Secondary magnetic inclusions in detrital zircons from the Jack Hills, Western Australia, and implications for the origin of the geodynamo

Benjamin P. Weiss¹, Roger R. Fu², Joshua F. Einsle³,⁴, David. R. Glenn⁵,⁶, Pauli Kehayias⁵,⁶, Elizabeth A. Bell⁷, Jeff Gelb⁸, Jefferson F.D.F. Araujo¹,⁹, Eduardo A. Lima¹, Cauê S. Borlina¹, Patrick Boehnke¹⁰,¹¹, Duncan N. Johnstone⁴, T. Mark Harrison², Richard J. Harrison³, and Ronald L. Walsworth⁵,⁶

¹Department of Earth, Atmospheric, and Planetary Sciences, Massachusetts Institute of Technology, Cambridge, Massachusetts 02139, USA
²Department of Earth and Planetary Sciences, Harvard University, Cambridge, Massachusetts 02138, USA
³Department of Earth Sciences, University of Cambridge, Cambridge CB2 3EQ, UK
⁴Harvard-Smithsonian Center for Astrophysics, Cambridge, Massachusetts 02138, USA
⁵Department of Physics, Harvard University, Cambridge, Massachusetts 02138, USA
⁶Department of Earth, Planetary, and Space Sciences, University of California, Los Angeles, California 90095, USA
⁷Department of Physics, Pontifical Catholic University of Rio de Janeiro, Rio de Janeiro 22451-900, Brazil
⁸Department of the Geological Sciences, University of Chicago, Chicago, Illinois 60637, USA
¹⁰Chicago Center for Cosmochemistry, Chicago, Illinois 60637, USA
¹¹Chicago Center for Cosmochemistry, Pleasanton, California 94588, USA

© 2018 Geological Society of America. For permission to copy, contact editing@geosociety.org.

GEOLOGY, May 2018; v. 46; no. 5; p. 427–430 | GSA Data Repository item 2018135 | https://doi.org/10.1130/G39938.1 | Published online 1 March 2018

ABSTRACT

The time of origin of Earth’s dynamo is unknown. Detrital zircon crystals containing ferromagnetic inclusions from the Jack Hills of Western Australia have the potential to contain the oldest records of the geodynamo. It has recently been argued that magnetization in these zircons indicates that an active dynamo existed as far back as 4.2 Ga. However, the ages of ferromagnetic inclusions in the zircons are unknown. Here we present the first detailed characterization of the mineralogy and spatial distribution of ferromagnetic minerals in Jack Hills detrital zircons. We demonstrate that ferromagnetic minerals in most Jack Hills zircons are commonly located in cracks and on the zircons’ exteriors. Hematite is observed to dominate the magnetization of many zircons, while other zircons also contain significant quantities of magnetite and goethite. This indicates that the magnetization of most zircons is likely to be dominantly carried by secondary minerals that could be hundreds of millions to billions of years younger than the zircons’ crystallization ages. We conclude that the existence of the geodynamo prior to 3.5 Ga has yet to be established.

INTRODUCTION

The unknown early history of Earth’s magnetic field has important implications for our understanding of the planet’s thermal evolution and the process of dynamo generation. In particular, inner core crystallization, the likely power source for today’s dynamo, is thought to have only initiated at <1.5 Ga (Davies et al., 2015). Therefore, identification of an early field would indicate that the core was stirred by other power sources, such as precipitation of Mg (O’Rourke and Stevenson, 2016), or perhaps that the dynamo was generated by exotic processes like a convecting basal magma ocean (Ziegler and Stegman, 2013). Furthermore, because Earth’s field controls the penetration of the solar-wind electric field into the ionosphere, the dynamo’s history may have strongly influenced Earth’s water budget and oxidation state (Tarduno et al., 2014).

Although paleomagnetic studies of Archean rocks indicate that a dynamo with an intensity of at least half that of the present day existed by 3.45 Ga (Tarduno et al., 2014), the earlier history of the field is uncertain. With U-Pb ages ranging from ca. 3.0 Ga to 4.38 Ga (Holden et al., 2009), detrital zircon crystals from the Jack Hills of Western Australia have the potential to retain geodynamo records from the missing first billion years of Earth’s history. Although zircon is itself not ferromagnetic, magnetization could be carried by ferromagnetic inclusions within the zircons (Fu et al., 2017; Sato et al., 2015).

It was recently proposed that the Jack Hills zircons contain records of the dynamo dating back to their oldest U-Pb crystallization ages of 4.2 Ga (Dare et al., 2016; Tarduno et al., 2015). However, it is currently unknown whether these zircons have escaped thermal and chemical remagnetization during the intervening time since their formation. In fact, many Jack Hills rocks were pervasively remagnetized sometime after 3.0 Ga (Weiss et al., 2015) (Appendix DR1 in the GSA Data Repository1). Although Tarduno et al. (2015) conducted a “micro-conglomerate test” in an attempt to demonstrate a lack of post-depositional remagnetization, this employed 0.5–0.8-mm-size specimens consisting predominantly of quartzite pebble material enclosing zircons with sizes of just 0.2–0.3 mm. As such, the result of their test rests on the unverified assumption that the magnetization of the specimens is dominated by inclusions within the embedded zircon. Furthermore, although Tarduno et al. (2015) and Bono et al. (2018) argued that thermal remagnetization of the zircons would have resulted in Pb/U variations during secondary ion mass spectrometry (SIMS) depth-profiling that they did not observe, their instrumentation should have been incapable of detecting such variations (Weiss et al., 2016). In any case, even if such variations could have been detected by Tarduno et al. (2015), such Pb/U depth-profiling is not a sensitive test for thermal remagnetization because of lead’s extremely low diffusivity at 600 °C in non-metamict zircons under both dry and hydrous conditions (Cherniak and Watson, 2003).

¹GSA Data Repository item 2018135, Figures DR1–DR12, Tables DR1–DR4, Movie DR1, and Appendices DR1–DR3, is available online at http://www.geosociety.org/datarepository/2018/ or on request from editing@geosociety.org.
Along with demonstrating a lack of thermal remagnetization, another key requirement for establishing that the bulk natural remanent magnetization (NRM) of a zircon crystal is a robust indicator of magnetic fields at the time of zircon crystallization is the demonstration that its ferromagnetic inclusions are dominantly primary rather than alteration products of primary inclusions or deposits in cracks and voids. Here we characterize the ferromagnetic mineral assemblage in Jack Hills zircons using compositional and magnetic analyses to assess whether magnetization in most Jack Hills zircons is carried dominantly by primary or secondary inclusions.

METHODS
We sought to identify the ferromagnetic mineralogy of the zircon inclusions, establish whether they are primary or secondary by focusing on their relationships to cracks and alteration textures, and test the efficacy of acid-washing for removing secondary inclusions. We conducted magnetic, compositional, and mineralogical analyses on 11 sets of Jack Hills detrital zircons (425 total zircons newly analyzed in this study, along with re-analysis of 2450 zircons previously studied by Bell et al. [2015]; Table DR1) from quartz pebble conglomerates sampled at the Eravandoo Hill Hadean-zircon discovery outcrop [site W74 of Weiss et al. 2016, their figure S2]). Eleven sets of zircons were mounted in several different ways for our magnetic measurements (Appendix DR2). We mapped the three components of the isothermal remanent magnetization (IRM) and NRM fields above 381 zircons using quantum diamond microscopy (QDM) (Fu et al., 2017; Glenn et al., 2017) (Appendix DR2). QDM employs optically addressable nitrogen vacancy centers in diamond that are sensitive to magnetic fields via the Zeeman effect. We also mapped the vertical component of the NRM field of 109 zircons using superconducting quantum interference device (SQUID) microscopy (SM). SM enables ultra-sensitive measurements of net magnetic moments (Lima and Weiss, 2016; Fu et al. 2017). Curie temperatures of inclusions were estimated by SM mapping of thermal demagnetization of IRM.

Of the zircons imaged with QDM, 34 grains were subsequently analyzed with backscattered scanning electron microscopy (BSEM), energy dispersive spectroscopy (EDS), and wavelength dispersive spectroscopy (WDS). QDM is most sensitive to magnetic materials located up to tens of microns below the polished grain surfaces, while electron microscopy is only sensitive to the top <2 µm of the grains. Following these analyses, the three-dimensional Fe inclusion distribution in one zircon was then imaged using X-ray tomography using Carl Zeiss Xradia 520 Versa and Ultra XRM-L200 microscopes (spatial resolutions of 750 and 150 nm, respectively).

RESULTS
Zircons Not Treated with Concentrated Acid
We begin by discussing zircons not washed with acid and those washed with weak (0.5 N) HCl (Table DR1). SM measurements show that non-acid-washed zircons from set 4 have a mean NRM of 8.3 x 10⁻¹³ Am², 23% of which are >1 x 10⁻¹² Am² (Fig. DR10A; Table DR3). QDM imaging of the non-acid-washed zircons from set 1 carrying IRM (Fig. DR3) and set 3 carrying NRM (Figs. DR4A–DR4D) was conducted in a lower-sensitivity reconnaissance (261 zircons) mode followed by higher-sensitivity imaging (84 zircons) (see Glenn et al. [2017] and Table DR2). Of the 147 and 76 such zircons detected in the reconnaissance and higher-sensitivity modes, respectively, 122 (83%) and 55 (72%) respectively, exhibited magnetic anomalies centered on locations that are within ~20 µm of the grains’ exteriors (Figs. 1A–1C; Figs. DR1A–DR1J). We observed similar results for zircons washed with 0.5 N HCl (i.e., sets 5 and 6): 67% of the 9 zircons detected with QDM showed exterior-only NRM (bottom grains in Figs. DR4E and DR4J; and both grains in Figs. DR4G and DR4D). Of the 23 non-acid-washed and 0.5 N HCl-washed zircons analyzed with WDS, 91% (including 93% of the 15 zircons with exterior-only magnetic sources) have secondary Fe-rich rims located within <5 µm of the grain exteriors (Figs. 1A–1C; Figs. DR1A, DR1B, DR1D–DR1J, DR2, DR5, and DR6). These rims have thicknesses ranging from <2 µm for most zircons (e.g., Figs. 1B–1D) and up to 10 µm for one zircon (e.g., Fig. DR1). Additionally, X-ray tomography of an uncracked, optically clear Hadean zircon with exterior-only magnetic sources, which showed no sign of secondary mineralization based on optical inspection, identified high-X-ray absorption grains (consistent with Fe-rich materials) exclusively on the zircon exterior (Fig. 2). The spatial association of magnetic anomalies and Fe-rich secondary materials suggests that the latter carry most of the magnetization in these zircons. Although some exterior magnetic anomalies are not associated with Fe-rich materials detectable with WDS (e.g., anomaly at upper right of grain in Figure 1B), the difference

![Figure 1. Magnetization, texture, and composition of Jack Hills (Western Australia) zircons not washed with acid (i.e., set 1). Shown are quantum diamond microscopy (QDM) maps of the vertical component of the magnetic field at ~1–10 µm above the samples overlain on backscattered electron microscopy (BSEM) images (left), BSEM images (middle), and maps of Fe abundance from wavelength dispersive spectroscopy (WDS) (right). A: Zircon RSES 199–4–15 (RSES—Australian National University Research School of Earth Sciences) (Pb-Pb age of <3900 Ma); B: Zircon RSES 199–10–2 (Pb-Pb age of 4050 ± 8 Ma); C: Zircon RSES 199–4–16 (Pb-Pb age of 3973 ± 8 Ma); D: Zircon RSES 199–13–3 (Pb-Pb age of <3900 Ma). See Figures DR1 and DR2 (see footnote 1) for more QDM and BSEM analyses of set 1 zircons, and see Figure DR3 for QDM data on all set 1 zircons. See Table DR4 for the Pb-Pb ages of these zircons.](image-url)
in depth sensitivity between these techniques (see Methods) implies that many of these anomalies may be likely associated with secondary Fe-rich materials located ≥2 µm beneath the polished grain surfaces.

We found that just 21% of detected zircons not washed with strong HCl contain interior magnetic sources (i.e., that lie deeper than 20 µm from the rim) (e.g., Fig. 1D; Figs. DR1M–DR1P; Table DR2). Although the bulk magnetizations of the latter zircons are better candidates for being dominantly carried by primary ferromagnetic materials, the exteriors of many of these zircons nevertheless carry substantial magnetization (e.g., Fig. 1D; Figs. DR1M–DR1P). In particular, 100% (5 out of 5) of these zircons with interior magnetic sources analyzed with electron microscopy have Fe-rich rims (e.g., Fig. 1D; Figs. DR1M, DR1O, and DR1P). Furthermore, we found that 100% (5 out of 5) of these zircons analyzed with electron microscopy host Fe-rich secondary minerals in interior cracks and metamict zones (e.g., Fig. 1D; Figs. DR1M, DR1O, and DR1P). QDM maps of the zircon host conglomerate found that the IRM of *in situ* zircons is significantly weaker than that associated with quartz grain boundaries that are commonly filled with Fe oxides (Fig. DR7). Therefore, until it is demonstrated that the NRM of the Tarduno et al. (2015) micro-conglomerate test samples are dominated by primary inclusions in the zircon rather than by the surrounding rock, the outcome of that test should be regarded as uncertain.

Raman spectroscopy indicates the presence of hematite in at least two zircons prior to any lab heating (Fig. DR8). Furthermore, SM measurements of thermal demagnetization of IRM (Fig. 3; Fig. DR9), found that 100% of 9 grains with clearly identified Curie temperatures contained hematite (Curie temperature 675 °C) while 22% also contained magnetite (Curie temperature 580 °C). These data also demonstrate that several zircons contain hematite (Curie temperatures 50–120 °C) and possibly pyrrhotite (Curie temperature 325 °C). During repeat heating experiments, it was observed that a zircon dominated by hematite during the first heating became dominated by magnetite during the second heating, indicating that heating severely altered the magnetization carriers (Fig. DR9C).

These observations collectively indicate that the NRM and IRM in most of our Jack Hills zircons not washed with concentrated HCl are predominantly carried by secondary Fe oxides deposited on the zircon exterior or within cracks and voids in the zircon interior. Our identification of hematite as a major remanence carrier contrasts with the observations of Tarduno et al. (2015), who found that essentially all of their analyzed zircons had remanence apparently dominated by magnetite. A possible explanation for this discrepancy is that hematite was originally present in the zircons of Tarduno et al. (2015), but was altered to magnetite by their heating experiments (e.g., Fig. DR9C) prior to their lowest-temperature checks for alteration (i.e., 550 °C).

**Zircons Treated with Concentrated (6N) Acid**

SM measurements of set 9 find that zircons washed in concentrated HCl have a mean NRM only 59% of that of non-acid-washed zircons (Fig. DR10B; Table DR3). Furthermore, only 12% of acid-washed zircons have moments ≥1 × 10^-12 Am². QDM measurements of sets 7 and 8 show that IRM is also weakened by acid-washing, with only 58% of such zircons detected (compared to 90% of unwashed set 1 zircons analyzed with QDM in the high-sensitivity mode).

Even so, QDM imaging showed that of the 14 zircons with detectable IRM, 29% still have magnetic sources confined largely to their exteriors (Fig. 4C; Fig. DR12A [both grains], and DR12C [bottom grain]). Furthermore, 36% of the 11 grains analyzed with EDS still have Fe-rich exterior rims (Figs. 4B and 4C; Figs. DR11E and DR11H). Also, 100% of the 8 zircons analyzed with EDS and having interior magnetic sources contain Fe-rich cracks and alteration textures in their interiors (Figs. 4A and 4B; Figs. DR11A, DR11C–DR11G). Again, we cannot exclude the possibility that interior anomalies not associated with Fe-rich surface alteration visible in electron microscopy are instead associated with such alteration minerals below the polished surface. Overall, our analyses demonstrate that washing with concentrated HCl reduces the NRM and IRM of the zircons particularly, on the grain exteriors. Unfortunately, this often still leaves large quantities of Fe-rich alteration materials behind that could carry significant remanence. As described in Appendix DR3, these results are broadly consistent with the observations of Fe oxide inclusions by Bell et al. (2015).


We thank A. Steele for use of his Raman microscope and N. Chatterjee for assistance with the microprobe.

REFERENCES CITED


We thank A. Steele for use of his Raman microscope and N. Chatterjee for assistance with the microprobe.

REFERENCES CITED


We thank A. Steele for use of his Raman microscope and N. Chatterjee for assistance with the microprobe.

REFERENCES CITED


We thank A. Steele for use of his Raman microscope and N. Chatterjee for assistance with the microprobe.

REFERENCES CITED


We thank A. Steele for use of his Raman microscope and N. Chatterjee for assistance with the microprobe.

REFERENCES CITED


We thank A. Steele for use of his Raman microscope and N. Chatterjee for assistance with the microprobe.

REFERENCES CITED


We thank A. Steele for use of his Raman microscope and N. Chatterjee for assistance with the microprobe.