Evidence from detrital zircons for the existence of continental crust and oceans on the Earth 4.4 Gyr ago

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No crustal rocks are known to have survived since the time of the intense meteor bombardment that affected Earth[1] between its formation about 4,550 Myr ago and 4,030 Myr, the age of the oldest known components in the Acasta Gneiss of northwestern Canada[2]. But evidence of an even older crust is provided by detrital zircons in metamorphosed sediments at Mt Narryer[3] and Jack Hills[4–8] in the Narryer Gneiss Terrane[9], Yilgarn Craton, Western Australia, where grains as old as ~4,276 Myr have been found[4]. Here we report, based on a detailed micro-analytical study of Jack Hills zircons[10], the discovery of a detrital zircon with an age as old as 4,404 ± 8 Myr—about 130 million years older than any previously identified on Earth. We found that the zircon is zoned with respect to rare earth elements and oxygen isotope ratios (δ^{18}O values from 7.4 to 5.0‰), indicating that it formed from an evolving magmatic source. The evolved chemistry, high δ^{18}O value and micro-inclusions of SiO_2 are consistent with growth from a granitic melt[11,2] with a δ^{18}O value from 8.5 to 9.5‰. Magmatic oxygen isotope ratios in this range point toward the involvement of supracrustal material that has undergone low-temperature interaction with a liquid hydrosphere. This zircon thus represents the earliest evidence for continental crust and oceans on the Earth.

We extracted a new aliquot of zircon from the original heavy mineral concentrate of the Jack Hills conglomerate from which the oldest documented crystal (~4,276 Myr; ref. 4) was obtained, and identified several grains with ages in excess of 4 Gyr. One of these is a deep purple zircon (W74/2-36), measuring 220 by 160 μm, that is a broken fragment of a larger crystal (Fig. 1). It shows few internal

complexities or inclusions, a feature previously noted in zircons older than 4 Gyr from the Jack Hills conglomerate[4,13].

We performed U-Th-Pb zircon analyses on the Perth Consortium SHRIMP II ion microprobe at Curtin University of Technology in Western Australia, following standard operating techniques[14–16]. Six analyses of grain W74/2-36 were initially made and five of these gave $^{207}Pb/^{206}Pb$ ages in excess of 4.3 Gyr (Table 1); the oldest and most concordant (97% concordance, Table 1) had an age of 4,363 ± 8 Myr (2σ), approximately 90 Myr older than the oldest known terrestrial material[4]. Other sites yielded more discordant ages and fell on a discordia line that passed through zero, indicative of recent lead loss (Fig. 2). A detailed cathodoluminescence (CL) image made after analysis indicated that all but the oldest site overlapped cracks within the crystal (Fig. 1a). However, crack-free domains greater than 50 μm in diameter were present and, after oxygen isotope and rare earth element (REE) analysis, approximately 20 μm was ground off the surface of the zircon to remove all previous analytical pits; the grain was then re-analysed on SHRIMP II in an attempt to obtain more concordant data. Care was taken to locate new analytical sites away from identifiable cracks and this proved partially successful, with four analyses obtained from such areas (Fig. 1b). Three of these sites yielded data that are 100, 98 and 95% concordant (Table 1), and confirm the initial estimate of the age, giving $^{207}Pb/^{206}Pb$ ages of 4,355 ± 4 Myr, 4, 341 ± 6 Myr and 4,364 ± 6 Myr (2σ), respectively (Table 1 and Fig. 2). Importantly, the fourth site, located near the pointed, broken termination of the crystal (right corner of Fig. 1b), was also nearly concordant (99%) and this gave a $^{207}Pb/^{206}Pb$ age of 4,404 ± 8 Myr (2σ) (Fig. 2), about 40 Myr older than the other results and only about 150 Myr younger than the oldest high-temperature inclusions known in meteorites[17] (~4,560 Myr), which constrain the maximum age for the Earth.

The chemistry of this crystal therefore provides important insights into early crustal processes. Because the internal cracks that are evident in CL and back-scattered electron (BSE) images (Fig. 1) may affect the chemistry, they were investigated using a high-resolution scanning electron microscope (SEM) and electron microprobe. Unlike the cracks in the xenocrysts older than 4 Gyr that were recently discovered in granitoids from the Narryer and Murchison Terranes of Western Australia[18], which are infilled with recrystallized zircon, the cracks in W74/2-36 are open. They contain thin (generally less than 300 nm thick), discontinuous films of phosphates, resulting in slightly elevated values of Fe, Al, P and Y. These are, however, too small to have a significant effect on the oxygen budget of 25-μm analytical sites; thus they do not compromise our interpretation of the oxygen data.

Grain W74/2-36 has U and Th values ranging from 127–487 and

Table 1 Shrimp U-Pb-Th isotopic analytical data

| Spot	U (p.p.m.)	Th (p.p.m.)	Th/U ratio	Pb (p.p.m.)	f206%	$^{204}Pb/^{206}Pb$	$^{207}Pb*/^{206}Pb*$	$^{208}Pb*/^{232}Th$	$^{208}Pb*/^{206}Pb*$	$^{206}Pb*/^{238}U$	$^{207}Pb*/^{235}U$	Conc. (%)	$^{206}Pb*/^{238}U$ age (Myr)	$^{207}Pb*/^{235}U$ age (Myr)	$^{208}Pb*/^{232}Th$ age (Myr)	$^{207}Pb*/^{206}Pb$ age (Myr)
Session 1																
74-36	258	178	0.69	355	0.22	0.00014	0.5432 ± 1	0.222 ± 5	0.1645 ± 12	0.928 ± 18	69.5 ± 1.4	97	4,233 ± 61	4,321 ± 20	4,058 ± 80	4,363 ± 4
74-37	449	347	0.77	615	0.048	0.00003	0.5386 ± 1	0.225 ± 5	0.1895 ± 8	0.919 ± 18	68.2 ± 1.3	97	4,201 ± 59	4,303 ± 20	4,109 ± 75	4,350 ± 3
74-38	450	1,224	2.72	544	0.098	0.00006	0.5345 ± 1	0.065 ± 1	0.2227 ± 9	0.797 ± 15	58.8 ± 1.2	87	3,780 ± 55	4,153 ± 20	1,277 ± 25	4,339 ± 3
74-58	487	1,731	3.56	217	1.142	0.00071	0.5088 ± 2	0.012 ± 0	0.1419 ± 2	0.304 ± 6	21.4 ± 0.4	40	1,713 ± 29	3,155 ± 19	244 ± 6	4,267 ± 5
74-59	454	765	1.68	335	0.781	0.00049	0.5297 ± 1	0.048 ± 1	0.1637 ± 17	0.496 ± 10	36.2 ± 0.7	60	2,595 ± 41	3,672 ± 20	952 ± 21	4,326 ± 4
74-60	390	1,336	3.43	120	1.9	0.00119	0.5394 ± 3	0.010 ± 0	0.1641 ± 41	0.200 ± 4	14.9 ± 0.3	27	1,177 ± 21	2,808 ± 20	193 ± 6	4,353 ± 8
Session 2																
36-1	361	262	0.73	515	0.002	0.00001	0.5401 ± 8	0.232 ± 5	0.1743 ± 6	0.965 ± 18	71.9 ± 1.4	100	4,356 ± 60	4,355 ± 19	4,211 ± 74	4,355 ± 2
36-2	258	174	0.67	351	0.01	0.00006	0.5353 ± 10	0.226 ± 5	0.1641 ± 7	0.929 ± 18	68.6 ± 1.3	98	4,235 ± 59	4,307 ± 19	4,125 ± 75	4,341 ± 3
36-3	184	117	0.64	204	0	0	0.5143 ± 12	0.194 ± 4	0.1612 ± 10	0.768 ± 15	54.5 ± 1.1	86	3,674 ± 53	4,078 ± 20	3,588 ± 68	4,283 ± 4
36-4	250	188	0.75	333	0	0	0.5436 ± 10	0.218 ± 4	0.1831 ± 7	0.897 ± 17	67.2 ± 1.3	95	4,126 ± 58	4,287 ± 19	3,986 ± 72	4,364 ± 3
36-5	208	304	1.46	153	0	0	0.5163 ± 13	0.067 ± 1	0.1959 ± 10	0.498 ± 9	35.4 ± 0.7	61	2,604 ± 40	3,651 ± 19	1,306 ± 25	4,288 ± 4
36-6	346	940	2.71	182	0.001	0	0.5147 ± 11	0.026 ± 1	0.2005 ± 9	0.356 ± 7	25.2 ± 0.5	46	1,961 ± 32	3,317 ± 19	524 ± 10	4,284 ± 3
36-7	127	75	0.59	180	0	0	0.5587 ± 14	0.237 ± 5	0.1437 ± 9	0.968 ± 19	74.6 ± 1.5	99	4,364 ± 61	4,392 ± 20	4,291 ± 83	4,404 ± 4
36-8	329	339	1.03	337	0.013	0.00001	0.5272 ± 9	0.141 ± 3	0.2134 ± 8	0.683 ± 13	49.6 ± 0.9	78	3,355 ± 49	3,985 ± 19	2,672 ± 49	4,319 ± 3

* Common lead corrected using ^{204}Pb.
Data for zircon grain W74/2-36. f206% is (common ^{206}Pb/total ^{206}Pb) × 100. Conc. (%) is percentage concordance defined as [($^{206}Pb/^{238}U$ age)/($^{207}Pb/^{206}Pb$ age)] × 100. All errors are quoted at 1 σ level. Errors given for Pb/Pb and Pb/Th ratios are based on counting statistics. Errors in Pb/U ratios also include an estimate of the Pb/U reproducibility error based on multiple analyses of the standard zircon CZ3 during the analytical sessions. During the first analytical session, all spots were given a unique number. In the second session, the grain was identified as W74-36 and each site was numbered consecutively, 36-1 to 36-8.

75–1,731 p.p.m., respectively (Table 1), reaching values considerably higher than those recorded from the ~4,276-Myr-old crystal[4]. There is no correlation between the $^{207}Pb/^{206}Pb$ age of the various analytical sites and the U, Th and Pb contents, or the Th/U ratio (Table 1), although the oldest site has the lowest values for all of these except Pb. These results suggest complex micrometre to submicrometre variations in composition, as indicated by several detailed studies[18–20], and also preclude any estimate of the composition of the host rock based on isotopic characteristics. The Th/U

ratio varies from 0.59 to 3.56, with those sites in the range 0.59 to 0.77 having $^{208}Pb/^{232}Th$ ages greater than 3,588 Myr and being the least discordant (Table 1). The large differences in Pb/U for similar $^{207}Pb/^{206}Pb$ ages (Table 1) indicate recent lead loss. This is especially evident within the combined light and dark rectangular area visible in the CL image, which may have formed part of the central region of the original zircon (Fig. 1b). The three spots from the second analytical run (36-3, 36-5 and 36-6), which partially overlap this zone, define a weighted $^{207}Pb/^{206}Pb$ age of 4,289 ± 7 Myr (2σ) that is younger than the $^{207}Pb/^{206}Pb$ age of all other sites (Table 1). A similar feature was noted in the core of a xenocrystic zircon older than 4.0 Gyr in granitic gneiss from Churla Well in the Narryer Terrane[18] and was interpreted as reflecting an ancient episode of lead loss resulting from an event at high temperature. Unlike Churla Well, our data show no evidence of subsequent lead loss during Precambrian time, suggesting that the zircon was not affected by later igneous or metamorphic processes before its deposition in the conglomerate.

We interpret the concordant $^{207}Pb/^{206}Pb$ age of 4,404 ± 8 Myr (2σ) as recording the time of crystallization of zircon W74/2-36. Although this is represented by only one analysis, it is concordant (99%), is not affected by cracks, and there is no evidence from the analytical data that this site, rather than any other measured, may be anomalous. The crystal was subsequently affected by one or more episodes of ancient lead loss, but the timing of these is unresolved. The concordant and near-concordant ages of 4,364 ± 6 Myr,
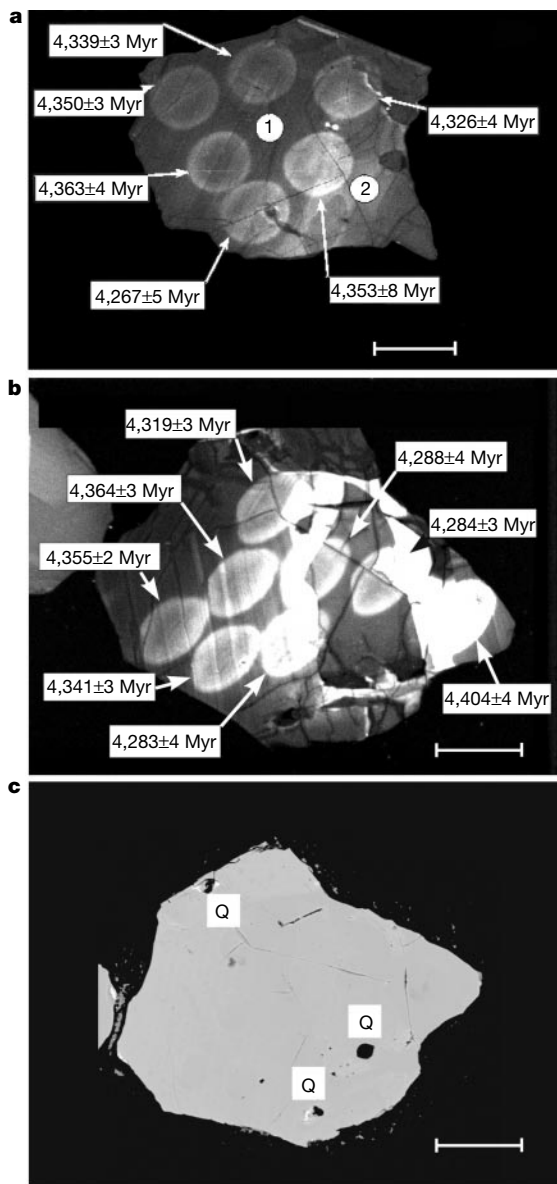
Figure 1 Cathodoluminescence and back-scattered electron images of zircon crystal W74/2-36. Scale bars are 50 μm. **a**, Image taken subsequent to first SHRIMP analysis. We note that lighter circular areas are the SHRIMP analytical sites and the values record the $^{207}Pb/^{206}Pb$ age (1σ) of each site. The two white areas represent the approximate location of the oxygen analytical spots, with δ^{18}O of 5‰ at point 1 and 7.4‰ at point 2. **b**, Cathodoluminescence image taken after the second SHRIMP analytical session showing the sites of analysis (as in **a**) and the $^{207}Pb/^{206}Pb$ ages (1σ) for each spot. We note the larger area showing light luminescence, the well defined cracks and the oscillatory zoning in both the light and dull portions of the crystal. **c**, Back-scattered electron image obtained after the second SHRIMP analytical session. We note the circular outline of the SHRIMP analytical sites and the lighter rectangular area, near the pointed termination, which corresponds to the dark area in the cathodoluminescence image (compare with **b**). The black areas (marked Q) are SiO_2 inclusions.
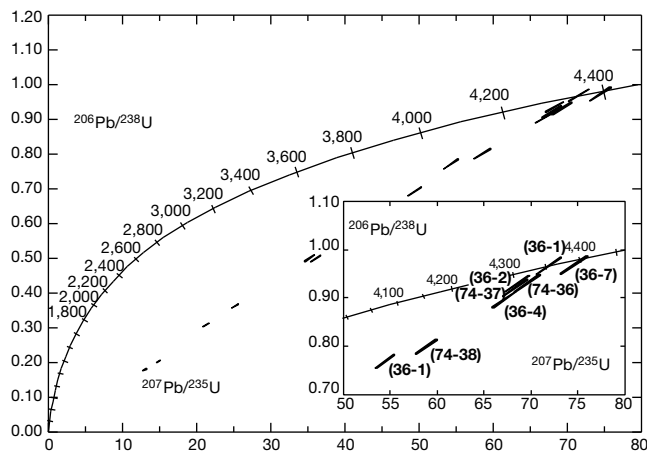
Figure 2 Combined concordia plot for grain W74/2-36, showing the U-Pb results obtained during the two analytical sessions. The inset shows the most concordant data points together with their analysis number (as in Table 1). Error boxes are shown at 1σ.
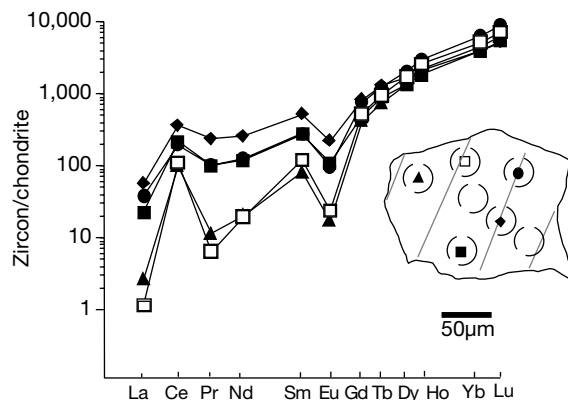
Figure 3 Rare earth element data for Jack Hills zircon W74-2/36 measured by ion microprobe. We note that spacing of elements along the x-axis is based on radii of 3$^+$ cations (in Å).

4,355 ± 4 Myr and 4,341 ± 6 Myr (2σ) may represent actual geological events, possibly triggered by meteor bombardment[18], or they may indicate slight changes in ^{207}Pb/^{206}Pb without generating much discordance[2], because of their position on the concordia curve (Fig. 2). The ^{207}Pb/^{206}Pb age of 4,289 ± 7 Myr (2σ) for the three more discordant points from the light and dark area in the CL image (Fig. 1b) were most probably reset at this time by a high-temperature event, and subsequently underwent recent lead loss.

Most of the crystal exhibits weak banding in the CL images (Fig. 1a and b), indicating elemental variation marked by differences in luminescence which usually extend fully across the crystal, suggesting that the zircon was originally much larger. The development of banding parallel to the two sharp crystal boundaries in the top left-hand corner of the image and also within the bright area (Fig. 1b) suggests that it reflects oscillatory zoning of magmatic origin. The bright area almost entirely encloses the dark central region, which is devoid of any CL pattern.

Variation in the CL image is confirmed by the REE data (Fig. 3), which were obtained from the floors of five of the initial SHRIMP analytical pits. The analyses yielded prominent positive Ce anomalies, negative Eu anomalies, and heavy (H)REE-enrichment relative to light (L)REE contents; these are features typical of zircons analysed by ion microprobe[11] and from other Jack Hills detrital zircons[13]. The crystal is zoned with respect to LREE (La by about 10-fold), with greater LREE enrichment within and around the bright portion of the crystal. Calculated partition coefficients[11] yield magma compositions with marked LREE-enrichment for this part of the crystal (Lu/La$_n$ (magma) is 238 to 616) and negative Eu anomalies, features indicative of evolved granitic melts. The crystal's growth in a silica-saturated environment is further supported by the identification of three areas, up to 20-μm in diameter, with SiO_2 inclusions (Fig. 1c).

Four analyses of oxygen isotope ratio were made on the Edinburgh Cameca ion microprobe on two spots close to two of the initial SHRIMP sites. One spot was located near the 4,339 ± 3 Myr site in the low LREE region that is dull and banded in CL (Fig. 1a). This has a δ^{18}O of 5.0 ± 0.7‰ (1σ), which is indistinguishable from the δ^{18}O values of mantle-derived zircon[21] and zircon from juvenile, 3.0 to 2.7 Gyr tonalite-trondhjemite-granodiorite plutonic rocks of the Superior Province[22]. The second spot was located in the high LREE region of the grain, which is brighter in the CL image (Fig. 1a), close to the site yielding a ^{207}Pb/^{206}Pb age of 4,353 ± 8 Myr (2σ). This has a δ^{18}O value of 7.4 ± 0.7‰ (1σ), consistent with equilibrium with a magma of about 8.5 to 9.5‰. Magmatic oxygen isotope ratios in this range are indicative of involvement of supracrustal material which has undergone low-temperature interaction with a liquid hydrosphere; there is no known primitive or mantle reservoir of this composition.

REE and oxygen isotope compositions in grain W74/2-36 provide unique insights into the Earth's crust at 4.4 Gyr ago. They indicate formation in a granitic melt derived by partial melting of pre-existing crust. Calculated magma compositions show characteristics distinctive of evolved melts (such as LREE enrichment, prominent negative Eu anomalies, silica saturation), and are not consistent with the REEs of primitive, mafic rocks[10]. The variation from relatively high to low LREEs, coupled with a 2.4‰ decrease in the oxygen isotope ratio, is consistent with igneous zoning associated with melting and assimilation and subsequent equilibration with a mantle-derived melt. The initially high-δ^{18}O magma (~9‰) could result from melting of ocean crust that was hydrothermally altered at low temperatures[23], altered or evolved continental crust, or sediments. The high δ^{18}O value cannot result from closed-system fractional crystallization by a normal mantle melt. In the case of simple melting without assimilation, zircons in the melt would have a similar δ^{18}O value to zircons in its protolith. An alternative hypothesis, involving assimilation coupled with fractional crystallization (AFC) by a normal basalt of high δ^{18}O wallrock, is unlikely, as it would require either energetically unrealistic amounts of assimilation (>50%) or wallrocks with average δ^{18}O values above 12‰ which are uncommon even in the late Archaean[22]. The correlation of high δ^{18}O values and enriched LREEs is most consistent with the melting of continental crust or sediments, but whichever of these processes dominated, a large reservoir of liquid water is required on the surface of the Earth.

The zoning of zircon W74/2-36 provides further insights into magmatic processes at 4.4 Gyr ago. Such zones could form during AFC, but we suggest that the zircon first crystallized in a magma derived from the melting of existing continental crust at 4,404 ± 8 Myr ago, which subsequently formed a magmatic overgrowth when mixed with, or remelted by, a more primitive magma between 4,364 ± 6 Myr ago and 4,289 ± 7 Myr ago. This indicates that at 4.4 Gyr ago there were already intermediate to granitic, high-δ^{18}O continental rocks to contaminate the magma in which grain W74/2-36 grew.

The existence of liquid water at 4.4 Gyr ago could have important implications for the evolution of life. Microfossils as old as 3.5 Gyr are known[24]. Metasediments and carbonaceous materials with biogenic carbon isotope ratios as low as δ^{13}C = −28‰ are known at 3.8 Gyr ago[25]. Zircon crystal W74/2-36 is over 500 Myr older than this organic matter and if liquid water was available to cause the evolved geochemistry that we have measured, then such water was also available for possible biological processes. High-energy asteroid bombardment before 3.9 Gyr ago is consistent with periodic formation and destruction of early oceans and the possibility that primitive life, if it evolved in the oceans, was globally extinguished more than once. □

Table 2 Rare earth element and oxygen isotope data

Trace element data (p.p.m.)

Spot number	La	Ce	Pt	Nd	Sm	Eu	Gd	Tb	Dy	Ho	Yb	Lu
m2-13	5.5	134	9.4	55	41.4	6.3	100	34	338	106	666	135
m2-14	9.2	122	9.5	59	42.6	5.6	155	47	518	173	1065	225
m2-17	0.6	61	1.1	9	12.3	1.0	85	28	347	124	768	159
m2-30	13.6	226	21.8	119	78.4	12.7	170	49	424	119	672	130
m2-31	0.3	69	0.6	9	18.4	1.4	108	36	438	149	877	182

Oxygen isotope data

Spot number	Analysis number	Measured ^{18}O/^{16}O (×10^{-3})	δ^{18}O (VSMOW)
m2-1	2(15)	1.9378	4.8
m2-2d	2(16)	1.9388	5.3
			Avg. 5.0
m2-3	2(21)	1.9414	6.8
m2-4d	2(22)	1.9436	8
			Avg. 7.4

Data were measured by ion microprobe for crystal W74-2/36.

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Methods

Zircon data collection

Approximately 100 zircon grains were hand picked from a previously prepared +135-μm concentrate and mounted onto double-sided adhesive tape, along with pieces of the Curtin University Sri Lankan gem zircon standard (CZ3) with a conventionally-measured U–Pb age of 564 Myr (ref. 26). They were enclosed in epoxy resin disks, ground and polished so as to effectively cut all zircon grains in half, and then gold coated. Samples were imaged by cathodoluminescence (CL), resulting in a map that allowed us to identify grains, as well as providing information on internal structure that could be tested during analysis. During the first analytical session, a mass resolution of 5,400 was obtained and the error associated with the measurement of Pb/U isotopic ratios for the standard, at 1 standard deviation, was 1.96% for seven standards. After discovery of a grain with an age in excess of 4.3 Gyr, and following the collection of oxygen isotope and trace element data, the sample was reground, repolished and gold coated and, on the basis of a new CL image, the grain was reanalysed on SHRIMP II, with a total of eight new sites selected so that most were away from cracks in the crystal. During this session, the mass resolution was 4,885 and the error on the standard, at 1 standard deviation, was 1.86% for six standards. The relationship between measured Pb/U and UO/U ratios on SHRIMP follows a power-law equation with the exponent equal to two (ref. 27). The Pb/U ratios on the unknowns were normalized to those measured on the standard zircon (CZ3 − (^{206}Pb/^{238}U = 0.0914)). Both data sets were reduced following the methods of Nelson[16], using the single-stage model Broken Hill common Pb correction for mass ^{204}Pb, since this is considered to be introduced chiefly through the gold coating[16]. The analytical spot size averaged 30 μm during each analytical run and each spot was rastered over 100 μm for five minutes before analysis to remove common Pb on the surface or contamination from the gold coating. All stated uncertainties and data listed in Table 1, and the error bars shown in Fig. 2, are at 1σ; ages discussed in the text are all 2σ.

Oxygen isotope analysis

Four analyses were made by Cameca ims 4f ion microprobe on two spots on grain W74/2-36 using an energy offset of 350 eV. These were analysed for a total of 2 × 10^6 counts of ^{18}O for each analysis, yielding precision close to 0.7‰ (1σ), based on gaussian counting statistics[28]. Internal precision for each analysis was ±0.3 and ±0.6‰ (1σ), comparing 80-cycle analysis halves on each full analysis, in agreement with theoretical counting statistics. The two point-analyses of the zircon crystal were interspersed with 11 analyses of Kim-5, a homogeneous zircon standard (δ^{18}O = 5.04 ± 0.07‰ VSMOW by laser fluorination) mounted in a separate standard block. Five standard zircons with 1.06 to 1.52 wt% HfO$_2$ were also analysed by ion microprobe and laser fluorination[10], and no statistically significant dependence of instrumental mass fractionation on HfO$_2$ content was found[29] for the narrow range of Hf in these samples.

Rare earth element analysis

In situ determination of REEs was performed by Cameca ims 4f ion microprobe[11]. Five ion microprobe REE analyses of the zircon crystal were made using a 14.5-keV primary beam of O⁻ defocused to an approximately 20 to 30 μm spot. Positive secondary ions were collected using an energy offset of 125 V. Analyses were standardized to the SRM-610 glass standard. Energy filtering and strategies to avoid and correct for isobaric interferences were used[11].

Received 1 August; accepted 24 November 2000.

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Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4,300 Myr ago

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Granitoid gneisses and supracrustal rocks that are 3,800–4,000 Myr old are the oldest recognized exposures of continental crust[1]. To obtain insight into conditions at the Earth's surface more than 4 Gyr ago requires the analysis of yet older rocks or their mineral remnants. Such an opportunity is presented by detrital zircons more than 4 Gyr old found within 3-Gyr-old quartzitic rocks in the Murchison District of Western Australia[2,3]. Here we report *in situ* U–Pb and oxygen isotope results for such zircons that place constraints on the age and composition of their

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