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Secondary magnetite in ancient zircon precludes analysis of a Hadean geodynamo

Fengzai Tang^a, Richard J. M. Taylor^{a,1}, Josh F. Einsle^{a,b}, Cauê S. Borlina^c, Roger R. Fu^d, Benjamin P. Weiss^c, Helen M. Williams^a, Wyn Williams^e, Lesleis Nagy^f, Paul A. Midgley^b, Eduardo A. Lima^c, Elizabeth A. Bell^g, T. Mark Harrison^g, Ellen W. Alexander^g, and Richard J. Harrison^a

^aDepartment of Earth Sciences, University of Cambridge, CB2 3EQ Cambridge, United Kingdom; ^bDepartment of Materials Science and Metallurgy, University of Cambridge, CB2 3EQ Cambridge, United Kingdom; ^cDepartment of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, MA 02139; ^dDepartment of Earth and Planetary Sciences, Harvard University, Cambridge, MA 02138; ^eSchool of Geosciences, University of Edinburgh, EH9 3FE Edinburgh, United Kingdom; ^fGeoscience Research Division, University of California, San Diego, La Jolla, CA 92093; and ^gDepartment of Earth, Planetary, and Space Sciences, University of California, Los Angeles, CA 90095

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Zircon crystals from the Jack Hills, Western Australia, are one of the few surviving mineralogical records of Earth's first 500 million years and have been proposed to contain a paleomagnetic record of the Hadean geodynamo. A prerequisite for the preservation of Hadean magnetization is the presence of primary magnetic inclusions within pristine igneous zircon. To date no images of the magnetic recorders within ancient zircon have been presented. Here we use high-resolution transmission electron microscopy to demonstrate that all observed inclusions are secondary features formed via two distinct mechanisms. Magnetite is produced via a pipe-diffusion mechanism whereby iron diffuses into radiation-damaged zircon along the cores of dislocations and is precipitated inside nanopores and also during low-temperature recrystallization of radiation-damaged zircon in the presence of an aqueous fluid. Although these magnetites can be recognized as secondary using transmission electron microscopy, they otherwise occur in regions that are indistinguishable from pristine igneous zircon and carry remanent magnetization that postdates the crystallization age by at least several hundred million years. Without microscopic evidence ruling out secondary magnetite, the paleomagnetic case for a Hadean–Eoarchean geodynamo cannot yet be made.

Hadean | paleomagnetism | Jack Hills | zircon | correlative microscopy

The earliest paleomagnetic evidence for an active geodynamo comes from circa (c.) 3.45-billion-year-old (Ga) rocks from the Barberton Greenstone Belt and the Pilbara Craton (1–3). According to many core formation models, the fields recorded by these rocks predate inner-core solidification, the process that powers the present-day geodynamo through the release of light elements at the inner-core/outer-core boundary. Before inner-core solidification, the geodynamo may have been powered by thermal convection alone. Recent upward revision of core thermal conductivity (4–6) means that high heat flux is needed to meet paleomagnetic constraints for a pure thermal dynamo. This leads to surprising predictions of a very young inner core (<600 Ma) and initial core temperatures that were hot enough to melt substantial portions of the lower mantle (7–9). As debate surrounding core thermal conductivity and implications for Earth's earliest magnetic fields continues (10), there is an ever-increasing need to place robust paleomagnetic constraints on the early geodynamo.

The lack of data before 3.45 Ga leaves a gap of over a billion years in the paleomagnetic record. Attempts to fill this gap have recently focused on the Jack Hills, Western Australia (11), where 2.65–3.05 Ga metaconglomerates contain detrital zircon grains with U–Pb ages as old as 4.4 Ga (12). Although zircon (ZrSiO₄) is not itself magnetic, zircon crystals contain inclusions of magnetic minerals that make them potential targets for single-crystal paleomagnetic analysis (13). Tarduno et al. (11) presented a single-crystal paleomagnetic study of Jack Hills detrital zircons, arguing that zircons dated between 3.3 and 4.2 Ga contain

primary thermoremanent magnetization (TRM) imparted by an active Hadean to Paleoproterozoic geodynamo. No microscopy images of primary magnetic carriers within Jack Hills zircon have been presented to date. Rather, there is abundant evidence for secondary magnetic sources on surfaces, along internal cracks, around multiphase microgranite inclusions, and within metamict zones particularly for grains that have not been cleaned with HCl (14). Constraining the source of magnetization—and demonstrating the lack of interference by secondary remanent carriers (15)—is an essential step in confirming the robustness of Hadean paleomagnetism. To this end, we performed a direct study to determine the origin and setting of ferromagnetic carriers in Jack Hills zircon using correlative magnetic measurements and electron microscopy.

Zircon crystals were extracted from metaconglomerates of the Erawaddoo Hill Hadean-zircon discovery outcrop (16, 17). We focus primarily on two grains (A and B) that are >3.9 Ga and that passed strict initial selection criteria for potential paleomagnetic targets: lack of evidence for alteration from scanning electron microscopy (SEM) images, concordant U–Pb ages (*SI Appendix, section E*), and treatment with 6M HCl to remove Fe in cracks (14), and a stable natural remanent magnetization (NRM) component (*SI Appendix, section C*). Three broadly defined textures are seen in SEM images: (i) primary oscillatory

Significance

The Earth's geodynamo is critical in protecting our atmosphere, and thus plays an important role in the habitability of our planet. As such, the Earth's magnetic field has likely played a crucial role in the emergence of life around 4 billion years ago during the Hadean–Archean Eons. However, we know little about the behavior of the geodynamo during this critical period. Recent efforts have focused on the magnetic signals harbored by Jack Hills zircon crystals, the oldest terrestrial material. Here we show the magnetic carriers in such grains. Our results demonstrate that although ancient zircon grains may contain ideal magnetic recorders, they do not record the magnetic field strength at the time of zircon growth.

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¹To whom correspondence should be addressed. Email: rjt79@cam.ac.uk.

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zoning, (ii) recrystallized zones with bright cathodoluminescence (CL; grain B only), and (iii) strongly radiation-damaged metamict zones (individual oscillatory zones in grain A and the entire rim of grain B). Specific areas (Fig. 1) were targeted for scanning transmission electron microscopy (STEM) because of strong magnetic signals observed in the zircon interior using quantum diamond microscopy (QDM) (18). TEM lamellae were extracted from two grains targeting QDM signals within zones displaying primary oscillatory zoning (Fig. 1 *A* and *E*). Sample extraction was after thermal demagnetization experiments for grains A and B, but not for grain C (*SI Appendix, SI Appendix, section A*, and *SI Appendix, Figs. S7–S11*). Both heated and nonheated grains displayed identical features. Magnetic regions are observed in areas that display primary zoning and recrystallized zones. Additional images are available in *SI Appendix, section A*.

Grain A ($^{207}\text{Pb}^*/^{206}\text{Pb}^*$ age = 3979 Ma) clearly displays magnetic signals hosted by primary magmatic zoning in SEM images (Fig. 1 *A–D*). However, at the TEM scale, the lamella shows unequivocal microstructural evidence of partial recovery from radiation damage with clearly observed porosity and dislocations (Fig. 2 *A–C*). This fluid-absent lattice recovery leads to the formation of nanoscale pores that preferentially nucleate on dislocations, forming strings of pores linked by a common dislocation line that crosscuts primary zonation (Fig. 2*A*). Dislocation cores concentrate nonstructural elements such as Fe and provide fast pipe-diffusion pathways to deliver these elements from external sources to an internal sink (19–21). Direct evidence of this mechanism is seen during the earliest stages of

infilling, where Fe accumulates at the intersection of the pore and the dislocation core (Fig. 2*F*). Pores are frequently partially or fully filled with precipitate phases such as magnetite, ilmenite (FeTiO_3), and crystalline ZrO_2 (potentially baddeleyite). The result is secondary, dislocation/pore-hosted, nanoscale magnetite grains within zircon that appears unaltered at SEM scale. No magnetite was found that does not lie on secondary microstructures, hence these observations demonstrate that all of the magnetite observed here postdates primary zircon crystallization. A comprehensive set of images of secondary magnetite and associated microstructures in grain A can be found in *SI Appendix, Fig. S2*.

Grain B ($^{207}\text{Pb}^*/^{206}\text{Pb}^*$ age = 3973 Ma) shows similar features to A in primary oscillatory zoned areas, along with an additional fluid-mediated recrystallization zone also hosting magnetic signals. Recrystallization proceeds as a diffusion–reaction process in which hydrous species diffuse inward and catalyze structural recovery (22, 23). We observe sinuous recrystallization fronts with bright CL, often closely associated with metamict areas that facilitate fluid ingress (Fig. 1*J* and *SI Appendix, Fig. S5A*). These recrystallized areas contain defect-rich crystalline zircon and crystallographically oriented precipitates of magnetite with elongated morphology due to preferential growth along intersecting dislocations (*SI Appendix, Fig. S5F*). These characteristics are typical of oxide inclusions precipitated from a silicate host by heterogeneous nucleation on dislocations (24, 25) and support a secondary origin for the magnetite in the recrystallized zones. A comprehensive set of images of secondary magnetite and associated microstructures

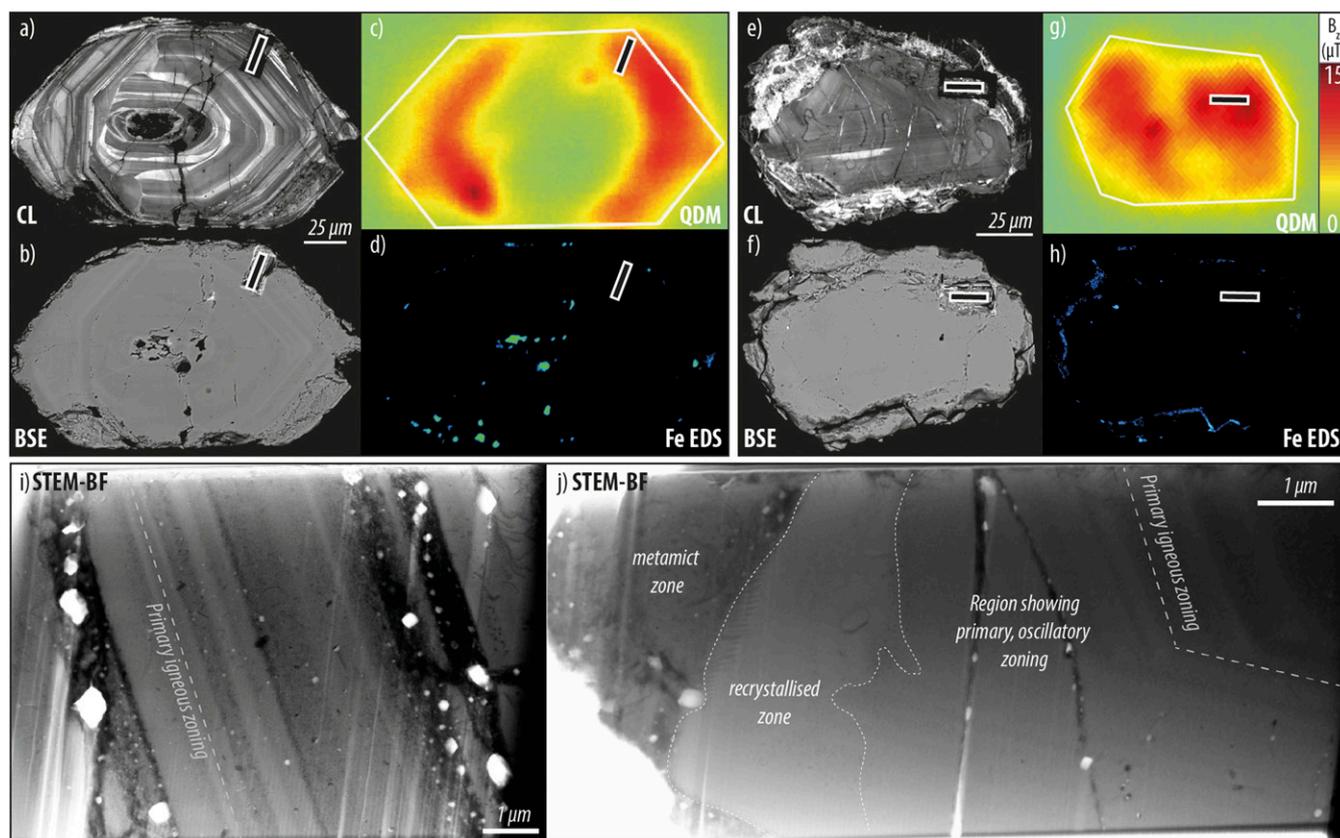


Fig. 1. Summary of SEM (*A–H*) and TEM (*I* and *J*) images of Jack Hills zircon grains A and B in this study. White outline rectangles mark original location of TEM lamellae. SEM—grain A: (*A*) CL image showing primary igneous zoning; (*B*) BSE image; (*C*) QDM magnetic anomaly map; and (*D*) compositional map of Fe intensity. Grain B: (*E*) CL image showing primary igneous zoning; (*F*) BSE image; (*G*) QDM magnetic anomaly map; and (*H*) compositional map of Fe intensity. Note that *E* and *F* were taken after a final polish, so that the TEM foil location appears less central than in *G*, which was taken before final polish. (*I*) TEM lamella showing primary zoning and associated secondary inclusions in grain A; and (*J*) TEM lamella showing primary zoning (RHS) and secondary inclusions in grain B. Metamict areas and a fluid-assisted recrystallization zone appear on the LHS. Color scale in *G* also applies to *C*.

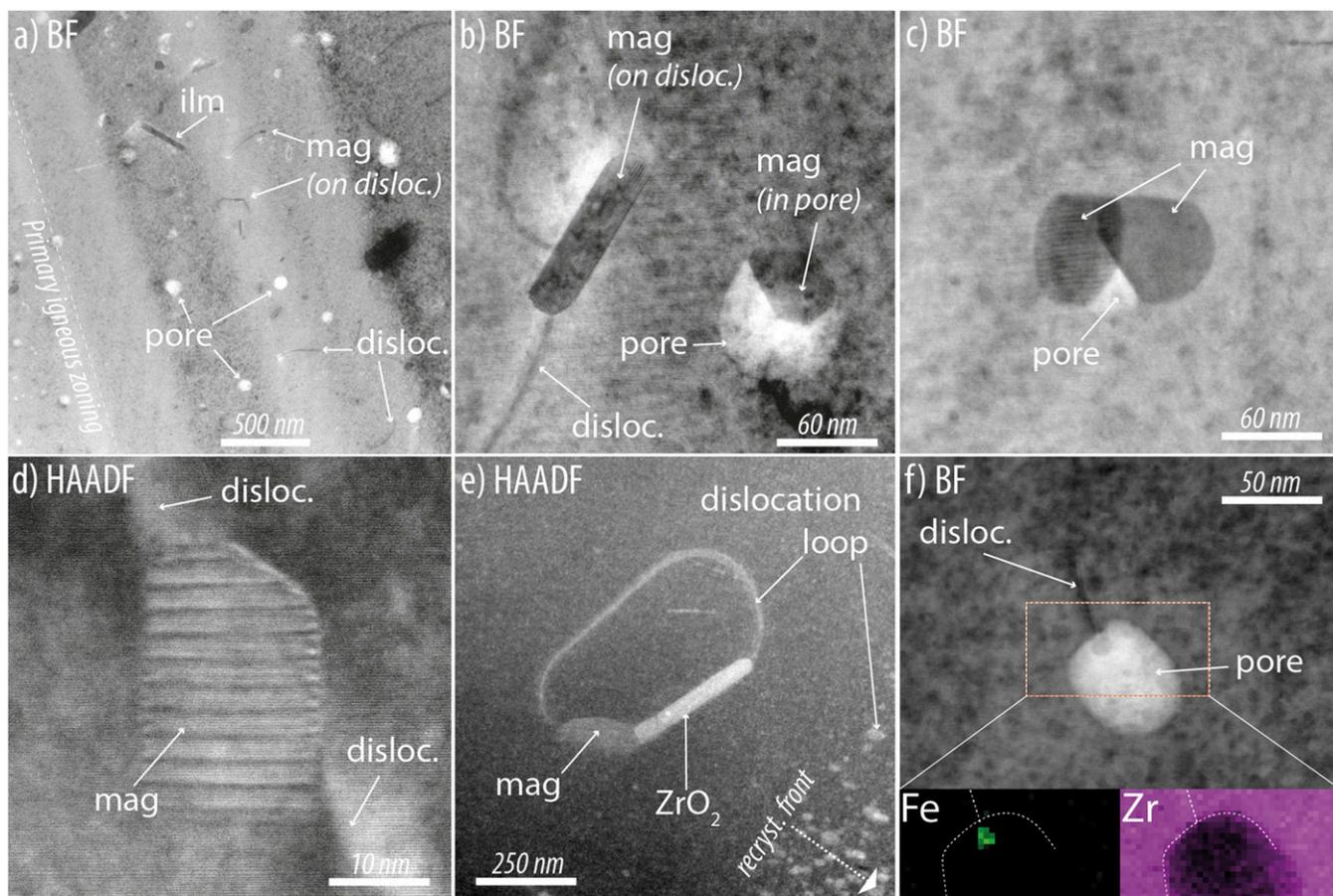


Fig. 2. High-resolution STEM images of nanoscale features and inclusions in this study. Background matrix is zircon. (A) Broad view of primary zoning with secondary features related to recovery of radiation damage. (B) Secondary magnetite grains along dislocations and filling pore spaces. (C) Multiple magnetite crystals in single pore. (D) Example of moiré fringe data used to identify magnetite. (E) Dislocation loop with magnetite and ZrO_2 near recrystallization front (Fig. 3E). (F) Intersection of dislocation and pore demonstrating pipe diffusion of secondary Fe into pore spaces; *Insets* show Fe and Zr EDS maps. Mineral abbreviations: ilm, ilmenite; mag, magnetite. Images A–D from grain A; image E from grain B; images D and F are from additional grain C (*SI Appendix, section A*). Images A–C, grain A; image E, grain B; images D and F, grain C (*SI Appendix, section A*).

in grain B can be found in *SI Appendix, Figs. S4–S6*. Fig. 3 demonstrates the schematic progression of features seen in grain B (Fig. 3A). The initial zircon grain shows oscillatory zoning in CL, which reflects a variation in trace element content, e.g., U, and a high-U rim (Fig. 3B). Radiation damage slowly accumulates in the core, and the high-U rim becomes totally metamict. Partial annealing of the core results in linked pore-dislocation networks, and the high-U rim facilitates fluid ingress at a later stage, reorganizing the annealing microstructures (Fig. 3C and F and *SI Appendix, Fig. S5A*). Magnetite growth in the core can only take place once this network of secondary features has accumulated (Fig. 3D, F, and G and *SI Appendix, Fig. S4 A–D*), and must therefore significantly postdate zircon crystallization.

Clear identification of the Fe-oxide as magnetite is the result of correlating the various datasets. Fe-oxides observed chemically from STEM energy dispersive spectroscopy (EDS) were observed using moiré fringe lattice interference patterns between the zircon and oxide. The resultant moiré fringe d-spacing (Fig. 2D and *SI Appendix, Fig. S11*) defines the Fe-oxide as most likely magnetite, with a possibility of being maghemite. However, the paleomagnetic data showing complete NRM demagnetization by 580 °C means it is only possible for the inclusions to be magnetite (*SI Appendix, Fig. S13*). The extraction of robust Hadean paleomagnetic signals from zircon single crystals relies on the following assumptions about any given magnetic particle: (i) iron oxide grains became trapped as primary inclusions in igneous

zircon; (ii) inclusions within the zircon acquired a primary TRM during postcrystallization cooling and have not been subsequently reheated above the Curie temperature; (iii) armoured magnetic inclusions remained chemically and thermally unaltered by pre- and postdepositional high-temperature metamorphic and low-temperature aqueous alteration/recrystallization events; and (iv) the high-temperature component of primary TRM can be separated from overlapping sources of secondary magnetization. If all these conditions are met, then the Jack Hills zircons have the potential to constrain the properties of the Hadean geodynamo. If any one of these conditions is violated, the case for primary magnetization cannot be made.

We have observed two pathways for the formation of secondary single-domain magnetite in Jack Hills zircon, circumventing criteria (i) and (iii) above. Formation of secondary magnetite in the presence of a magnetic field will generate a chemical remanent magnetization (CRM). An important property of CRM is that its thermal unblocking temperature is not limited by the temperature of its acquisition, but by the volume of the particles formed (26). Magnetite particles of sufficient size acquire CRM with laboratory unblocking temperatures that overlap with the 550–585 °C window attributed to primary Hadean remanence (27). A representative (but not exhaustive) summary of magnetite particles observed using TEM is given in *SI Appendix, Table S1*. Measurements of the length (L) and width (W) of each particle were taken directly from the TEM images. Fig. 4 compares the 2D projected lengths and

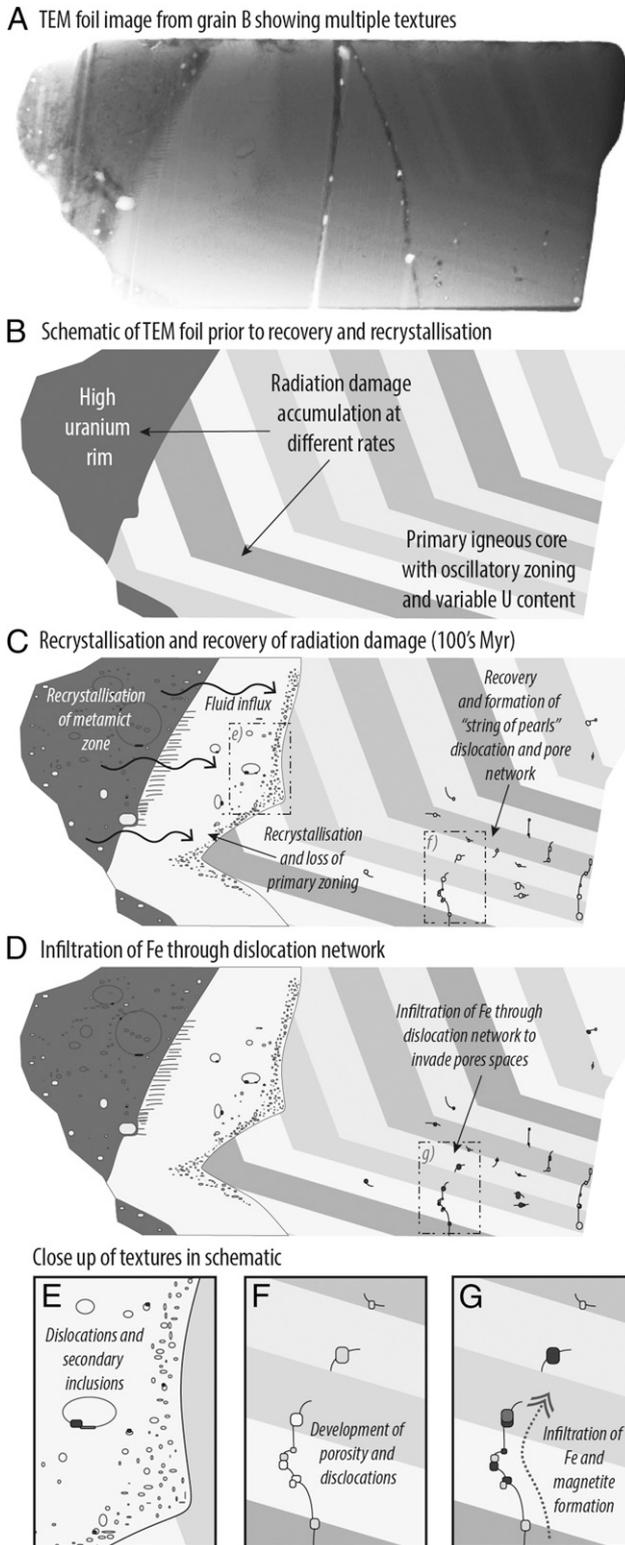


Fig. 3. Summary diagram showing order of events forming secondary inclusions in grain B. (A) TEM BF image of lamella. (B) Schematic of zonation in zircon. Oscillatory zoning with variable U content (light = low U) accumulating radiation damage at different rates. High-U rim area accumulates damage most rapidly. (C) Fluid-mediated recrystallization and fluid-absent recovery process occur 100s My after grain formation. (D) Fe infiltrates dislocation-pore network forming magnetite. (E–G) Close up of processes *Inset* areas in C and D. Features shown in F and G are clear in images from *SI Appendix, Fig. S4 A–D*.

aspects ratios of the observed particles with the calculated thresholds for superparamagnetic, single-domain, and vortex behavior in isolated magnetite particles (28). The majority of observed particles are predicted to be single domain (Fig. 4A), with 40% of grains having blocking temperatures >500 °C (Fig. 4B). Two of the largest particles observed are predicted to lie above the threshold for single-vortex behavior for noninteracting magnetite (28). Micromagnetic simulations confirm that these particles adopt either single-domain or single-vortex states at remanence, that both adopt vortex states during magnetization reversal, and that their blocking temperatures are 570–575 °C (*SI Appendix, section D*). Single-vortex particles of a similar size have been observed to retain their remanence all of the way to the Curie temperature (29). Thermal demagnetization of grain A demonstrates that 30–40% of its NRM is retained after heating to 550 °C in zero field and that the NRM is fully demagnetized by 580 °C (*SI Appendix, section C*), confirming the presence of magnetite remanence carriers with high blocking temperatures. This means that a putative primary Hadean TRM and secondary CRM would have overlapping blocking spectra, making it difficult to discriminate primary and secondary remanence, violating criteria (iv) above.

Given these observations of secondary ferromagnetism, recognizing the presence of (or demonstrating the lack of) secondary magnetite via high-resolution magnetic, compositional, and mineralogical analyses are now essential steps in the quest for Hadean paleomagnetism. Although most magnetite particles formed through fluid-mediated recrystallization that we observed fall well within the stable single-domain size range, their frequently low volumes yield blocking temperatures that mostly lie outside the 550–585 °C window used to isolate Hadean remanence. Therefore, CRM acquired via this mechanism might be avoided through careful sample characterization and thermal demagnetization to 550 °C (27). However, the formation of secondary magnetite in crystalline zircon via the pipe-diffusion mechanism cannot be recognized using CL imaging, is not associated with Pb loss, and produces magnetite particles with sizes and aspect ratios spanning the stable single-domain to single-vortex range, with blocking temperatures that fall within the 550–585 °C window.

Evaluation of the TEM images in this study enables an estimate to be made of the volume expansion of the crystal lattice due to radiation damage. Image analysis of the ratio of zircon to observed pore spaces shows a volume expansion of $\sim 0.7\%$, used as a proxy for lattice expansion, which can be converted to the time taken to accumulate this damage based on the original actinide content (30). Back-calculated U and Th concentrations give a lower estimate of c. 950 and c. 500 My for grains A and B, respectively, to produce the observed porosity (*SI Appendix, section B* provides more details). This means that the Fe source may be from fluid alteration within precursor igneous rocks, but also allows for the source of Fe to be the Jack Hills sediment itself, consistent with deep weathering estimates (31). This estimate provides an upper age limit for magnetite formation, and is clearly significantly later than zircon crystallization (Fig. 3).

The distinct possibility that the secondary Fe source predates sedimentation at 3.0 Ga is important, as it negates the use of microconglomerate tests on the Jack Hills sediments as evidence for primary magnetization. The observed radiation damage in Jack Hills zircon is much lower than that expected on the basis of their actinide content and age (32). Therefore, this pipe-diffusion mechanism is expected to be widespread, a natural consequence of the build up and subsequent recovery of radiation damage that will affect all ancient zircon crystals. Therefore, unless primary magnetite can be confirmed, the existence of a magnetic field during Eoarchean and Hadean remains an unknown.

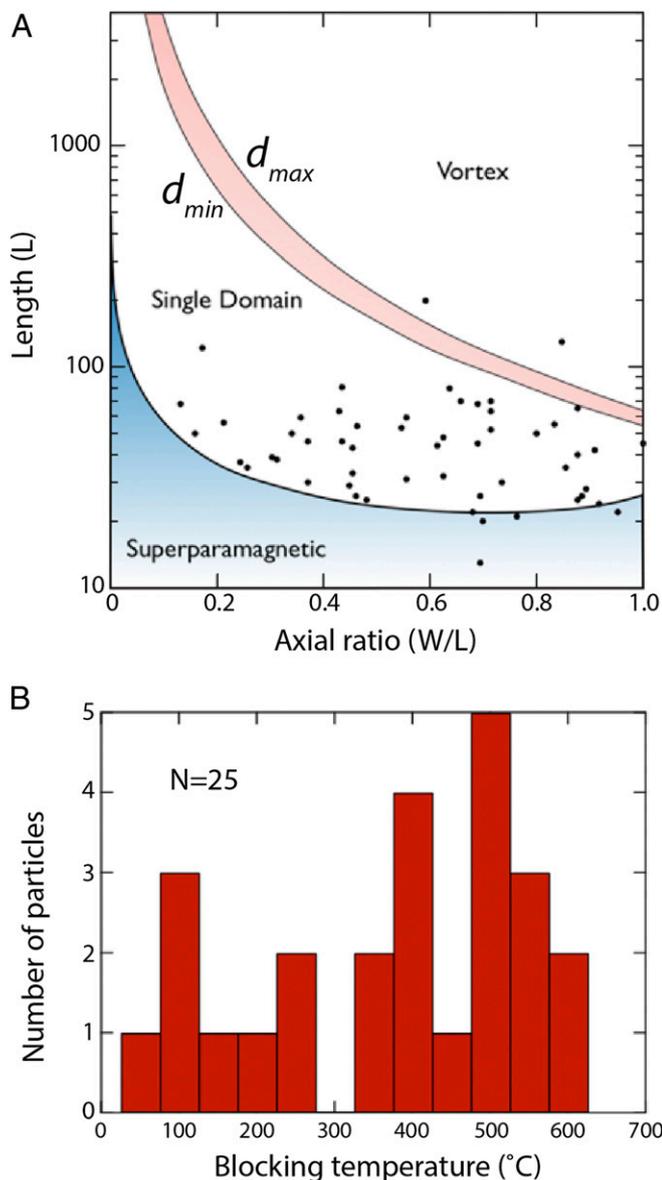


Fig. 4. Magnetic information on secondary magnetite particles observed in Jack Hills zircon. (A) L vs. aspect ratio (W/L) for magnetite particles observed using TEM (SI Appendix, Table S1). Boundaries between superparamagnetic, single-domain, and vortex states are based on micromagnetic simulations of noninteracting magnetite (28). (B) Histogram of calculated blocking temperatures (50 °C bin width), excluding SP particles. Blocking temperatures were calculated for laboratory observation times (taken to be $t_{\text{obs}} = 100$ s). A significant number of the particles observed have $T_B > 500$ °C, consistent with the rapid loss of NRM observed using superconducting quantum interference device (SQUID) magnetometry (SI Appendix, Fig. S13).

Methods

SEM. An FEI Quanta 650 field emission gun SEM was used to collect both energy dispersive spectroscopy elemental maps (at 20 kV accelerating voltage), back-scattered electron (BSE), and cathodoluminescence micrographs (collected at 5 kV). The BSE and CL maps were collected in parallel, and the EDS maps were collected subsequently. EDS maps were collected using two Bruker 6j30 EDS detectors simultaneously to increase the overall counts and improve throughput. For grain C, each pixel's spectrum was denoised using a Python-based nonnegative matrix factorization algorithm, background subtracted, and then peak integration performed on the $\text{Fe}_{\text{K}\alpha}$ window of 6.0–6.7 keV (33, 34).

TEM. The TEM specimen was site-precisely prepared from a zircon grain using a dual beam focused ion beam (FIB) scanning electron microscope field

electron and ion (FEI), now Thermo Fisher Scientific, Helios NanoLab. An in situ lift-out technique was applied to extract and transfer the specimen onto a standard TEM molybdenum half grid, and a platinum bar was deposited on the surfaces of target areas before FIB processing. The TEM lamella was made with the reduced FIB voltages down to ~2–5 kV to minimize FIB-induced damage (35), and was cleaned for about 3–5 min in a plasma chamber before being loaded into the TEM microscope. The TEM study was carried out using two microscopes: FEI Tecnai Osiris and FEI Titan³ (80–300 kV), and both were dedicated to scanning TEM operation. The Osiris microscope fitted with four silicon drift detectors for energy dispersive X-ray spectrometry analysis was used for STEM high-angle annular dark field (HAADF) and STEM-bright field (BF) imaging and fast STEM chemical mapping operating at 200 kV. The Titan microscope had a probe-forming corrector for spherical aberration, allowing for high resolution imaging in STEM configuration at 300 kV. To obtain optimum contrast for identifying nanometer-sized particles, the STEM imaging was typically taken at the combination of the camera length between 80 and 250 mm and the screen currents of 0.05–0.3 nA; whereas, the STEM chemical mapping was performed at the screen currents larger than about 0.1 nA.

U–Pb Geochronology. Grains were prescreened for ancient Pb isotope signatures on the CAMECA ims1270 ion microprobe using a 15-nA O-primary beam and a mass resolution of 5000. This used more rapid count times to analyze a large number of grains but at lower than normal precision. Oxygen flooding to $c. 1 \times 10^{-5}$ torr was used to enhance Pb ionization. Following a 2-min presputter to clean the zircon surface, Pb isotopes were counted for 30 s in monocollection mode. During a later session, U–Pb ages were measured under the more typical instrumental conditions and count times, using the AS3 zircon standard (36) for Pb/U relative sensitivity factor calibration. More details on the U–Pb method can be found in Quidelleur et al. (37).

QDM. We use the quantum diamond microscope at the Harvard Paleomagnetism Laboratory to obtain high-resolution magnetic field maps of zircon grains A and B (Fig. 1 C and G). Both grains are first subjected to a 0.25 T isothermal remanent magnetization oriented out of the imaging plane. The polished surface of the zircons is then placed in contact with the sensing diamond, which has nitrogen-vacancy ($N-V$) centers implanted uniformly in a 4- μm layer. We then optically excite the ($N-V$) centers with a 500-mW 532-nm wavelength laser and image the fluorescence at a spatial resolution of 1.17 μm per pixel. To maximize the signal-to-noise ratios, we perform the experiments in projective magnetic microscopy mode (18) that directly measures the magnetic field projection in the [111] direction of the diamond lattice. This protocol involves two measurements taken under bias fields of 900 μT oriented in opposing directions parallel to the [111] axis. The two maps are then summed to isolate the ferromagnetic component. The reversal accuracy of the bias field is 1 part in 1500, resulting in a residual bias field of 600 nT, which is then subtracted from the summed map. The residual bias field in the final map is therefore at least 10^3 smaller than the zircon signals and can be neglected. We then convert these projected magnetic field values to the magnetic field perpendicular to the measurement plane using spectral domain algorithm (38).

Laser Ablation. U and Th measurements were made for the zircon grains alongside the TEM locations to calculate radiation damage times. Analyses were carried out using an ESI UP193UC laser system coupled to a Perkin–Elmer Nexion 350D inductively coupled plasma mass spectrometer (LA-ICP-MS) in the Department of Earth Sciences at the University of Cambridge. The LA-ICP-MS data acquisition settings were 1 sweep per reading, 80 readings, 1 replicate, and total data acquisition lasted 50 s (~1 data point for each element per second). The instrument was set up for background data followed by ablation for 20 s, at a rep rate of 10 Hz, and power on the sample of ~3 joules per cm^2 . Data were processed using Iolite software with the trace element DRS (39), with concentrations calibrated against KLDF standard zircon (Curtin University internal standard; U 507 ppm, Th 75 ppm) and 91500 (40). National Institute of Standards and Technology glasses SRM 610 and 612 (41) were run to monitor instrument stability. U and Th concentrations were calculated for the crystallization ages of the grains.

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