

Magmatic $\delta^{18}\text{O}$ in 4400–3900 Ma detrital zircons: A record of the alteration and recycling of crust in the Early Archean

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Abstract

Ion microprobe analyses of $\delta^{18}\text{O}$ in 4400–3900 Ma igneous zircons from the Jack Hills, Western Australia, provide a record of the oxygen isotope composition of magmas in the earliest Archean. We have employed a detailed analysis protocol aimed at correlating spatially related micro-volumes of zircon concordant in U/Pb age with $\delta^{18}\text{O}$ and internal zoning. Simultaneous analysis of ^{18}O and ^{16}O with dual Faraday cup detectors, combined with frequent standardization, has yielded data with improved accuracy and precision over prior studies, and resulted in a narrower range of what is interpreted as magmatic $\delta^{18}\text{O}$ in >3900 Ma zircons. Preserved magmatic $\delta^{18}\text{O}$ values from individual zircons (Zrc) range from 5.3‰ to 7.3‰ (VSMOW), and increasingly deviate from the mantle range of $5.3 \pm 0.3\text{‰}$ as zircons decrease in age from 4400 to 4200 Ma. Elevated $\delta^{18}\text{O}$ (Zrc) values up to 6.5‰ occur as early as 4325 Ma, which suggests that evolved rocks were incorporated into magmas within ~230 Ma of Earth's accretion. Values of magmatic $\delta^{18}\text{O}$ (Zrc) as high as 7.3‰ are recorded in zircons by 4200 Ma, and are common thereafter. The protoliths of the magmas these zircons crystallized in were altered by low temperature interaction with liquid water near Earth's surface. These results provide the strongest evidence yet for the existence of liquid water oceans and supracrustal rocks by approximately 4200 Ma, and possibly as early as 4325 Ma. The range of magmatic $\delta^{18}\text{O}$ values in the 4400–3900 Ma zircons is indistinguishable from Archean igneous zircons, suggesting similar magmatic processes occurred over the first two billion years of recorded Earth history. Zircons with sub-solidus alteration histories, identified by the presence of disturbed internal zoning patterns, record $\delta^{18}\text{O}$ values both below (4.6‰) and above (10.3‰) the observed range for primary magmatic zircon, and are unreliable indicators of Early Archean magma chemistry.

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1. Introduction

While the earliest history of Earth is poorly constrained due to the absence of any known rocks older than 4030 Ma [1], detrital zircons preserve evidence of magmatic processes as early as 4400 Ma [2]. The rock-forming events recorded by Early Archean zircons (>3800 Ma) have been interpreted as marking the emergence of proto-continental crust [2–4]. Here we use the oxygen isotope composition ($\delta^{18}\text{O}$) of Early Archean igneous zircons to track the alteration and recycling of this early formed crust on the young Earth. Oxygen isotope ratios are sensitive to the recycling of altered crust into magmas, a process that produces zircons with diverse $\delta^{18}\text{O}$ values that deviate from the mantle range. Using zircon to document the effects of surface processes on >3900 Ma magma compositions can place absolute time constraints on when evolved crust formed and also when surface waters appeared, the latter being a pre-requisite for supporting life on Earth.

The ability to study igneous processes older than 3900 Ma from detrital zircons is made possible by the refractory behavior of zircon, which can preserve the primary magmatic chemical/isotopic composition inherited from its parental melt at the time of crystallization, despite enduring long time spans in complex geologic systems. Due to the slow diffusion of oxygen in zircon in most crustal environments [5,6], unaltered igneous zircon retains the oxygen isotope ratio ‘locked in’ during crystallization, which is a function of the oxygen isotope composition of the parent magma, $\delta^{18}\text{O}$ (magma) [7]. Thus, by analyzing the $\delta^{18}\text{O}$ of >3900 Ma detrital igneous zircons the oxygen isotope composition of Early Archean magmas can be determined in the absence of preserved rocks. Magmatic zircon crystallizing from melts in equilibrium with the mantle preserves a narrow range of $\delta^{18}\text{O}$ = $5.3 \pm 0.3\text{‰}$, one standard deviation (1 S.D.) [7], and is insensitive to closed-system crystallization processes that can elevate the $\delta^{18}\text{O}$ of melts by up to $\sim 1\text{‰}$ [8–10]. As a consequence, $\delta^{18}\text{O}$ values higher than $\sim 6.3\text{‰}$ in igneous zircon require a component of supracrustal rock in the melt, based on equilibrium fractionation of $\delta^{18}\text{O}$ between melt and zircon [11].

Large variations in $\delta^{18}\text{O}$ have been proposed for Early Archean magmas. Twelve >4000 Ma zircons have previously been analyzed for $\delta^{18}\text{O}$, with values ranging from 5.0‰ to 15.0‰ [2,3,12]. Calculated $\delta^{18}\text{O}$ (magma) compositions range from 6‰ to 9‰ [3] up to 17‰ [12]. However, as $\delta^{18}\text{O}$ has been reported for only 12 >4000 Ma zircons, it is difficult to establish how representative these values are for Early Archean magmas. Moreover, grain images have been published for only one of the 12 zircons [2,3], thereby precluding a detailed evaluation of whether or not the micro-volumes analyzed for $\delta^{18}\text{O}$ represent magmatic chemistry or secondary alteration. Establishing if these $\delta^{18}\text{O}$ (Zrc) values are products of magmatism or alteration is critical for understanding magmatic processes in general, and in particular for Early Archean magmas, as values of $\delta^{18}\text{O}$ (Zrc) above 8‰ have not been found in zircons separated from over 120 Archean igneous rocks analyzed by laser fluorination, and the value of 15.0‰ is substantially higher than zircon from any igneous rock analyzed to date [7,13,14].

The goal of this paper is to better constrain the oxygen isotope composition and evolution of >3900 Ma zircon-crystallizing magmas by closely correlating the $\delta^{18}\text{O}$ of zircons in concordant U/Pb domains with internal zoning. We present high spatial resolution analyses of $\delta^{18}\text{O}$ (Zrc) by ion microprobe for 44 >3900 Ma detrital zircons from the Jack Hills, Western Australia, previously characterized for U/Pb age and internal zoning. By analyzing the portions of zircons most likely to preserve magmatic chemistry, the $\delta^{18}\text{O}$ values can be used to constrain when evolved crust was extant, and demonstrate the effects of surface processes on the chemical diversity of magmas older than 3900 Ma.

2. Samples and analytical methods

2.1. Early Archean zircon samples

The forty-four detrital zircons from Jack Hills range in age from 4400 to 3900 Ma. Aspects of these grains, including details of their field locations, rock descriptions, zircon separation techniques, cathodoluminescence (CL) images, and U/Pb analyses have been described previously [4]. The zircons are

from metasediment samples W74, 01JH36, 01JH54, and 01JH60, and are contained in five polished round epoxy grain mounts.

The majority of the zircons in this study have previously been interpreted as magmatic in origin based on internal zoning observed in CL images and Th–U chemistry [4]. Internal zoning patterns are an important criterion for demonstrating that a zircon has not been altered, as primary growth patterns are usually present in unaltered igneous zircon. Typically, magmatic growth zoning is regular, geometric and symmetrical; alteration can result in irregular, patchy, or cloudy zoning (see review by [15]). Thirty-one of the zircons analyzed here display oscillatory zoning in CL that is attributed to growth in a magma [16] [Appendix 1(a)–(ae)], including five grains that also display varying degrees of sector zoning [Appendix 1(p), (z), (ac)–(ae)]. Thirteen grains have irregular zoning [Appendix 1z, (af)–(ao)]. Ten of the thirteen irregularly zoned crystals have partially banded zoning patterns that may represent growth zoning, but are ambiguous (the other three grains have patchy zoning, which is strongly indicative of alteration [Appendix 1 (ap)–(ar)] [17]). Part of the ambiguity arises from the random orientation of the exposed grain surface. Crystals that are polished parallel to the *c*-axis tend to produce images that allow better evaluation of the overall zoning patterns (see examples in [15]); randomly oriented grain fragments may expose surfaces within the crystal that do not display a regular pattern.

Some of the zircons in this study record evidence of recrystallization. Grain 01JH54-37 [Appendix 1(ad)] displays a non-concentric sector zoning pattern, with remnants of concentric oscillatory zoning preserved near both grain terminations. Other zircons that display CL patterns with sector-zonation and concentric oscillatory zoning appear magmatic in origin [Appendix 1(p), (z), (ac), and (ae)], although partial recrystallization cannot be ruled out.

These samples present an ideal opportunity to not only establish the range of magmatic $\delta^{18}\text{O}$ (Zrc) in >3900 Ma zircons based on concordant igneous grains with preserved growth zoning, but also to document the $\delta^{18}\text{O}$ of zircons with disturbed zoning, as the effects of secondary processes (e.g. alteration, recrystallization) on the preservation of magmatic $\delta^{18}\text{O}$ are currently unknown.

2.2. Standard zircon KIM-5

Each zircon mount contained a 0.5 to 1.0 mm chip of oxygen isotope standard zircon KIM-5. The chips were obtained from a single cm-size kimberlite megacryst zircon from Kimberley, South Africa, with a $\delta^{18}\text{O}$ value of $5.09 \pm 0.06\text{‰}$ [7,18]. Fifteen age determinations by SHRIMP II were made on two chips of KIM-5 (Fig. 1a). The data were reduced with SQUID [19] and plotted using Isoplot/Ex [20]. The $^{206}\text{Pb}/^{238}\text{U}$

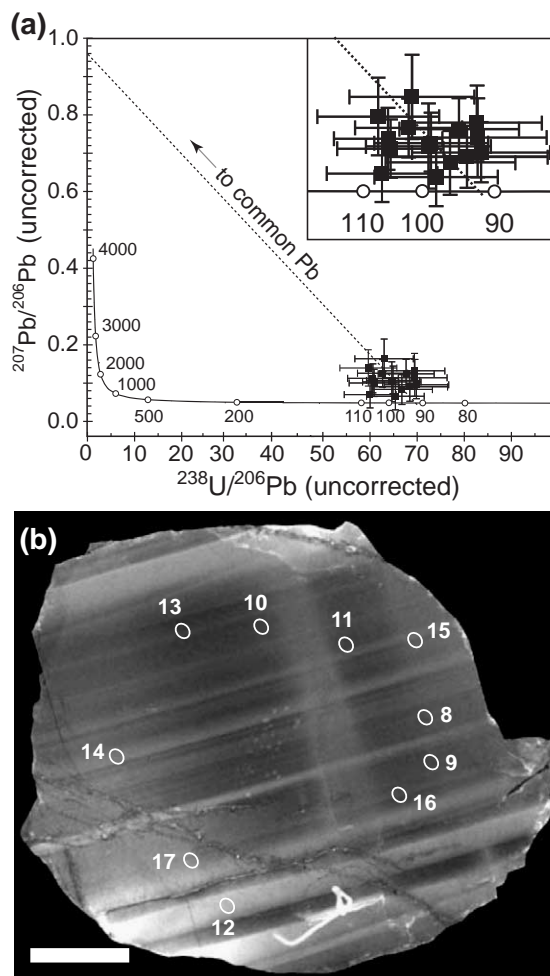


Fig. 1. SHRIMP II U–Pb analyses of zircon standard KIM-5. (a) Tera–Wasserburg concordia plot of 15 SHRIMP II analyses of two different chips of KIM-5 made in two different sessions. Ages along concordia are in Ma. Error bars are 2σ . (b) CL image of one of the KIM-5 chips used as an oxygen standard in this study (embedded in mount 01JH36). Numbered analyses correlate to U–Pb analyses 8 through 17 listed in Appendix 2. Scale bar is 200 μm .

ages corrected for common Pb using both ^{204}Pb measured values (88 ± 11 Ma, 2σ) and ^{208}Pb -corrected values (92 ± 3 Ma, 2σ) are indistinguishable within error. The ^{208}Pb -corrected value of 92 ± 3 Ma coincides with the concordia intercept of a line regressed through the data from common Pb and is our preferred age, and also identifies KIM-5 as originating from the Group I kimberlites in the Kaapvaal craton [21]. One of the KIM-5 chips used as an oxygen isotope standard in this study is one of the two chips analyzed by SHRIMP II (embedded in mount 01JH36). This chip preserves oscillatory zoning in CL (Fig. 1b) and, aside from a few fluid and/or mineral inclusions, does not appear to have experienced the pervasive alteration of some Group I kimberlite zircons reported by [21]. SHRIMP II U–Th–Pb analyses of KIM-5 were made at Curtin University, calibrated with zircon standard CZ3 (U/Pb age = 564 Ma), and closely follow the analytical protocols outlined in [22]. Results of the U/Pb isotopic analyses are listed in Appendix 2.

2.3. Electron beam techniques

Individual zircons were imaged with a scanning electron microscope (SEM) in back-scattered electron (BSE), secondary electron (SE) and cathodoluminescence (CL) mode. Images were collected using standard operating conditions with a Phillips XL30CP SEM (BSE, CL, SE) at the University of Edinburgh, and also with a LEO 1550 SEM (BSE, SE) at the Synchrotron Radiation Center, University of Wisconsin-Madison. The reported HfO_2 concentrations are the average of three analyses on each crystal made in different spots using wavelength dispersive spectroscopy with a CAMECA SX50 electron microprobe at the University of Wisconsin (data for other major and minor elements will be reported elsewhere). The analytical conditions during the Hf analyses were 18 kV and 20 nA, and a combination of synthetic and natural standards were used to calibrate the elemental data.

2.4. Ion microprobe analytical conditions

Oxygen isotope analyses of zircon were made with the CAMECA ims-1270 ion microprobe at the Edinburgh Ion Microprobe Facility (EIMF), University of Edinburgh. A primary beam of $^{133}\text{Cs}^+$ with a

2.5–3.0 nA current was used, with charge compensation of the Au-coated samples accomplished using a normal incidence electron flood gun. A pre-sputtering time of 45 s to remove the Au-coat was identical for all analyses. Sputtering with a fixed beam produced roughly elliptical 15×20 μm pits 2–3 μm deep. Ions were extracted with a 10 kV voltage, and low energy secondary ions of ^{16}O and ^{18}O were selected using an energy window of 60 eV. During each analysis, the secondary beam was automatically scanned across a small field aperture for centering along the ion-optic axis, followed by scanning the entrance slit across the contrast aperture. The daily mass resolving power was 2400, sufficient to resolve hydride interferences (e.g. ^{17}OH , ^{16}OD , $^{16}\text{OH}_2$). Secondary ions were simultaneously collected on Faraday collectors (FC) with average count rates from 1.2 to 2.5×10^9 cps for $^{16}\text{O}^-$ and 2.4 to 5.0×10^6 cps on $^{18}\text{O}^-$ (depending on session, see below). The background of the FC was measured at the beginning of each session. Each spot measurement was divided into 2 blocks consisting of 5 cycles/block (totaling 10 cycles) with a count time of 4 s/cycle resulting in a total count time of 40 s. Moving the sample, selecting the next grain and area to analyze, adjusting the sample height (Z-focus), pre-sputtering, and ion counting resulted in a total analysis time of approximately 6 min.

Seven analytical sessions were conducted over a 72-h period from March 15–17, 2004. The term ‘session’ refers to a period of time over which no major instrumental adjustments were made (e.g. sample exchange, beam re-alignment) during the calibration of a series of samples by analyses of standards embedded in the same mount. A new session began each time a sample mount was exchanged (sessions 3, 5, 6 and 7), when the ion microprobe was started up ‘cold’ (sessions 1 and 2), or after the primary or secondary column was re-tuned beyond minor focusing (session 4). Standards in the same mount as the samples were analyzed to bracket sample analyses, with an average of 8 sample analyses between each standardization (Fig. 2). During the seven analytical sessions a total of 194 analyses of KIM-5 were made to calibrate 172 sample analyses of 44 zircons. An additional 38 analyses of KIM-5, made during ‘tuning’ periods, were not used for standardization and are omitted.

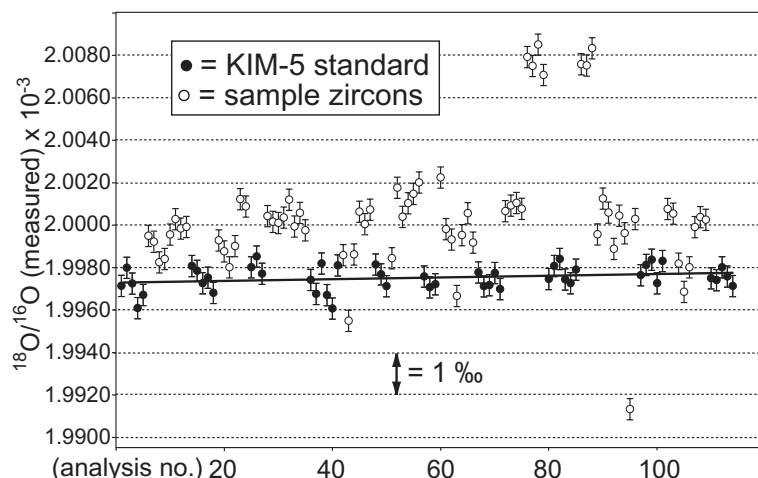


Fig. 2. Example of bracketing sample analyses with standard analyses during an ion microprobe session. During this 12 h session (session 5) on sample mount 01JH54, 114 analyses were made: standards ($n=46$) and samples ($n=68$). The solid line is a regression through all of the standard analyses to quantify drift throughout the session. In this session, the drift of $0.002\text{‰}/\text{analysis}$ was minimal. In other sessions, drift approached $0.05\text{‰}/\text{analysis}$, and the average of drift from all sessions was $0.006\text{‰}/\text{analysis}$ (Table 3). Note in particular the consistency of the standards bracketing analyses no. ~ 70 through ~ 100 , where the range of the samples varied by over 8‰ .

External precision refers to the spot-to-spot reproducibility of $\delta^{18}\text{O}$ values from analyses made in different locations on the same crystal under the same analytical conditions (i.e. in the same session), and internal precision refers to the precision of any single analysis based on the number of ions counted during the analysis [23]. Thus, with the same analytical conditions, the internal precision is identical for both standard and sample analyses, whereas external precision may vary for a variety of sample-related (e.g. sample heterogeneity, number of analyses) and/or instrumental reasons. In this study, estimates of the best possible internal precision for ^{18}O range from 0.07‰ to 0.10‰ (1 SD) based on counting statistics. This ideal precision was not achieved due to other limiting factors, including suspected variation of the background on the FC.

2.5. Oxygen isotope analysis: ion microprobe vs. laser fluorination

Typically zircons are analyzed for $\delta^{18}\text{O}$ by laser fluorination with analytical precision of $\pm 0.05\text{‰}$ (1 S.D.), e.g. [7,11,24], which is superior to published ion microprobe data for $\delta^{18}\text{O}$ (Zrc), but requires >1 mg of zircon. Ion microprobe studies of $\delta^{18}\text{O}$ (Zrc) using a CAMECA ims-4f with a single detector have

reported external precision for zircon standard KIM-5 of $\pm 1.0\text{‰}$ to $\pm 1.4\text{‰}$ (1 S.D.) [25] and $\pm 0.7\text{‰}$ to $\pm 1.0\text{‰}$ (1 S.D.) [2,3]. Ion microprobes are thus less precise than laser fluorination, however, the small penalty in precision is more than compensated by the ability to make high spatial resolution in situ analyses ($\sim 20\text{ }\mu\text{m}$ spots) on single zircons in multiple locations while consuming one million times less material than laser analysis ($1\text{--}2\text{ ng}$ vs. $1\text{--}2\text{ mg}$).

Analysis of $\delta^{18}\text{O}$ in zircon by ion microprobe presents new opportunities and challenges with respect to distinguishing magmatic oxygen isotope ratios from non-magmatic values that can result from secondary processes (e.g. hydrothermal alteration, recrystallization, radiation damage). Zircons are known to vary by over 20‰ in $\delta^{18}\text{O}$ (e.g. -10.0‰ to $+13.0\text{‰}$) and thus $\delta^{18}\text{O}$ alone is not sufficient for identification of magmatic values [26–28]. The analysis of primary (magmatic or otherwise) $\delta^{18}\text{O}$ (Zrc) by laser fluorination can be accomplished by pre-treating $\sim 2\text{ mg}$ aliquots of non-magnetic grains in concentrated acids (e.g. HF, HNO_3 , HCl) that dissolve radiation damaged areas of crystals, crack-filling materials, and other contaminants, leaving behind gemmy, refractory zircon of primary composition [7,24]. For igneous rocks that contain abundant zircons of a single generation, bulk analysis of 2 mg by laser fluorination

yields consistent and reproducible magmatic $\delta^{18}\text{O}$ values [7,24,29]. Zircons analyzed in situ for $\delta^{18}\text{O}$ by ion microprobe typically do not undergo acid treatment; targeting areas that preserve primary values and avoiding altered areas of crystals, inclusions, and crack-filling materials requires a beam positioning strategy.

2.6. Protocol for characterizing ion microprobe targets

Most zircons previously analyzed for $\delta^{18}\text{O}$ by ion microprobe were chosen because of their age [2–4,6,12]. For zircons dated in situ by the U–Pb method, the concordance of the U–Pb systems (agreement between the $^{207}\text{Pb}/^{206}\text{Pb}$ and the $^{206}\text{Pb}/^{238}\text{U}$ age) provides a reliable measure of how closed the U–Pb system has remained since crystallization for the volume analyzed, as both ages will agree if the isotopic ratios have remained undisturbed. A determination of U–Pb concordance thus allows undisturbed domains within individual crystals to be identified for oxygen isotope analysis.

To increase the likelihood of sampling micro-volumes in individual zircons that contain magmatic $\delta^{18}\text{O}$ values, the following 3-stage protocol was developed and adopted in this study for analyzing detrital grains by ion microprobe. (1) Polished zircons were first imaged in CL to identify magmatic grains, and then analyzed for their U/Pb age by ion microprobe, ideally (but not always) in multiple locations (see [4] for additional details of the U/Pb analyses). Afterward, the grains were imaged in BSE/SE to document analysis locations. This allows the age, Th/U chemistry, and concordance of $\sim 25\ \mu\text{m}$ diameter domains to be correlated with internal zoning, and also evaluated for the presence of cracks and inclusions. (2) Sample mounts were then re-ground and re-polished to expose a surface $\sim 5\ \mu\text{m}$ below the previous one. This ensures that any oxygen implanted in the zircon surface from the ^{16}O beam used for U/Pb analysis is removed, and that the surface is smooth and flat. The grains were then re-imaged in CL and BSE/SE prior to $\delta^{18}\text{O}$ analysis to characterize internal zoning at the new surface, and also to identify cracks and inclusions. (3) Analyses of $\delta^{18}\text{O}$ were made, which in most cases specifically targeted the same $\sim 25\ \mu\text{m}$ diame-

ter domains of crystals that yielded concordant U/Pb ages, while avoiding irregularities such as cracks, inclusions, and discordant zones. In other words, for most of the zircons $\delta^{18}\text{O}$ was analyzed in spots either directly below or very near where the age was measured on the prior surface. Multiple analyses of $\delta^{18}\text{O}$ on single crystals were also made to test for $\delta^{18}\text{O}$ homogeneity, resulting in some $\delta^{18}\text{O}$ analyses not being associated with a micro-volume that was previously characterized for U/Pb age. After $\delta^{18}\text{O}$ analysis, all analysis pits were individually imaged in BSE/SE to document analysis locations and also to allow inspection of ion microprobe pits for irregularities. Analyses made on concordant areas of zircon free of cracks were then accepted; analyses found to be located on cracks, inclusions, or in discordant areas of crystals were rejected.

2.7. Laser fluorination analysis of quartz

The detrital zircons analyzed in this study occur in metamorphosed quartz-rich siliciclastic rocks, including conglomerates and quartzites [4]. Quartz from three samples, including two which yielded zircons for this study (01JH36, 01JH54), was investigated for $\delta^{18}\text{O}$ to determine if primary compositions were preserved in any of the grains. Metaconglomerate samples 01JH54 and 01JH42 contain heterogeneous populations of 1–10 cm-sized clasts, including chert, vein quartz, and quartzite, which likely had a large range of primary (pre-sedimentation) $\delta^{18}\text{O}$ (Qtz) values. Quartzite sample 01JH36 is primarily composed of quartz, with the exception of conspicuous heavy mineral layers of detrital chromite. Clean separates of quartz were obtained from slabbed hand-samples by drilling 3 mm diameter cores and hand-picking inclusion-free grains after the cores were lightly crushed (see slab images in Appendix 3). Hand-picked grains of quartz were then pre-treated with concentrated HF at room temperature overnight. Analyses for $\delta^{18}\text{O}$ of $\sim 2\ \text{mg}$ aliquots of quartz were made at the University of Wisconsin by gas source mass spectrometry using BrF_5 and a 32 W CO_2 laser [30,31]. All samples were corrected for accuracy with UWG-2 garnet ($\delta^{18}\text{O}=5.8\text{‰}$) [30], analyzed multiple times at the beginning of each run. The reproducibility of UWG-2 ranged from 0.03‰ to 0.04‰ (1 SD).

3. Oxygen isotope results

3.1. Quartz $\delta^{18}\text{O}$ values

Quartz separates from each of the three samples are remarkably homogenous in $\delta^{18}\text{O}$, considering the analyzed material was targeted as possibly preserving differences in primary $\delta^{18}\text{O}$ (i.e., pre-Jack Hills sedimentation) (Table 1). When grouped by sample, clasts from the conglomerates have average $\delta^{18}\text{O}$ (Qtz) values of $10.9 \pm 0.08\text{‰}$ (1 S.D., $n=13$, 01JH54) and $12.7 \pm 0.12\text{‰}$ (1 S.D., $n=10$, 01JH42). A similar result was found in quartzite 01JH36 which yielded a value of $12.7 \pm 0.04\text{‰}$ (1 S.D., $n=6$) for 3 samples from a 10 cm slab. These samples are homogenous with precisions approaching that of the oxygen isotope standard UWG-2 (Appendix 4). These data suggest that pervasive exchange and equilibration of $\delta^{18}\text{O}$ (Qtz) occurred at the decimeter-scale in these rocks during regional metamorphism.

Quantitative estimates of the metamorphic conditions experienced by rocks at Jack Hills are not well constrained, however, mineral assemblages suggest that upper greenschist to amphibolite facies conditions were attained [4]. Extensive deformation textures in the quartz clasts (see images in Appendix 3; also described in [4]) are additional evidence that pervasive oxygen isotope exchange accompanied recrystallization in these samples.

In contrast to quartz, previous studies have demonstrated that detrital zircons from quartzites can preserve primary magmatic $\delta^{18}\text{O}$ values through amphibolite or even granulite facies metamorphism

[6,11]. The large range of $\delta^{18}\text{O}$ preserved in the Jack Hills zircons (see below) from samples that are homogenous in $\delta^{18}\text{O}$ (Qtz) is evidence that these two minerals did not exchange oxygen with each other owing to the refractory nature of zircon [7].

3.2. Ion microprobe data: standards and precision

The instrumental mass fractionation (IMF) of measured vs. true isotope ratios for the zircon standard used in this study ranged from -2.92‰ to -9.53‰ , depending on session (see below). Thus, reducing ion microprobe data for samples requires that analyses of a well-characterized oxygen isotope standard be interspersed repeatedly with sample analyses throughout the course of each analytical session. Zircon standard KIM-5 has been shown to be homogenous in oxygen isotope ratio at the mg-scale by laser fluorination [7]. KIM-5 is also suitable as an ion microprobe oxygen standard for most zircons as its HfO_2 content (~ 1.23 wt.% [3]) is similar to the range found in most natural zircons, as well as 19 randomly selected zircons from this study ($\text{HfO}_2=0.83$ to 1.41 wt.%, $n=19$, see Table 2) and thus obviates the need to correct for variations in the IMF due to large variations in Hf content [3,25]. Oxygen isotope ratios are expressed in delta notation, $\delta^{18}\text{O}$, relative to Vienna standard mean ocean water (VSMOW). As all zircon samples analyzed by ion microprobe were standardized with KIM-5, the $\delta^{18}\text{O}$ value for each sample is calculated relative to VSMOW according to the following relation:

$$\begin{aligned} \delta^{18}\text{O}_{(\text{sample}, \text{VSMOW})} &= (\delta^{18}\text{O}_{(\text{KIM-5}, \text{VSMOW})} + 1000) \\ &\quad * \left[({}^{18}\text{O}/{}^{16}\text{O}_{(\text{sample}, \text{meas})}) / ({}^{18}\text{O}/{}^{16}\text{O}_{(\text{KIM-5}, \text{meas})}) \right] \\ &\quad - 1000 \end{aligned} \quad (1)$$

The measured ${}^{18}\text{O}/{}^{16}\text{O}$ ratio of the KIM-5 standard requires close attention, as this value can vary over the course of an analytical session. Indeed, a small, but detectable, instrumental ‘drift’ in the measured ${}^{18}\text{O}/{}^{16}\text{O}$ ratio of KIM-5 over the duration of most sessions was observed. A linear fit through the

Table 1
 $\delta^{18}\text{O}$ of Jack Hills quartz by laser fluorination

Sample	01JH54	01JH42	01JH36
Rock type	Cong.	Cong.	Quartzite
wt.% SiO_2^a	94.90	96.40	96.90
Analyses (n)	13	10	6
$\delta^{18}\text{O}$ (quartz)	10.90‰	12.73‰	12.71‰
1 S.D. ^b	± 0.08	± 0.12	± 0.04

Cong.=(meta) conglomerate.

‰ values relative to VSMOW.

Standard results are in Appendix 4.

^a Additional whole-rock data for these and other Jack Hills samples are published in [4].

^b S.D. of multiple analyses (see Appendix 4).

Table 2

Ion microprobe analyses of $\delta^{18}\text{O}$ from Jack Hills zircons

Sample-grain	$^{207}\text{Pb}/^{206}\text{Pb}$ age [Ma]	U/Pb conc. [%]	Th/U	HfO ₂ [wt.%]	Total anal.	Accepted anal.	Grain area	$\delta^{18}\text{O}$ [‰] (VSMOW)	1 S.D.	Comment on $\delta^{18}\text{O}$ analysis
Session 1: Mount W74/2										
W74/2-36	4404 ± 4 ^a	99 ^a	0.59 ^a	1.07 ^a	32	12	Core (Avg, $n=12$)	5.4	0.4 ^b	Drift/Anal. = 0.002‰
KIM-5 (1–51)				1.23 ^a	51	51	Avg ($n=51$)	5.1	0.3	
Session 2: Mount W74/2										
W74/2-52	4163 ± 6 ^a	100 ^a	0.52 ^a	1.16 ^a	10	10	Core (Avg, $n=10$)	5.3	0.4 ^b	Drift/Anal. = 0.047‰
KIM-5 (57–66)				1.23 ^a	10	10	Avg ($n=10$)	5.1	0.2	
Session 3: Mount W74/3										
W74/3-143	4159 ± 12	101	0.26	n.a.	3	1	Core ($n=1$)	6.7	0.4	Undated area of grain
W74/3-32	4091 ± 4	65	1.59	n.a.	3	1	Core ($n=1$)	6.7	0.4	
W74/3-30	4102 ± 22	93	0.41	n.a.	2	2	Core (Avg, $n=2$)	7.3	0.4	
W74/3-36	3964 ± 7	94	0.33	n.a.	2	2	Core (Avg, $n=2$)	5.5	0.4	
W74/3-41	4112 ± 6	96	0.64	1.10	2	2	Core (Avg, $n=2$)	7.3	0.4	All analyses rejected
W74/3-154	4164 ± 33	95	0.30	n.a.	3	3	Core (Avg, $n=3$)	6.3	0.9 ^b	
W74/3-154	4075 ± 8	98	0.30	n.a.	1	1	Rim ($n=1$)	6.1	0.4	
W74/3-7	4078 ± 5	98	0.43	1.22	1	0	–	–	–	
W74/3-74	4035 ± 11	77	0.89	n.a.	1	1	Core ($n=1$)	6.6	0.4	Drift/Anal. = – 0.007‰
W74/3-13	4008 ± 5	97	0.77	n.a.	1	1	Core ($n=1$)	6.3	0.4	
W74/3-15	4017 ± 14	97	0.19	1.41	3	3	Core (Avg, $n=3$)	7.3	0.3 ^b	
KIM-5 (83–122)				1.23 ^a	40	40	Avg ($n=40$)	5.1	0.4	
Session 4: Mount W74/3										
W74/3-17	4013 ± 4	84	0.71	n.a.	2	1	Core ($n=1$)	6.4	0.6	Undated area of grain
W74/3-58	4045 ± 4	91	0.53	n.a.	2	2	Core (Avg, $n=2$)	6.2	0.6	
W74/3-62	4133 ± 6	87	0.28	n.a.	2	2	Core (Avg, $n=2$)	6.9	0.6	All analyses rejected
W74/3-114	4027 ± 5	94	0.33	1.18	1	0	–	–	–	
W74/3-174	4094 ± 7	99	0.74	1.24	3	3	Core (Avg, $n=3$)	5.5	0.2 ^b	
W74/3-170	4069 ± 7	88	0.31	n.a.	1	1	Core ($n=1$)	5.8	0.6	
W74/3-134	3984 ± 6	96	0.52	n.a.	2	1	Core ($n=1$)	6.3	0.6	Drift/Anal. = – 0.012‰
W74/3-133	3996 ± 6	94	0.38	n.a.	1	1	Core ($n=1$)	5.7	0.6	
W74/3-131	4130 ± 7	96	0.20	n.a.	3	2	Core (Avg, $n=2$)	4.6	0.6	
W74/3-152	4029 ± 6	96	0.46	n.a.	2	2	Core (Avg, $n=2$)	6.1	0.6	
KIM-5 (123–141)				1.23 ^a	19	19	Avg ($n=19$)	5.1	0.6	

Session 5: Mount 01JH54

01JH54-D2	4042 ± 5	94	0.75	n.a.	2	1	Core (<i>n</i> = 1)	6.2	0.3	
01JH54-D90	4263 ± 4	88	1.36	n.a.	4	1	Core (<i>n</i> = 1)	6.3	0.3	
01JH54-D90	4030 ± 6	85	0.64	n.a.	2	1	Rim (<i>n</i> = 1)	6.4	0.3	
01JH54-D7	4348 ± 3	94	0.63	0.89	4	1	Core (<i>n</i> = 1)	5.4	0.3	
01JH54-77	4324 ± 6	101	0.76	0.84	10	8	Core (Avg, <i>n</i> = 8)	6.5	0.4 ^b	
01JH54-77	3688 ± 11	96	0.25	1.20	3	0	–	–	–	Rim analyses rejected
01JH54-66	4195 ± 4	100	0.35	1.12	3	2	Core (Avg, <i>n</i> = 2)	6.5	0.3	
01JH54-81	4103 ± 5	95	0.43	1.03	3	2	Core (Avg, <i>n</i> = 2)	6.9	0.3	
01JH54-81	–	–	–	n.a.	1	1	Rim (<i>n</i> = 1)	6.9	0.3	Undated area of rim
01JH54-78	4167 ± 5	95	0.39	1.20	3	3	Core (Avg, <i>n</i> = 3)	7.3	0.2 ^b	
01JH54-78	3362 ± 10	93	0.41	n.a.	2	1	Rim (<i>n</i> = 1)	6.2	0.3	
01JH54-68	4176 ± 5	96	0.64	1.18	3	3	Core (Avg, <i>n</i> = 3)	6.2	0.4 ^b	
01JH54-58	4063 ± 7	103	0.79	1.22	4	3	Core (Avg, <i>n</i> = 3)	6.8	0.1 ^b	
01JH54-37	3904 ± 3	98	0.52	1.11	7	5	Core (Avg, <i>n</i> = 5)	10.3	0.3 ^b	
01JH54-40	4078 ± 5	102	0.72	n.a.	3	3	Core (Avg, <i>n</i> = 3)	6.5	0.4 ^b	
01JH54-34	4165 ± 6	100	0.37	n.a.	3	3	Core (Avg, <i>n</i> = 3)	6.2	0.4 ^b	
01JH54-34	–	–	–	0.83	2	1	Rim (<i>n</i> = 1)	6.1	0.3	Undated area of rim
01JH54-20	4110 ± 3	99	0.49	n.a.	2	2	Core (Avg, <i>n</i> = 2)	6.6	0.3	
01JH54-17	4178 ± 6	98	0.31	n.a.	3	1	Core (<i>n</i> = 1)	5.3	0.3	
01JH54-10	4123 ± 5	100	0.82	1.02	3	3	Core (Avg, <i>n</i> = 3)	6.3	0.1 ^b	
KIM-5 (142-187)				1.23 ^a	46	46	Avg (<i>n</i> = 46)	5.1	0.3	Drift/Anal. = 0.002‰

Session 6: Mount 01JH60

01JH60-51	4116 ± 8	100	0.31	1.07	3	3	Core (Avg, <i>n</i> = 3)	6.5	0.1 ^b	
01JH60-39	4177 ± 18	100	0.48	1.11	3	3	Core (Avg, <i>n</i> = 3)	6.3	0.3 ^b	
01JH60-39	3906 ± 5	92	0.35	n.a.	1	1	Rim (<i>n</i> = 1)	7.3	0.3	
01JH60-64	4040 ± 6	101	0.74	1.26	3	3	Core (Avg, <i>n</i> = 2)	6.5	0.3	
01JH60-68	4097 ± 13	93	0.27	1.37	3	2	Core (Avg, <i>n</i> = 2)	6.7	0.3	
01JH60-47	4038 ± 7	69	2.42	n.a.	2	1	Core (<i>n</i> = 1)	6.0	0.3	Undated area of grain
KIM-5 (192-208)				1.23 ^a	17	17	Avg (<i>n</i> = 17)	5.1	0.3	Drift/Anal. = 0.000‰

Session 7: Mount 01JH36

01JH36-69	4324 ± 18	85	0.75	n.a.	5	1	Core (<i>n</i> = 1)	4.6	0.3	
01JH36-115	4065 ± 15	89	0.29	n.a.	2	1	Core (<i>n</i> = 1)	5.3	0.3	
KIM-5 (209-219)				1.23 ^a	11	11	Avg (<i>n</i> = 11)	5.1	0.3	Drift/Anal. = 0.012‰

Conc.=concordance.

Anal.=analysis, Avg=average, S.D.=standard deviation.

n.a.=not analyzed.

^a Data from Peck et al. [3].^b 1 S.D. based on sample reproducibility, not standard.

KIM-5 data for each session provides a drift-corrected value of $^{18}\text{O}/^{16}\text{O}$ (KIM-5, meas) for use in Eq. (1) (see example in Fig. 2). The magnitude of drift correction per analysis is small, ranging from 0.000‰ (session 6, $n=32$) to 0.047‰ (session 2, $n=20$), with an average of 0.006‰ for all seven sessions. Summary statistics for KIM-5 results by session are listed in Table 3. Appendix 5 contains the measured (i.e. uncorrected) $^{18}\text{O}/^{16}\text{O}$ ratios and values of $\delta^{18}\text{O}$ (VSMOW) for all samples and standards listed by session, in the order analyses were made.

Table 2 lists corrected $\delta^{18}\text{O}$ values for standards and samples by session, and also includes other grain characteristics such as the $^{207}\text{Pb}/^{206}\text{Pb}$ ages, U/Pb concordance, HfO_2 content, and description of where the oxygen analyses were made in each grain (e.g. core vs. rim). Table 3 lists both the internal and external precision for each session in this study, with the external precision based on KIM-5 results. External precision in all cases is larger than the internal precision by factors ranging from two to seven, and so approaches, but does not match, the internal precision. The external precision of KIM-5 is therefore considered the best measure of precision for any given analysis, and is assigned to samples with only one or two analyses. The external precision of sample zircons based on multiple analyses is quoted for grains with at least three analyses (marked by a superscript 'b' in Table 2), and serves as a useful comparison of the standard for evaluating grain-scale homogeneity.

Of the 44 zircons listed in Table 2, 15 grains have three or more analyses that allow a comparison with the external precision of the standard. Six of the 15 grains have external precision of $\pm 0.1\%$ to $\pm 0.3\%$ (1 S.D.), which is smaller than the precision for KIM-5 in the same session. Nine zircons have external precision of $\pm 0.3\%$ to $\pm 0.9\%$ (1 S.D.), values less precise than KIM-5 in the same session, but none by more than a factor of three, and most by less than a factor of two (Table 3). The similarity of the external precision of the 15 zircon samples with that determined for KIM-5 demonstrates that most of the grains are as homogenous as KIM-5 at the level of sampling. Thus, within a session, the external precision measured on KIM-5 is a reasonable estimate for the precision for sample zircon analyses.

Table 3
Oxygen isotope standard results: KIM-5 summary statistics

Session	Total analyses (n)	Standard analyses (n)	KIM-5 analysis number	$^{18}\text{O}/^{16}\text{O}$ avg (drift corr.)	Internal precision, 1 S.D. (‰) ^a	External precision, 1 S.D. (‰)	External precision, 1 S.E. (‰)	IMF [‰]	Drift/analysis (‰)	Ext. precision of sample zircons (‰) ^b
1	85	51	1–51	0.002006745	0.10	0.35	0.05	–4.10	0.002	0.4 (n=1)
2	20	10	57–66	0.002009110	0.07	0.16	0.05	–2.92	0.047	0.4 (n=1)
3	62	40	83–122	0.002000161	0.07	0.36	0.06	–7.36	–0.007	0.3, 0.9 (n=2)
4	38	19	123–141	0.001998974	0.08	0.62	0.14	–7.95	–0.012	0.2 (n=1)
5	114	46	142–187	0.001997526	0.08	0.28	0.04	–8.67	0.002	0.1–0.4 (n=8)
6	32	17	192–208	0.001996574	0.07	0.25	0.06	–9.14	0.000	0.1, 0.3 (n=2)
7	18	11	209–219	0.001995787	0.08	0.30	0.09	–9.53	0.012	–
Avg.	53	28	(n=194)	0.002000697	0.08	0.33	0.07	–7.10	0.006	0.33 (n=15)

S.D.=standard deviation of average (external precision) for analyses on different spots.

S.E.=standard error ($\text{S.D.}/(n^{1/2})$).

IMF=Instrumental Mass Fractionation = $[(^{18}\text{O}/^{16}\text{O})_{\text{meas}} - (^{18}\text{O}/^{16}\text{O})_{\text{actual}}]/(^{18}\text{O}/^{16}\text{O})_{\text{actual}} \times 10^3$.

^a Internal precision is theoretical, based on counting statistics for average primary beam intensity during session.

^b External precision only calculated for zircon samples with at least 3 analyses measured in the same session (n=# of grains).

3.3. Evaluation of ion microprobe pits

In a previous ion microprobe study of $\delta^{18}\text{O}$ in magnetite, post-analysis SEM imaging demonstrated a correlation between micro-volumes affected by open-system exchange of $\delta^{18}\text{O}$ and morphologically ‘irregular’ pits [32]. Although care was taken in each step of the analysis protocol in this study, post-analysis SEM imaging revealed that 57 of 172 (33%) pits on sample zircons were located in discordant domains or were otherwise morphologically ‘irregular’. These ‘irregular’ pits include spots located on cracks ($n=35$), spots that overlap onto epoxy ($n=3$), spots in areas less than 85% concordant in U/Pb age (see [4]), and/or with high Th/U ratios >1.5 ($n=6$), or spots that have a combination of these features ($n=14$) (Fig. 3; see ‘comment’ column in Appendix 5). A comparison of $\delta^{18}\text{O}$ values for the 57 ‘irregular’ pits reveals that over half ($n=38$, 67%) overlap at 1 S.D. with the accepted average for the grain, which suggests that not all ‘irregular’ pits have been isotopically disturbed. However, a number of the ‘irregular’ pits ($n=12$, 21%) yield both lower ($n=8$) and higher ($n=4$) $\delta^{18}\text{O}$ values than the grain average by up to 12.0‰ (Appendix 5). For example, three pits which overlap onto epoxy (Appendix 5: sample 01JH54, grains 34 and 77) are lighter in $\delta^{18}\text{O}$ than neighboring pits in the same CL domain by up to 4‰. Data from pits located on cracks or in discordant and/or high Th/U domains are more variable, and can be lighter or heavier in $\delta^{18}\text{O}$ than ‘regular’ pits by $\sim 0.5\%$ to 2‰. Seven additional ‘irregular’ pits (12%) are from grain cores or rims where only one analysis was made, and therefore can not be evaluated by comparison. The most extreme $\delta^{18}\text{O}$ values identified were from two ‘irregular’ pits on zircon W74/3-143, which displays ‘ambiguous’ internal zoning. The pits are located on cracks in a bright CL domain, which yielded $\delta^{18}\text{O}$ values of 17.7‰ and 18.4‰ (Appendix 5). While no prior U/Pb analyses were made in the bright CL domain of this grain, a $\delta^{18}\text{O}$ value of 6.7‰ in a crack-free, dark CL, concordant U/Pb domain suggests the cracked area of the grain is disturbed.

It is tempting to accept the results from the ‘irregular’ pits along with other data, since 67% fall within 1 S.D. of the grain average (see example in Fig. 4). However, the non-systematic and sometimes large shifts (e.g. up to +12‰) observed in $\delta^{18}\text{O}$ from other

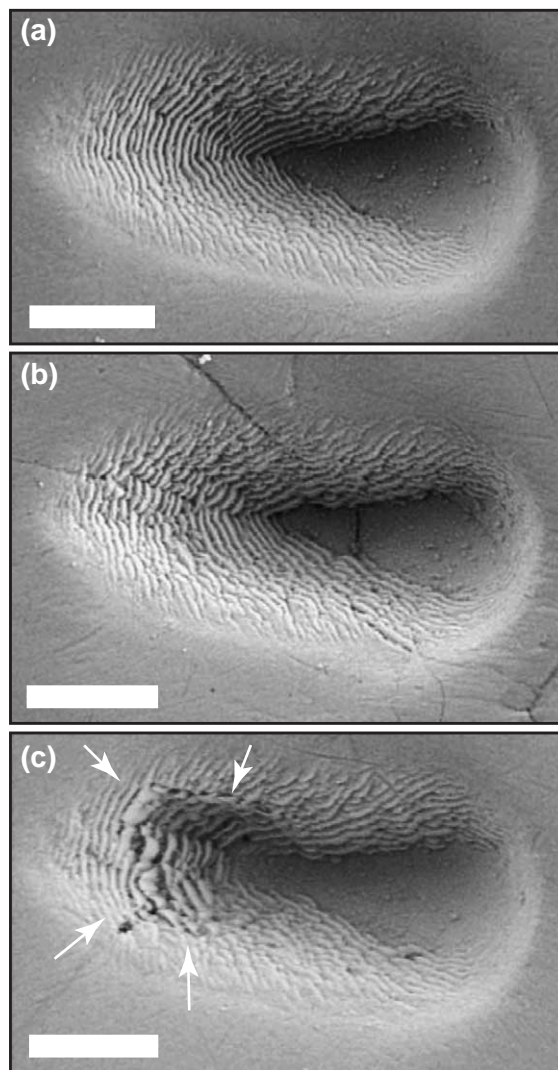


Fig. 3. Examples of ‘regular’ and ‘irregular’ ion microprobe pits in zircon following $\delta^{18}\text{O}$ analysis, as imaged with secondary electrons (SE). (a) ‘Regular’ pit, showing slight asymmetry due to inclination of primary beam. (b) ‘Irregular’ pit with through-going cracks, visible in the crater walls and floor. (c) ‘Irregular’ pit with circular ‘cavity’ at left side (defined by arrows). The analysis hit a mineral inclusion, visible in a prior image. Preferential sputtering of the inclusion is thought to have caused this unusual feature. Pits are approximately 2–3 μm in depth. Scale bar in all images is 5 μm .

‘irregular’ pits persuade us to exercise caution and reject all data from ‘irregular’ pits given the uncertainty over preservation of primary $\delta^{18}\text{O}$, regardless of the measured $\delta^{18}\text{O}$. Despite rejecting nearly a third of the data set (Appendix 5), precise $\delta^{18}\text{O}$ analyses from

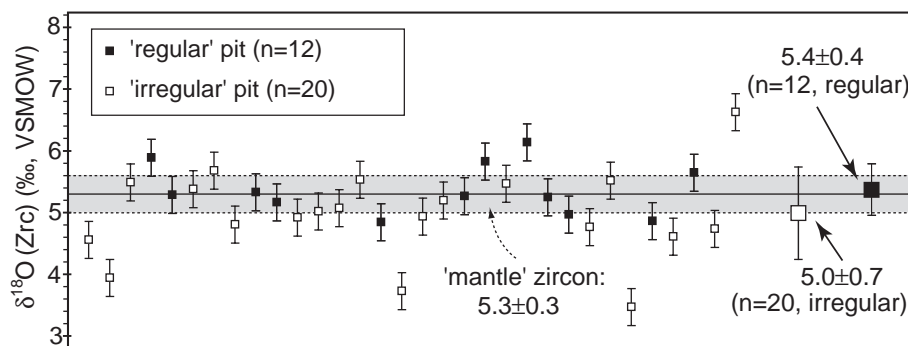


Fig. 4. Example of characterizing 32 $\delta^{18}\text{O}$ analyses made on zircon W74/2-36 as 'regular' or 'irregular' based on imaging the ion microprobe pit after analysis. The two values quoted on the right side are the averages with external precision (1 S.D.) of the data from 'regular' pits ($n=12$, upper) and 'irregular' pits ($n=20$, lower). The shaded field is 'mantle' zircon, $5.3 \pm 0.3\text{‰}$ (1 S.D.), as defined in [7,18]. See text for discussion.

'regular' pits were made in 42 of the 44 analyzed zircons.

3.4. Comparison with previous work

Two zircons in this study were analyzed for $\delta^{18}\text{O}$ in 1999 by Peck et al. [3]. The first is W74/2-36, an oscillatory zoned zircon with concordant U–Pb domains as old as 4404 Ma. W74/2-36 was previously analyzed for $\delta^{18}\text{O}$ in two locations; two analyses were made at each spot resulting in four separate analyses. Each of the individual analyses had an internal precision of $\pm 1.0\text{‰}$ (1 S.D.) [3]. The authors combined the duplicate analyses for each spot to obtain higher total counts, resulting in a $\delta^{18}\text{O}$ value of $7.4 \pm 0.7\text{‰}$ in the core (1 S.D., internal precision), and $5.0 \pm 0.7\text{‰}$ in the rim (1 S.D., internal precision), which led to the interpretation that the crystal was zoned in $\delta^{18}\text{O}$ [2,3]. Analysis of REEs and CL showed matching core-to-rim zonation. The second crystal is W74/2-52, with concordant U–Pb domains as old as 4163 Ma. W74/2-52 was previously analyzed in eight locations, with average $\delta^{18}\text{O} = 7.2 \pm 0.7\text{‰}$ (1 S.D., $n=8$, internal precision [3]).

A total of 32 spot analyses were made on a new surface of grain W74/2-36 (Fig. 4). The average $\delta^{18}\text{O}$ value for regular pits in W74/2-36 in this study is $5.4 \pm 0.4\text{‰}$ (1 S.D., $n=12$, external precision) (Fig. 5). Zoning in $\delta^{18}\text{O}$ was not detected in grain W74/2-36, although the CL image of the new surface shows the oscillatory nature of the zoning pattern more clearly than in previous images [Appendix 1(n)]. The average of ten new analyses on W74/2-52 is

$\delta^{18}\text{O} = 5.3 \pm 0.4\text{‰}$ (1 S.D., $n=10$, external precision), $\sim 2\text{‰}$ lower than the previous average. Several important analytical aspects of this comparison merit discussion.

- (1) Grain surface. The mount containing grains W74/2-36 and W74/2-52 was re-ground and re-polished twice following the original $\delta^{18}\text{O}$ measurements. This 'double-grinding' resulted in an estimated removal of $\sim 20\text{ }\mu\text{m}$ of material, significantly more than what was removed from other mounts re-ground only once after U/Pb analysis. The portions of the crystals where the

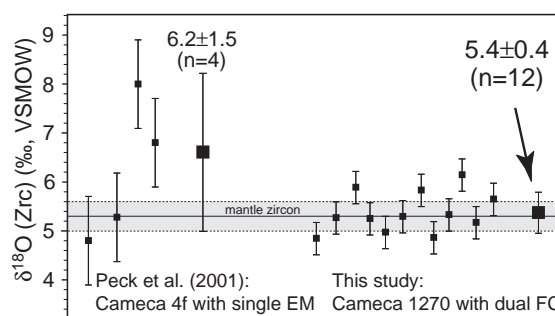


Fig. 5. Comparison of $\delta^{18}\text{O}$ values for zircon W74/2-36 analyzed by multi-collector CAMECA ims-1270 ion microprobe (this study) and by single-collector CAMECA ims-4f [3]. For both groups, the smaller symbols are individual analyses. The larger symbol after each group is the group average. Error bars for individual analyses are the external precision of the standard from the session (1 S.D.). Error bars for group averages are external precision of the individual analyses (1 S.D.). EM=electron multiplier, FC=Faraday cup. See text for discussion.

original oxygen data were collected [2,3] are thus no longer in existence, and given the unknown orientation of these two grains, it is possible that the removed areas preserved a different oxygen isotope composition.

- (2) Internal precision. The previous analyses were made with a CAMECA ims-4f ion microprobe using a single electron multiplier ion detector. Secondary ion beam intensities were limited by deadtime to $\sim 1 \times 10^6$ cps for $^{16}\text{O}^-$ and $\sim 2 \times 10^3$ cps for $^{18}\text{O}^-$. Collecting $\sim 1 \times 10^6$ total counts on ^{18}O for a theoretical precision of 1.0‰ (1 SD) required counting times of 500 s on ^{18}O , resulting in ~ 20 min analyses. The use of dual Faraday collectors on the CAMECA ims-1270 in this study allowed higher secondary ion beam intensities (e.g. 5.0×10^6 vs. 2.0×10^3 cps for ^{18}O) which resulted in shorter counting times (40 s), better theoretical precisions of $\sim 0.1\%$ (1 S.D.), and an analysis time of ~ 6 min.
- (3) Analytical drift. The ~ 20 min analyses for $\delta^{18}\text{O}$ and different instrument configuration of the ims-4f resulted in instrumental drift ranging from 0.01‰ to 0.14‰ per analysis [3]. With dual Faraday collectors on the ims-1270, the shorter analysis time of ~ 6 min to simultaneously collect ^{16}O and ^{18}O ions resulted in reduced drift, which ranged from 0.00‰ to 0.05‰ per analysis.
- (4) External Precision. Peck et al. [3] bracketed analyses of sample zircons with analyses of KIM-5. They reported external precisions for five sessions that ranged from $\pm 0.69\%$ (1 S.D., $n=23$, session 2) to $\pm 0.95\%$ (1 S.D., $n=11$, session 5). The external precisions for seven sessions in this study are smaller by up to a factor of four, and range from $\pm 0.16\%$ (1 S.D., $n=10$, session 2) to $\pm 0.62\%$ (1 S.D., $n=19$, session 4).

The three other >4000 Ma zircons of Peck et al. [3] were not re-analyzed in this study, and previously yielded $\delta^{18}\text{O}$ values from 5.6‰ to 6.8‰. One of the grains (W74/1-43, $\delta^{18}\text{O}=5.9\%$) was highly discordant in U/Pb age (61% concordant), and based on the rejection criteria outlined above will not be considered further.

In another study of 4000 to 4278 Ma zircons from Jack Hills, Mojzsis et al. [12] analyzed 7 grains for $\delta^{18}\text{O}$ with dual Faraday collectors on a CAMECA ims-1270 ion microprobe and reported values ranging from 5.4‰ to 9.0‰ for zircon cores, and 8.5‰ to 15.0‰ for rims. These samples were standardized with standard zircons KIM-5 and 91500, however, no table of measured isotope ratios was published for either samples or standards. The details of analytical protocol described in their report and accompanying supplementary data, particularly regarding which standards calibrated which samples, are insufficient to critically evaluate the quality of these results. Nonetheless, the four concordant (U/Pb) zircons range from $\delta^{18}\text{O}=5.4\%$ to 7.6‰. The three zircons with $\delta^{18}\text{O} > 8\%$ have highly discordant ages (U/Pb concordance from 16% to 34%) and very high Th/U ratios (Th/U=2.4 to 3.1), which indicate open system behavior for U/Pb in these crystals. There is no way to evaluate if these crystals have retained primary magmatic $\delta^{18}\text{O}$ values, and they will not be considered further.

Taken together, the $\delta^{18}\text{O}$ values for six previously published zircons (not including the two re-analyzed in this study [3]) with concordant U–Pb ages >4000 Ma and magmatic Th/U ratios (0.25 to 0.87) range from 5.4‰ to 7.6‰.

3.5. Zircon $\delta^{18}\text{O}$ values and CL zoning patterns

Fig. 6 displays the single or average $\delta^{18}\text{O}$ (Zrc) value for 42 Jack Hills zircons analyzed in this study vs. crystallization age [4], along with the data for the six previously published zircons described above. The field of ‘mantle’ zircon identifies the range of $\delta^{18}\text{O}$ values for zircon in equilibrium with mantle melts [7,18]. The ‘supracrustal’ field indicates a range in magmatic $\delta^{18}\text{O}$ (Zrc) that is elevated relative to zircon in equilibrium with mantle melts, and thus requires an input to the melt source of rocks that have been altered to higher $\delta^{18}\text{O}$ (WR) values by low-temperature processes at (or near) Earth’s surface [7,13,14]. The upper limit for the ‘supracrustal’ zircon field of 7.5‰ is based on laser fluorination analysis of zircon samples separated from >120 Archean igneous rocks of known origin, and here applies only to Archean (or older) zircons, as no concordant zircons separated from Archean igneous rocks have yielded $\delta^{18}\text{O} >$

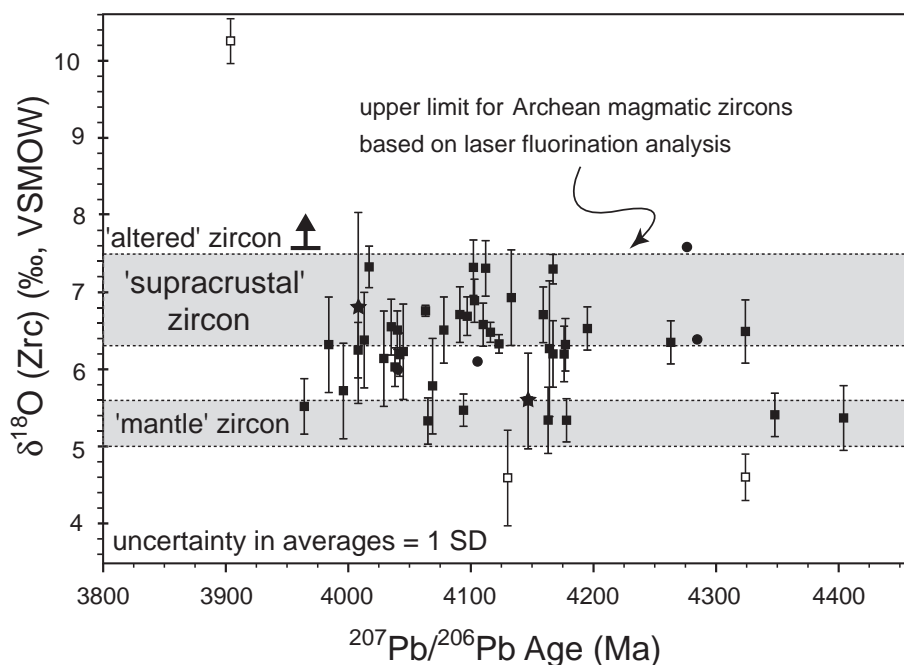


Fig. 6. Average $\delta^{18}\text{O}$ vs. age for Jack Hills zircons (squares are from this study). Filled squares are zircons interpreted to preserve magmatic $\delta^{18}\text{O}$. Open squares are zircons interpreted to be altered, with non-magmatic $\delta^{18}\text{O}$. Uncertainty in $\delta^{18}\text{O}$ values = 1 S.D. Uncertainty in the Pb/Pb ages are smaller than the symbol, typically ± 3 to ± 7 Ma (1 S.D.) [4]. Previously published data for samples that meet the criteria outlined in this study: stars ($n=2$) [3], and circles ($n=4$) [12]. Uncertainties are only assigned to data for which the bracketing standard analyses have also been published. The 'mantle' zircon field is $5.3 \pm 0.3\text{‰}$ (1 S.D.), as defined in [7,18]. The 'supracrustal' field indicates a range in magmatic $\delta^{18}\text{O}$ (Zrc) that is elevated relative to zircon in equilibrium with mantle melts (see text). The upper limit for the 'supracrustal' zircon field of 7.5‰ is based on analysis of zircon samples separated from >120 Archean igneous rocks of known origin, and applies only to Archean (or older) samples [7,13,14] (see text for discussion). The identification of $\delta^{18}\text{O}$ (Zrc) > 7.5‰ in >2500 Ma zircons as 'altered zircon' is based on the observation that analyses of zircon samples from >120 Archean igneous rocks by laser fluorination have not yielded values >7.5, and that all previously reported >2500 Ma zircons above 7.5‰ are discordant in U/Pb age or have non-magmatic CL patterns.

7.5‰ [7,13,14]. The identification of zircons older than 2500 Ma with $\delta^{18}\text{O}$ values > 7.5‰ as 'altered' (Fig. 6) is based on the above observation and also the evidence that all previously reported >2500 Ma zircons above 7.5‰ are discordant in U/Pb age or have non-magmatic CL patterns.

For the zircons analyzed in this study, values of $\delta^{18}\text{O}$ (Zrc) range from 4.6‰ to 7.3‰ , with one exception at 10.3‰ . Most zircons are between 5.3‰ and 7.3‰ , and aside from the high $\delta^{18}\text{O}$ grain, no analysis is above 7.5‰ . Seven grains fall within the 'mantle' field, 24 zircons lie in the 'supracrustal' field, 8 grains have intermediate $\delta^{18}\text{O}$ values, and 3 are interpreted as 'altered' (based on CL). Fig. 7(a)–(x) displays CL images with location of $\delta^{18}\text{O}$ analysis for all zircons in the 'supracrustal' field of Fig. 6 ($\delta^{18}\text{O}=6.3\text{‰}$ to 7.3‰ , $n=24$), as well as other selected grains [Fig. 7(y)–

(ab)]. The majority of the zircons with 'supracrustal' $\delta^{18}\text{O}$ values (16 of 24, 67%) display regular magmatic zoning patterns in CL, whereas the other 8 'supracrustal' zircons have 'ambiguous' zoning, but do not include the three previously identified 'altered' grains.

The only zircon with a $\delta^{18}\text{O}$ value above 7.5‰ , 01JH54-37 (Fig. 7y), is interpreted to have recrystallized, based on the overprinting of fine concentric zoning by broad sectors visible in the CL pattern. The value of $\delta^{18}\text{O}=10.3 \pm 0.3\text{‰}$ recorded in this grain may have resulted from recrystallization in the presence of a fluid phase (e.g. [33]), although this is speculative. The unusually high $\delta^{18}\text{O}$ value in grain 01JH54-37 is not regarded as representative of magmatic $\delta^{18}\text{O}$, given the uncertain origin of the grain as inferred from the CL pattern. The two zircons that plot below the mantle range in Fig. 6 are grains 01JH36-69

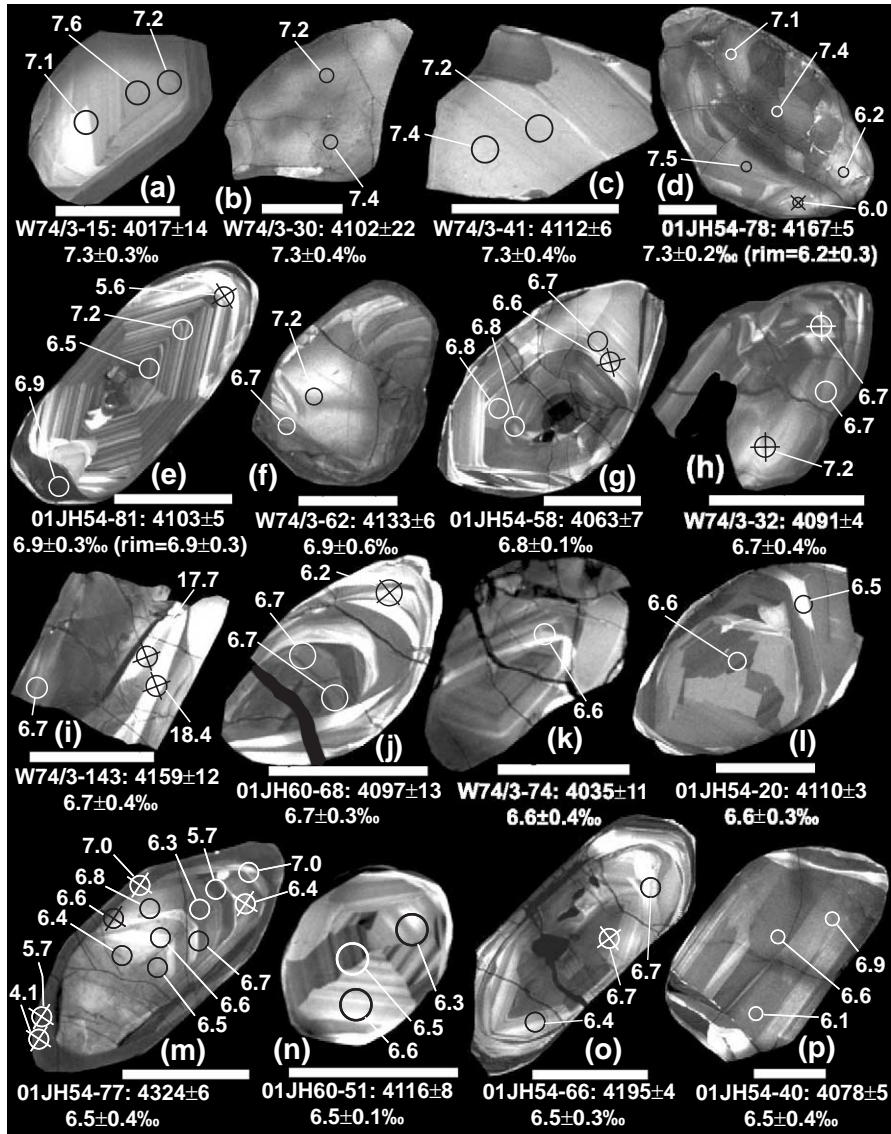


Fig. 7. Cathodoluminescence (CL) images with $\delta^{18}\text{O}$ spot values for selected Jack Hills zircons discussed in the text (see Appendix 1 for CL images with $\delta^{18}\text{O}$ spots for all zircons). Spots are crossed-through with an 'X' if the analysis was rejected (as discussed in the text). Grains (a) to (x) are all zircons in the 'supracrustal' field of Fig. 6 (e.g. $\delta^{18}\text{O} > 6.3\text{‰}$). Grains (y), (z), and (aa) are interpreted as altered zircons with non-magmatic $\delta^{18}\text{O}$ values. Grain (ab) is zircon W74/2-36, with CL images of surfaces 1 and 2 previously analyzed by [2,3], and CL and BSE images of the surface analyzed in this study (surface 3). All four images are in the same orientation and at the same scale. The $\delta^{18}\text{O}$ values for the twelve accepted analyses for this grain are labeled on the CL image of surface 3. Scale bar in all images is 100 μm . The age and U/Pb concordance (if known) associated with each $\delta^{18}\text{O}$ analysis are listed in Appendix 5.

(Fig. 7z) and W74/3-131 (Fig. 7aa), both of which were identified at the onset of this study as having disturbed CL zoning. The $\delta^{18}\text{O}$ values of these two grains may have been altered during the disturbance that perturbed the zoning, and are not regarded as

representing magmatic values. With the exception of the three zircons with non-magmatic $\delta^{18}\text{O}$ values described above, all other grains, including those with 'ambiguous' CL zoning, yield an average $\delta^{18}\text{O}$ value of $6.31 \pm 0.57\text{‰}$ (1 S.D., $n=39$).

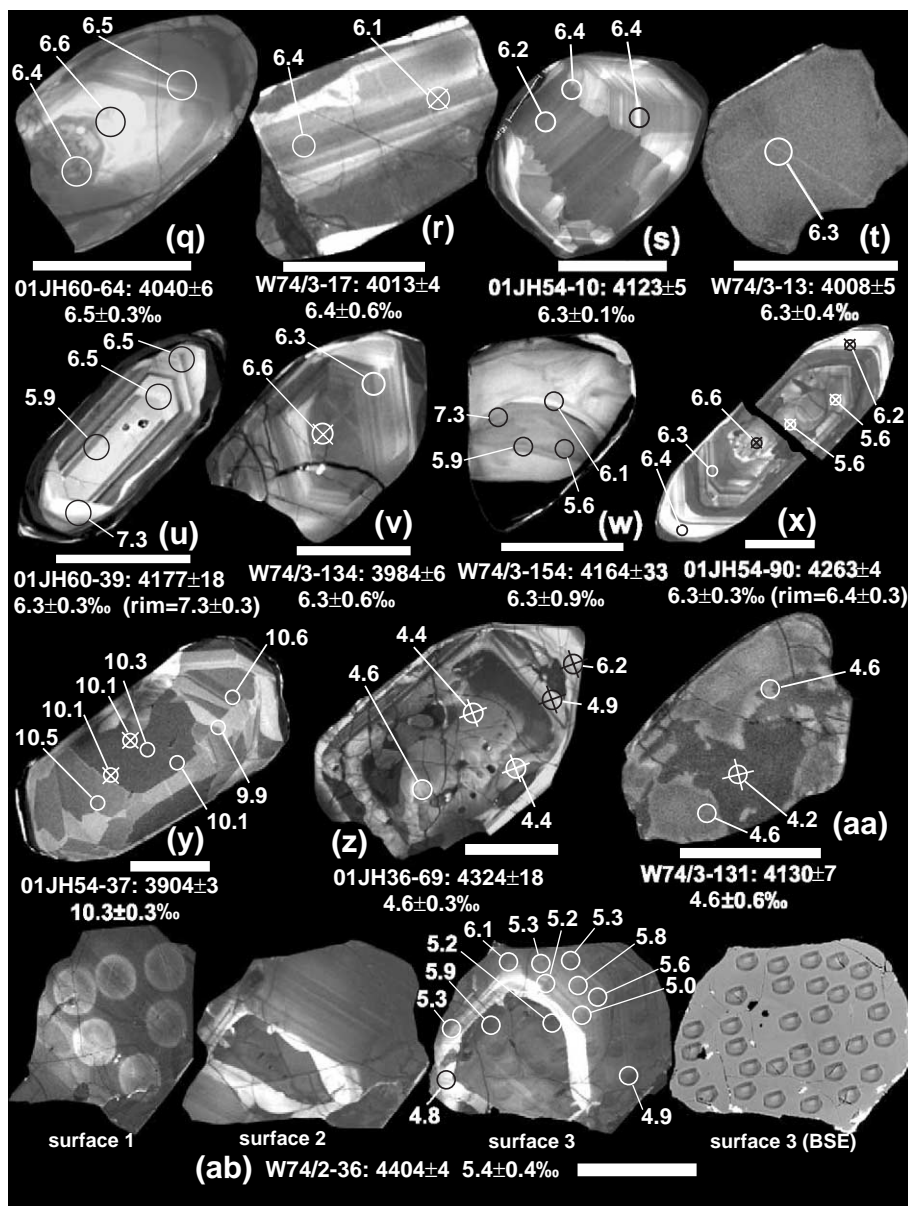


Fig. 7 (continued).

The observed deviation from the mantle range to higher $\delta^{18}\text{O}$ values in igneous zircons increases as their age decreases from 4400 to 4200 Ma (Fig. 6). The two oldest grains range in age from 4400 to 4350 Ma and preserve mantle $\delta^{18}\text{O}$ values of 5.4‰. From 4325 to 4200 Ma, the range increases from 5.3‰ to 6.5‰ ($n=4$ grains). The largest observed range in

$\delta^{18}\text{O}$ occurs from 4200 to 3950 Ma [5.3‰ to 7.3‰ ($n=32$ grains)].

3.6. Zircon rims

Attempts were made to analyze rims of grains with CL patterns distinct from the core. The bright, oscil-

latory zoned overgrowth on grain 01JH54-90 (Fig. 7x) yields a $\delta^{18}\text{O}$ value of $6.4 \pm 0.3\text{‰}$ for the 4030 Ma rim, which is indistinguishable from the 4263 Ma core value of $6.3 \pm 0.3\text{‰}$. The bright rim on grain 01JH54-78 (Fig. 7d) truncates core zoning, and is lower in $\delta^{18}\text{O}$ (4176 Ma core = $7.3 \pm 0.2\text{‰}$, 3362 Ma rim = $6.2 \pm 0.3\text{‰}$). The bright ‘inner rim’ in grain 01JH60-39 (Fig. 7u) truncates core zoning, and is higher in $\delta^{18}\text{O}$ (4177 Ma core = $6.3 \pm 0.3\text{‰}$, 3906 Ma rim = $7.3 \pm 0.3\text{‰}$). An undated dark rim on grain 01JH54-81 (Fig. 7e) yielded the same $\delta^{18}\text{O}$ value as the core ($\delta^{18}\text{O} = 6.9 \pm 0.3\text{‰}$), and a bright, undated rim (recrystallized?) on grain 01JH54-34 [Appendix 1(q)] also yielded the same value as the core ($\delta^{18}\text{O} = 6.1\text{‰}$ vs. 6.2‰). All rim analyses on grain 01JH54-77 (Fig. 7m) and 01JH36-69 (Fig. 7z) produced ‘irregular’ pits (i.e. located on cracks or epoxy) and were rejected.

Of the three rims that yielded the same $\delta^{18}\text{O}$ value as their respective cores, the rim on grain 01JH54-90 (Fig. 7x) appears texturally to be magmatic in origin, whereas the rims on grains 01JH54-34 and 01JH54-81 (both undated) appear to be the result of a sub-solidus disturbance that did not affect $\delta^{18}\text{O}$. A sub-solidus origin based on textural evidence also seems likely for the rims of grains 01JH54-78 and 01JH60-39, which both yield younger U/Pb ages than their cores, and moreover, there is no evidence that exchange of $\delta^{18}\text{O}$ occurred between the cores and rims in these grains given the observed zonation in $\delta^{18}\text{O}$.

4. Oxygen isotope composition of Early Archean magmas

The main finding of this study is that evidence for the recycling of altered crust is preserved in igneous zircons from Jack Hills with magmatic $\delta^{18}\text{O}$ values as high as 6.5‰ by 4325 Ma, and up to 7.3‰ by 4200 Ma. The $\delta^{18}\text{O}$ values in these zircons are indistinguishable from the range of igneous zircons found throughout the Archean [13,14], and demonstrate from an oxygen isotope perspective that no fundamental, planetary-scale change in magmatic process is recorded in zircon from at least 4325 to 2500 Ma. The detrital magmatic zircons in this study likely represent many igneous rocks, and are clearly not from the same magmatic event given the spread in age. The mag-

matic $\delta^{18}\text{O}$ values were obtained from micro-volumes of zircon interpreted to preserve igneous chemistry based on multiple lines of evidence, including U–Pb concordance, Th/U chemistry, and internal zoning. Although some grains have internal zoning patterns that are ambiguous, both the lower (5.3‰) and upper (7.3‰) limits of magmatic $\delta^{18}\text{O}$ values for the zircons in this study are defined by multiple grains (Fig. 6), many of which preserve typical growth zoning patterns (Fig. 7). Thus, interpreting the few ‘supracrustal’ zircon grains that have ‘ambiguous’ zoning patterns as ‘altered’ does not change our main conclusion. The range of magmatic $\delta^{18}\text{O}$ (Zrc) defined in this study is within, but smaller than, the range previously reported for detrital zircons of similar age from Jack Hills [2,3,12]. The non-magmatic character of the only zircon with $\delta^{18}\text{O} > 7.5\text{‰}$ in this study (grain 01JH54-37) suggests that previously reported $\delta^{18}\text{O}$ (Zrc) values above $\sim 7.5\text{‰}$ are likely a consequence of alteration processes [12,34].

At igneous temperatures (e.g., approximately 800–1000 °C), the magmatic $\delta^{18}\text{O}$ (Zrc) values correspond to calculated $\delta^{18}\text{O}$ [Whole Rock (WR)–magma] values from 5.8‰ to 8.0‰ for mafic parent magmas (e.g. $\Delta^{18}\text{O}$ (WR–Zrc) $\approx 0.5\text{‰}$ for $\text{SiO}_2 = 50$ wt.%) and 6.8‰ to 9.0‰ if more evolved magmas are considered [e.g. $\Delta^{18}\text{O}$ (WR–Zrc) $\approx 1.5\text{‰}$ for $\text{SiO}_2 = 70$ wt.%] [11]. Although closed-system differentiation of basalt to form a felsic rock can increase the $\delta^{18}\text{O}$ (magma) by up to 1‰ [10], at constant temperature the $\delta^{18}\text{O}$ of zircon is insensitive to this process as $\Delta^{18}\text{O}$ (WR–Zrc) increases at the same rate as $\delta^{18}\text{O}$ (WR); thus $\delta^{18}\text{O}$ (Zrc) remains constant. Regardless of host-rock composition, magmatic $\delta^{18}\text{O}$ (Zrc) $> 6.3\text{‰}$ is too high to represent uncontaminated mantle-derived melts in isotopic equilibrium with peridotite ($\delta^{18}\text{O}$ WR $\approx 5.5\text{‰}$) [18,35,36]. Modern basalts from mid-ocean ridges and ocean islands show a narrow range of $\delta^{18}\text{O}$ (WR–magma) values from 5.3‰ to 6.0‰ despite the addition of subducted sediments and altered crust to the upper mantle [37]. In other words, the Jack Hills zircons with $\delta^{18}\text{O} > \sim 6.3$ could not have formed in evolved melts from closed-system fractional crystallization of uncontaminated mantle-derived basalt. The values of $\delta^{18}\text{O}$ (Zrc) as high as 7.3‰ , if magmatic, are unambiguous evidence for liquid water and the existence of supracrustal rocks on Earth by 4200 Ma.

Through development and use of a detailed analytical protocol, we emphasize the approach of attempting to correlate micro-volumes of concordant igneous zircon with $\delta^{18}\text{O}$ and CL zoning pattern. The majority of the $\delta^{18}\text{O}$ analyses constitute a high-resolution temporal record of magmatic recycling of crust prior to 3900 Ma. Components of altered, high $\delta^{18}\text{O}$ crust were recycled into many of the >3900 Ma magmas represented by the zircons in this study. The major element composition of these magmas is unknown [3,38], however the presence of SiO_2 inclusions in the zircons indicates the melts were quartz-saturated, and fractionated REE patterns [3,38] and elevated $\delta^{18}\text{O}$ (WR-magma) values are usually associated with more silica-rich rocks [7]. The findings from this study show that elevated $\delta^{18}\text{O}$ (Zrc) values existed by 4325 Ma as a consequence of melting of rock previously altered at the Earth's surface, requiring the presence of liquid water, and that crustal recycling was firmly established by 4200 Ma. All previously reported $\delta^{18}\text{O}$ (Zrc) values over 8‰ for >3900 Ma zircons are interpreted here to not represent magmatic $\delta^{18}\text{O}$; evidence of preserved igneous chemistry has not been demonstrated for any Archean zircon with $\delta^{18}\text{O} > 7.5\text{‰}$. The existence of mildly enriched magmas with $\delta^{18}\text{O}$ (Felsic WR) = 7‰ to 9‰ in the Early Archean as inferred from $\delta^{18}\text{O}$ (Zrc) supports the hypothesis that the Jack Hills zircons are a record of the emergence of continental crust on the early Earth.

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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.2005.04.028](https://doi.org/10.1016/j.epsl.2005.04.028).

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