LETTERS

Low heat flow inferred from >4 Gyr zircons suggests Hadean plate boundary interactions

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The first ~600 million years of Earth history (the 'Hadean' eon) remain poorly understood, largely because there is no rock record dating from that era. Detrital Hadean igneous zircons from the Jack Hills[1], Western Australia, however, can potentially provide insights into the conditions extant on our planet at that time. Results of geochemical investigations[2–13] using these ancient grains have been interpreted to suggest the presence of a hydrosphere[2–4,7,8] and continental crust[9,10] before 4 Gyr. An underexploited characteristic of the >4 Gyr zircons is their diverse assemblage of mineral inclusions[14–17]. Here we present an examination of over 400 Hadean zircons from Jack Hills, which shows that some inclusion assemblages are conducive to thermobarometry. Our thermobarometric analyses of 4.02–4.19-Gyr-old inclusion-bearing zircons constrain their magmatic formation conditions to about 700 °C and 7 kbar. This result implies a near-surface heat flow of ~75 mW m^{-2}, about three to five times lower than estimates of Hadean global heat flow. As the only site of magmatism on modern Earth that is characterized by heat flow of about one-quarter of the global average is above subduction zones, we suggest that the magmas from which the Jack Hills Hadean zircons crystallized were formed largely in an underthrust environment, perhaps similar to modern convergent margins.

Geochemical and mineralogical investigations of Hadean zircons, including oxygen isotopes[2–4], fission Xe[5,6], zircon thermometry[7,8], Lu–Hf[9,10], Sm–Nd[11,12], trace elements[13] and mineral inclusion studies[14–17], are beginning to reveal insights into the physical and environmental conditions on the early Earth. The ~100 Hadean zircons that have previously been examined for mineral inclusions have been documented to contain quartz, apatite, monazite, K-feldspar, xenotime, rutile, biotite, muscovite, chlorite, FeOOH, Ni-rich pyrite, thorite, amphibole, plagioclase and diamond[14–17]. Two broad inclusion assemblages are consistent with their forming in 'I-type' (for example hornblende, quartz, biotite, plagioclase, apatite, ilmenite) and 'S-type' (quartz, K-spar, muscovite, monazite) granitoids[2]. The observation of diamond inclusions in Hadean Jack Hills zircons may imply thick, cool lithosphere before 4 Gyr ago[17].

We examined 403 Jack Hills zircons from this period (4.02–4.19 Gyr) for inclusion type and abundance (see Methods). Of these, 85 possessed inclusions that intersected the polished surface. Although only about a quarter of the polished zircon surfaces exposed inclusions, optical examination showed that most grains contain subsurface inclusions. In selected cases we used laser Raman confocal imaging of the zircons embedded in their epoxy mounts but found that epoxy fluorescence could interfere with signals from subsurface phases. Some subsurface minerals, such as titanite, do yield clearly identifiable spectra.

The type and abundance of inclusions identified by energy-dispersive spectroscopy and optical imaging methods are as follows (number, average size, size range): 37% muscovite (31, ~4 μm, 1–10 μm); 36% quartz (30, ~13 μm, 4–25 μm); 12% biotite (9, ~5 μm, 2–10 μm); 7% apatite (5, ~4 μm, 2–10 μm), 2% hornblende (2, 2 and 10 μm); 2% rare-earth element oxide (2, 4 and 25 μm), 1% monazite (1, ~10 μm); 1% albite (1, ~4 μm); 1% ilmenite (1, ~25 μm). Although we have examined over ten times as many Hadean zircons as Menneken *et al.*[17], we have not identified any diamond inclusions. We obtained chemical analyses on inclusions that were both relevant to barometric methods and large enough to obtain reliable results (that is, >5 μm). Only seven zircons met these criteria: six containing muscovite (+ other phases) and one containing hornblende (+ biotite + titanite).

Six muscovites associated with minerals including quartz, biotite, rutile and feldspar were analysed by electron microprobe analyser (EMPA) for silicon content and fall into two broad groups characterized by Si_{pfu} (per formula unit normalized to 11 oxygens) values of about 3.12 (Group I) and 3.4 (Group II). The inclusions are generally small but yield results consistent with muscovite structural formula (Table 1). Sodium loss seems to be small. The high TiO_2 contents

Table 1 | Electron microprobe results for muscovite and hornblende inclusions in Hadean Jack Hills zircons

	Muscovite						Hornblende
	RSES55_6.15	RSES67_19.5	RSES67_15.16	RSES77_5.7	RSES67_3.2	RSES61_10.8	RSES58_ 7.9
SiO_2	47.5	46.67	45.77	46.46	50.62	51.20	42.16
TiO_2	0.4	0.19	0.40	0.40	1.52	0.22	0.46
Al_2O_3	35.69	34.55	34.14	34.84	25.36	26.30	11.97
MgO	0.92	0.93	0.71	1.11	1.33	1.68	8.08
CaO	0.05	0.05	0.03	0.00	1.29	0.08	11.86
MnO	0.01	0.00	0.00	0.02	0.00	0.05	0.65
$\sum$Fe as FeO	1.73	1.52	1.02	1.30	4.12	6.37	21.53
Na_2O	0.45	0.42	0.50	0.36	1.29	0.04	0.71
K_2O	9.51	9.49	9.92	9.80	9.69	8.44	0.83
Total	96.26	93.82	92.50	94.28	95.20	94.39	98.20
Si_{pfu}	3.11	3.13	3.12	3.11	3.42	3.46	

Si_{pfu} is normalized to 11 oxygens.

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(typically ≥0.4%) are characteristic of derivation from peraluminous granites containing Ti-bearing phases[18]. One hornblende inclusion yields 2.25 Al per 13 cations (Table 1; Fig. 1m,n). Titanium concentrations for the seven zircons, measured by ion microprobe[8] (only analytical errors quoted), range from 3 to 9 p.p.m., yielding apparent crystallization temperatures[7] (T_{zir}) of 665–745 °C (assuming a rutile activity (a_{TiO_2}) of 1). None of the analysed inclusions (Fig. 1) are associated with imperfections in the zircon (cracks, growth zone boundaries). Because of this, and the fact that included white micas were not affected by the widespread alteration of muscovite to fuchsite (a Cr-mica) in the host-rock matrix[1], we conclude that the analysed inclusions remained closed chemical systems since deposition. Details of inclusion mineralogy, zircon age and Ti temperatures are given in Fig. 1.

Experimental results in the system K-feldspar + phlogopite + quartz indicate a broadly linear increase of Si content in white mica (that is, the celadonite component) with pressure[19]. Thermodynamic parameters derived from experimental studies[19] are incorporated into THERMOCALC[20] version 3.26 (2007), permitting construction of pseudo-sections for relevant rock compositions. Using the Bullenbalong cordierite granite as a representative peraluminous magma composition[21], we have calculated Si_{pfu} values as a function of temperature and pressure using a Na-free solution model[22], modified to include ideal mixing of Fe and Mg on octahedral sites. The average values of $T_{zir} = 690 \pm 15$ °C and $Si_{pfu} = 3.12 \pm 0.01$ of the four Group I muscovites indicate formation at $P = 6.9 \pm 0.8$ kbar. Incorporation of Na mixing for K in muscovite[22] yields pressure about 1 kbar higher; TiO_2 and Fe_2O_3 are not accounted for but are negligible (Table 1). Thus, we interpret our result as a minimum estimate of pressure. We found that varying the bulk composition of peraluminous silicic melts had little effect on these calculations provided Na/K was low (that is, muscovite composition was controlled by pressure, temperature, and solid-solution energetics, not bulk composition). This is potentially important as low-degree partial melts from amphibolites yield trondhjemitic[23] magmas with Na/K that is too high to stabilize muscovite on the liquidus, offering further evidence in support of a metasedimentary magma source.

Calculations based on subsolidus experiments suggest that the higher Si_{pfu} values of ~3.4 in Group II muscovites (Table 1) could correspond to pressures of over 20 kbar. However, these calculations are more indicative than conclusive as thermodynamic data for these

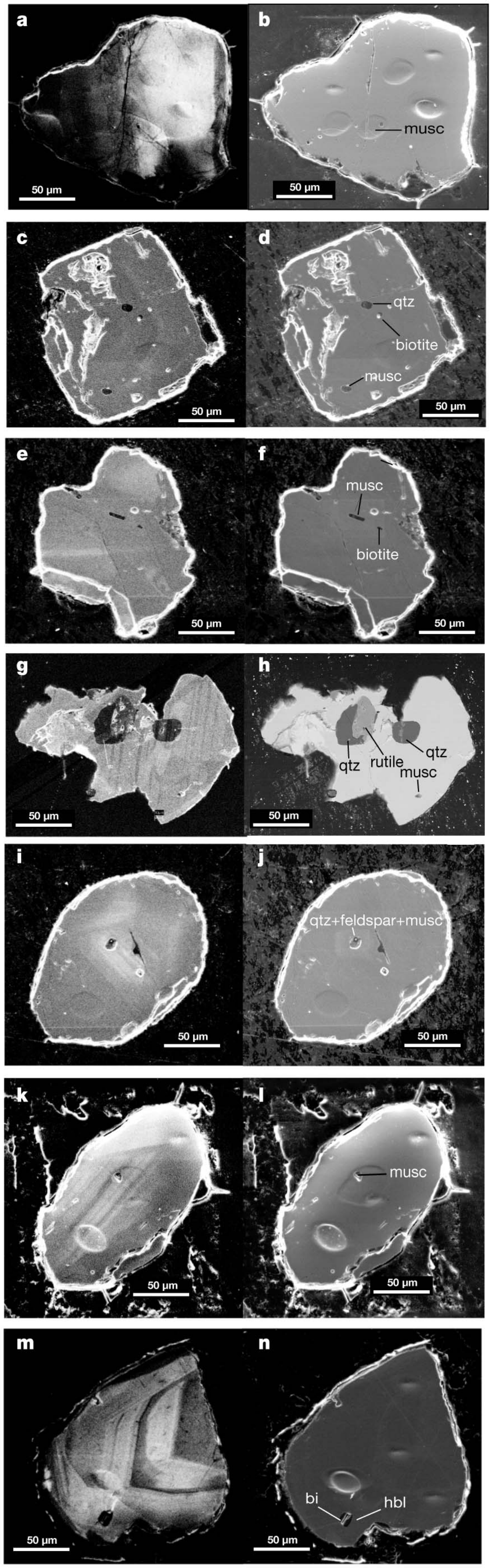

Figure 1 | Cathodoluminescence and secondary electron micrographs of inclusion-bearing Jack Hills zircons. Sample identification ($^{207}Pb/^{206}Pb$ age, percentage discordance, Ti-in-zircon crystallization temperature) is as follows. **a**, **b**, RSES55_6.15 (4,017 ± 19 Myr, −7% discordant, $T_{zir} = 695 \pm 15$°C), muscovite $Si_{pfu} = 3.11$. Only muscovite inclusions were seen. **c**, **d**, RSES67_19.5 (4,151 ± 5 Myr, 3% discordant, $T_{zir} = 665 \pm 15$ °C), muscovite $Si_{pfu} = 3.13$. This zircon contains inclusions of quartz, muscovite and biotite ranging in size from 5 to 8 μm. **e**, **f**, RSES67_15.16 (4,192 ± 7 Myr, −3% discordant, $T_{zir} = 723 \pm 15$ °C), muscovite $Si_{pfu} = 3.12$. Both muscovite and biotite are present and range in size from 4 to 10 μm. **g**, **h**, RSES77_5.7 (4,061 ± 14 Myr, 1% discordant, $T_{zir} = 667 \pm 15$ °C), muscovite $Si_{pfu} = 3.11$. This zircon contains a large inclusion with coexisting quartz, rutile (that is, $a_{TiO_2} \approx 1$), and muscovite ranging in size from 10 to 80 μm. The calculated temperature of ~670 °C in a zircon coexisting with rutile is evidence of crystallization from a water-saturated magma[8]. The TiO_2 content (~0.4%) is similar to two of the other three inclusions with muscovite $Si_{pfu} \approx 3.12$ (Table 1) suggesting that they too formed under conditions close to rutile saturation. **i**, **j**, High-Fe muscovites RSES67_3.2 (coexisting quartz, biotite and muscovite; 4,008 ± 6 Myr, −2% discordant, $T_{zir} = 745 \pm 15$ °C). This analysis seems to contain a contaminating Ca-bearing phase. **k**, **l**, RSES61_10.8 (4,028 ± 11 Myr, 0% discordant, $T_{zir} = 693 \pm 15$ °C) yields muscovite Si_{pfu} values of ~3.4 (Table 1). **m**, **n**, RSES58_7.9 (4,025 ± 21 Myr, −9% discordant, $T_{zir} = 700 \pm 15$ °C) contains hornblende with 2.2 Al per 13 cations, indicating an apparent pressure of 7 ± 2 kbar. Although quartz was not directly seen, coexisting biotite and titanite imply quartz saturation in the host melt. musc, muscavite; qtz, quartz; bi, biotite; hbl, hornblende.

conditions are incomplete (for example, Fe treated as ferrous rather than ferric state).

The empirically calibrated Al-in-hornblende barometer[18] for low-variance granitoids seems to be valid provided that quartz is present and Fe/(Fe+Mg) < 0.65. The total aluminium content of the hornblende inclusion (2.25 Al per 13 cations; Table 1), coupled with the Ti-in-zircon temperature of 700 ± 15 °C, suggests a pressure of 7 ± 2 kbar (ref. 18).

Perhaps the most surprising result of our extensive survey is the observation that coequally abundant muscovite and quartz make up nearly three-quarters of all inclusions in Hadean Jack Hills zircons. The limited stability field of muscovite + quartz in peraluminous granitoids[23] alone restricts temperatures to below 800 °C and pressure to more than 4 kbar (Fig. 2).

Ignoring for the moment the two higher-pressure data, the thermobarometric results indicate a formation environment of ~7 kbar and ~690 °C. For a surface temperature of 0 °C and rock density of 3 g cm^{-3}, the average geotherm to the site of zircon crystallization would be ~30 K km^{-1} (Fig. 3). Because this value is very similar to the slope of the Si_{pfu} isopleths (Fig. 2), underestimation of crystallization temperature due to sub-unity a_{TiO_2} (in those cases where rutile is not present) would be almost exactly compensated by lower calculated pressure; that is, the apparent gradient of about 30 K km^{-1} is insensitive to changes in T_{zir}. The two muscovite inclusions suggesting even higher pressures (Table 1) imply an even lower geotherm. Although the report of diamonds[17] in Hadean Jack Hills zircons (Fig. 3) might also be indicative of very low heat flow, we believe that the lack of a calibrated solution model for muscovite under such conditions makes it premature to speculate on their significance.

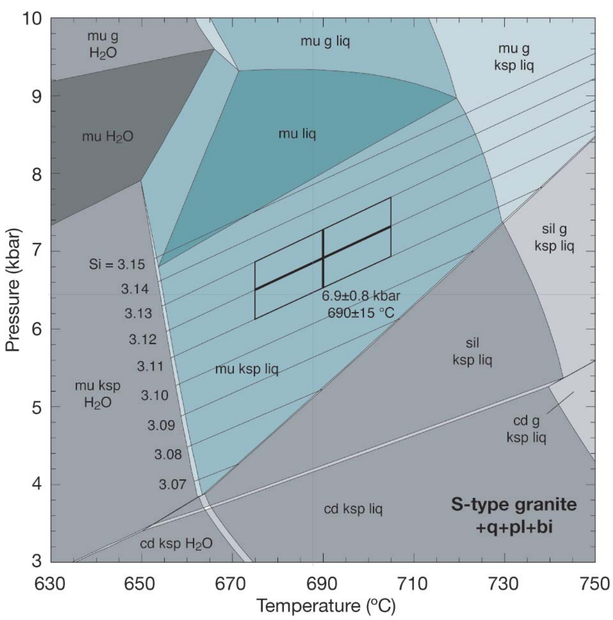

Figure 2 | Pressure–temperature pseudo-section for model S-type granite. Phase relations in the Bullenbalong cordierite granite[25] in the presence of q, pl and bio (solution models are from Holland and Powell[20] and White *et al.*[32]). Shading becomes lighter with decreasing variance. Phase regions depicted with grey shading denote muscovite unstable with melt, whereas blue colours show regions where muscovite and melt stably coexist. Selected contours of predicted Si content in muscovite (3.07–3.17, in moles per formula unit) are shown with light lines. The highlighted polygon gives the pressure calculated from combination of Si content of muscovite (3.12 ± 0.01) with the temperature from Ti in zircon (690 ± 15 °C). Phase abbreviations: bi, biotite; mu, muscovite; sil, sillimanite; q, quartz; pl, plagioclase; liq, granitic melt; g, garnet; cd, cordierite; ksp, K feldspar. The error box represents one standard deviation in both temperature and pressure.

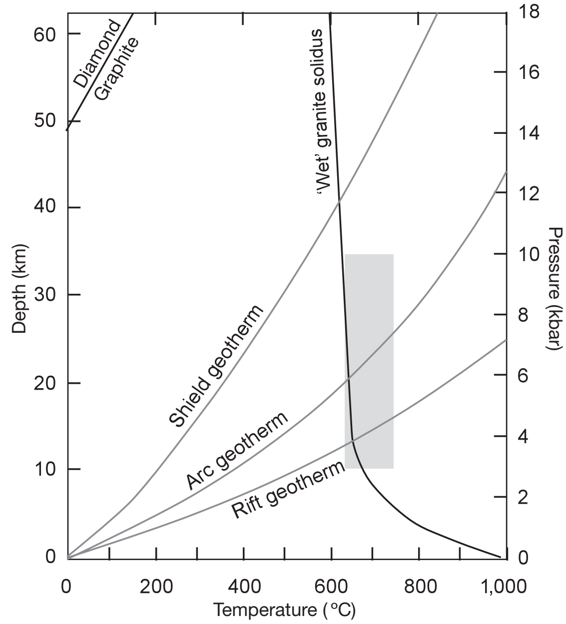

Figure 3 | Pressure–temperature diagram. The position of the pseudo-section from Fig. 2 is shown in grey relative to approximate modern geotherms, the 'wet' granite solidus and the graphite–diamond stability boundary.

Note that both a Hadean surface temperature of >0 °C and mechanisms associated with granitoid plutonism (for example crystallization following buoyant magma ascent) would lead us to overestimate the average geotherm to the site of melting. In contrast, we have not identified a plausible mechanism that would have the opposite effect, and thus regard 30 K km^{-1} as an upper bound. For a typical rock conductivity[24] of 2.5 W m^{-1} K^{-1}, 30 K km^{-1} translates into a near-surface (≤40 km) heat flow of ~75 mW m^{-2}. This value, slightly lower than the Earth's average heat loss today[25], is substantially less than that inferred for global heat flow during both the Archean[26,27] (150–200 mW m^{-2}) and Hadean[28,29] (160–400 mW m^{-2}).

As radioactive heat generation was about three times as great at 4.1 Gyr ago as at present[24] and the Earth is generally thought to have cooled by 50–100 K Gyr^{-1} (ref. 30), it is difficult to conceive that Hadean global heat flow was less than about three times higher than our upper bound of ~75 mW m^{-2}. Today, the only magmatic environment characterized by heat flow of around 25–30% of the global average is where subducting oceanic lithosphere refrigerates the overlying wedge as it descends into the mantle[25,31] (note that although volcanic arcs have greater near-surface heat flow because of the advection of magmatic heat, the average geotherm to the site of magmagenesis is about 15 K km^{-1}). Given that the inclusion mineralogy of ancient Jack Hills zircons points towards their origin from hydrous, SiO_2-saturated, meta- and peraluminous melts similar to the two distinctive type of convergent margin magmas observed today (arc-type andesites and Himalayan-type leucogranites), we interpret our results as evidence that many of the Jack Hills Hadean zircons crystallized from magmas generated in an underthrust environment, possibly similar to modern convergent margins.

METHODS SUMMARY

Sample preparation. We hand-picked zircon grains from heavy mineral concentrates, placed them on double-sided adhesive tape, and mounted them in 1-inch-diameter epoxy disks together with AS-3 standards[2,4]. The disks were then ground with SiC paper and polished only with 1 μm diamond paste.

Ion microprobe. The epoxy mounts were gold-coated and surveyed for $^{207}Pb/^{206}Pb$ age using high-resolution ion microprobes at the Australian National University and the University of California, Los Angeles. Precise U-Th-Pb ages were then determined on zircons found to be more than about

4 Gyr old. Titanium and rare-earth element measurements were undertaken using methods described previously[4].

Electron imaging. Mounts with zircons >4 Gyr old were cleaned of their gold coatings and carbon-coated. Samples were imaged in a LEO 1430VP with secondary and backscattered electrons and using cathodoluminescence to identify inclusions and provide information on internal structure of the zircon. We qualitatively chemically characterized inclusions by using energy-dispersive spectroscopy.

Electron microprobe. We obtained quantitative chemical compositions of inclusions *in situ* using a JEOL 8200 electron microprobe equipped with five wavelength-dispersive spectrometers. An electron beam ~1 μm in diameter was used with an accelerating voltage of 15 kV. Standard corrections were used.

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