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Evidence for oceans pre-4300 Ma confirmed by preserved igneous compositions in Hadean zircon

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Abstract

Detrital zircons from the Jack Hills are the dominant source of Hadean (pre-4000 Ma) terrestrial material available for study today. Values of $\delta^{18}O$ in many of these zircons (6.0 to 7.5‰) are above the mantle-equilibrated value. For two decades, these mildly elevated values have been the primary evidence that protoliths of the zircon-forming magmas interacted at low temperature with liquid water before burial and melting, implying that the surface of Earth cooled quickly after core and Moon formation and that habitable conditions for life existed within 250 Myr of the formation of Earth, over 800 Myr before the oldest generally accepted microfossils. These conclusions are based on oxygen isotope analyses of zircon domains with well-defined growth zoning and nearly concordant U-Pb ages within zircon grains with low magnetic susceptibility, which are further inferred to be unaltered by various tests. However, no studies of Jack Hills zircons have directly correlated oxygen isotope ratios and radiation damage, which facilitates alteration in zircon. Several previous studies have selected zircons that show radiation-damaged, discordant, and/or hydrous domains and have shown that such altered material is not reliable as a record of igneous composition. In contrast, this study targeted zircons that are interpreted as not altered and demonstrates the importance of testing zircons for radiation damage and alteration as part of any geochemical study, regardless of age. This study expands on existing data and presents the first comprehensive evaluation of $\delta^{18}O$, OH/O, CL imaging, U-Pb concordance, and radiation-damage state within Jack Hills zircons. A total of 115 Hadean zircon grains in this study have water contents similar to nominally anhydrous standard reference zircons and are interpreted as pristine. Raman band broadening correlated with $\delta^{18}O$ reveals low levels of radiation damage, indicating significant annealing. The present-day effective doses (D_{eff}) are uniformly less than the first percolation point [dose where damage domains, that are isolated at lower damage state, overlap to form a continuous pathway through the crystal, ~2×10^{15} α-decays/mg (Ewing et al. 2003)] and most zircons have D_{eff} <1×10^{15} α-decays/mg. Modeling of representative α-recoil damage and annealing histories indicates that most zircons in this study have remained below the D_{eff} of the first percolation point throughout their history. The $\delta^{18}O$ values for these primary zircons include many that are higher than would be equilibrated with the mantle at magmatic temperatures and average 6.32 ± 1.3‰ in the Hadean and 6.26 ± 1.6‰ in the Archean. There is no correlation in our suite of unaltered Hadean zircons between $\delta^{18}O$ and OH/O, D_{eff}, age, or U-Pb age concordance. These carefully documented Hadean-age zircons have low amounts of radiation damage in water-poor domains sampled by $\delta^{18}O$ analysis. The mildly elevated $\delta^{18}O$ values are a primary magmatic geochemical signature. These results strengthen the conclusion that mildly elevated-$\delta^{18}O$ magmas existed during the Hadean, supporting the hypothesis that oceans and a habitable Earth existed before 4300 Ma.

Keywords: Zircon, oxygen isotopes, Hadean, SIMS, ion microprobe, Jack Hills, Raman, radiation damage, alteration, annealing; Isotopes, Minerals, and Petrology: Honoring John Valley

Introduction

The Hadean Jack Hills detrital (JHD) zircons from Western Australia include the oldest-dated samples of Earth at 4400 Ma (Wilde et al. 2001; Valley et al. 2014). Although Hadean detrital zircons have been found in other localities (e.g., Iizuka et al. 2006; Duo et al. 2007; Maier et al. 2012; Paquette et al. 2015; Harrison and Wielicki 2016; Harrison 2020; Harrison et al. 2017; Cavosie et al. 2019; Drabon et al. 2022), the most plentiful source remains the Jack Hills (Holden et al. 2009; Cavosie et al. 2019). Wilde et al. (2001) and Peck et al. (2001) reported the first 4400 Ma terrestrial zircon and a suite of Hadean zircons with $\delta^{18}O$ values up to 7.5‰ that are above the value equilibrated with primitive, mantle-derived magmas (4.7 to 5.9‰) (Valley et al. 1998, 2005). The existence of zircons with mildly elevated $\delta^{18}O$ values (6.3 to 7.5‰; i.e., above 5.9 within analytical precision) has been confirmed in many studies (see, Cavosie et al. 2019) and interpreted to indicate that parent magmas assimilated

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material with elevated $\delta^{18}O$. Such high-$\delta^{18}O$ assimilants can only form through low-temperature interactions with surface water. The discovery of elevated $\delta^{18}O$ in Hadean zircons led to the Cool Early Earth hypothesis that proposes liquid-water oceans existed before 4300 Ma (Valley et al. 2002).

The JHD zircons have been extensively studied and analyzed, including U-Pb age; isotopes of O ($^{16}O/^{17}O/^{18}O$), Li, Si, and Hf; scanning electron microscopy (SEM) imaging of cathodoluminescence (CL), backscattered electrons (BSE), and electron backscatter diffraction (EBSD); atom probe tomography (APT); electron probe microanalysis (EPMA); magnetic susceptibility; and trace elements (including B, Al, Ca, Fe, Li, Ti, REE, Nb, Sc, halogens, Eu*, and Ce*) (Compston and Pidgeon 1986; Wilde et al. 2001; Peck et al. 2001; Mojzsis et al. 2001; Cavosie et al. 2004, 2005, 2006, 2019; Turner et al. 2004; Watson and Harrison 2005; Nemchin et al. 2006; Valley et al. 2007, 2015, 2023; Trail et al. 2007, 2012; Menneken et al. 2007; Hopkins et al. 2008; Harrison et al. 2008; Ushikubo et al. 2008; Fu et al. 2008; Holden et al. 2009; Kemp et al. 2010 ; Ortiz-Cordero 2010; Bouvier et al. 2012; Bell et al. 2016, 2019; Pidgeon et al. 2017, 2019; Ge et al. 2018, 2019; Blum 2018; Bellucci et al. 2018; Keller et al. 2019; Turner et al. 2020; Tang et al. 2019; Harrison 2020; Chowdhury et al. 2020; Ackerson et al. 2021; Spencer at al. 2022; Drabon et al. 2022). Mineral inclusions in JHD zircons have also been identified and analyzed for isotopes of O and C (Ortiz-Cordero 2010; Dobrzhinetskaya et al. 2014; Valley et al. 2015; Bell et al. 2015a, 2015b, 2017, 2018; Cameron 2017; Menneken et al. 2007, 2017) and age (Rasmussen et al. 2010). Despite such varied and detailed characterization, questions remain regarding the degree of alteration and the ability to distinguish primary vs. secondary signatures in zircon, both for the JHD data set and for zircons in general.

Zircon ($ZrSiO_4$) is a refractory, highly durable mineral (Speer 1980), which, when not heavily radiation-damaged, exhibits very slow diffusion for most elements and isotopes, including oxygen. In situ measurements of oxygen isotopes ($\delta^{18}O$) in zircon have become increasingly common and, more recently, have been paired with simultaneous measurements of H in the same SIMS pit (reported as $^{16}O^{1}H/^{16}O$ ~OH/O) (Wang et al. 2014). When calibrated by secondary ion mass spectrometry (SIMS) analysis of a zircon standard for hydrogen, OH/O is a quantitative measure of "water" content (i.e., OH and H_2O) (Xia et al. 2019). In the absence of a calibrated standard, OH/O provides an indication of relative differences that are useful to identify alteration and inclusions. Undamaged zircon is nominally anhydrous, but amorphous, glass-like domains created by radiation damage are susceptible to hydrous alteration and high OH/O often correlates with high degrees of radiation damage and alteration (Wang et al. 2014). SIMS pits that fall on cracks or inclusions can also yield elevated OH/O due to the presence of other phases (Pidgeon et al. 2019), but such analyses are readily identified by post-analysis SEM examination of pits. Large-radius, multi-collector SIMS instruments, such as the CAMECA IMS-1280 (Cavosie et al. 2005; Page et al. 2007) provide in situ measurement of $\delta^{18}O$ in zircon with high spatial resolution (1–10 μm spot size) and high spot-to-spot precision (0.2‰ 2SD), which allows spatially resolved analyses to be correlated with imaging and other in situ analyses of specific domains within individual zircons.

At high spatial resolution, U and Th concentrations can vary at the micrometer scale, leading to a heterogeneous damage state, discordance, and alteration, possibly affecting $\delta^{18}O$ and other geochemistry. Analysis of a small suite of radiation-damaged JHD zircons has shown correlations between $\delta^{18}O$ and OH/O, leading to the suggestion that all mildly elevated $\delta^{18}O$ values within Jack Hills zircons might be due to hydrous alteration of weathered zircon and that they do not reflect primary $\delta^{18}O$ values (Pidgeon et al. 2017). Anomalous values of $\delta^{18}O$ can also result from alteration along cracks that were intersected by the SIMS pits (Pidgeon et al. 2019). Thus, deciphering the record in zircons requires the ability to distinguish altered vs. primary (igneous) domains. In some studies, significant steps have been taken to identify and selectively analyze domains in low-magnetic-susceptibility grains that preserve chemical and textural evidence of primary chemical compositions (e.g., Cavosie et al. 2004; Valley et al. 2015). This is especially important for old zircons, including those that have been used to make inferences about the Hadean Earth, but criteria and tests sufficient to identify alteration are not uniformly applied or agreed upon (Gao et al. 2014; Davies et al. 2015; Liebmann et al. 2023).

This paper focuses on the micrometer-scale correlation of $\delta^{18}O$ and U-Pb age in Hadean zircons with Raman spectroscopy, water content, and SEM imaging to better describe aspects of JHD zircon crystallinity, thermal history, and geochemistry. These data significantly expand the correlated $\delta^{18}O$, OH/O, and Raman data set for JHD zircon and build upon published work, enabling a more thorough understanding of (1) the fidelity and interpretation of elevated $\delta^{18}O$ in the Jack Hills record and (2) the wider application of the $\delta^{18}O$ and OH/O record for zircons with other ages and localities outside of the Jack Hills. This comprehensive comparison of $\delta^{18}O$ to radiation damage and water content in Hadean zircons provides new criteria to evaluate the fidelity of geochemical data for zircons of any age.

Background information: Radiation damage in zircon

Radioactive decay is the basis for U-Pb geochronology, but its effects on the zircon structure can also promote alteration of geochemical records from Hadean and younger zircons. U-Th-Pb geochronology is based on the decay of U and Th through a series of intermediaries to isotopes of Pb. The nuclear transmutations in these decay chains generate nanometer-scale damage domains, principally by the recoil of daughter atoms after the emission of an α particle (α-recoil) (Ewing et al. 2003). If not annealed, amorphous (noncrystalline) domains accumulate, leading to various chemical and physical changes, including an increase in volume and faster rates of diffusion and dissolution. If a zircon accumulates damage of ~2×10^{15} α-decay events/mg (Salje et al. 1999; Ewing et al. 2003; Nasdala et al. 2004) and is not annealed, these nanometer-scale damage domains form an overlapping continuous network. The beginning of the three-dimensional interconnection of damage clusters is referred to as the first percolation point, and the network of damage domains can form fast pathways for diffusion and hydrous alteration (Salje et al. 1999). More advanced stages of damage accumulation open a zircon to elemental and isotopic exchange, facilitating alteration of primary U-Pb ages, trace element concentrations, and stable isotope ratios (e.g., Valley et al. 1994, 2015; Ewing et al. 2003). At extreme levels of radiation damage, zircon becomes amorphous and glass-like and is often referred to as metamict. Though they may retain external crystal form, metamict zircon are not reliable as a geochemical record of parent magmas.

The emission of heavy daughter nuclei during α-decay causes most of the damage to the zircon structure (Nasdala et al. 2001; Ewing et al. 2003). The number of α-decay events experienced by a zircon throughout its history (i.e., the total α-dose, D_{total}) can be calculated from equations for $^{238}U \rightarrow {}^{206}Pb$, $^{235}U \rightarrow {}^{207}Pb$, and $^{232}Th \rightarrow {}^{208}Pb$ decay based on the zircon age, U and Th concentrations:

$$D_{total} = 8 \times {}^{238}N[\exp(\lambda_{238}t) - 1] + 7 \times {}^{235}N[\exp(\lambda_{235}t) - 1] + 6 \times {}^{232}N[\exp(\lambda_{232}t) - 1] \quad (1)$$

where D_{total} is the number of α-decay events per milligram; λ_{238}, λ_{235}, and λ_{232} are the decay constants for ^{238}U, ^{235}U, and ^{232}Th, respectively; t is the age of the zircon (or zircon domain); and ^{238}N, ^{235}N, and ^{232}N are the present-day number of ^{238}U, ^{235}U, and ^{232}Th atoms per milligram of zircon (Holland and Gottfried 1955; Nasdala et al. 2001; Ewing et al. 2003). The concentrations of U and Th are variable in Jack Hills zircons, but in this study, zircons were selected for bright CL that correlates with lower values (typically 50–200 ppmw U and 20–100 ppmw Th; Online Materials[1] Appendix C) and thus less radiation damage.

Zircon crystals commonly form by concentric growth with individual bands that can differ significantly in the concentrations of uranium [U] and thorium [Th] (and other trace elements), and thus the zircon radiation-damage state can be highly variable at the micrometer- and sub-micrometer scale within a single grain (Chakoumakos et al. 1987; Nasdala et al. 1996; Palenik et al. 2003; Hofmann et al. 2009; Valley et al. 2015; Ge et al. 2018). Zoning or less-systematic heterogeneity in composition and damage state can be identified through various techniques, including imaging by SEM (CL, BSE, and SE), EBSD, APT, TEM, spectroscopy (IR and Raman), identification of anomalous inclusions, optical examination (for micro-cracks, porous zircon, and/or reduced birefringence), and etching with HF. Analyses of leachates and residual zircon obtained by chemical abrasion (annealing at 900 °C followed by HF leach) of Jack Hills zircons show that dissolution selectively removes components with lower (discordant) ages and LREE's (Keller et al. 2019). In situ analyses coupled with careful imaging make it possible to identify and avoid many, but not all damaged domains. However, taking all possible precautions is tedious, and simplified protocols are generally employed. Ratios of OH/O are commonly measured as one indicator of alteration (Wang et al. 2014; Pidgeon et al. 2013, 2017; Liebmann et al. 2021). Wang et al. (2014) measured ^{16}O, $^{16}O^{1}H$, and ^{18}O simultaneously by SIMS and showed that background-corrected ratios of OH/O, based on bracketing analyses of nominally anhydrous zircon, are a sensitive measure of relative water contents and correlate with radiation damage and alteration.

Raman spectroscopy, specifically measurement of band shift and band broadening for the $\nu_3(SiO_4)$ vibrational mode, can be done in situ at a sub-micrometer-scale (Kim et al. 2020) to estimate the present-day zircon crystallinity and damage state (e.g., Nasdala et al. 2001; Ewing et al. 2003). From the full-width at half maximum (FWHM) of the $\nu_3(SiO_4)$ band (FWHM hereafter), one can calculate an "effective dose," D_{eff}, which corresponds to the *current* amount of damage. Values of D_{eff} are often significantly less than the total α-dose (D_{total}, Eq. 1) due to partial or complete annealing of the zircon structure over geologic time (Nasdala et al. 2014). Annealing in zircon can happen over geologic periods of time, even at relatively low temperatures (down to 200–300 °C), and most ancient zircons are at least partly annealed (Nasdala et al. 2001 and references therein).

Samples and methods

Overview of new and previously described samples

Zircons in this study were separated from seven samples of meta-sandstone and metaconglomerate collected within 1 km of the "Discovery" outcrop on Eranondoo Hill in the Jack Hills, where the first zircon with an age of ~4400 Ma was collected (Wilde et al. 2001). Hadean zircons have been found in abundance at this location (Compston and Pidgeon 1986; Cavosie et al. 2004, 2019; Holden et al. 2009). Many, though not all, of the 200 zircons in this study (including 115 pristine Hadean zircon grains) were previously analyzed and underwent significant pre-screening (magnetic separation, SEM-CL imaging, U-Pb age concordance) before in situ analysis of $\delta^{18}O$ to identify domains suspected to be pristine vs. radiation-damaged and/or altered [see data and methods in Cavosie (2005) and Cavosie et al. (2004, 2005, 2006, 2007)]. The oxygen isotope data presented here are unpublished and were all made on the same SIMS instrument, in many cases repeating analysis of zircons from Cavosie et al. (2005). Rock descriptions and locations are compiled in Online Materials[1] Appendix A.

A majority of analyses in this study targeted domains previously analyzed and interpreted to preserve primary igneous compositions based on several criteria including being in grains with low overall magnetic susceptibility (Frantz magnetic separator), high degree of U-Pb-age concordance by SIMS (average = 98% for Hadean zircons), magmatic CL textures [concentric and sector zoning (Corfu et al. 2003)], Th/U ratios >0.1, and appearance under reflected light (Cavosie et al. 2004, 2005, 2006; Cavosie 2005). Settings used by Frantz vary by sample and instrument. In general, for the Jack Hills detrital zircons, we set a steep forward tilt (20°), full current to the magnet (1.85 A), and varied side tilt (10 to –1°) to select the least magnetic zircon grains. Although concordance averaged 98% for selected zircons, Cavosie et al. (2004) show that $^{207}Pb/^{206}Pb$ ages and Th/U ratios appear unaffected for Jack Hills zircons even at 85% concordance and thus only domains more than 15% discordant are rejected. Analyses suspected to overlap damaged or altered domains (as identified by criteria above) are not interpreted as primary.

The in situ analyses reported here were targeted using SEM-CL images so that age and geochemistry correlate as closely as possible within the individual growth domains of each zircon. Identification of two different domains in a single zircon grain (e.g., core vs. overgrowth) is often clear, however, the small size and internal complexity of some zircons complicate easy correlation. Figure 1 and Online Materials[1] Appendix E show images and spot locations in representative zircons.

SIMS analysis of $\delta^{18}O$ and OH/O

Zircon grains were cast in 25.4-mm round epoxy mounts, ground to approximately their midsections, and polished with 0.25-μm diamond suspension. After zircons were cast and polished, epoxy mounts were coated with 20 nm of carbon for BSE-SE and CL imaging. Before coating, mounts were cleaned using a 70% ethanol solution, followed by deionized water. The same cleaning procedure was utilized between analysis sessions and before coating with Au for SIMS analysis or coating with carbon for SEM imaging. After SIMS analysis, BSE and SE imaging by SEM was employed to evaluate SIMS pits; carbon coating was again added to the mounts, but only after Au was removed from the mount surface by dissolution in ethaline [two 15 min soaks (Jones et al. 2012)] and an additional ethanol cleaning. Zircons were cleaned again and were subsequently analyzed by Raman spectroscopy; Raman spots were selected adjacent to $\delta^{18}O$ analysis pits in similar CL domains (see below). Oxygen isotope analyses of zircons were performed on a CAMECA IMS-1280 large-radius multi-collector ion microprobe at the WiscSIMS Laboratory, University of Wisconsin, Madison, over eight analysis sessions of 12–48 h each. One four-day session (hereafter identified as session 1) was completed in 2006 before the OH/O analysis protocol was developed (Online Materials[1] Appendix B). Sample preparation and analysis conditions were the same as described previously (Kita et al. 2009; Valley and Kita 2009; Kitajima et al. 2012). Seven 12-h analytical sessions (no. 2–8) were completed from January 2016 to March 2017, where OH/O was analyzed simultaneously with $\delta^{18}O$ (Online Materials[1] Appendix B); OH/O ratios were measured and background-corrected against the nominally anhydrous running standard approximately every 2 h as described by Wang et al. (2014). For all zircons, a 2 nA primary beam of $^{133}Cs^{+}$ ions (20 keV impact energy) was focused to a diameter of ~10 μm on the gold-coated sample surface. Currents for $^{16}O^-$, $^{18}O^-$, and $^{16}O^1H^-$ were collected simultaneously with three Faraday cups. Mass calibrations were performed every 12 h. Instrument stability during analytical sessions was monitored by sets of four spot-analyses of KIM-5 running standard zircon ($\delta^{18}O$ = 5.09‰ VSMOW; Valley 2003) that were repeated at ~90 min intervals throughout each of the seven sessions (Online Materials[1] Appendix B). The analytical precision for $\delta^{18}O$ in each sample analysis is reported as two standard deviations (2 SD) of typically eight standard analyses that bracket each set of 10–15 sample analyses. The measured ratios of ^{18}O to ^{16}O are corrected for instrumental bias as calculated from bracketing KIM-5 zircon analyses and reported in standard $\delta^{18}O$ notation on the Vienna Standard Mean Ocean Water (VSMOW) scale.

The OH signal within a SIMS analysis originates from both the sample itself and the sample environment (i.e., small amounts of H-species adsorbed on the sample surface even after cleaning and degassing at ultrahigh vacuum). Wang et al. (2014) demonstrated that the background OH levels vary with the age and type of mounting medium, and the length of time a sample is in the analysis chamber. For this study, the OH/O ratio of each sample analysis is background-corrected by subtracting the ratio measured on bracketing KIM-5 zircon standard analyses. The KIM-5 standard preserves finely banded igneous zonation in CL (Cavosie et al. 2005), has low degrees of radiation damage and is nominally anhydrous.

The adsorption of volatiles on the sample surface is influenced by vacuum quality. Thus, uncorrected OH background signals measured during zircon analysis correlate with pressure in the analysis chamber, and OH backgrounds can drift even for a single sample as vacuum pressure changes. Frequent monitoring of background OH/O by use of bracketing standard analyses leads to more accurate measurement of background-corrected OH/O than corrections based on daily averages. Within this study, pressures in the analysis chamber typically decreased by ~14% over 12 h (at 10^{-7} to 10^{-8} torr) for individual sample mounts. Cycle-to-cycle variability in OH/O is monitored for each of the 20 4-s cycles in a single SIMS analysis, to screen for anomalous spikes or down-pit variability in ^{16}OH or ^{16}O. Fluid inclusions can generate short-lived spikes in OH as volatiles are rapidly pumped away. Denny et al. (2020) found that spikes in OH/O ratios from supposed fluid inclusions in quartz were less than 10 s in duration and do not affect resulting $\delta^{18}O$ values. In this study, six zircon analyses have one 4-s cycle that is greater than the 5-SD value of OH/O for the 20 cycles, suggesting that some of the samples contain sub-micrometer-scale hydrous inclusions. These limited spikes in OH/O did not correspond to anomalous $\delta^{18}O$ values, so the six analyses with OH/O spikes are not excluded.

Ratios of OH/O can be used to evaluate [H] or "water" content in zircons. However, many of the samples in this study were cast in epoxy (Cavosie 2005), which leads to slightly elevated backgrounds and compromises quantitative analysis of water at parts per million levels in nominally anhydrous zircon by SIMS. The recent use of Sn-Bi alloys to cast zircon mounts (Zhang et al. 2018) and calibrated zircon standards (Xia et al. 2019) allow quantitative analysis of [H_2O] in zircon, however, these procedures were not available at the start of this project and are not necessary to evaluate the much-higher wt% levels of water often found in zircon with high amounts of radiation damage. Without calibration against homogeneous zircon standards, background-corrected OH/O ratios are a measure of relative hydrogen content from zircon-to-zircon but are only qualitative measures of wt% H_2O. In this study, negative ratios of background-corrected OH/O are all within the uncertainty of zero and are not statistically significant.

Zircons were analyzed for $\delta^{18}O$ by placing one or more 10-μm SIMS-analysis spots on each grain (Fig. 1; Online Materials[1] Appendix E). The spots are correlated with U-Pb domains previously determined as >85% concordant by Cavosie et al. (2004) (Online Materials[1] Appendix C).

Post-analysis SEM imaging of SIMS pits was used together with secondary-ion yield (Gcps/nA, see Online Materials[1] Appendix B) to further evaluate the reliability of individual analyses. Analysis pits that overlapped a second phase (e.g., mineral inclusion, epoxy) are irregular and unreliable; these analyses are indicated in Online Materials[1] Appendix B and are not considered further. Filtering for low- or high-ion yields (>5% different from the average yield for bracketing analyses of the matching KIM-5 standard), as well as unusual SIMS pit shape or anomalous grain behavior, were additional considerations for generating a robust $\delta^{18}O$ and OH/O data set.

Raman analysis of zircons

The local radiation-damage state of zircon domains is monitored by measurement of the full-width at half maximum of the $\nu_3(SiO_4)$ vibrational mode [$FWHM_{\nu_3(SiO_4)}$] (e.g., Nasdala et al. 1995, 2001). In zircons with no radiation damage at ambient pressure, this Raman band is positioned at about 1008 cm^{-1} (Zeug et al. 2018; Ende et al. 2021). Both band position and band broadening vary systematically with the accumulation of radiation damage (e.g., Nasdala et al. 1995, 2001; Wopenka et al. 1996; Geisler et al. 2001; Palenik et al. 2003). The full α-dose (D_{total}) follows an exponential curve of the form:

$$FWHM_{\nu_3(SiO_4)} = A[1 - \exp(-BD_{total})] \quad (2)$$

where A and B are constants (35.64 cm^{-1}, 5.49 × 10^{-16}/mg, respectively), FWHM is in units of cm^{-1}, and D_{total} is in units of α-decays/mg (Palenik et al. 2003). However, it should be noted that Equation 2 was derived from results obtained from a suite of Sri Lankan zircons that share a particular annealing history (Nasdala et al. 2004). Furthermore, the complete damage retention line from Equation 2 starts at the origin, whereas unirradiated (zero dose) and hence undamaged zircon has a FWHM of 1.7–1.8 cm^{-1} (Zeug et al. 2018; Ende et al. 2021). In spite of these uncertainties, Equation 2 can be rearranged and used to calculate the effective α-dose (D_{eff}) based on measured $FWHM_{\nu_3(SiO_4)}$ of both annealed and unannealed zircon unknowns, which may not preserve damage from their full α-dose.

$$D_{eff} = -1/B \ln [1 - FWHM_{\nu_3(SiO_4)}/A] \quad (3)$$

By comparing the total calculated α-dose (D_{total} from Eq. 1) and the D_{eff} (from Eq. 3 for the measured Raman bandwidth), it is possible to determine whether a specific zircon domain preserves all its radiation damage and an approximate percentage of annealing. For zircons that are not annealed, D_{total} is expected to equal D_{eff}.

Raman spectra, specifically targeting the $\nu_3(SiO_4)$ vibrational mode, were collected on 147 of the 200 grains analyzed for $\delta^{18}O$ to characterize the present damage state in the same domains as SIMS $\delta^{18}O$ analyses. Analyses were made on a LabRAM HR confocal Raman microscope in spot mode in the Department of Geoscience, University of Wisconsin-Madison. Analyses used a 632.8 nm He-Ne laser, with a 100× objective, confocal aperture set at 100 μm, a spectrometer entrance slit of 100 μm, and an 1800 groove/nm grating. Spike correction for cosmic ray hits on the detector was done by accumulation of multiple spectra (between two and four spectra). Total acquisition times for each spectrum ranged between 4 and 80 s; times varied based on the time required to generate spectra sufficient for reliable spectral processing. Between one and four Raman spots were targeted adjacent to each SIMS $\delta^{18}O$-pit (Online Materials[1] Appendix D); some Raman analysis locations correlate well with multiple, closely spaced $\delta^{18}O$ analyses. Since the $\delta^{18}O$ SIMS analyses were originally placed nearby or beneath prior U-Pb SIMS analyses, comparisons were also made between Raman and U-Pb data, including age, [U], [Th], and concordance (Online Materials[1] Appendix D). No significant difference is seen for Raman spots correlated to $\delta^{18}O$ pits vs. those adjacent to U-Pb pits within a given zircon domain. Raman analyses employed SEM-based CL imaging to position analyses; any zoning apparent in CL imaging that intersected corresponding SIMS $\delta^{18}O$ analyses was targeted for independent Raman spot analysis. Individual Raman analyses were positioned a minimum of 1 μm away from correlated $\delta^{18}O$ SIMS pits. Processing of Raman spectra was done within the software LabSpec6, and included background subtraction, followed by band fitting, assuming bands represent a convolution of Gaussian (instrumental) and Lorentzian (physical) shapes. The fitted FWHM values were corrected for the apparatus function using the approximation of Váczi (2014).

RESULTS

Oxygen isotopes and water in zircon

A total of 924 SIMS $\delta^{18}O$ analyses were made on 200 detrital zircon grains; many, though not all, of these zircons have previously been dated by SIMS, yielding domains as old as 4374 Ma (Cavosie et al. 2004; Cavosie 2005; Valley et al. 2014, 2015; Online Materials[1] Appendix C). In their entirety (including altered domains), these individual analyses yield a total range in $\delta^{18}O$ from 0.9 to 10.3‰ (Fig. 2), though most are between 5 and 8‰. The full range in $\delta^{18}O$ includes analyses in which sampled domains are judged to be either altered zircon or non-igneous zircon (e.g., metamorphic, 01JH-54a 2.5M 37; Cavosie et al. 2018). A total of 523 analyses across a nearly identical set of domains include OH/O data documenting a range in background-corrected OH/O from –6.7 × 10^{-5} to 1.2 × 10^{-2}; most are <3 × 10^{-4} (Fig. 2). Note that negative values of OH/O are within analytical error of 0. Intragrain variability in $\delta^{18}O$ varies from 0.0 to a maximum of 3.0‰; we note that intragrain variability is expected, given that these data

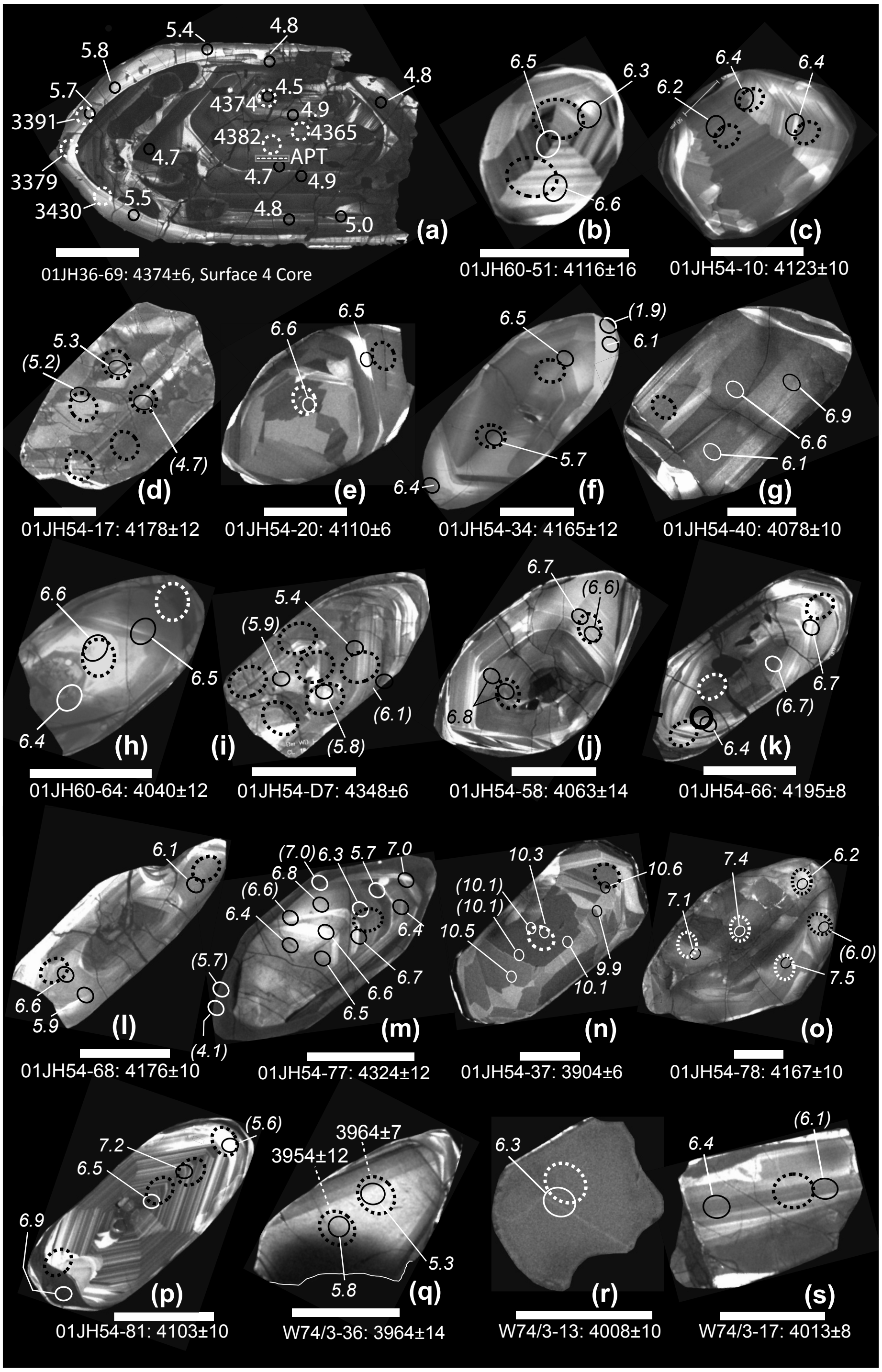

Figure 1. CL images of representative Jack Hills detrital zircons showing location of SIMS analysis pits for age (dashed circles, Ma) and $\delta^{18}O$ (solid circles, ‰ VSMOW, parentheses = rejected data). Images for 54 zircons from this study are shown in Online Materials[1] Appendix E. APT = atom probe tomography. (**a**) Valley et al. (2014). (**b–s**) Cavosie et al. (2006). All scale bars = 100 μm.

include both analyses that hit domains judged to be altered [e.g., W74/3-131, see also Cavosie et al. (2005)] and also several grains that show clear chemical and textural evidence for younger overgrowths (e.g., 01JH-36 69, Fig. 1a) (Valley et al. 2014).

The exclusion of altered domains by simple objective measures (Cavosie et al. 2004) was applied to $\delta^{18}O$ analysis in a subset of these zircon grains previously (Cavosie et al. 2005) and application of these criteria within this larger data set generates a more restricted range in δ[18]O and OH/O (see Online Materials[1] Appendices B, C, and D for tabulation of excluded data and rationale). The δ[18]O and OH/O values of individual-spot analyses in pristine zircon domains vary between 3.8 and 9.9‰, and -4.7×10^{-5} to 8.4×10^{-4}, respectively (Fig. 2). When assessing variability on a domain-specific scale (i.e., "cores"), intragrain δ[18]O variability is reduced—two zircons possess 3.9 and 2.5‰ variability, while all others show variability <1.8‰.

The average δ[18]O for the texturally primary Hadean zircon domains (>4000 Ma) analyzed in this study is 6.3 ± 1.3‰ VSMOW (2SD). The new data show excellent agreement with specific zircon domains from the smaller data set from Cavosie et al. (2005) (Fig. 3), who reported an identical average δ[18]O value of 6.3 ± 1.1‰ VSMOW (2SD).

Values of δ[18]O for unaltered (pristine) igneous zircons lower than 5.0‰ or higher than 7.5‰ are rare in this study (Figs. 2 and 3); most zircons plot within or slightly above the range for igneous zircons that equilibrated with mantle compositions (4.7 to 5.9‰) (Valley et al. 1998, 2005). A significant population of zircons plots in the mildly elevated range of 6.3 to 7.5‰, explored in detail by Cavosie et al. (2005) and referred to as "supracrustal." The δ[18]O

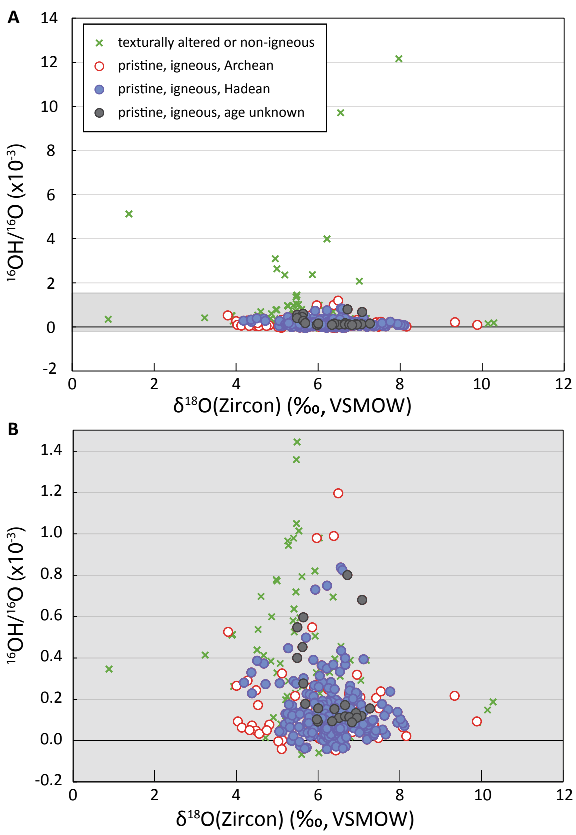

FIGURE 2. Values of $^{16}OH/^{16}O$ vs. δ[18]O for SIMS measurements for which OH/O was simultaneously measured with δ[18]O. The OH/O data are background-corrected ratios, but uncalibrated (see text for details). Negative ratios are within uncertainty of 0. There is a total of 522 data points, including 427 in "unaltered" domains and 296 in unaltered domains with Hadean ages. (**a**) All data within this study, including high-OH/O analyses corresponding to altered/non-igneous domains. (**b**) Expanded view of low-OH/O data.

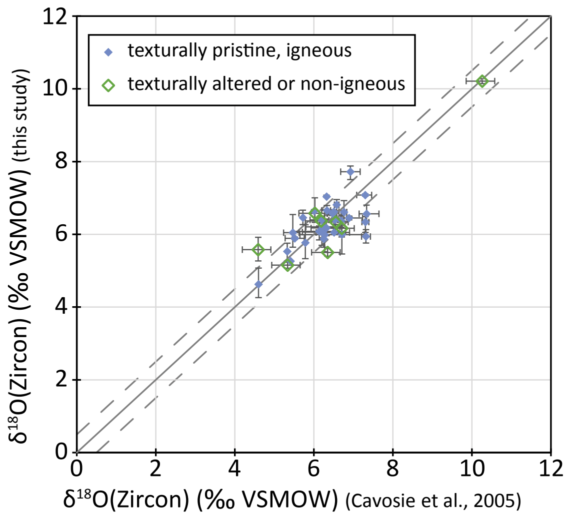

FIGURE 3. Comparison of average δ[18]O within zircon domains measured by IMS-1270 (Cavosie et al. 2005) and IMS-1280 (this study). Solid line is 1:1 and dashed lines show ±0.5‰. Error bars show the complete range in δ[18]O measured within each sampled domain. Total number of grains in comparison is 38, with ~180 individual δ[18]O analyses contributing to domain averages between both studies. There is no significant difference in δ[18]O(Zrn) values either for pristine or altered zircons.

SIMS values in Figure 2 show the same range as bulk analyses of unaltered Archean zircons from other terranes made by laser fluorination of ~2 mg aliquots of zircon separates (~100 zircons/analysis) (Valley et al. 1994, 2005, 2015). The laser data are more precise than SIMS because of larger sample sizes; however, they are bulk averages that do not resolve intra-grain or inter-grain variability, and they can't necessarily be correlated to other in situ data.

The average background-corrected OH/O ratio for unaltered igneous Hadean zircons is 0.15×10^{-3} (Fig. 2b); ratios range up to 0.8×10^{-3}. Most analyses have background-corrected OH/O values that are similar to the nominally anhydrous KIM-5 standard. Overall, these OH/O ratios are low and uniform within each of the Hadean zircon grains in this study. No correlation is observed between the corrected ratios of OH/O and values of δ[18]O(Zrn) (Fig. 2), the vacuum in the analysis chamber, U-Pb age (Fig. 4), or the polishing relief between zircon grains and epoxy (as measured by profilometer), which averages ~2 μm.

Raman measurements

A total of 956 Raman analyses were paired with 417 SIMS-based measurements of δ[18]O + OH/O on 147 of the 200 zircon grains (86 of the 147 have Hadean ages). The Raman analysis spots were selected to be adjacent to and surrounding SIMS pits to characterize the same domains. When assessing all Raman measurements that were paired to a δ[18]O spot for Hadean and Archean zircons without removing altered and non-igneous domains, individual Raman spectra have a large range of band shifts and band broadenings. Values for FWHM plotted against Raman shift for the $\nu_3(SiO_4)$ mode consistently fall along a typical "Radiation Damage Accumulation" trend (black arrow in Fig. 5b) (Zhang et al. 2000; Nasdala et al. 2001; Geisler et al. 2003; Ende et al. 2021). Values of FWHM range between 2.9 and 28.0 cm^{-1}, corresponding to D_{eff} from 0.15 to 3.03 × 10^{15} α-decays/mg for primary and altered domains. These FWHM values encompass micrometer-scale heterogeneity in domains analyzed for $\delta^{18}O$, reflecting heterogeneity in damage state on a scale of <10 µm, consistent with U and Th zoning on the micrometer scale (Online Materials[1] Appendix D).

When excluding altered or non-igneous domains (see criteria above), variability in damage state on the scale of individual SIMS spots is significantly reduced with FWHM values ranging from 3.6 to 17.4 cm^{-1} and D_{eff} ranging from 0.15 to 1.24 × 10^{15} α-decays/mg (Eq. 3; Figs. 5a and 5b). These data document present-day damage states in domains at the scale of SIMS analyses, which are all below the first percolation point. Correlations between Raman data and [U] and [Th] concentrations measured during U-Pb SIMS analysis are approached conservatively. Because U and Th can vary over small spatial scales and Raman was specifically targeted to $\delta^{18}O$ pits that are, by necessity, slightly offset from U-Pb pits, we carefully examined textural relations to match Raman measurements with U-Pb data. Figure 5a shows the comparison of measured $FWHM_{v3(SiO_4)}$ (and equivalent D_{eff}) vs. calculated D_{total} for well-correlated Raman and [U]-[Th]-age data (Online Materials[1] Appendix D). A zircon domain that has retained 100% of the predicted radiation damage would plot on the "complete damage retention" line, while a zircon that is completely annealed would plot near the lower horizontal axis. The damage-retention line is poorly defined above ~5 × 10^{15} α-decays/mg, but zircons with such high values of D_{eff} are not likely to be reliable. The total α-dose calculated from U, Th, and $^{207}Pb/^{206}Pb$ ages (D_{total}) ranges from 0.47 × 10^{15} to 11.8 × 10^{15} α-decays/mg for individual U-Pb analyses. If not annealed, 58% of analyzed zircon domains would have exceeded the first percolation point. However, it is notable that all domains possessing paired [U]-[Th]-age data and Raman spectra fall well below the complete damage retention trend. There is no significant correlation between D_{eff}, OH/O, $\delta^{18}O$ (Fig. 6), age, or age concordance (Online Materials[1] Appendix D). There may be a faint correlation of OH/O and D_{eff} shown in Figure 6b for zircons that plot below the first percolation point and are water poor. Such a correlation would not be surprising at some level and will be explored further in future studies where zircons are mounted in indium or Sn-Bi to reduce OH backgrounds and thus obtain better accuracy and precision for low-OH domains.

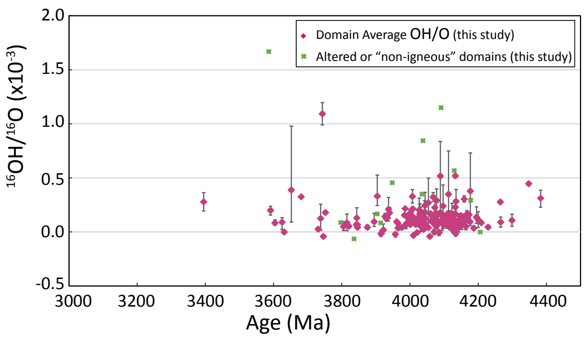

Figure 4. Summary of $^{16}OH/^{16}O$ and age for dated domains within this study. Data points represent the domain-average OH/O within individual zircons correlated to dated domains. Error bars show range in OH/O associated with each domain.

The doses experienced by the suite of zircon domains in this study are explored further below in the modeling of damage accumulation and annealing.

Discussion

Radiation damage and annealing in Hadean zircons

The Raman measurements of Hadean Jack Hills zircons document significant annealing (Figs. 5a and 5b; Online Materials[1] Appendix D); this is the largest Raman data set for JHD zircons published thus far and establishes that annealing is widespread. The prevalence of annealing in the JHD zircons is particularly important because it restricts the times when radiation damage might possibly have exceeded the first percolation point and facilitated oxygen isotope exchange. Alteration is well documented in some JHD zircons (Cavosie et al. 2004, 2005, 2006, 2019; Wang et al. 2014; Pidgeon et al. 2017; Ge et al. 2018), but there remain differing accounts of how widespread alteration is within the JHD zircons

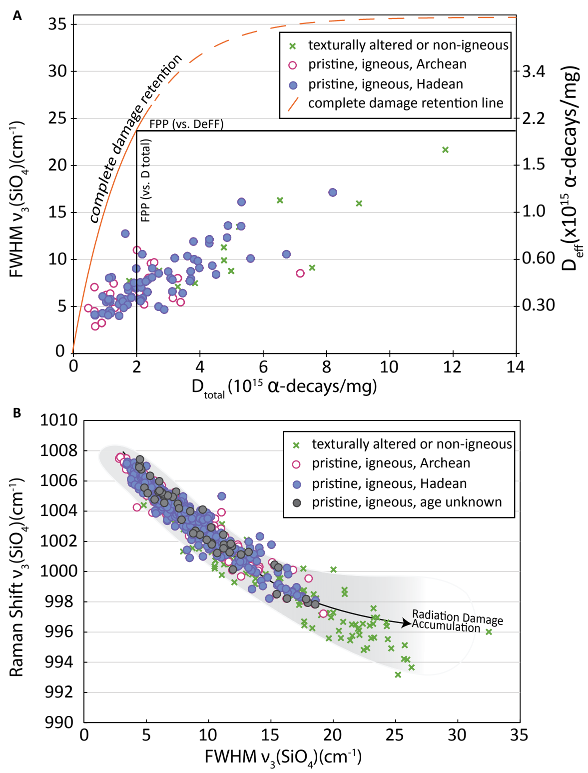

Figure 5. Summary of Raman spectroscopic measurements of zircon within this study. (**a**) Plot showing correlation between D_{total} calculated from [U]-[Th]-age data and average D_{eff} from correlated Raman measurements of FWHM (see text and Online Materials[1] Appendix D for additional details). The black lines are the approximate value of the first percolation point (FPP). None of the Jack Hills data show complete damage retention (i.e., none plot on the curve) indicating that these zircons experienced significant annealing (D_{eff} < D_{total}). These data include 350 individual Raman spot analyses that are correlated to 115 distinct U-Pb analyses. (**b**) Summary of band position (Raman shift) and FWHM for the v_3SiO_4 mode for all individual Raman spectra measured in this study [n = 956; open circles (Archean), n = 194; filled circles (Hadean), n = 498; undated, n = 17]. "Radiation Damage Accumulation" trend from Zhang et al. (2000), Nasdala et al. (2001), Geisler et al. (2003), and Ende et al. (2021).

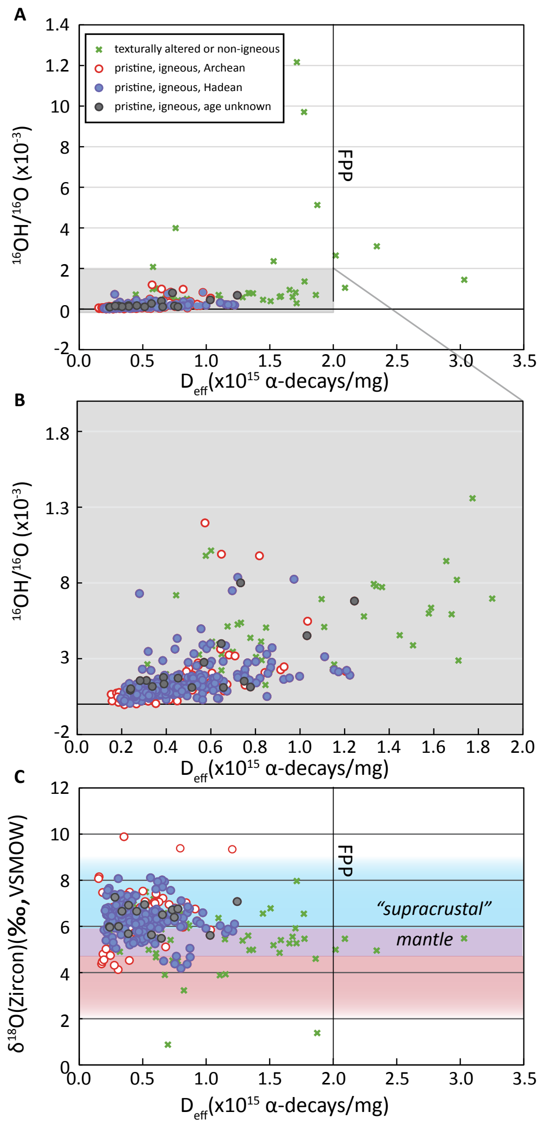

FIGURE 6. Correlated δ^{18}O, OH/O (background corrected), and D_{eff} for zircon. In all plots, D_{eff} is the average for all FWHM measurements surrounding each respective SIMS δ^{18}O pit. (**a**) Plot showing OH/O vs. D_{eff} for all data within the study. (**b**) Enlarged view of gray rectangle in **a** showing most data at low D_{eff} and low OH/O. (**c**) Plot of δ^{18}O(Zrn) vs. D_{eff} [all data, n = 417; open circles (Archean), n = 77; filled circles (Hadean), n = 220; undated, n = 17]. FPP = first percolation point.

as a whole and whether careful pre-screening reliably identifies unaltered zircon domains (e.g., Cavosie et al. 2019).

Raman data in this study place robust constraints on the radiation damage history of JHD grains. Regional metamorphism of the Jack Hills metasediments presumably caused complete annealing at ca. 2600 Ma (Rasmussen et al. 2010). Thermal events are also proposed to have induced widespread annealing within the Jack Hills zircons between 1000 and 830 Ma (e.g., Olierook et al. 2019). Complete annealing at 1000–830 Ma would heal much of the total damage (D_{total} in Fig. 5a) and is broadly consistent with the minimum amount of time necessary to generate the effective doses observed in this study (D_{eff}, Figs. 5a and 6; Online Materials[1] Appendices C and D). Assuming no more recent annealing, the present-day damage states (measured D_{eff}) represent the full dose that has accumulated since ca. 1000 Ma. Given that none of the oxygen isotope domains analyzed in this study have damage states (D_{eff}) exceeding the first percolation point, these zircons would have been highly resistant to alteration and recrystallization during the Neoproterozoic and Phanerozoic.

The uniformity of effective doses <1.2 × 10^{15} α-decays/mg in our data is particularly relevant to published proposals for aqueous alteration of JHD zircons. Cenozoic weathering has been invoked to explain both U-Th-Pb discordance and elevated δ^{18}O values in the Jack Hills zircons (e.g., Pidgeon et al. 2017). This correlation is strong for zircons with high degrees of radiation damage, however, the low measured damage states for zircons in Figures 5 and 6 show that radiation damage could not have created fast pathways for recent (i.e., Cenozoic) fluid-mediated oxygen exchange in the zircons of this study. This is consistent with previous interpretations that measured δ^{18}O values in carefully screened zircons, including mildly elevated values up to ~8‰, record primary isotope ratios and chemical compositions. Likewise, Pidgeon et al. (2017) concluded that a subset of their zircons with low-[U] and low-[Th] (Group 1) record primary δ^{18}O values, and they did not find elevated δ^{18}O above the mantle range in this group. Our study, with a much larger sampling of low-dose grains, demonstrates that: (1) existing protocols that utilize multiple lines of evidence, textural and chemical indicators, can effectively identify, and allow researchers to avoid, regions of radiation damage and alteration (e.g., Cavosie et al. 2004; Wang et al. 2014), and (2) the unaltered Hadean JHD zircon suite in this study records primary δ^{18}O values, many of which are mildly elevated above the mantle range, with ages that extend to before 4300 Ma (e.g., Cavosie et al. 2019).

Modeling Paleo-radiation damage

Present-day measurements of effective dose are uniformly less than total dose (Fig. 5a), which shows that annealing has occurred but does not indicate when. The history of accumulation and annealing of radiation damage in JHD zircons prior to the Neoarchean is only partially defined. The wide range of magmatic ages from ca. 3100 to 4400 Ma indicate multiple magmatic events, consistent with known rocks younger than 3700 Ma in the Narryer Gneiss Terrane. Possibly, these younger magmas annealed older zircons. Such heating is documented in JHD zircons where younger overgrowths are identified by CL and dated by U-Pb. For instance, zircon JH4.4 (01JH-36-69, Fig. 1a) has a core dated at 4374 Ma and a ~3400 Ma rim (Valley et al. 2014). Atom probe tomography demonstrates annealing in the core of this zircon and that the SIMS ages are not compromised. Annealing at ~1000 Ma may have overprinted evidence of prior annealing.

Raman measurements place constraints on levels of radiation damage in JHD zircons during the Hadean, Archean, and early- to mid-Proterozoic. This is particularly true for the JHD grains, which share the same thermal history after sedimentary deposition at ~3000 Ma. However, pre-depositional histories can vary from grain to grain. Early thermal episodes, when rates of radiation damage are highest, can have a dramatic influence on the maximum damage a given grain experiences at specific times in its history (e.g., Valley et al. 2014). This is investigated for zircons in this study by modeling damage accumulation after crystallization, as well as annealing during specific time points.

We model the accumulation of radiation damage through time for each SIMS U-Pb analysis accounting for up to two complete annealing events: during thermal activity at ~1000 Ma (Pidgeon 2014; Olierook et al. 2019) and during regional metamorphism at ~2600 Ma (Rasmussen et al. 2010). Three different annealing scenarios are compared (Fig. 7): (Model 1) no annealing since crystallization (Fig. 7a), (Model 2) complete annealing at both 2600 and 1000 Ma (Fig. 7b), and (Model 3) continuous annealing prior to 2600 Ma in which 50% of damage is retained, complete annealing at 2600 Ma, continuous annealing from 2600 to 1000 Ma in which 75% of damage is retained, complete annealing at 1000 Ma, followed by complete damage retention (Fig. 7c). Model 1 is disproven by greenschist facies metamorphism of Jack Hills metasediments and shown only for comparison. Model 2 represents the minimum amount of annealing that is consistent with geologic evidence. The levels of annealing in Model 3 (Fig. 7c) are geologically reasonable but largely unconstrained, particularly as they apply to a detrital suite with disparate ages and pre-depositional histories. Many other scenarios are possible, including ones with more annealing before 1000 Ma. Despite uncertainties, these scenarios represent end-member thermal histories and are instructive in comparison to published data. The doses accumulated by each [U]-[Th]-age domain between crystallization, 2600, 1000, and 0 Ma are tabulated in Online Materials[1] Appendix C.

The black curves in Figure 7 represent the accumulating dose for primary zircons of this study. The red curves represent the zircons judged unreliable by independent measures. The number of grains that are modeled to possibly have accumulated $>2.0 \times 10^{15}$ α-decays/mg varies significantly between each annealing scenario, as does the amount of time (if any) spent above the first percolation-point threshold. In the geologically unrealistic Model 1 with no annealing between crystallization and the present (Fig. 7a), only 46% of the primary zircon domains would have stayed below 2.0×10^{15} α-decays/mg (in contrast to 100% in Fig. 5a), and only 9% of the discordant and texturally altered domains would be below this limit. As discussed above, the measured values of D_{eff} demonstrate that the end-member Model 1 does not apply to the JHD suite (see also Pidgeon 2014). In the case of Model 2 (complete annealing at 2600 and 1000 Ma and no other annealing), 76% of the primary zircon domains analyzed by SIMS would never have exceeded the first percolation point (Fig. 7b). However, this model results in some zircons with retained damage $>1.0 \times 10^{15}$ α-decays/mg at 0 Ma, which are not supported by Raman measurements of D_{eff} (Fig. 5a) indicating (not unreasonably) that there was additional annealing and thus that the Jack Hills metasediments were buried and heated above ~250 °C at some time between 1000 Ma and the present day. Based on these calculations, relatively limited amounts of additional annealing (25–50%) would be sufficient to keep all domains below the first percolation point throughout geologic time. As mentioned above, evidence exists for pre-2600 Ma annealing in some grains with magmatic overgrowths.

An alternative, more realistic scenario (Model 3) is shown in Figure 7c where 50% of damage is retained prior to 2600 Ma, 75% of damage is retained between 2600 and 1000 Ma, and 100% is retained after 1000 Ma. These are reasonable levels of partial annealing that would occur if zircons were buried and continuously (or episodically) heated to temperatures of 250–300 °C (Ewing et al. 2003). This scenario would result in 96% of the primary zircon domains staying below the first percolation point. These results are one of many scenarios consistent with the interpretation that a vast majority of JHD zircons within this study spent all their history below the first percolation point. In fact, it is likely that the primary zircons were more annealed than shown in Figure 7c and that none exceeded the first percolation-point threshold at any time in their history. It is, however, also likely that if Jack Hills zircons are selected at random, many (especially with higher concentrations of U and Th) will show higher levels of radiation damage and alteration.

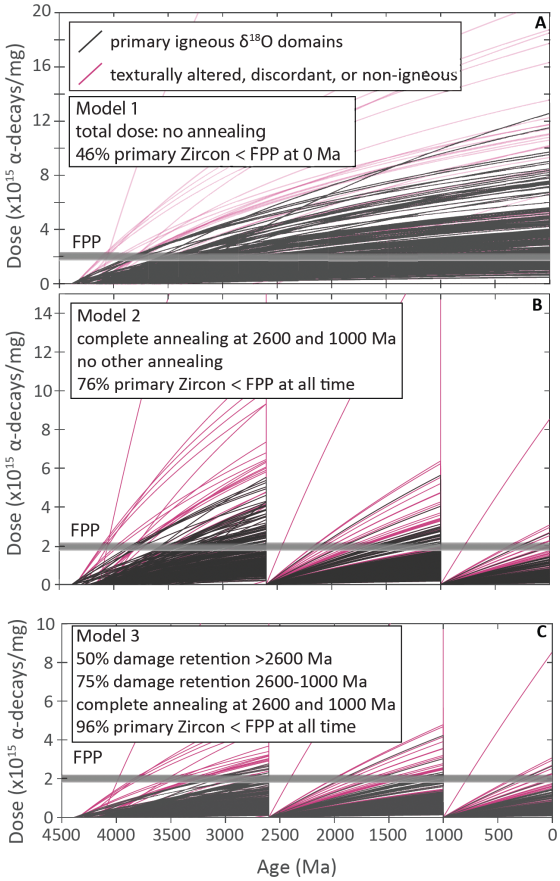

FIGURE 7. Summary of calculated maximum radiation damage accumulation for three annealing models (see text for details). Gray horizontal band at 2.0×10^{15} α-decays/mg shows the approximate location of the first percolation point (FPP).

Hadean zircons: $\delta^{18}O$ and OH/O

New data within this study allow close pairing of $\delta^{18}O$, OH/O, and Raman in Hadean zircons. The $\delta^{18}O$ values are in excellent agreement with previous measurements of these zircons (Cavosie et al. 2005) that were undertaken without measurement of OH/O. Ratios of OH/O are low ($<0.8 \times 10^{-3}$) in all the domains identified as preserving "primary" chemistry. Although the measured concentrations of OH are not quantitative, the measured values (Fig. 2) qualitatively suggest <<0.2 wt% H_2O in our zircons. Furthermore, there is no correlation of OH/O with age (Fig. 4), present-day radiation-damage state (D_{eff}, Figs. 6a and 6b), or $\delta^{18}O$ (Fig. 2). Thus, there is no indication that radiation damage has facilitated alteration of primary $\delta^{18}O$ values or hydration of these studied zircons. This assessment is the most quantitative demonstration to date, showing that $\delta^{18}O$ measurements of JHD zircons can preserve primary compositions.

These new results support previous proposals that, if carefully selected based on objective criteria, Jack Hills zircons can be identified that preserve primary unaltered $\delta^{18}O$ values representative of their growth in Hadean magmas (Fig. 8). This work also reinforces the utility of OH/O measurements by SIMS in assessing the potential for hydrous alteration and loss of primary $\delta^{18}O$ values. This approach can be applied to zircons of all ages but is a particularly important precaution for grains that have spent long periods of time at low temperatures, allowing accumulation of radiation damage followed by interaction with fluids.

These results provide a clear test and disprove the proposal that all Jack Hills zircons were altered by weathering and that all elevated $\delta^{18}O$ values are secondary. It is well established that Jack Hills zircons exist with high degrees of radiation damage, discordant ages, and altered oxygen isotope chemistry; however, the mildly elevated oxygen isotope ratios of 6 to 8‰ measured in Hadean zircons of this study (Fig. 8) are all in zircons with low ratios of OH/O and high degrees of crystallinity (D_{eff} below the first percolation point). If zircons are carefully selected by criteria described previously (Valley et al. 1994, 2005, 2015; Cavosie et al. 2004, 2005, 2006; Wang et al. 2014), they are likely to have low-OH/O ratios and to retain primary isotope and trace element compositions. There is no published evidence that Jack Hills zircons with low degrees of radiation damage are geochemically altered. The present data further demonstrate that the crystalline subset of the zircon population preserves reliable records of the Hadean Earth.

Implications

This study greatly expands the suite of Hadean zircon with sub-domains that have been evaluated for radiation damage and alteration by multiple tests. There are no other known materials from the first 500 Myr of Earth history. The compositions of Jack Hills detrital zircons allow far-ranging inferences about the early Earth. However, indiscriminate analysis of unscreened zircons will include many that are altered and can lead to spurious data and unjustified conclusions. The present study demonstrates that primary, well-preserved domains can be recognized by employing a range of standard methodologies even in zircons older than 4000 Ma.

There is little or no water in the analyzed domains in this study of 115 unaltered Hadean zircons, and there is no correlation of $\delta^{18}O$(Zrn) with age, OH/O, or radiation damage in this unaltered suite. These data disprove the hypothesis that mildly elevated $\delta^{18}O$ values in Hadean zircons result from alteration.

The Hadean zircon data helps constrain important, long-standing, and contentious questions on Early Earth relating to the interaction of the crust/mantle/hydrosphere/atmosphere/(biosphere?)/(extraterrestrial?) system. When did the first continental crust form? Was subduction or plate tectonics active in the Hadean? When were liquid water oceans formed from a steam atmosphere? When did Earth become habitable to life? The mildly elevated primary values of $\delta^{18}O$ in Hadean zircons from the Jack Hills support previous proposals that parent magmas for these zircons represent hydrous proto-continental crust, the surface of early Earth cooled and had liquid-water oceans before 4300 Ma, and conditions were habitable for life 800 Myr before the oldest known microfossils. The implications of these discoveries, in combination with other studies of the geochemistry of Hadean zircons and their inclusions, will continue in the future to add to our understanding of the earliest history of our planet.

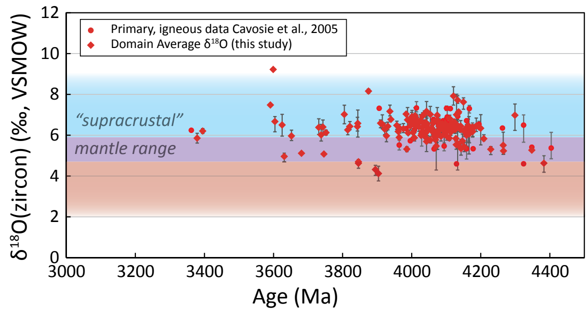

Figure 8. Summary of $\delta^{18}O$ and age for dated domains within this study and Cavosie et al. (2005). Data points represent the domain average $\delta^{18}O$ within individual zircons correlated to dated domains. Error bars show range in $\delta^{18}O$ for each domain.

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Endnote:

[1]Deposit item AM-24-109180. Online Materials are free to all readers. Go online, via the table of contents or article view, and find the tab or link for supplemental materials.