Hf results are shown as $\varepsilon_{Hf(T)}$ vs. age in Fig. 4A, coded as Hf–Pb or Hf-only. Also shown in Fig. 4A is the trajectory representing departures from CHUR at 4.56 Ga for Lu/Hf = 0. Several data plot within uncertainty of the Lu/Hf = 0, seemingly requiring derivation from an environment in which Lu was almost completely fractionated from Hf immediately following Earth accretion. In contrast to the earlier investigation (Harrison et al., 2005), we observed no positive $\varepsilon_{Hf(T)}$ values suggesting that zircons derived from a depleted reservoir are less abundant than previously thought. However, a follow-up study using the solution MC-ICPMS approach (Blichert-Toft and Albarède, 2008) documents additional positive values up to $\varepsilon_{Hf(T)} = 8$.

The use of coupled Hf–Pb measurements has given us enhanced confidence in the veracity of our earlier approach to appropriately identify the crystallization age associated with the initial Hf isotopic signal measured by MC-ICPMS methods. In Fig. 4B, we plot our new isotope data together with previously published Hf isotope studies of Jack Hills zircons (Amelin et al., 1999; Harrison et al., 2005).

4.4. Oxygen isotope results

Seventy-five oxygen isotope analyses of 33 zircons dated by ion microprobe to between 4.10 to 4.36 Ga yield a range of $\delta^{18}O$ values between 4.2 and 7.2‰ (Table 3). These data are shown as a probability density function in Fig. 5A along with previous ion microprobe $\delta^{18}O$ results for Jack Hills zircons (Trail et al., 2007; Cavosie et al., 2005; Peck et al., 2001) and

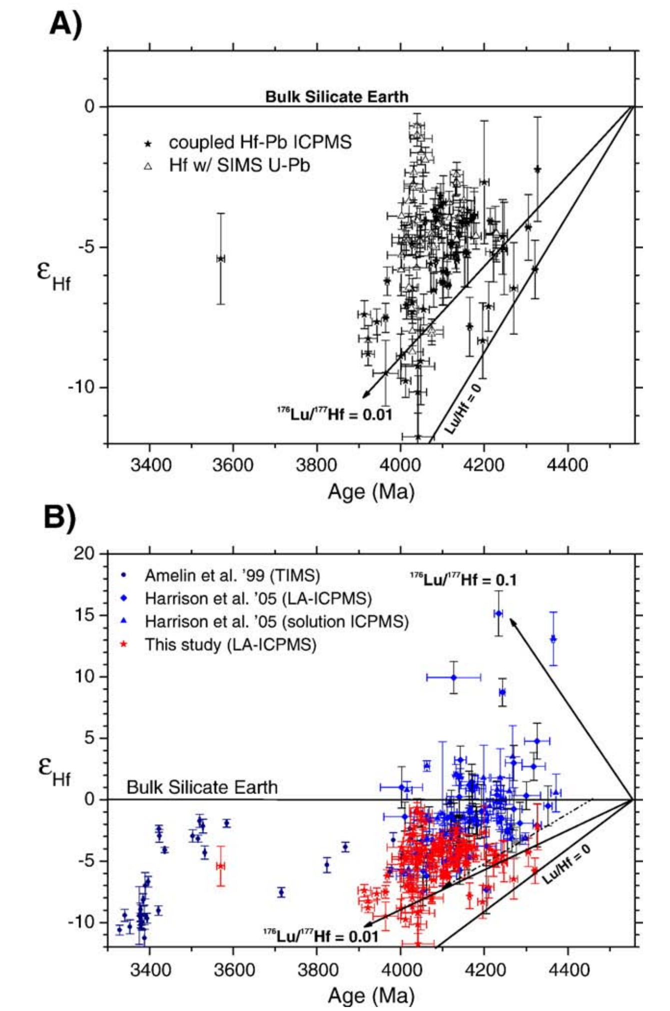

Fig. 4. A) Plot of $\varepsilon_{\mathrm{Hf}(T)}$ vs. age for 116 laser ablation Lu–Hf measurements on 87 zircons with $^{207}Pb/^{206}Pb$ ages up to 4.36 Ga. B) $\varepsilon_{\mathrm{Hf}(T)}$ data from A) together with results from Harrison et al. (2005) and Amelin et al. (1999). Black lines emerging at 4.56 Ga are trajectories showing *Hf* evolution for $^{176}Lu/^{177}Hf$ values of 0, 0.01, and 0.1. Dashed line from 4.46 Ga is from Caro et al. (2005).

data from lunar zircons (Nemchin et al., 2006) for reference. Note that not all of the zircons characterized by oxygen isotopes proved suitable for subsequent Lu–Hf analysis due to small grain size.

4.5. Ti thermometry

Ti concentrations were translated into temperature (Table 1) using the model of Watson and Harrison (2005). Results obtained prior to Lu–Hf–(Pb) analysis in the first analytical session (March 2006) were obtained in automated analysis mode and range from 602 to 1017 °C, roughly corresponding to the temperature spectrum previously seen, albeit with a higher proportion of >780 °C results (Watson and Harrison, 2005, 2006; Harrison et al., 2007). However, detailed ion imaging of >4 Ga Jack Hills zircons indicate that virtually all the very high temperature results are due to Ti contamination introduced along crystal imperfections (Harrison and Schmitt, 2007). The majority of zircons analyzed in the second Lu–Hf session were either ion imaged for Ti or subjected to multiple analyses permitting exogenous Ti to be identified. Once filtered for this effect, no apparent temperatures >780 °C were confirmed. We assume that the same relationship holds for the earlier analyses but cannot easily confirm this due to the semi-destructive nature of the laser ablation analysis.

5. Discussion

5.1. Relationships between Lu–Hf, $\delta^{18}O$, and Ti thermometry

In order to provide greater coverage of oxygen isotopes and Ti thermometry for >4.2 Ga zircons, we measured $\delta^{18}O$ for the grains used in session 2 which targeted older zircons. The new results (Table 2) show a broad range of $\delta^{18}O$ values, up to equivalent whole rock values of about +9‰. While consistent with earlier investigations (Mojzsis et al., 2001; Peck et al., 2001; Trail et al., 2007; Cavosie et al., 2005), we did not observe the even higher $\delta^{18}O$ values documented in those studies. As noted by Trail et al. (2007), the new data show that zircons with lower (<700 °C) apparent temperatures exhibit $\delta^{18}O$ values over the full 3‰ range with a tendency for the higher temperature zircons to cluster in a more restricted range of $\delta^{18}O$ (~1‰) close to mantle values (Fig. 5B). This is consistent with the fact that the full range of anatectic protoliths (i.e., altered basalts, orthogneisses, pelites) will all melt at ca. 650 °C under water-saturated conditions (and thus potentially show a broad range in $\delta^{18}O$) whereas zircons crystallizing from mafic and intermediate magmas will tend to yield higher crystallization temperatures (Harrison et al., 2007) and be characterized by juvenile oxygen isotope compositions.

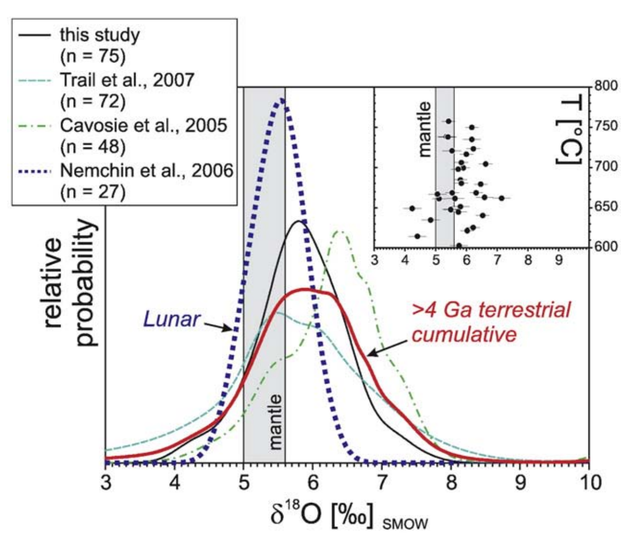

Fig. 5. Probability distribution functions for oxygen isotopes measurements on Hadean Jack Hills zircons from this study together with results from previous studies of Trail et al. (2007) and Cavosie et al. (2005). Data from the study of lunar zircons (Nemchin et al., 2006) are shown as possibly representative of the composition of Earth's Hadean mantle. Inset. Plot of crystallization temperature vs. $\delta^{18}O$ of Hadean zircons showing broad range of $\delta^{18}O$ values, up to equivalent whole rock values of about +9‰ and a tendency to range more widely at the lower end of the temperature spectrum.

The broad range of individual zircon $\delta^{18}O$ values within a single rock suggests that oxygen isotopes have been little affected by post-depositional exchange (Valley et al., 1994; cf. Watson and Cherniak, 1997). This is reinforced by the general homogeneity of intra-grain $\delta^{18}O$ (Table 3) which strongly contrasts with the highly variable Ti concentrated along cracks (Harrison and Schmitt, 2007). There is no obvious correlation between oxygen and *Hf*, but we note that values characteristic of mantle derivation ($\delta^{18}O \approx 5.6‰$) run the full spectrum of *Hf*, from −2 to −10 $\varepsilon_{Hf(T)}$, consistent with the derivation of zircons from the fusion of many different rock types.

5.2. Constraining terrestrial Lu/Hf fractionation

The confirmation that some 4.4–4.0 Ga terrestrial zircons contain extremely unradiogenic *Hf* is direct evidence that a significant silicate fractionation occurred early in Earth history leading to the production of at least some rocks of continental affinity. Our present dataset is dominated by results that are broadly bounded by bulk Earth evolution ($\varepsilon_{Hf(T)}=0$) and a reservoir with $0<{}^{176}Lu/{}^{177}Hf<0.02$. In principle, a two-stage model age for derivation of the enriched reservoir from a CHUR mantle can be made by extrapolating back in time using estimates of $^{176}Lu/^{177}Hf$. A limitation of this approach is that no isochronous relationship can be assumed among individual detrital zircons and thus there is no *a priori* statistical control gained from apparent correlations on Fig. 4B. However, the dataset is now sufficiently large that we can set conservative criteria to estimate when enriched (i.e., low Lu/Hf) zircon protoliths could have become isotopically isolated from the mantle.

We have recast the combined dataset (Harrison et al., 2005; this study) into a 2D probability function (*Hf* vs. age; Fig. 6, bottom) using Eq. B.4 (see Supplementary file B). Monte Carlo models were then performed by first randomly sampling a position in this 2D distribution. The approach we take is similar to that of Blichert-Toft and Albarède (2008), but sampling was restricted to *Hf* values greater than the initial chondrite ratio (Hf_o) and lower than CHUR ($\varepsilon_{Hf(T)}<0$). This value was then associated with a $^{176}Lu/^{177}Hf$ ratio obtained by random sampling of a second probability function, derived by compiling Lu/Hf from 8225 volcanic rocks with SiO_2 contents between 45–52% (Fig. 7; http://georoc.mpch-mainz.gwdg.de/georoc/). Note that the peak in this distribution at ~0.01, is also similar to the average $^{176}Lu/^{177}Hf$ of the tonalite–trondhjemite–granodiorite (TTG) suite (~0.008; Condie, 1993). In order that we not permit model separation ages to exceed the known age of chondrites, we restricted sampling of the $^{176}Lu/^{177}Hf$ distribution to values yielding ages ≤4.56 Ga. Note that the differences between the Lu/Hf distribution used and the empirical database that result from this choice are small (Fig. 7). Overall, 2000 Monte Carlo models were run in this fashion resulting in the spectrum of separation ages shown at the top of Fig. 6. The results are characterized by a broadly uniform distribution of ages between ~4.2 and 4.56 Ga (where the distribution is artificially truncated). Using instead the $^{176}Lu/^{177}Hf$ distribution for volcanic rocks with SiO_2 between 52–78% (i.e., assuming the direct formation of continental-type crust; Fig. 7) does not shift the distribution to appreciably older ages. However, assuming extraction from a depleted mantle (DM) composition rather than CHUR does increase the average extraction age in the distribution (Blichert-Toft and Albarède, 2008).

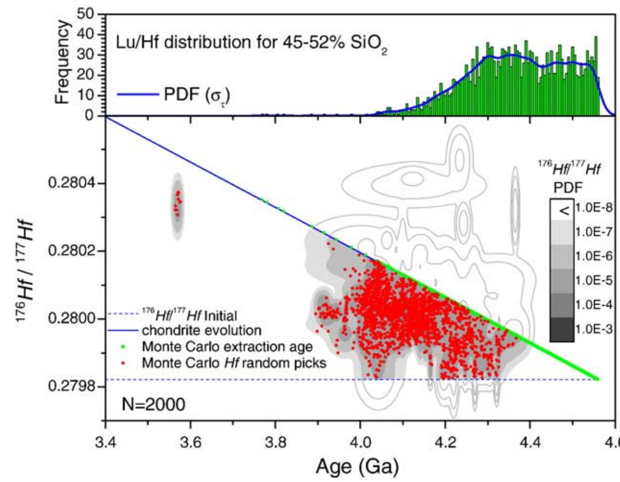

Fig. 6. Top) Extraction ages of zircon protoliths from CHUR obtained from 2000 Monte Carlo models. The distribution is broadly uniform between ~4.2 and 4.56 Ga. Bottom) Combined Jack Hills initial Hf dataset shown as a 2D probability function. Red dots show location of 2000 random samples of the probability distribution. Green dots show projections back to CHUR of those sampled locations using a $^{176}Lu/^{177}Hf$ randomly sampled from the black distribution in Fig. 7.

Given the conservative nature of our assumptions, we interpret the age spectrum in Fig. 6 as supportive of the view that the >4 Ga Jack Hills zircons were derived from crustal protoliths that formed essentially continuously during the Hadean, and beginning almost immediately upon planetary formation. This conclusion is essentially independent of the relatively few data representing the least radiogenic Hf. That is, ignoring data within error of the 'forbidden zone' (see Fig. 4) does not appreciably alter this conclusion. However, to further quantify the meaning of 'almost immediately upon planetary formation' requires further scrutiny of these results.

5.3. Statistical assessment of the $\varepsilon_{Hf(T)}$ dataset

As already noted, geochemical data derived from detrital samples present special challenges for statistical analysis. We do not *a priori* know the relationship of an individual datum to the rest of the population and thus determining whether a specific result is a statistical outlier is problematic. We present below a model with which to address this issue.

We begin by noting the case of ANU125_11.3 ($\delta^{18}O=5.6‰$, Table 1; $T_{min}=700°C$, Harrison and Schmitt, 2007) which yields a concordant U–Pb ion microprobe age in the core (Fig. 1C and D) of 4.328±0.012 Ga and an identical, and more precise, laser ablation $^{207}Pb/^{206}Pb$ date, also restricted to the core, of 4.321± 0.004 Ga (Fig. 1C). However, when corrected for radiogenic ingrowth, the Hf value of 0.279821 ($\varepsilon_{Hf(4.32\ Ga)}=-5.8\pm1.0$) is identical to the calculated solar system initial (Supplementary file A; Blichert-Toft and Albarède, 1997). The in run data are unexceptional (e.g., $^{174}Hf/^{177}Hf$ is well within 2σ of the

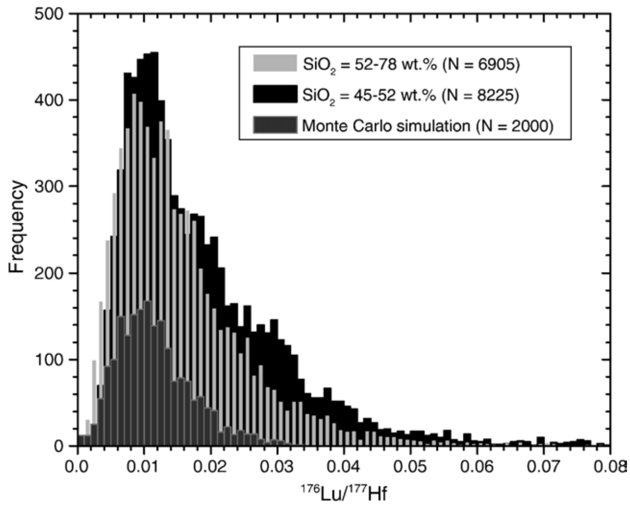

Fig. 7. $^{176}Lu/^{177}Hf$ distributions of volcanic rocks with SiO_2 contents between 45–52% and 52–78% are shown together with the distribution used in the Monte Carlo modelling to calculate the extraction age distribution (top of Fig. 6).

average; Yb and Hf mass bias corrections are nominal), although the ^{176}Yb correction and $^{176}Lu/^{177}Hf$ of 0.002 (from which correction for radiogenic ^{176}Hf ingrowth is made) are both on the high side of the zircons measured. Propagating the uncertainties in age and isotope ratios yields a limiting bound of $^{176}Lu/^{177}Hf = 0.002$ at 4.56 Ga for the protolith of this sample. For the limiting case of Lu/Hf = 0, at the conservative 2σ error limits of both Lu/Hf and Hf that would maximize the calculated value of Hf for ANU125_11.3, the *lower* limit for the time of extraction from CHUR is 4.52 Ga. To confirm the origin of this grain, we measured REE in both the core and rim (Fig. 1E) which revealed Ce anomalies characteristic of a terrestrial origin.

Four other data (ANU81-10.9, ANU121-8.11, ANU51-6.12, Supplementary data Table 2; ANU66-9.10, Harrison et al., 2005) plot at ~0.5 ε_{Hf} from the forbidden zone, with uncertainties that extend across it. The first three were analysed by the coupled Hf–Pb method and yield ion microprobe and MC-ICPMS $^{207}Pb/^{206}Pb$ ages that are concordant within uncertainty. Thus we are confident that the appropriate age is being ascribed to $\varepsilon_{Hf(T)}$. The last datum, from the study of Harrison et al. (2005), was measured for Hf only by laser ablation MC-ICPMS and thus the bulk age of the analysis pit is unconfirmed.

To examine these and other data, we have defined a new differential quantity, $\varepsilon_o(Hf)$, that represents the difference between the measured *Hf* ratio at time *t* and the calculated initial chondritic Hf ratio (Hf_o) (Supplementary file A). Note that in a traditional $\varepsilon_{Hf(T)}$ vs. age plot, this difference is the distance of each point to the line defined by Lu/Hf = 0 (Fig. 4A). This line defines the limit of the 'forbidden region' (Harrison et al., 2005) since values below this line imply the existence of samples with *Hf* ratios *less than* the chondritic initial ratio. We have calculated $\varepsilon_o(Hf)$ values and propagated the various uncertainties using Eq. B.3 (Supplementary file B), including the variance in chondritic Lu–Hf systematics and its influence on estimating Hf_o (i.e., the solar system initial ratio). We then calculated the 1D probability density function (PDF) for the complete dataset (Fig. 8A) by summing the Gaussian distributions associated with each measurement. For comparison, we show a histogram of the raw $\varepsilon_o(Hf)$ values (Fig. 8A).

The PDF (Fig. 8A) can also be used to gain further insight into the probability of obtaining a datum adjacent or within the forbidden zone ($\varepsilon_o(Hf) < 0$). Examining the first few percent of the PDF shows that our data have a probability greater than zero (~0.6%) of containing a negative $\varepsilon_o(Hf)$ result (Fig. 8B). Furthermore, recalculation of the PDF omitting the ANU125_11.3 datum still yields a probability of observing a negative $\varepsilon_o(Hf)$ result of ~0.5% (i.e., one should expect at least one negative ε_o (Hf) result for $N = 221$, even if no actual sample is within ~1/2 ε of the forbidden zone). To illustrate this, we have recalculated the PDF by removing the points closest to zero (i.e., the ANU125_11.3 datum plus the four data within 1 $\varepsilon_o(Hf) = 0$). This new cumulative PDF (Fig. 8B) yields a value of ~0.25% at $\varepsilon_o(Hf) = 0.5$, implying that we would need at least 1600 measurements to get four values within $\varepsilon_o(Hf) \approx 0.5$.

We used the cumulative PDF obtained from all the positive results ($N = 220$) as a proxy for the actual distribution of $\varepsilon_o(Hf)$ in Nature. We then followed the method of Press et al. (1988; p. 200) in transforming a random uniform distribution into one associated with the assumed $\varepsilon_o(Hf)$ distribution. Monte Carlo modelling of this distribution (Fig. 9) shows a high probability of getting at least one negative result for every ~200 measurements. We thus conclude that while the ANU125_11.3 datum may be

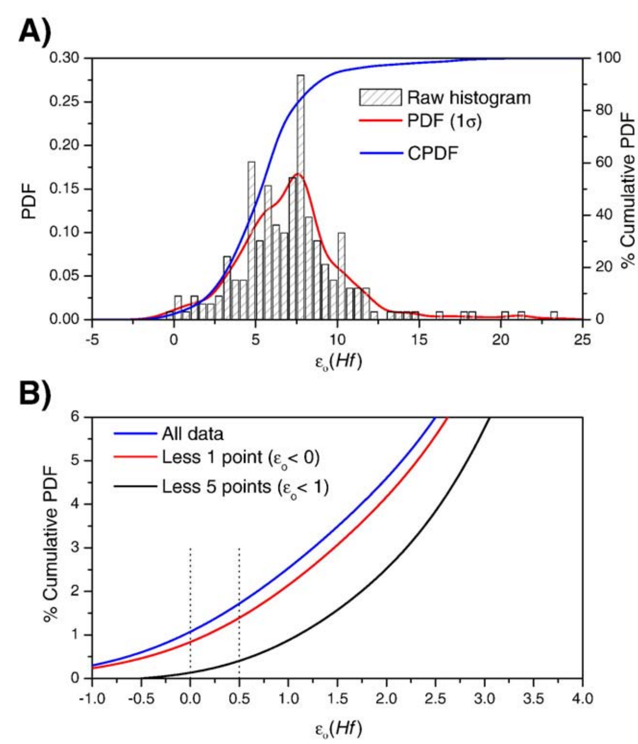

Fig. 8. A) Histogram of the 221 raw ε_o values together probability density function (PDF) of summed Gaussian distributions (red curve) using propagated errors as discussed in the text and the cumulative PDF (blue curve). B) Close-up of the cumulative PDF plot highlighting values close to zero. Note that removing the one datum with a negative $\varepsilon_o(Hf)$ (red curve) drops the cumulative PDF only slightly such that there is still an expectation at the ~0.6% level of a negative value occurring. When the four data with $\varepsilon_o \approx +0.5$ are removed, the tail of the PDF no longer extends to values significantly <0.

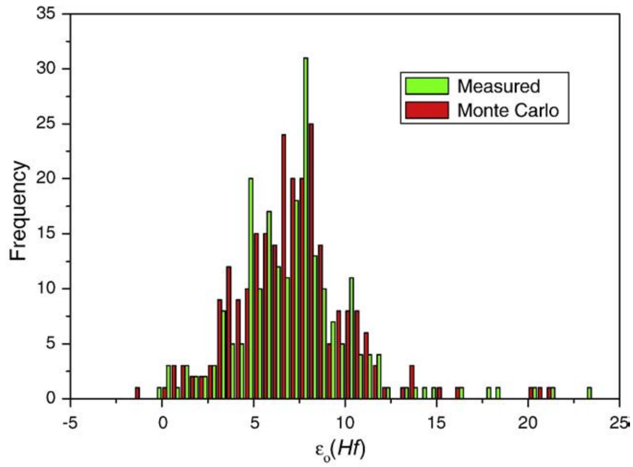

Fig. 9. Histogram from Fig. 8A together with Monte Carlo simulations obtained from 200 random selections from the cumulative PDF which show the high probability of getting at least one negative result for every ~200 measurements.

the expected outlier, the four data clustering at ~0.5 $\varepsilon_o(Hf)$ are likely real. Even assuming Lu/Hf=0 subsequent to separation, this implies the protolith(s) of these zircons was removed from a CHUR reservoir prior to 4.5 Ga.

On a cautionary note, we point out that the overall PDF (Fig. 8A) is remarkably close to a Gaussian distribution centred at $\varepsilon_o(Hf)=7\pm5$ (2σ) ($R^2=0.95$). If we assume that the real $\varepsilon_o(Hf)$ is given by this Gaussian function, a Kolmogorov–Smirnov statistical test gives a 98% probability that our measured $\varepsilon_o(Hf)$ distribution is Gaussian. Two contrasting interpretations are suggested. The first is that there are unaccounted for errors in our calculation of $\varepsilon_{Hf(T)}$ at the level of 5 ε (2σ). If so, the data set would be broadly consistent with sequestration of zircon protoliths from CHUR at 4.3–4.4 Ga, assuming Lu/Hf=0. For a Lu/Hf characteristic of TTG's (~0.008; Fig. 7), the separation age increases to >4.4 Ga. However, it is unclear how we might be underestimating errors by a factor of ~5 and the highly non-linear relationship between Pb–Pb age and Hf in the calculation of $\varepsilon_{Hf(T)}$ (Harrison et al., 2005) acts to produce heterogeneity rather than a normal distribution (Fig. 8A). Alternatively, this distribution may reflect essentially continuous Hadean crustal growth of which the detrital zircon record is a random sample.

5.4. Other evidence for early silicate Earth differentiation

Other recent results support the conclusion, albeit indirectly, that a profound differentiation event affected the early silicate Earth. Observed $^{142,143}Nd/^{144}Nd$ variations in early Archean rocks (Caro et al., 2003; Boyet et al., 2003), together with assumptions regarding the Sm/Nd of key terrestrial reservoirs, suggest a major silicate differentiation within ~150 m.y. of planetary accretion. To explain the apparent lack of co-variance of Nd and Hf isotopes in ~3.7 Ga West Greenland gneisses, Caro et al. (2005) proposed a multi-stage model involving melt segregation from a crystallizing magma ocean, with Ca-perovskite playing a key role in fractionating the two isotopic systems. The predicted trajectory for Lu/Hf in the resulting protocrust (shown in Fig. 4B) is broadly consistent with all but the dozen or so least radiogenic of our Hf isotopic results. Given that mantle-derived Archean rocks are characterized by both enriched and depleted signatures (Vervoort and Blichert-Toft, 1999; Blichert-Toft and Arndt, 1999; Blichert-Toft et al., 2004), the specificity of their model may not be justified. The strongly negative $\varepsilon_{Hf(T)}$ values throughout the Hadean are equally consistent with garnet fractionation (Draper et al., 2003) dominating trace element partitioning in the Hadean upper mantle.

Boyet and Carlson (2005, 2006) observed that average chondrite $^{142}Nd/^{144}Nd$ is ~20 ppm lower than that of the observable silicate Earth. The restricted range of Sm/Nd in terrestrial reservoirs and the short (103 Ma) half-life of ^{146}Sm would require the superchondritic terrestrial Sm/Nd inferred responsible for this difference to have formed by 4.53 Ga, consistent with our estimate of ≥4.5 Ga. Continental-type crust cannot be the complementary subchondritic reservoir *in toto* (i.e., it does not contain the 'missing' Nd and thus Hf), but could account for up to ~20% of an early enriched LREE reservoir. Alternatively, the 20 ppm difference in $^{142}Nd/^{144}Nd$ between chondrites and Earth could be due to Sm–Nd fractionation in the solar nebula.

The existence of Hadean zircons has been known for a quarter of a century (Froude et al., 1983) but were long considered ambiguous evidence of pre-4 Ga continental crust. For example, Galer and Goldstein (1991) noted that Hadean zircons did not "unequivocally prove the existence of some continental crustal material at ~4.2 Ga" as they could have formed in an ocean island setting. However, zircon crystallization thermometry results (Watson and Harrison, 2005; Harrison et al., 2007; Harrison and Schmitt, 2007; Grimes et al., 2007) essentially rule out the possibility that Hadean zircons are largely derived from mafic, or even intermediate, magmas (cf. Taylor and McLennan, 1985; Galer and Goldstein, 1991; Valley et al., 2006; Coogan and Hinton, 2006). Clearly, by 4.35 Ga, sialic crust had begun to form on Earth. While we cannot state unambiguously that rocks of continental affinity were among the earliest formed, our data indicate that crust formed by 4.5 Ga was later reworked to generate hydrated granitoids during the Hadean.

6. Conclusions

We have measured initial *Hf* in 116 zircons ranging in age from 3.5 to 4.36 Ga from Jack Hills, Western Australia, by laser ablation inductively-coupled plasma mass spectrometry. Most of these measurements involved use of coupled Hf–Pb analysis that permit a direct test of the use of ion microprobe ages in characterizing $\varepsilon_{Hf(T)}$ from Hf isotope data obtained from a much larger sampled region. We observe a broad range of $\varepsilon_{Hf(T)}$ values varying from close to bulk Earth to strongly negative deviations from CHUR confirming earlier results and allaying concerns that the large range in $\varepsilon_{Hf(T)}$ previously seen was due to calculation artefacts from analysis of mixed age domains within zircons. Negative values of $\varepsilon_{Hf(T)}$ observed between 4.36 and 4.0 Ga indicate the development of a low Lu/Hf reservoir by 4.5 Ga. We interpret these data as documenting a major fractionation of the silicate Earth at that time, including creation of crust. The characteristics of Hadean zircons (inclusion assemblage, oxygen isotopes, crystallization temperature, etc.) are most consistent with formation in an environment not unlike modern continental crust by 4.35 Ga. Thus the emerging scenario for the Hadean is one of crust formation by 4.5 Ga followed by essentially continuous 1) formation of new crust, 2) internal crustal reworking, and 3) rapid crustal recycling into the mantle, possibly by mechanisms analogous to the era of plate tectonics.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.epsl.2008.02.011.

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