

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 - $^{206}\text{Pb}/^{238}\text{U} = 0.0914$). Both data sets were reduced following the methods of Nelson¹⁶, 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 coating¹⁶. 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 statistics²⁸. 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 ($\delta^{18}\text{O} = 5.04 \pm 0.07\text{‰}$ VSMOW by laser fluorination) mounted in a separate standard block. Five standard zircons with 1.06 to 1.52 wt% HfO₂ were also analysed by ion microprobe and laser fluorination¹⁰, and no statistically significant dependence of instrumental mass fractionation on HfO₂ content was found²⁹ 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 microprobe¹¹. 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 used¹¹.

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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 crust¹. 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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sources and may therefore provide information about the nature of the Earth's early surface. We find that 3,910–4,280 Myr old zircons have oxygen isotope ($\delta^{18}\text{O}$) values ranging from $5.4 \pm 0.6\text{‰}$ to $15.0 \pm 0.4\text{‰}$. On the basis of these results, we postulate that the $\sim 4,300$ -Myr-old zircons formed from magmas containing a significant component of re-worked continental crust that formed in the presence of water near the Earth's surface. These data are therefore consistent with the presence of a hydrosphere interacting with the crust by 4,300 Myr ago.

The Narryer Gneiss Complex, Western Australia, contains 3.73–3.30-Gyr-old granitic to tonalitic gneisses and about 3.0-Gyr-old metasedimentary rocks in the Mt Narryer and Jack Hills regions (Fig. 1). Previously, detrital zircons ranging in age from 4.27 to 3.05 Gyr (refs 2–5) have been described from these two regions. The source rocks of these zircons have not been identified and may not have been preserved.

Because zircon is a common accessory phase in granitoids and their volcanic equivalents, these rocks are generally considered to be the dominant source of detrital zircons. But zircon can form in other rock types (albeit of low abundance in most cases) such as syenites, carbonatites, and mafic rocks⁶, and can also grow in hydrothermal veins and during metamorphism. Residual plagiogranites from Iceland-type melts more than 4 Gyr old within a predominantly mafic crust have been suggested as the source of the oldest detrital zircons from the Narryer Gneiss Complex⁷, but this view has been challenged on trace-element and mineralogical grounds⁸.

Zircon has been extensively studied because it provides reliable U–Pb crystallization ages and can survive both high-grade metamorphism and sedimentary transport processes. Measurements of oxygen isotopes in rocks and minerals help us to understand the magmatic, fluid and thermal history of the crust. Exchange rates for oxygen are very slow⁹ in zircon, which may permit preservation of the protolith oxygen isotope composition through high-grade metamorphism¹⁰. Oxygen isotopes are used to discriminate among possible granitoid sources (mantle, metasedimentary, hybrid); thus, measurements of ancient zircons from the Narryer Gneiss Complex could allow us to directly explore crust–hydrosphere interactions before 4 Gyr ago.

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 margin¹¹ that were subsequently metamorphosed to upper greenschist facies^{8,13}. At least three distinct age groupings of ancient zircons have been described^{3,8,11,13} (~ 4.3 Gyr, 4.15 Gyr and 3.9 Gyr) that could represent discrete source terranes, although no rocks

older than ~ 3.75 Gyr have been found in the region^{4,5,12}. We collected quartz-pebble conglomerates rich in heavy mineral indicators (such as Cr-spinel, fuchsite) from a locality in the Erawondoo region of the Jack Hills (Fig. 1) that was previously sampled for investigations of the trace element composition and inclusion mineralogy of detrital zircons more than 4 Gyr old^{2,3,8,13}. In order to minimize the loss of zircon during sample preparation, we crushed, powdered and sieved 15 kg of sample JH992 and processed all fractions through heavy liquids without pre-washing. This yielded about 80 zircons kg^{-1} in the size range 50–700 μm , most with low aspect ratios. For each sample mount, we placed 100 zircon grains on adhesive tape together with standard zircon AS3¹⁴ and filled an enclosing one-inch diameter mould with epoxy. After curing, the mount was cleaned and polished following our usual procedures¹⁵ and the internal features of the zircons were imaged using optical and back-scattered electron microscopy.

Because the very oldest grains are less than 10% of the total zircon population, we developed a new multi-collector ion microprobe technique to rapidly identify the oldest grains by determining $^{207}\text{Pb}/^{206}\text{Pb}$ ages by simultaneous measurement of ^{207}Pb and ^{206}Pb on adjacent electron multipliers. Using a primary O^- beam of 3 nA focused to an approximately 20 μm diameter spot together with O_2 flooding¹⁶, this new approach yielded precise (typically ± 10 Myr) $^{207}\text{Pb}/^{206}\text{Pb}$ ages in 3.5 minutes, permitting us quickly to survey 200 zircons. The oldest candidate grains were then targeted for conventional U–Pb ion microprobe measurements. Our search revealed 17 zircons more than 3.9 Gyr old. Grains JH992_95 and JH992_48 (Table 1) showed very ancient and essentially concordant ages of $4,279 \pm 5$ Myr (2σ) and $4,280 \pm 5$ Myr (2σ), respectively, suggesting that $\sim 1\%$ of the zircons in our sample are about 4.3 Gyr old.

We used a multi-collector method to obtain precise oxygen isotope compositions of microscale domains within the zircons. This new method provides the spatial resolution to determine isotopic heterogeneity at the sub-grain scale and avoid metamict zones or later metamorphic overgrowths that might complicate interpretation of the isotopic data. After the U–Pb measurements, the zircon mounts were re-polished, cleaned, and gold-coated and then analysed for oxygen isotopes using a 6-nA Cs^+ primary beam focused to a 25 μm diameter spot. In most cases, the oxygen isotope measurement was made directly adjacent to the spot on which a U–Pb age was determined. A mass resolving power of $\sim 2,000$ was sufficient to separate $^{18}\text{O}^-$ and $^{16}\text{O}^-$ from molecular interferences. Each beam was focused into a Faraday cup with a typical count rate

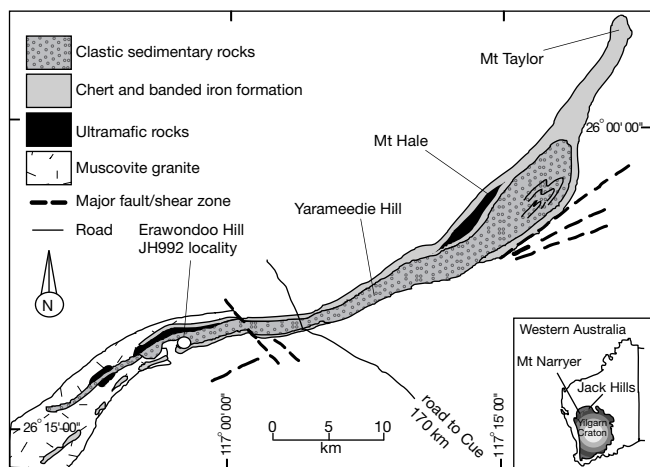


Figure 1 Schematic geological map of the Erawondoo region, Western Australia, showing the location of quartz-pebble conglomerate sample JH992 containing detrital zircons more than 4 Gyr old. The Jack Hills and the Mt Narryer quartzitic units are part of an arcuate metasedimentary belt near the northwestern margin of the Yilgarn Craton (see inset).

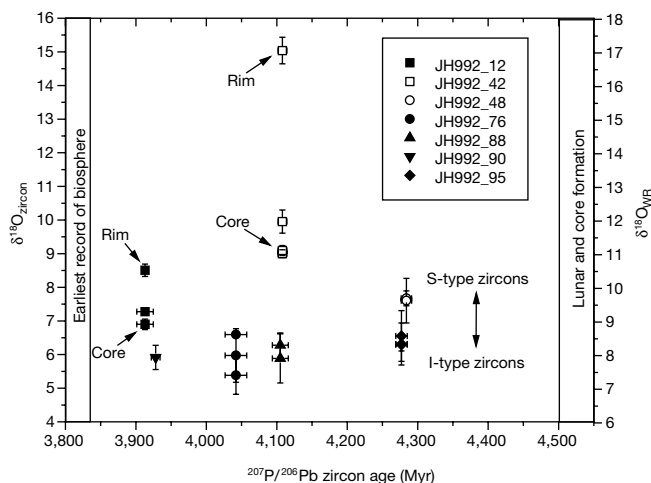


Figure 2 Ion microprobe $\delta^{18}\text{O}$ data for individual zircon spot analyses versus $^{207}\text{Pb}/^{206}\text{Pb}$ zircon age (Supplementary information available at <http://www.nature.com>). The right vertical axis shows the estimated $\delta^{18}\text{O}$ data for the whole rock^{10,25} ($\delta^{18}\text{O}_{\text{WR}}$) from which the zircon crystallized. High $\delta^{18}\text{O}_{\text{WR}}$ values are consistent with the incorporation of recycled crustal material that had interacted with low-temperature water in the magmatic source of the zircons.

of 2 GHz for $^{16}\text{O}^-$ and 4 MHz for $^{18}\text{O}^-$; the total integration time for each analysis was less than 6 min. Backgrounds on the Faraday cup system were monitored periodically and the uncertainty in this correction was always less than 0.1‰. Instrumental mass fractionation was corrected by reference to standard zircons KIM5 ($5.04 \pm 0.05\text{‰}$)¹⁷ and 91500 ($9.8 \pm 0.2\text{‰}$; S. Claesson, personal communication), which were interposed between analyses of unknowns. Daily reproducibility determined from more than 15 spots was typically better than $\pm 0.2\text{‰}$ for both standards. Uncertainties in oxygen isotope data are reported at the 2σ level. Most zircons were examined for intracrystal homogeneity by analysing multiple spots. Two zircons (JH992_12, and JH992_42) were found to have core to rim variability over about 50 μm that correlates with observed overgrowths (Table 1), emphasizing our need for the highest possible spatial resolution. The values of $\delta^{18}\text{O}$ for 3.90–4.28-Gyr-old zircon cores ranged from $5.4 \pm 0.6\text{‰}$ (JH992_76) to $9.0 \pm 0.2\text{‰}$ (JH992_42) for seven zircons from sample JH992. Figure 2 shows the data for these zircons plotted as $\delta^{18}\text{O}_{\text{zircon}}$ versus $^{207}\text{Pb}/^{206}\text{Pb}$ age.

The $\delta^{18}\text{O}_{\text{SMOW}}$ of the mantle, estimated to be 5.5‰ ¹⁸, is unlikely to have changed over time as contemporary mid-ocean ridge and ocean island basalts have identical $\delta^{18}\text{O}$ values of $5.7 \pm 0.2\text{‰}$ (refs 19, 20). Crustal contamination can strongly affect oxygen isotopes in igneous rocks. Phanerozoic granitoids derived largely from orthogneiss protoliths (I-types) tend to have $\delta^{18}\text{O}$ values below 9‰, whereas those derived by melting of clay-rich sedimentary rocks (S-types) have higher $\delta^{18}\text{O}$ values²¹. Granitoids with $\delta^{18}\text{O}$ values significantly less than 6‰ probably reflect interaction with meteoric water²². In general, S-type granitoids form by partial melting of metasediments enriched in ^{18}O , as opposed to I-type granitoids, which form by melting of igneous rocks derived from arc processes²³. As the average $\delta^{18}\text{O}$ values of Archean sedimentary rocks varies from 9 to 12‰ (ref. 24), only small inputs of this component to a primitive source magma will measurably raise its $\delta^{18}\text{O}$.

The $\delta^{18}\text{O}$ values of the zircons we examined range from 5.4‰ to 15.0‰ (Table 1; Fig. 2). In the two most discordant grains (JH992_12, JH992_42), we identified core–rim relationships and analysed both. In these cases, rim compositions were systematically higher in $\delta^{18}\text{O}$ than cores. In the five other zircons investigated, multiple analyses undertaken on optically continuous grains range in $\delta^{18}\text{O}$ from 5.4 to 7.7‰. The oxygen isotope fractionation between zircon and a granitoid host rock is approximately -2‰ (refs 10, 25), permitting us to estimate the $\delta^{18}\text{O}$ value of the melt from which the zircon crystallized. Source $\delta^{18}\text{O}$ values calculated in this fashion for all seven zircon cores analyzed range from about 7 to

11‰. These results indicate the presence in these zircons of recycled crustal material that had interacted with liquid water under surface, or near-surface, conditions. This conclusion is consistent with the results of a Hf isotope study of detrital zircons from the Narryer Gneiss Complex²⁶ that shows that many Hadean zircons formed by re-melting of significantly older crust. If the rims of grains JH992_12 and JH992_42 also reflect crystallization from a melt, then a source $\delta^{18}\text{O}$ value as high as 17‰ is possible.

We note that mineral assemblages (including muscovite and monazite) suggestive of derivation from a peraluminous melt were found as inclusions in 4.2-Gyr-old zircons from the Narryer Gneiss Complex⁸. Peraluminous granitoids form mainly from melting of a graywacke protolith²⁷; therefore, this observation is also consistent with the presence of a hydrosphere on Earth before 4.2 Gyr ago.

The crystallization of Hadean zircons containing heavy oxygen isotopic compositions suggests the existence of a hydrosphere at or near the Earth's surface within about 200 Myr of terrestrial core formation and the origin of the Moon at 4.50 Gyr (ref. 28). Liquid water, a source of energy, and organic raw materials are assumed to be necessary for the origin and propagation of life. Our results thus raise the possibility that a biosphere could have arisen on Earth at least 400 Myr earlier than is now thought²⁹. □

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Table 1 U–Pb geochronology and oxygen isotope compositions

Grain spot	$\%^{206}\text{Pb}^*$	$^{206}\text{Pb}/^{238}\text{Pb}$ age	$^{207}\text{Pb}/^{235}\text{U}$ age	$^{207}\text{Pb}/^{206}\text{Pb}$ age	Th/U	$\delta^{18}\text{O}_{\text{zircon}}$
U–Pb	(%)	(Myr)	(Myr)	(Myr)		(‰)
12_1	98.9	780 ± 97	2126 ± 118	3913 ± 12	2.6	7.3 ± 0.1 6.9 ± 0.2 $8.5 \pm 0.2^\dagger$
42_1	99.0	657 ± 97	2081 ± 137	4108 ± 6	2.4	$10.0 \pm 0.3^\dagger$ 9.0 ± 0.1 9.0 ± 0.2 $15.0 \pm 0.4^\dagger$
48_1	99.9	3582 ± 209	4045 ± 76	4284 ± 7	0.92	7.7 ± 0.2
48_2	99.9	3970 ± 101	4175 ± 33	4276 ± 6	0.88	7.6 ± 0.7
48_3	99.9	4147 ± 167	4238 ± 55	4282 ± 6	0.87	
76_1	99.7	3567 ± 288	3877 ± 106	4042 ± 15	0.30	6.6 ± 0.1 6.0 ± 0.8 5.4 ± 0.6
88_1	99.9	3928 ± 237	4046 ± 78	4105 ± 11	0.52	5.9 ± 0.7 6.3 ± 0.4
90_1	98.6	1345 ± 132	2676 ± 102	3928 ± 6	3.1	5.9 ± 0.4
95_1	99.9	4284 ± 143	4283 ± 46	4282 ± 7	0.31	6.3 ± 0.2
95_2	99.9	3730 ± 236	4093 ± 81	4277 ± 8	0.44	6.6 ± 0.8 6.3 ± 0.6

Data is from detrital zircons that are more than 3.9 Gyr old from sample JH992, Jack Hills, Western Australia.

Uncertainties in ages are reported at 1σ . Oxygen isotope values are expressed in per mil deviations from standard mean ocean water (SMOW); uncertainties in $\delta^{18}\text{O}$ are reported at 2σ .

* Radiogenic lead.

† $\delta^{18}\text{O}_{\text{zircon}}$ data measured at the rim of the zircon; all others measured at the core.

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Supplementary information is available on Nature’s World-Wide Web site (<http://www.nature.com>) or as paper copy from the London editorial office of Nature.

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Fossil that fills a critical gap in avian evolution

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Despite the discoveries of well-preserved Mesozoic birds^{1–5}, a key part of avian evolution, close to the radiation of all living birds (Aves), remains poorly represented⁶. Here we report on a new taxon from the Late Cretaceous locality of Ukhaa Tolgod, Mongolia⁷, that offers insight into this critically unsampled period. *Apsaravis* and the controversial alvarezsaurids⁸ are the only avialan⁹ taxa known from the continental deposits at Ukhaa Tolgod, which have produced hundreds of fossil mammals, lizards and other small dinosaurs⁷. The new taxon, *Apsaravis ukhaana*, is the best-preserved specimen of a Mesozoic ornithurine bird discovered in over a century. It provides data important for assessing morphological evolution across Avialae, with implications for,

first, the monophyly of Enantiornithes and Sauriurae; second, the proposition that the Mesozoic sister taxa of extant birds, as part of an ‘ecological bottleneck’, inhabited exclusively near-shore and marine environments²; and third, the evolution of flight after its origin.

Systematic paleontology
 Theropoda Marsh 1881
 Avialae Gauthier 1986
 Ornithurae Chiappe 1991
Apsaravis ukhaana new taxon

Type specimen. IGM (Institute of Geology, Mongolia) 100/1017 (Figs 1–3).

Etymology. ‘Apsara’ (sanskrit), winged consorts prominent in Buddhist and Hindu art, plus ‘avis’ from the Greek *aves* for bird. ‘Ukhaana’ refers to the type locality Ukhaa Tolgod.

Type locality. Camels Humps amphitheater, Ukhaa Tolgod, Mongolia, ?Campanian⁷.

Diagnosis. *Apsaravis* is differentiated from other avialans by the derived presence of a strong tubercle on the proximal posterior surface of the humerus directly distal to the humeral head (Fig. 1), a hypertrophied trochanteric crest on the femur and well-projected wings of the sulcus cartilaginis tibialis on the posterodistal tibiotarsus (Figs 1 and 3). Nine additional characters optimize as local apomorphies in the phylogenetic analysis (Fig. 4).

Description. The holotype specimen is three-dimensionally preserved and partially articulated (Figs 1 and 2). The fragmentary skull has a ring of scleral ossicles in the left orbit. A fragment (the left quadrate?), lies against the cranium close to the first of 12 preserved heterocoelic cervical vertebrae (Fig. 2). Part of the right jaw is a crushed arch of bone near the first phalanx of right manual digit II (Fig. 1). Another fragment includes the tips of toothless dentaries joined in an ossified symphysis (Fig. 1).

Seven opisthocoelel dorsal vertebrae and ten ankylosed sacral vertebrae are visible ventrally. Five free caudal vertebrae and a pygostyle, broken at its base and distal tip, complete the series. The pectoral and pelvic arches are nearly complete. The V-shaped ulnare and radiale are preserved and metacarpals I–III are fused (at least proximally) into a carpometacarpus (Figs 1 and 2). The proximal tarsals and tibia are coossified (Figs 1 and 3). The right tibiotarsus is in articulation with the tarsometatarsus (Fig. 3). In both tarsometatarsi, the distal tarsals and metatarsals II–IV are coossified completely and enclose the distal vascular foramen. Metatarsal V is not present, and pedal digit I was not present or is not preserved. Distal to the area of the hypotarsus, an ossified tendon lies against metatarsal III. Semi-articulated pedal phalanges (Figs 1 and 3) decrease in length distally.

The phylogenetic position of *Apsaravis* close to crown-clade Aves (Fig. 4) is strongly supported. *Apsaravis* uniquely and unambiguously shares with Aves, and the only other well-preserved Mesozoic ornithurines¹ *Ichthyornis* and *Hesperornithiformes*¹⁰ (for example, *Hesperornis* and *Baptornis*), at least ten ankylosed sacral vertebrae; pubis and ischium sub-parallel and closely appressed; pubis medio-laterally compressed; a patellar groove on the distal femur; lateral condyle of the tibiotarsus equal to, or surpassing, the width of the medial; and metatarsal III pinched proximally between II and IV.

Other derived forelimb characters present in *Apsaravis*, *Ichthyornis* and Aves are indeterminable in the highly apomorphic, diving Hesperornithiformes. These include a globose humeral head; an extensor process on the proximal surface of metacarpal I; phalanx 1 of manual digit II posteriorly compressed; and a flat, and posteriorly bowed, metacarpal III less than one-half the diameter of metacarpal II. *Apsaravis* shares with *Ichthyornis* and Aves the derived presence of an anteriorly developed midline ridge associated with an anterior sternal keel, which is absent in flightless Hesperornithiformes, missing data in *Patagopteryx deferrariisi*¹¹ and unknown in more basal avialans where a keel, if present, is posteriorly developed^{5,12}. *Apsaravis*, *Ichthyornis* and Aves also share the derived