



Recovering the primary geochemistry of Jack Hills zircons through quantitative estimates of chemical alteration

Elizabeth A. Bell^{*}, Patrick Boehnke, T. Mark Harrison

Dept. of Earth, Planetary, and Space Sciences, University of California, Los Angeles, Los Angeles, CA 90095, United States

Received 24 September 2015; accepted in revised form 12 July 2016; available online 19 July 2016

Abstract

Despite the robust nature of zircon in most crustal and surface environments, chemical alteration, especially associated with radiation damaged regions, can affect its geochemistry. This consideration is especially important when drawing inferences from the detrital record where the original rock context is missing. Typically, alteration is qualitatively diagnosed through inspection of zircon REE patterns and the style of zoning shown by cathodoluminescence imaging, since fluid-mediated alteration often causes a flat, high LREE pattern. Due to the much lower abundance of LREE in zircon relative both to other crustal materials and to the other REE, disturbance to the LREE pattern is the most likely first sign of disruption to zircon trace element contents. Using a database of 378 (148 new) trace element and 801 (201 new) oxygen isotope measurements on zircons from Jack Hills, Western Australia, we propose a quantitative framework for assessing chemical contamination and exchange with fluids in this population. The Light Rare Earth Element Index is scaled on the relative abundance of light to middle REE, or $LREE-I = (Dy/Nd) + (Dy/Sm)$. LREE-I values vary systematically with other known contaminants (e.g., Fe, P) more faithfully than other suggested proxies for zircon alteration (Sm/La, various absolute concentrations of LREEs) and can be used to distinguish primary compositions when textural evidence for alteration is ambiguous. We find that zircon oxygen isotopes do not vary systematically with placement on or off cracks or with degree of LREE-related chemical alteration, suggesting an essentially primary signature. By omitting zircons affected by LREE-related alteration or contamination by mineral inclusions, we present the best estimate for the primary igneous geochemistry of the Jack Hills zircons. This approach increases the available dataset by allowing for discrimination of on-crack analyses (and analyses with ambiguous or no information on spot placement or zircon internal structures) that do not show evidence for chemical alteration. It distinguishes between altered and unaltered samples in ambiguous cases (e.g., relatively high Ti), identifying small groups with potentially differing provenance from the main Jack Hills population. Finally, filtering of the population using the LREE-I helps to more certainly define primary correlations among trace element variables, potentially relatable to magmatic compositional evolution.

© 2016 Elsevier Ltd. All rights reserved.

Keywords: Zircon; Hadean; Early Earth; Rare earth element; Trace element

1. INTRODUCTION

Detrital zircons from Jack Hills, Western Australia range up to nearly 4.4 Ga in age and record an abundance

of geochemical information about the crust during Earth's first few hundred million years (Holden et al., 2009; Harrison, 2009). High $\delta^{18}O$ among some zircons has been interpreted as evidence for low-temperature rock–water interactions during this time (e.g., Mojzsis et al., 2001; Peck et al., 2001; Harrison et al., 2008), and low average Ti-in-zircon crystallization temperatures (T^{zln}) suggest near

^{*} Corresponding author.

E-mail address: ebell21@ucla.edu (E.A. Bell).

granitic minimum melting conditions for the source magmas of the zircons (Watson and Harrison, 2005). The granitic primary mineral inclusion suite, dominated by quartz and muscovite (Hopkins et al., 2008, 2010; cf. Rasmussen et al., 2011; Bell et al., 2015b), further supports granitic source rocks for the zircons. Their relatively unradiogenic Lu-Hf systematics have been interpreted as indicating continental-like material in the source throughout the Hadean (>4 Ga) eon (e.g., Harrison et al., 2005, 2008; cf. Kemp et al., 2010; Bell et al., 2014) and among the more numerous younger zircons (e.g., Amelin et al., 1999; Bell et al., 2011).

Zircon incorporates many petrologically useful minor and trace elements, such that they are a potentially rich yet currently underexploited source of petrologic information on Earth's first few hundred million years. However, the extent to which chemical alteration may have obscured the primary chemistry of the Jack Hills population, and thus its implications for the Hadean, has been a source of controversy. Although many studies have used the trace element contents of the zircons to argue for various igneous or metamorphic origins (e.g., Peck et al., 2001; Crowley et al., 2005; Watson and Harrison, 2005; Cavosie et al., 2006; Coogan and Hinton, 2006; Grimes et al., 2007; Bell and Harrison, 2013), some aspects of zircon trace element chemistry are susceptible to chemical alteration during metamorphism or metasomatism (e.g., Hoskin, 2005 for Jack Hills zircons; Vavra et al., 1999; Hoskin and Black, 2000; Hoskin and Schaltegger, 2003 for zircon in general). For instance, hydrothermally altered zircon often shows a high, flat light rare earth element (LREE) pattern relative to the normal, high ratios of the heavy rare earth elements (HREE) to the LREE in magmatic zircons (e.g., Hoskin and Schaltegger, 2003). Such apparently altered LREE patterns are seen among a minority of Jack Hills zircons (Maas et al., 1992; Peck et al., 2001; Hoskin, 2005; Cavosie et al., 2006), prompting Hoskin (2005) to ascribe them to hydrothermal alteration rather than to high LREE contents among Hadean magmas. Cavosie et al. (2006) attributed similar high-LREE patterns among a minority of zircons to alteration processes other than hydrothermal, given their lack of correlation with anomalous $\delta^{18}\text{O}$. They instead attributed such patterns to contamination by phosphate inclusions or local LREE enrichment at very low water/rock ratios in radiation-damaged regions.

It is known that a variety of metamorphic events affected the ca. 3 Ga host conglomerate of the Jack Hills zircons and its surrounding environs during the Archean and Proterozoic (e.g., Myers, 1988a,b), with several recognized chemical effects on the zircons themselves and their host rocks (e.g., Rasmussen et al., 2011; Pidgeon, 2014). Metasediments at the Jack Hills discovery site fail the paleomagnetic conglomerate test, indicating that they were remagnetized after deposition (Weiss et al., 2015; cf. Tarduno et al., 2015). In addition to Archean and Proterozoic metamorphic events (Myers, 1988a,b; Fletcher et al., 1988), granitoids intruded the region at ca. 3.0 and 2.6 Ga (Myers, 1988a,b; Spaggiari et al., 2007) along with a phase of volcanism at 1.8 Ga (Wilde, 2010), and mafic dikes associated with the Marnda Moorn and Warrakurna Large

Igneous Provinces intruded the region at ca. 1.2 Ga (Spaggiari et al., 2007). Any of these tectonothermal events could potentially create conditions conducive to zircon alteration.

Many Jack Hills zircons contain cracks which are associated with higher Ti and Fe contents relative to the magmatic zircon lattice (Harrison and Schmitt, 2007) and appear to contain slightly lower $\delta^{18}\text{O}$ values (Trail et al., 2007). Cracks in the zircons are often mineralized (Rasmussen et al., 2011; Caro et al., 2008; Bell et al., 2015b), with the dominant phases being quartz, xenotime, Fe oxides, muscovite, and minor monazite (Bell et al., 2015b). These phases are common in the host metaconglomerate (Rasmussen et al., 2010, 2011). Some but not all inclusions in contact with cracks in the zircons have been altered by fluid ingress over geologic time (Bell et al., 2015b). It has so far been unclear, however, to what extent these crack-related zones of alteration may affect the Jack Hills zircon geochemical record as a whole and to what extent the zircons may indeed retain their primary igneous chemistry.

To address these issues, we present a database of published and new trace element and oxygen isotope compositions on a variety of Jack Hills zircon samples with U–Pb dates from 4.2 to 2.2 Ga which range from uncracked and magmatically zoned to highly cracked and/or metamict grains. We investigate the relationship of various trace element concentrations and $\delta^{18}\text{O}$ values to likely alteration features such as cracks, metamict regions, or disrupted zoning as shown by cathodoluminescence (CL) in order to define quantitative estimates for the degree and mechanisms of chemical alteration of Jack Hills zircons, and potential structural markers for such alteration.

2. TRACE ELEMENTS IN ZIRCON

Considerable effort has been expended in developing various aspects of zircon trace element chemistry as proxies for the conditions of zircon formation or for discriminating the provenance of detrital zircons. Several trace element contents and ratios in zircon are quantitative proxies for useful properties of magmas, including the Ti content as a proxy for crystallization temperature (Watson and Harrison, 2005; Ferry and Watson, 2007) and Ce/Ce* as a proxy for f_{O_2} (Trail et al., 2011). Other trace element concentrations and ratios, especially of the rare earth elements (REE), provide less certain and less quantitative information about igneous zircon origins. They may record useful information about magmatic compositional evolution or source region (e.g., cf. Hoskin et al., 2000; Claiborne et al., 2010; Barth et al., 2013). Their usefulness as provenance indicators is a subject of debate (e.g., Hoskin and Ireland, 2000; Belousova et al., 2002). However, in order to properly assess the potential of trace element chemistry as a discriminant of zircon provenance, it must first be established that the effects of later alteration can be distinguished from the original chemistry of the zircon as inherited from the magma (hereafter, 'primary chemistry').

Although normally robust, under certain circumstances zircons can be chemically altered. Damage to or

amorphization of the zircon crystal structure is a common factor, as radiation-damaged zircon will often swell progressively with accumulating damage. This may allow permeation by fluids, with consequent chemical alteration (e.g., Geisler et al., 2003a) and disturbance to the U–Pb system (Mezger and Krogstad, 1997). Swollen metamict regions may also cause the formation of cracks in surrounding, less U-rich zircon, allowing fluid ingress, as demonstrated at Jack Hills by the evidence for crack mineralization (Rasmussen et al., 2011; Harrison and Schmitt, 2007; Caro et al., 2008; Bell et al., 2015b). This process can lead to chemical alteration of metamict regions in the zircon or, in the case of mineralized cracks, contaminate in situ analyses which sample both pristine zircon and material residing in cracks due to accidental overlap. Recrystallization in the solid state may also occur under high-temperature metamorphism and result in some redistribution of trace elements within the zircon (e.g., Hoskin and Black, 2000), although not necessarily effecting exchange between zircon and the surrounding geologic environment. In this paper we will focus on the effects of contamination by and exchange with external fluids, as these processes likely affect zircon across a larger range of geologic settings than solid-state recrystallization.

Exposure to hydrothermal fluid may result in chemically altered zircon (Geisler et al., 2003a,b) or in replacement of the zircon by other phases such as zirconolite, various REE-phosphates, carbonates, oxides, and hydroxides (Gieré, 1996). Hydrothermal alteration of zircon commonly results in enrichments in LREE and various other incompatible elements, along with light elements such as Ca, Al, and Fe (Hoskin and Schaltegger, 2003; Geisler et al., 2003b; Hoskin, 2005; Yang et al., 2014), and a loss of REE, U, Th, and other heavy trace elements (Geisler et al., 2003a; Hoskin and Schaltegger, 2003). In addition, some studies of metamorphic zircon have also proposed effects of aqueous chemical alteration. Vavra et al. (1999) document CL-bright secondary features cross-cutting primary igneous zoning within altered zircons, and interpret them as resulting from fluid-related alteration and exchange of various trace elements. As an additional consideration, the diffusivity of oxygen in zircon is orders of magnitude higher in the presence of water, potentially leading to oxygen isotope exchange during fluid-related alteration (Watson and Cherniak, 1997).

3. MATERIALS AND METHODS

We combined new SIMS data for U–Th–Pb systematics, trace elements, and oxygen isotopes with literature data for Jack Hills zircons to assess relationships with microstructures ranging from likely pristine to clearly altered. Ion microprobe measurement craters were imaged via SEM and classified into those falling on cracks or obvious inclusions and those falling on uncracked and apparently inclusion-free regions of the host zircon. We chose this textural approach due to previous evidence for alteration of the zircons along cracks (e.g., Trail et al., 2007; Harrison and Schmitt, 2007). Cathodoluminescence (CL) imaging using a Tescan Vega 3 with a 3-channel color CL detector was

used to determine the type of zoning in regions sampled by SIMS measurements. We categorize the degree of CL alteration into the categories *Magmatic*, *Altered* (any potential former magmatic zoning obliterated), *Altered Magmatic* (magmatic zoning still recognizable but clearly altered in certain regions, e.g. blurring of originally fine oscillatory zoning or patches of faded zoning), and *Ambiguous* (showing no clear zoning; often homogeneous and CL-inactive) after the classification scheme of Bell et al. (2014). Samples are further grouped largely by the apparent style of altered zoning observed. This includes “patchy” structures (e.g., Corfu et al., 2003; irregular zoning subdividing the grain into smaller regions), faded/blurred/darkened magmatic zoning (e.g., broadening or fading of oscillatory zoning), and cloudy or hazy zoning (zoning indistinct in a bright and somewhat diffuse luminescence). We also include in the *Altered* category bright, sometimes cross-cutting features similar to those which have been interpreted as fluid-related alteration in other settings (e.g., Vavra et al., 1999). We use “patchy” as the default category for alteration as it is the most common type among our sample set as well as in the literature data we draw from. Grains with various types of alteration are put into the “patchy” category. *Ambiguous* grains are mostly homogeneous, and homogeneous grains are usually CL inactive. *Magmatic* zoning includes unaltered oscillatory zoning (e.g., Corfu et al., 2003). Sector zoning is also characteristic in many magmatic settings, but we use oscillatory zoning as the benchmark due to the lesser chance of mistaking it for another zoning style, particularly in broken zircons. Examples of the alteration microstructures used for our classifications are shown in Fig. 1. Literature data, including U–Pb age, multicollector oxygen isotope, and trace element results, were combined from a variety of sources which report the relationship of analysis spots to zoning style and/or cracks (Cavosie et al., 2004, 2005, 2006; Trail et al., 2007; Bell and Harrison, 2013; Bell et al., 2014, 2015a) and those which did not report these relationships (Peck et al., 2001; Crowley et al., 2005; Harrison et al., 2008; Bell et al., 2011). We use those analyses from regions containing various potential alteration features (cracks, zoning) to assess chemical markers for alteration. Since omitting analyses with uncertain placement may in many cases involve ignoring a large amount of data, we later evaluate these data by the same chemical markers to assess whether they can also be used for reconstructions of the primary zircon chemistry. All data may be viewed in the [Supplementary materials Tables EA-1 through EA-3](#).

3.1. Samples and CL zoning styles

The majority of data come from zircons taken from a ca. 3 Ga conglomeratic quartzite at the discovery site (Compston and Pidgeon, 1986). These samples constitute the most studied population at Jack Hills and are hereafter referred to as “discovery site zircons”. In the [Supplementary data Tables EA-1 through EA-3](#), all samples except those beginning with the designation “JHC2” are from this population. This population consists of typically rounded, translucent, colorless to deep red grains up to several

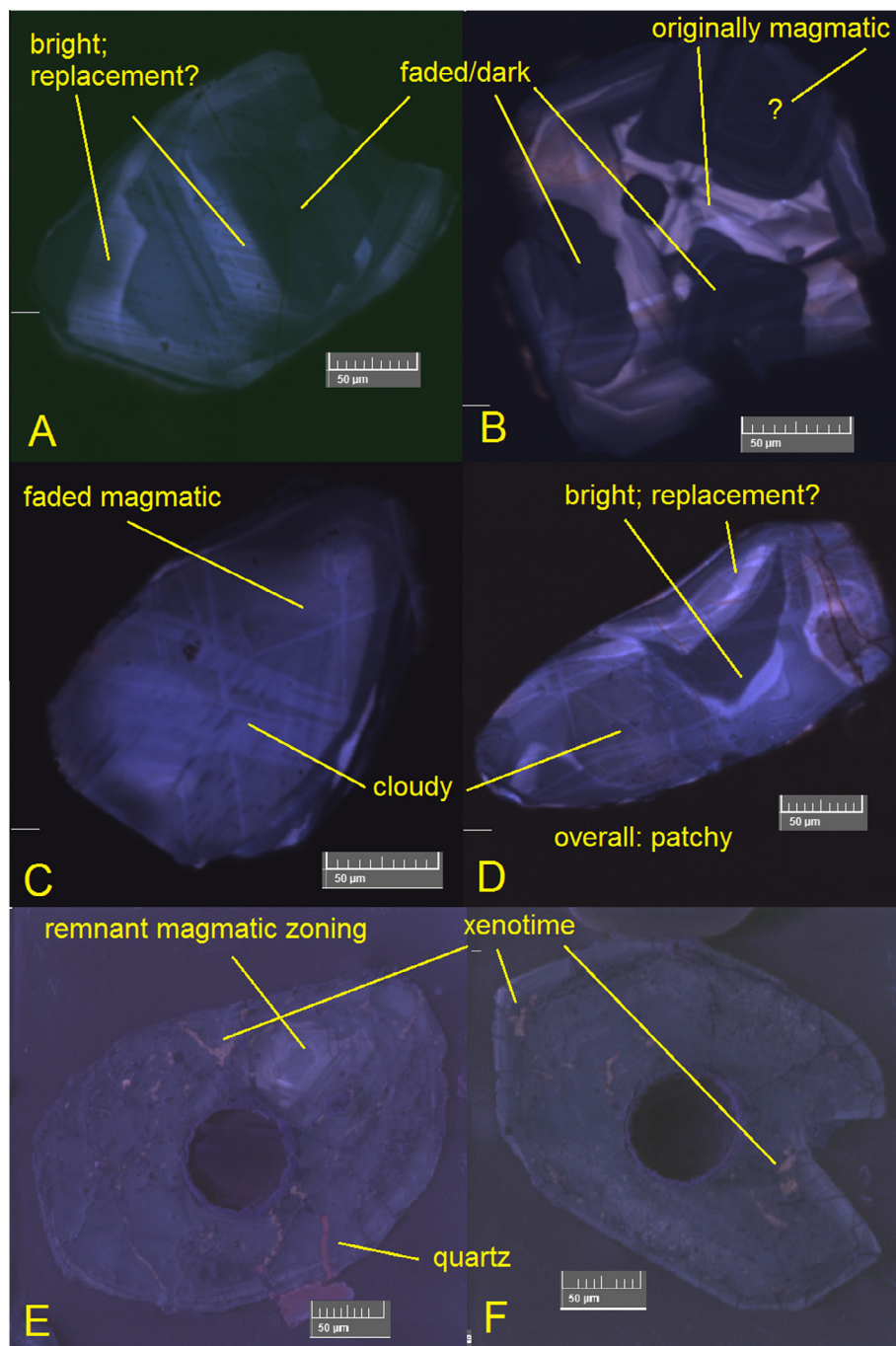


Fig. 1. Cathodoluminescence (CL) images of zircons showing examples of alteration features and remnant magmatic zoning. (A–D) discovery site zircons; (E–F) yellow series zircons. Samples shown are (A) RSES 82-5.14, (B) RSES 80-2.8, (C) RSES 82-15.19, (D) RSES 82-14.11, (E) JHC 2-2.5, and (F) JHC 2-4.5. Note dark CL, overprinted or absent magmatic zoning, and pervasive mineralization of yellow-series metamict zircons. Scale bars in each panel are 50 µm. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

hundred microns in their longest dimension. They range in age ca. 4.4–3.0 Ga, with a major age peak at ca. 3.4 Ga and a minor age peak at ca. 4.1 Ga (e.g., Holden et al., 2009). In addition to zircons from the discovery outcrop, we include zircons from a nearby metasediment (JHC2; [Supplementary Tables EA-2 and EA-3](#)) which are similar in size and

rounding to the discovery site zircons but largely opaque and yellow–brown. Like the discovery site zircon, these yellow zircons were separated using standard heavy liquid separation, with the exception that they were not subject to magnetic separation. Cathodoluminescence imaging reveals remnant magmatic zoning in several of these grains,

although it has been obliterated in many (see Fig. 1). Mineral inclusions are far more numerous among this population and commonly consist of quartz and xenotime. Because of their dominant coloring, this sample set is hereafter referred to as “yellow series” zircons. Age (EA-3) and trace element contents (EA-2) are reported for both discovery site and yellow series zircons. Oxygen isotope measurements are reported only for discovery site zircons (EA-1).

3.2. 210n microprobe analyses

All ion microprobe analyses were undertaken on the CAMECA *ims1270* ion microprobe at UCLA. U–Th–Pb dating was accomplished using a ca. 15 nA O[−] primary beam focused to a ca. 30 μm spot (e.g., Mojzsis et al., 2003). We used zircon age standard AS3 (1099 ± 1 Ma, *Paces and Miller, 1993*). We measured trace elements including Ti, Fe, Y, REE, Hf, Th, and U using a ca. 15 nA O[−] primary beam focused to a ca. 30 μm spot. A −100 V offset in the sample high voltage was used to suppress molecular interferences. Instrumental mass fractionation and relative sensitivity factors for various elements were determined using standard glass NIST 610 with additional comparison to the 91500 standard zircon (e.g., *Wiedenbeck et al., 2004*) for accuracy. The use of NIST 610 glass allows for the standardization of all studied trace elements except for Fe, since there is a potentially unresolved interference of ⁴⁰CaOH⁺ at mass ⁵⁷Fe. We therefore present estimated Fe concentrations for zircons as Fe*. Oxygen isotopes were measured in multicollection mode with a ~2 nA Cs⁺ primary beam focused into a ~20 μm spot. For more details on the analytical method see *Trail et al. (2007)*. The AS3 zircon standard (5.34‰; *Trail et al., 2007*) was used for sample-standard comparison.

4. RESULTS

We present 201 new oxygen isotope analyses on Jack Hills discovery site zircons, along with 600 published analyses (see Table EA1). In addition, we present 148 new trace element analyses on Jack Hills zircons, along with 230 published analyses (see Table EA2). U–Pb isotopic data for newly dated grains are shown in Table EA3. Yellow-series and discovery site zircons are distinguished in Tables EA-2 and EA-3 and in Figs. 2–6. Results for crack-free and crack-intersecting analyses among the discovery site zircons, as well as yellow series samples, are shown separately in Figs. 2–4. We do not at this time include those analyses on discovery site zircons with uncertain spot placement with respect to cracks or other features (either from this study or previous studies) in Figs. 4–6 so as not to obscure potential microstructural origins of variations in trace chemistry. Yellow series zircons are similar enough in chemistry and SEM imaging reveals nearly universally disrupted, highly cracked surfaces (see e.g. Fig. 1E, F) such that we consider them as one group regardless of microstructural features. For most trace element variables there is considerable overlap among the analyses on crack-free surfaces, those falling on cracks, and those on the yellow series grains (see Figs. 2–4). However, despite the many similarities, the on-crack versus crack-free

discovery site zircon analyses differ significantly (using the Mann–Whitney *U* test, a nonparametric statistical test for whether two samples come from the same population) in several trace element variables: P, LREE/HREE (as shown by Nd/Yb), T^{xln}, Fe, HREE/MREE (shown by Yb/Gd), and U. Certain signals are seen mainly or exclusively among the crack-intersecting measurements: high P (>1000 ppm), high LREE/HREE (Nd/Yb > 0.01), high Ti (>900 °C apparent T^{xln}), high Fe (>1000 ppm), and low HREE/MREE (Yb/Gd < 10). Analysis spots on cracks and uncracked but CL-altered regions in the discovery site zircons are slightly more likely to show high Th/U, low Ce/Ce*, and low δ¹⁸O, but these differences are not statistically significant. Each of the aforementioned trace chemistry differences is also seen between the crack-free and yellow-series analyses, with the exception that the Mann–Whitney *U* test shows the differences to be significant even for Th/U and Ce/Ce*. Y and HREE contents are similar between on-crack and crack-free analysis spots. Comparison of yellow-series and discovery site zircons on Figs. 3–6 reveals that many of the differences between the cracked and uncracked discovery site analyses also hold for yellow-series versus uncracked discovery site zircons: yellow-series grains are more likely to show higher P, LREE/HREE, Ti, Fe, and low HREE/MREE. They also tend to be higher in Y and HREE contents than discovery site zircons regardless of spot placement. Yellow series zircons are on average higher in U, and range up to 20,000 ppm U. Based both on their U contents and their highly disrupted microstructures they are most likely metamict. U above 1000 ppm is only seen among crack-intersecting analyses in discovery site zircons. Among most analyses, Nd/Yb correlates directly with P and inversely with Ce/Ce*, while T^{xln} correlates with Fe (and also Mn, although this is not shown on Fig. 4). Sm/La varies between ~1 and 1000 (Fig. 4E, F). Among cracked and metamict analyses Sm/La varies inversely with the other likely alteration signals of P and Fe, but there is little evidence of a relationship between these variables among crack-free analysis spots at similar Sm/La values. Zircons vary between 2 and 11 ‰ in δ¹⁸O_{SMOW}.

Crack-free analyses falling in regions of different CL zoning (see Fig. S3 of Electronic Annex EA4) show few chemical distinctions by group, with the exception that regions characterized by bright features are typically low in U and that dark, homogeneous regions are typically low in T^{xln} and high in U and Hf (similar to the observations of *Bell and Harrison, 2013* for their study specifically of ca. 3.9 Ga zircons).

5. DISCUSSION

Jack Hills zircons display a variety of geochemical signatures potentially related to alteration, magmatic compositional evolution, or distinct provenances. Although δ¹⁸O does not differ significantly between cracks and uncracked surfaces, several trace element concentrations and ratios show distinct trends among the cracked, uncracked, and yellow-series populations. However, the significant overlap in the ranges of many elemental concentrations and ratios

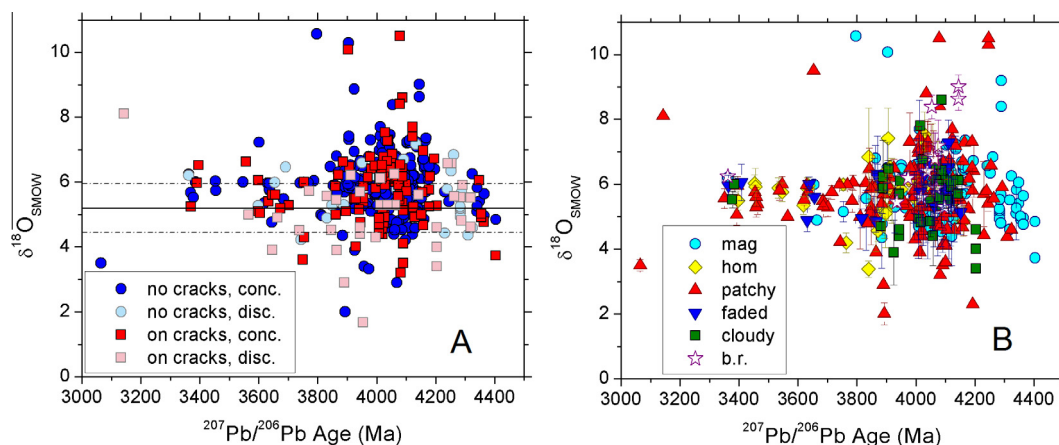


Fig. 2. $\delta^{18}\text{O}$ vs. age for Jack Hills zircons. (A) By relationship to cracks and U–Pb discordance. Mantle-derived zircon values shown in panel (A) (solid line: average; dashed lines: $\pm 1\sigma$). “Conc.” = $\leq 10\%$ discordant; “Disc.” = $> 10\%$ discordant. (B) By relationship to CL zoning, undifferentiated by relationship to cracks. “Mag” = magmatically zoned; “hom” = homogeneous; “b.r.” = bright replacement.

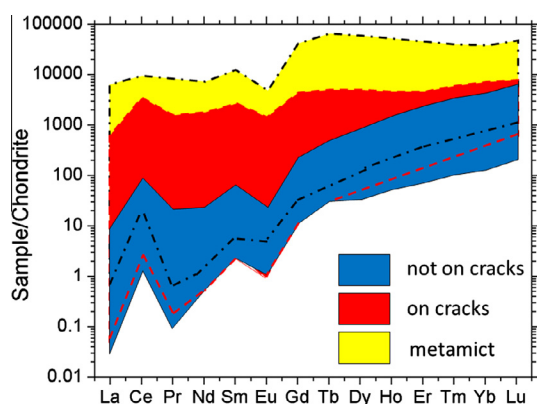


Fig. 3. REE plot fields for crack-free, on-crack, and metamict SIMS analysis spots on Jack Hills zircons.

between cracked and non-cracked regions suggests that discarding analyses for which the analysis spot overlaps cracks (e.g., Bell and Harrison, 2013) removes a significant amount of unaltered chemical data.

Deconvolving the primary trace element chemistry of zircons from alteration overprints and interpreting that data in terms of Hadean magma chemistry would be strengthened by knowing alteration signatures. Steep, primary REE patterns similar to the Type I patterns of Hoskin (2005) and Cavosie et al. (2006) are the most common and make up the vast majority of analyses not falling on cracked regions (see Fig. 3). High, flat-LREE patterns (Type II, Hoskin, 2005; Cavosie et al., 2006) are displayed by a small minority of analyses not falling on cracks but are more common among analyses on cracks and nearly universal for the yellow series zircons (see Fig. 3). We therefore focus on the LREE as an alteration indicator.

5.1. An LREE-based alteration index

High, flat LREE patterns are commonly associated with zircon alteration (e.g., Hoskin and Schaltegger, 2003;

Hoskin, 2005; Cavosie et al., 2006). This observation is consistent with the lower abundance (and opposite slope) of LREE in zircon compared to many other materials – for example, the average continental crust has a negative REE slope and varies between $85 \times$ chondritic for La and $27 \times$ chondritic for Sm (crust: Rudnick and Gao, 2003; chondrites: Anders and Grevesse, 1989), an order of magnitude or more above La contents often seen in primary zircon. Hoskin (2005) reported $(\text{Sm}/\text{La})_{\text{N}}$ values for hydrothermal zircon from the Boggy Plain Zoned Pluton of 1.5–4.4, contrasted with the values of 22–110 for magmatic zircon, demonstrating the relative LREE-flatness of hydrothermally altered zircon and the covariance of $(\text{Sm}/\text{La})_{\text{N}}$ with quantities such as Ce/Ce^* . Similarly, Cavosie et al. (2006) defined their altered “Type II” samples as those with chondrite-normalized $\text{La}_{\text{N}} > 1$ and $\text{Pr}_{\text{N}} > 10$, and observed that these were generally intermediate between Hoskin (2005)’s fields for magmatic and hydrothermal signatures.

Analyses on cracks and the yellow series Jack Hills zircons do show generally lower $(\text{Sm}/\text{La})_{\text{N}}$, but there is considerable overlap with the crack-free analyses such that a substantial number of crack-free analyses with otherwise magmatic trace element signatures (low U, low T^{XIIIn}) also display low $(\text{Sm}/\text{La})_{\text{N}} < 10$ (below the magmatic range suggested by Hoskin (2005)) and have variable La and Pr contents. Along with the similar ranges of Sm/La among on-crack and crack-free analyses, differing trends of on-crack and crack-free analyses at similar low Sm/La (on-crack analyses trending toward higher P and Ti contents with lower Sm/La, and no obvious trend among the crack-free analyses; Fig. 4C,D) suggests that Sm/La is an ambiguous signal of alteration and thus microstructural context is needed to appropriately interpret it. By contrast, all three categories display similar trends between La and Ti or P (Fig. 4A, B), although the on-crack and yellow-series analyses do trend toward higher overall La contents. Similar behavior is seen in plots of Nd/Yb vs. Ti (Fig. 4E), with the on-crack and yellow-series analyses again trending toward higher Nd/Yb.

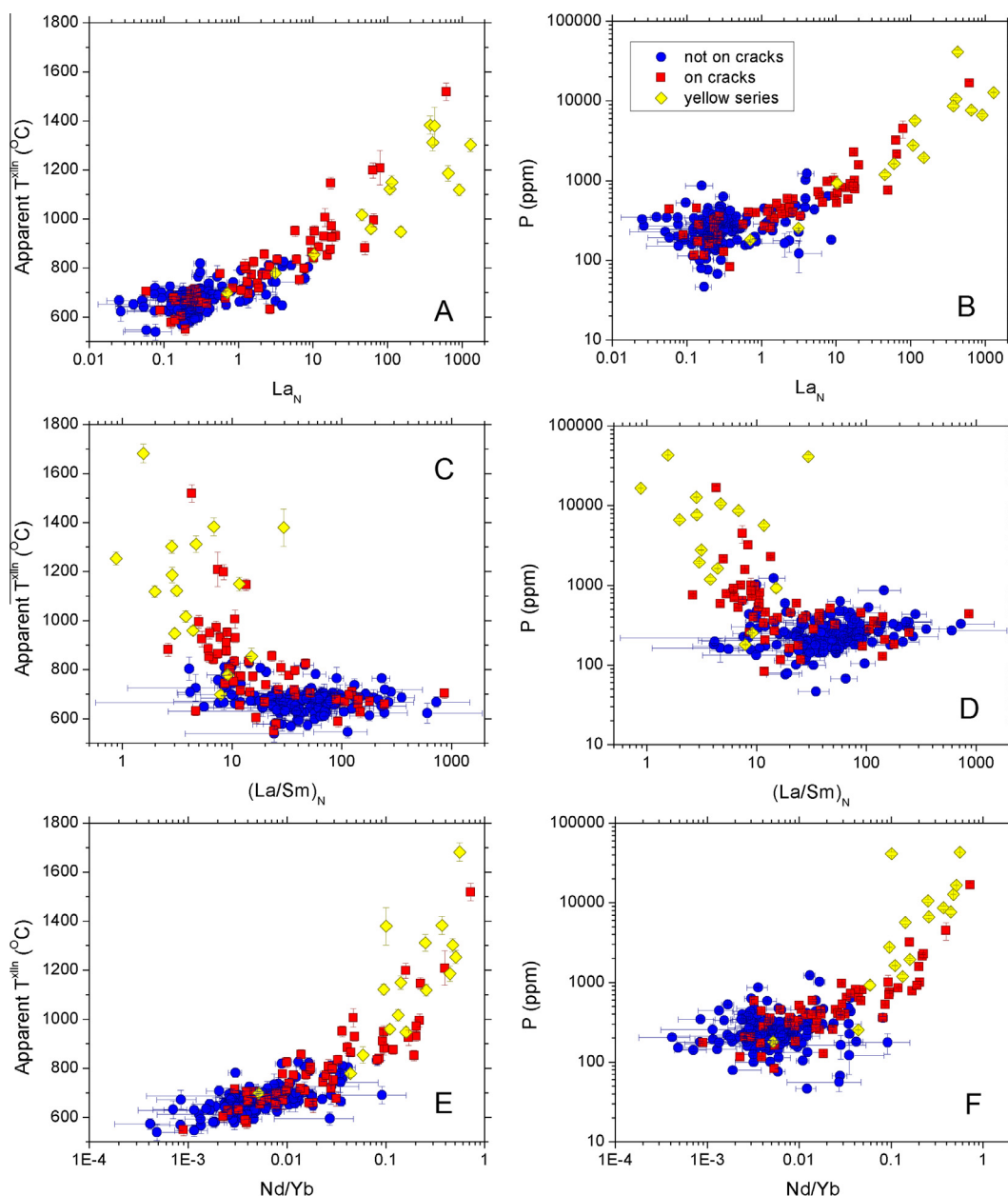


Fig. 4. Various trace element quantities and their variation among the crack-free, on-crack, and yellow series analysis spots. (A) apparent T^{xlin} vs. La_N ; (B) P vs. La_N ; (C) apparent T^{xlin} vs. $(Sm/La)_N$; (D) P vs. $(Sm/La)_N$; (E) apparent T^{xlin} vs. Nd/Yb; (F) P vs. Nd/Yb. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

Given these results coupled with the potential for a range in overall primary REE contents among zircons of differing provenance, the relative abundance of LREE versus the other REE is the preferred predictor for the other aspects of chemical alteration (high Ti, P) identified among the zircons. Since separate processes may change the HREE/MREE slope in zircon as a primary magmatic effect (e.g., Claiborne et al., 2010; Barth et al., 2013) and Yb/Gd varies among our microstructural categories, comparing the LREE to an element intermediate between Yb and Gd in ionic radius may help to avoid the effects of other processes. We propose a simple Light Rare Earth

Element Index for hydrothermal alteration and contamination (LREE-I) defined by $LREE-I = (Dy/Nd) + (Dy/Sm)$.

Of the LREE, only Sm and Nd are used in the calculation in order to decrease the uncertainties associated with Ce's f_{O_2} dependency and the typical very low abundances of La and Pr. Dy is chosen as a relatively abundant MREE intermediate between Yb and Gd. Nonetheless, LREE-I variants using Gd or Yb instead of Dy correlate well with the LREE-I over most of its range except at very low (altered) values in the Jack Hills population (see Fig. S5 in EA4).

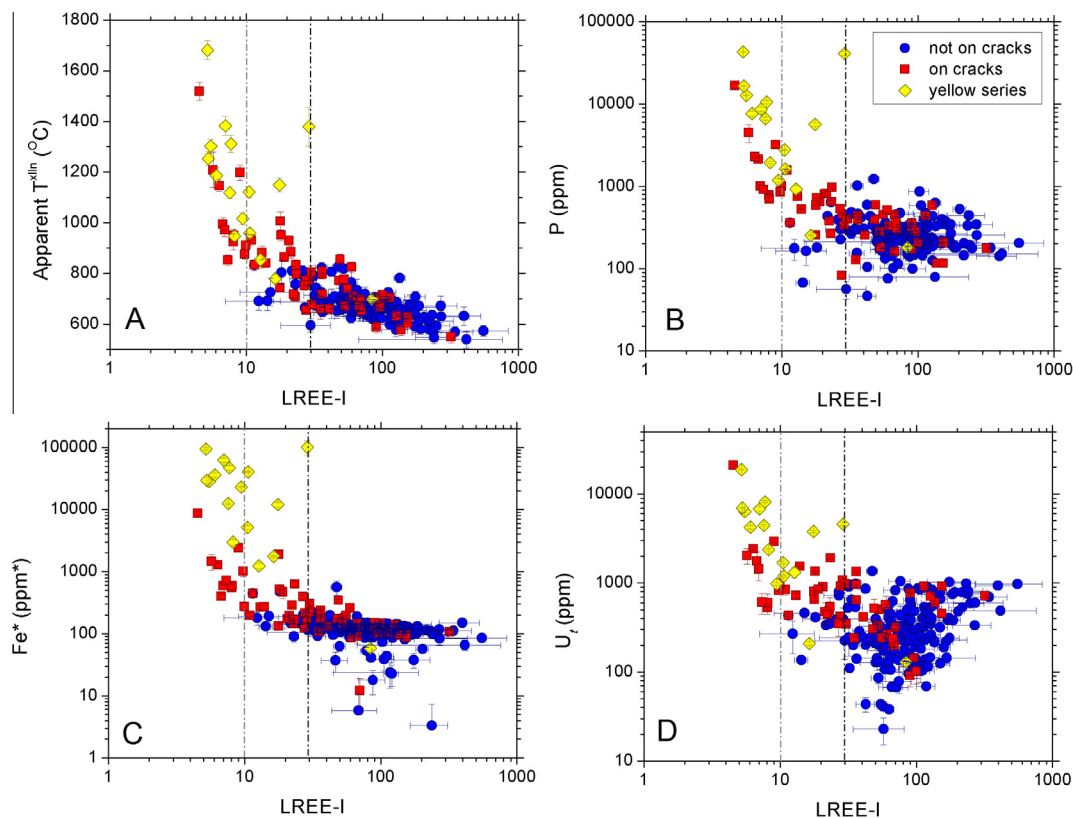


Fig. 5. Various trace element ratios and other quantities associated with alteration in Jack Hills zircons versus the LREE-I parameter. Breaks in slope are common between LREE-I values of 10–30. (A) apparent T^{xln} ; (B) P; (C) Fe^* ; (D) time-corrected U. Subscript 't' indicates decay-corrected value for crystallization age. Asterisk on Fe^* indicates this is an estimated concentration because the NIST 610 standard glass may have an unresolved interference on mass ^{57}Fe lending uncertainty to the absolute concentration calculations.

As formulated, the LREE-I should decrease with increasing degree of hydrothermal alteration or contamination. Indeed, it exhibits the appropriate correlations with the other indicators of alteration noted among Jack Hills zircons (P, Ti, Fe, U contents; Fig. 5). However, there is a break in slope at $LREE-I < 30$ for most investigated quantities, below which alteration indicators increase precipitously as LREE-I decreases (Fig. 5). We interpret this break in slope as separating distinct sets of processes for producing the LREE-I variation, with LREE-I below 30 indicating alteration. Analyses on cracks or metamict surfaces constitute the vast majority of $LREE-I < 10$. Samples with low LREE-I (mostly cracked and metamict surfaces) generally have lower $(Sm/La)_N$ below 10 and high contents of LREE, although some grains falling into an uncertain region between 10 and 30 range to low LREE contents (Fig. 7A). At higher LREE-I values, no correlation is apparent (Fig. 7). Other trace element quantities which respond slightly to alteration, or which relate also to magma chemistry and thus may not be clear diagnostic indicators for alteration, also show contrasting relationships with LREE-I above and below 30 (Fig. 6). Among samples with $LREE-I > 30$, Th/U and Ce/Ce^* are negatively correlated and Yb/Gd is slightly positively correlated with LREE-I. However, below $LREE-I = 30$, Th/U shows no covariance with LREE-I while Ce/Ce^* and Yb/Gd

become much more strongly correlated with LREE-I, pointing again to alteration processes dominating the trace element signatures at $LREE-I < 30$. The lower Ce/Ce^* at $LREE-I < 30$ does not lead to erroneously low estimates for f_{O_2} , however, owing to the nearly universally high apparent T^{xln} among these same samples (Fig. 6D).

For the remainder of this paper we consider analyses with $LREE-I < 10$ to be clearly altered and those with $LREE-I$ between 10 and 30 to be uncertain. $LREE-I > 30$ indicates a sample that has not undergone contamination or hydrothermal alteration processes and are referred to as primary. Samples with $LREE-I < 30$ are not further considered outside of discussions of alteration. We now also include 125 additional trace element measurements both new and from the literature with no or uncertain microstructural context, 96 of which have $LREE-I > 30$. All trace element analyses are classified into the categories *primary*, *altered*, and *uncertain* in Table EA-5 of the Supplementary materials. Better elimination of altered samples using the LREE-I helps to define the ranges of various trace element contents and ratios among the zircons and can help to identify small groups with chemistry that is otherwise of uncertain origin. For instance, after applying our criteria, apparent T^{xln} values above $\sim 850^\circ C$ are eliminated from the primary dataset, such that the relatively low-temperature (average $\sim 680^\circ C$; similar to that reported by

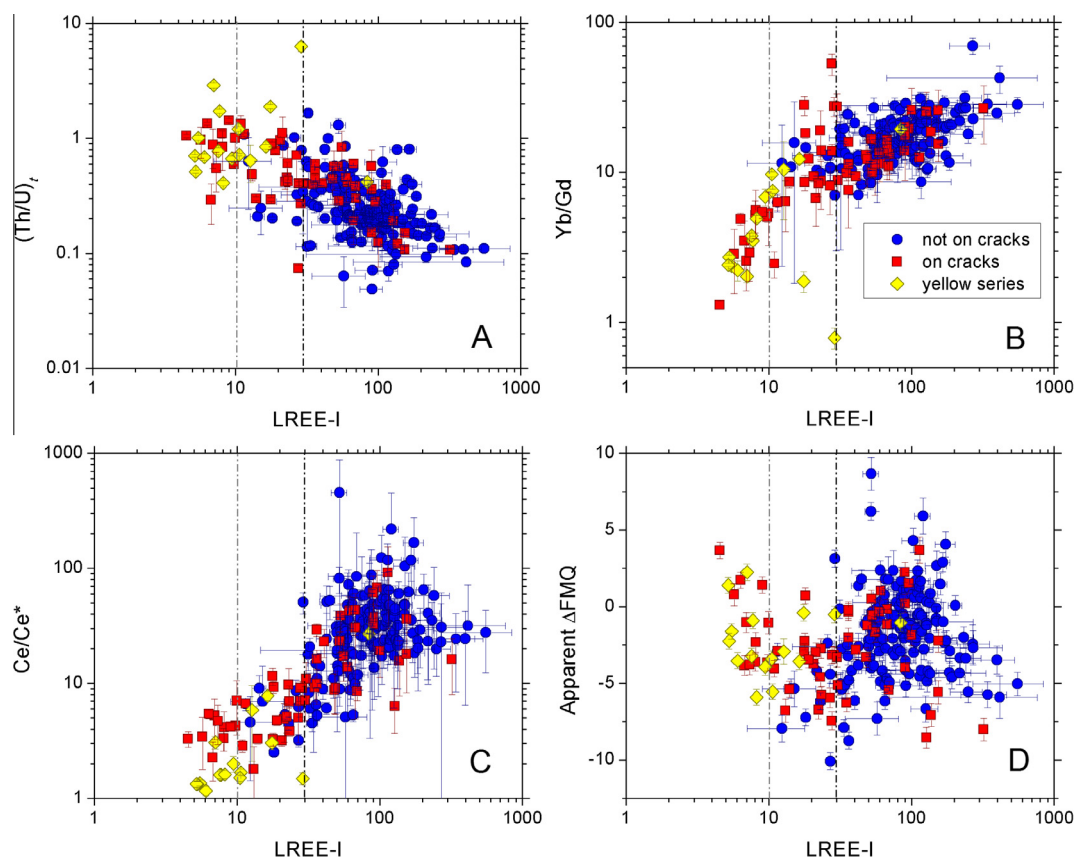


Fig. 6. Various quantities that may differ with either magmatic processes or alteration versus the LREE-I parameter. Breaks in slope or reversals in trends at high LREE-I are common at values of 30–10 (noted by dashed lines). (A) time-corrected Th/U; (B) Yb/Gd; (C) Ce/Ce*; (D) apparent Δ FMQ.

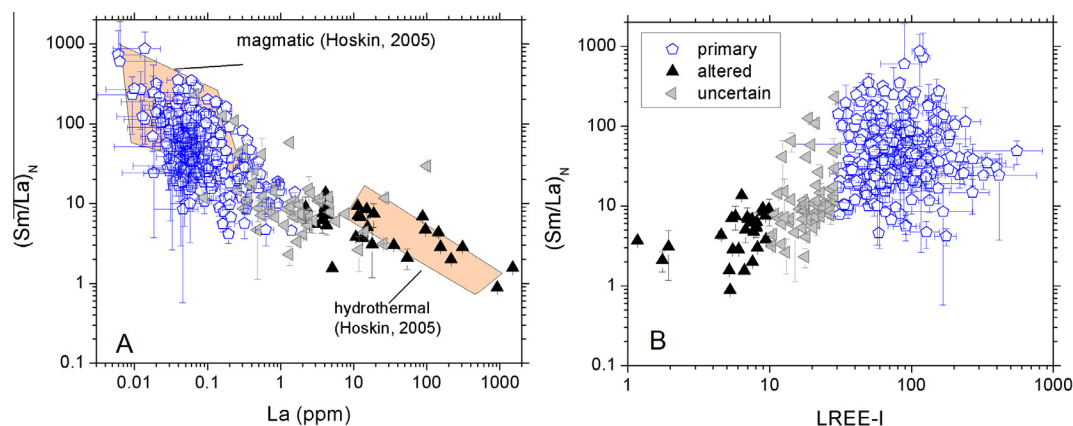


Fig. 7. Sm/La, a proposed criterion for recognizing hydrothermal alteration (Hoskin, 2005), versus (A) La concentration and (B) the LREE-I, along with approximate fields for magmatic and hydrothermal zircons from Hoskin (2005). For the most part, low-Sm/La zircons (i.e., likely to be hydrothermal) also display low LREE-I (i.e., altered), although a small group of high-LREE-I (i.e., apparently unaltered) zircons display low Sm/La. LREE-I values of 10 and 30 are noted by dashed lines.

Watson and Harrison, 2005) population resembles even less the temperature spectra of zircons from mafic or impact-related melts (Wielicki et al., 2012). Although the problem of high Ti due to alteration had been previously identified (Harrison and Schmitt, 2007), better establishing the origins

of the high-Ti signature will help to clarify ambiguities in the Jack Hills temperature record. There exists a small number of >800 °C zircons that might otherwise be assumed to reflect alteration but which screening with the LREE-I reveals is probably primary (Fig. 8A). Similarly,

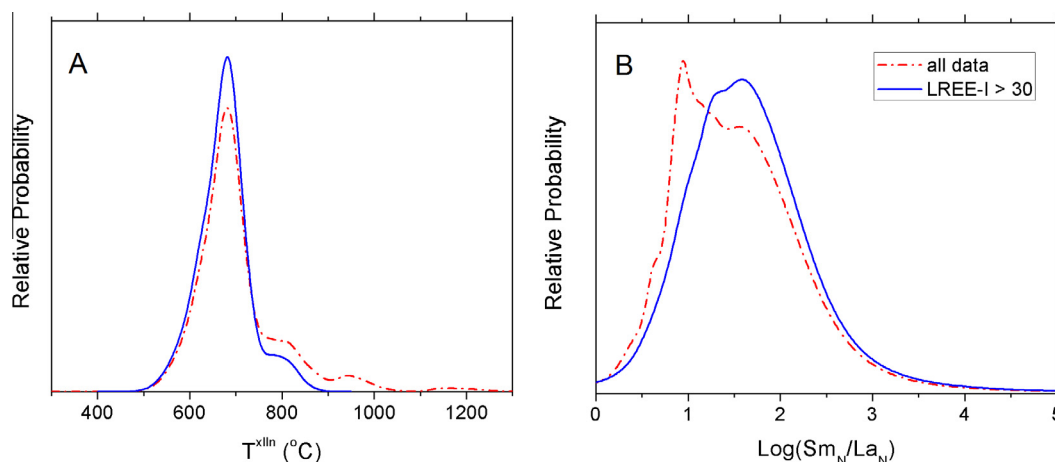


Fig. 8. Probability density functions for (A) apparent T^{xln} and (B) $\log_{10}(Sm/La)$ for both all Jack Hills zircons data and those data with LREE-I > 30 (primary).

although most altered samples have low Sm/La, zircons falling into the primary category also range to relatively low Sm/La (Fig. 8B).

5.2. Distinguishing types of alteration

Without prior knowledge, a search for regions in which primary zircon chemistry remains undisturbed would likely focus only on those regions with original magmatic zoning, concordant U–Pb systems, and no cracks. Indeed the vast majority of such regions show magmatic, high LREE-I. However, later alteration may be ambiguous in cases of ancient Pb loss or, apart from the Jack Hills population, among zircons too young for Pb loss to be reliably distinguished. The typical methods used for extracting zircon from bulk samples (involving pulverization by crushing or electricity) are also likely to produce some cracks which were not present during residence in the crust and thus do not represent sites of chemical alteration. Many regions of Jack Hills zircons showing potential predictors of later disturbance (mainly cracks, but also altered CL zoning, etc.) display high, primary LREE-I – although many cracked regions do show low LREE-I as expected. As such, the LREE-I can reduce ambiguity surrounding alteration of zircon. In addition to more readily identifying altered samples, when applied to populations of zircon it can help to distinguish mechanisms of alteration relevant for understanding the population's post-crystallization geologic history.

Known mechanisms of alteration and contamination in the Jack Hills zircons include mineralization of some cracks by foreign phases, consisting mainly of quartz, xenotime, Fe oxides, monazite, and muscovite (Rasmussen et al., 2011; Bell et al., 2015b). Although these phases were noted filling wide cracks, chemical alteration is evident even among some cracks where a separate phase cannot be identified. Fig. 9 shows correlations of various alteration-related trace element signatures with the concentration of Fe and P (also see plots S8–S10 in EA4). Fe correlates strongly with Ti content (as does Mn). P correlates well with Ti, HREE slope (as

shown by Yb/Gd), and most REE + Y contents. REE + Y and P covariance during magmatic evolution is expected since P^{+5} (along with H^{+} ; de Hoog et al., 2014) can charge-balance the substitution of REE^{+3} into tetravalent lattice sites (Finch and Hanchar, 2003), but the distinct slope and much stronger correlation among the altered signatures points to a separate process. Interestingly, Th/U correlates strongly with P among the altered samples only at $P < 1000$ ppm, with higher P values having relatively flat Th/U ~ 2.5 (~ 1.5 when time-corrected for decay, although this correction may or may not be appropriate for alteration features given that they are probably not the same age as their host zircon, to which the correction is presently pegged). A Ti-bearing Fe phase(s) and a REE- (and Ti-?) bearing phosphate(s) are likely. The phosphate is likely not monazite, since a very high Th/U ratio relative to zircon would lead to a much stronger correlation between P and Th/U. The moderate-Th/U xenotime seen in cracks in Jack Hills zircons (Rasmussen et al., 2011; Bell et al., 2015b) and the discovery site conglomerate matrix (Rasmussen et al., 2010) is a likely candidate, especially as shown by the high correlation among Y and P contents among altered samples in Fig. 9D. Host zircons of different age with LREE-I < 30 show some variation in their contents of P, Y, and Fe, with Hadean hosts mostly showing lower P, Y, and Fe. Of those <3.6 Ga zircons with very high Fe, P, Ti, and Y, many are from the yellow series, but some 4.0–3.6 Ga zircons fall into the same range. Although tentative at present, this might point toward slightly differing alteration styles for zircons of differing age. While the majority of altered signatures are thus traceable to contamination by known secondary phases in the Jack Hills zircons, there are also several samples that display the low LREE-I of hydrothermal alteration but lack the high Fe, Ti, and P contents of the other altered samples. These may be altered by a process that did not deposit phosphate or Fe oxides despite adding LREE, potentially contamination by phases not rich in Ti, Fe, and P or hydrothermal exchange/precipitation of zircon without elevated Ti, Fe, or P.

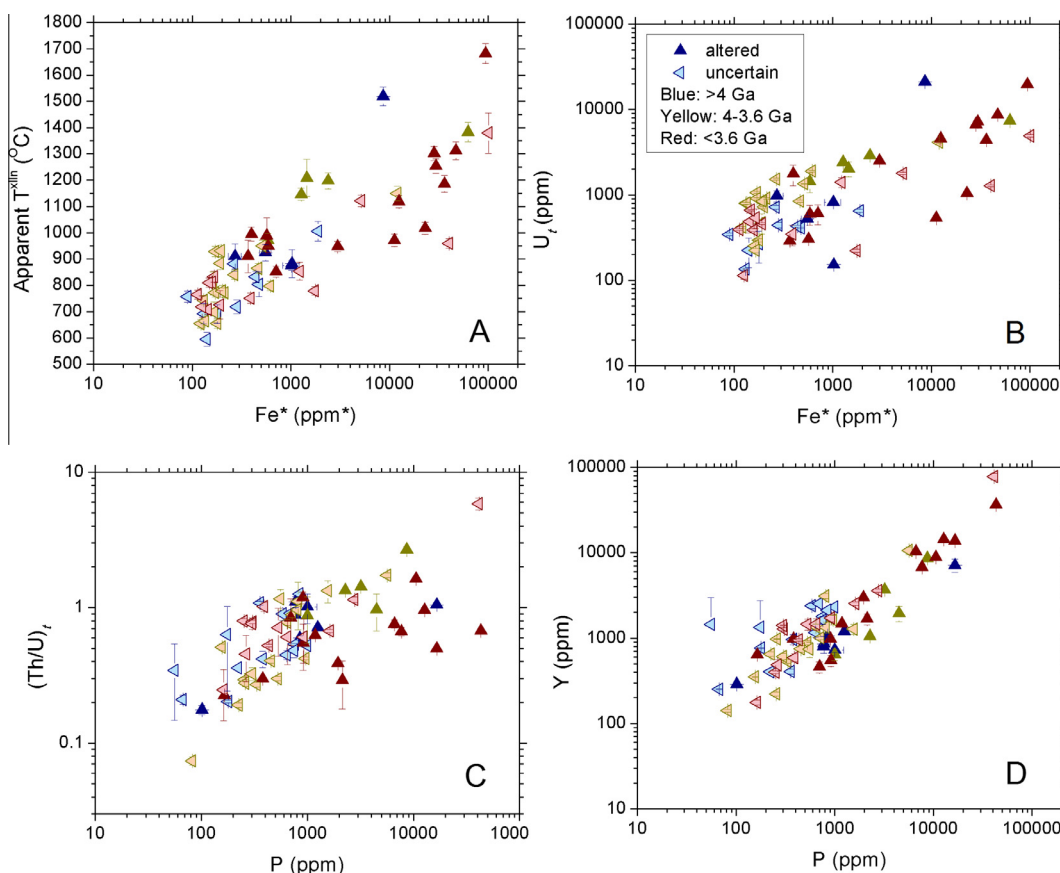


Fig. 9. The LREE-altered and ambiguous cases classified by age of the host zircon and showing Fe- and P-related alteration. (A) Apparent T^{xlin} versus Fe; (B) time-corrected U versus Fe; (C) time-corrected Th/U versus P; (D) Y versus P. Contamination with REE-Y-bearing phosphates (likely xenotime) and Ti-bearing Fe oxides is likely to account for most of the altered (LREE-I < 10) samples. Some variation in age of the host zircon is seen, with most Hadean cases having lower Fe*, P, Y, and Ti. Fe* is an estimated Fe concentration, as for Fig. 5.

The bright, transgressive CL features (similar to features potentially related to fluid alteration in other systems; in this study see, e.g., Fig. 1A, D) sampled away from cracks do not appear to have elevated levels of P, Fe, or Ti, although they fall largely to the high side of La content and to the low side of U and (Sm/La)_N. Whether these samples are related is unclear, as the analyses on bright uncracked regions do not differ significantly in other trace element contents or trends from the other uncracked analyses. The samples with low (Sm/La)_N yet high LREE-I, many of which do not fall on cracks but often on faded or bright CL features, are another interesting case. Whether this signature reflects potential alteration or if the low (Sm/La)_N is a magmatic effect is unclear. Interestingly, there is great chemical and oxygen isotopic similarity of many zircons with “altered” CL features (blurred/faded, cloudy, or patchy zoning) with those having magmatic, oscillatory zoning. This may mean that the alteration shown by most “altered” CL does not relate to chemical exchange with the environment. Blurred, faded, or patchy zoning may instead reflect local diffusion of CL-active trace elements without bulk exchange necessarily having occurred with external fluids, given the retention of similar chemistry in clearly magmatically zoned grains (see Figs. S3

and S6 in EA4). Although several patchy and bright regions display high $\delta^{18}O$ between 8 and 11‰ relative to SMOW (Figs. 2, 10D), a few magmatically zoned (two uncracked and U–Pb concordant) samples are also seen at these values. The slight if any differences between $\delta^{18}O$ on cracked and uncracked surfaces, and the lack of correlation between $\delta^{18}O$ and LREE-I and other trace element quantities (Fig. 10), suggest that post-formation alteration has not significantly affected $\delta^{18}O$. This is a similar result to that of Cavosie et al. (2006) in finding no correlation between altered trace element signatures and anomalous $\delta^{18}O$, and our data further suggest that the lower $\delta^{18}O$ found along cracks (e.g., Trail et al., 2007) is not a significant effect, suggesting essentially primary $\delta^{18}O$ regardless of spot placement in the Jack Hills zircons. Cavosie et al. (2006) consider the lack of correlation of $\delta^{18}O$ with chemical alteration features to be evidence against the production of the high-LREE signatures by hydrothermal alteration, since exchange with a hydrothermal fluid should in most cases lead to altered $\delta^{18}O$ in the zircon lattice (e.g., Valley, 2003). However, given that nearly all low-LREE-I signatures in the discovery site zircons occur in analysis pits overlapping cracks, it is likely that the small volume of material either precipitated in or affected by localized fluid

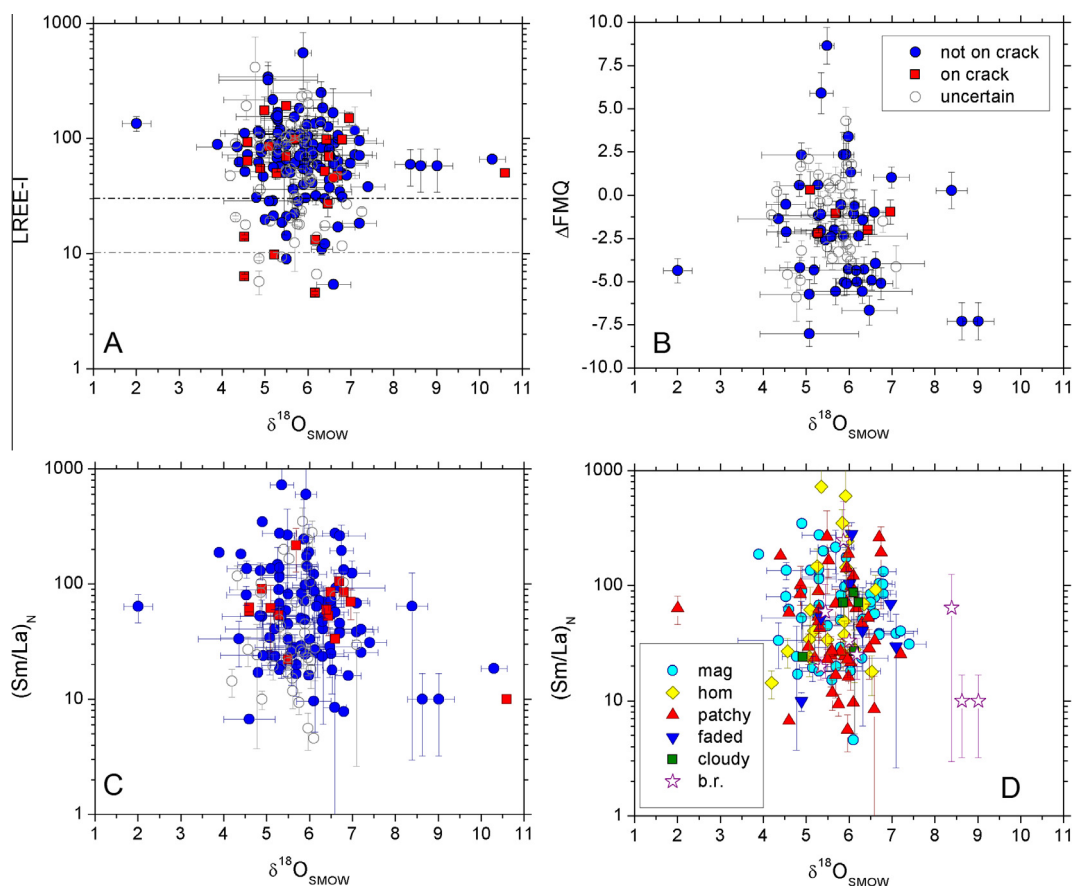


Fig. 10. Various trace element quantities versus $\delta^{18}\text{O}$, with groups classified in panels A–C by whether the $\delta^{18}\text{O}$ analysis spot fell on a cracked or uncracked surface. (A) LREE-I; (B) ΔFMQ ; (C) chondrite-normalized Sm/La; (D) chondrite-normalized Sm/La, grouped by zones and undifferentiated by $\delta^{18}\text{O}$ spot placement. Panel A shows trace element analyses regardless of LREE-I category. Panels B–D show trace element analyses falling into the “primary” category (LREE-I > 30) but undifferentiated by relationship to cracks. Zoning styles in panel D: “mag” = magmatic; “hom” = homogeneous; “b.r.” = bright replacement.

alteration along some cracks could have a large effect on trace elements (especially the very low-abundance LREE) while having little effect on zircon $\delta^{18}\text{O}$. Most of these altered signatures probably result from analytical mixing between altered material along (or contaminants precipitated in) cracks and that in the unaltered surrounding zircon volume, such that alteration signatures in the trace-level LREE, P, Ti, and Fe are much more likely to be expressed than in the structural component oxygen. It is clear that fluid ingress has affected the zircons along cracks at some point in their history, given the widespread mineralization of cracks in discovery site zircons (Rasmussen et al., 2011; Bell et al., 2015b). These data do, however, argue against contamination or fluid-related alteration of significant volumes of zircon away from cracks and metamict regions in discovery site zircons (as previously noted by Cavosie et al., 2006).

5.3. Primary trace element signatures

The reconstructed primary composition of Jack Hills zircons better defines provenance groups that are distinguished by distinct chemistry and clarifies covariations

among trace element concentrations or ratios which may be related to zircon provenance. Zircons of all ages show trends between Th/U, Sm/La, and various other trace element quantities (Fig. 11), notably the absolute concentrations of Y and HREEs (shown by Y, Fig. 11A) and their abundance relative to minor element Hf (shown by Yb/Hf, Fig. 11B). Correlations with Hf, often related to magmatic compositional evolution (Claiborne et al., 2010), appear to be limited (see Fig. S11 in EA4). The good correlations among Th/U, P, and most REE + Y (represented here relative to Hf as Yb/Hf) may be related to magmatic evolution or variations in source materials, such as fractionation or melting of monazite, apatite, or other phosphate minerals. Additionally, the fractionation of an MREE-concentrating phase such as amphibole (seen as a minor inclusion phase among Hadean zircons; Hopkins et al., 2008, 2010) or sphene (identified in one Hadean zircon inclusion; Hopkins et al., 2010) can decrease the Yb/Gd ratio of a magma and can also potentially lead to variations in zircon Yb/Gd. There is no clear correlation between Yb/Gd and Hf content among Hadean zircons of any age, but Yb/Gd and Th/U show an inverse relationship in all age ranges, as commonly seen in modern settings due

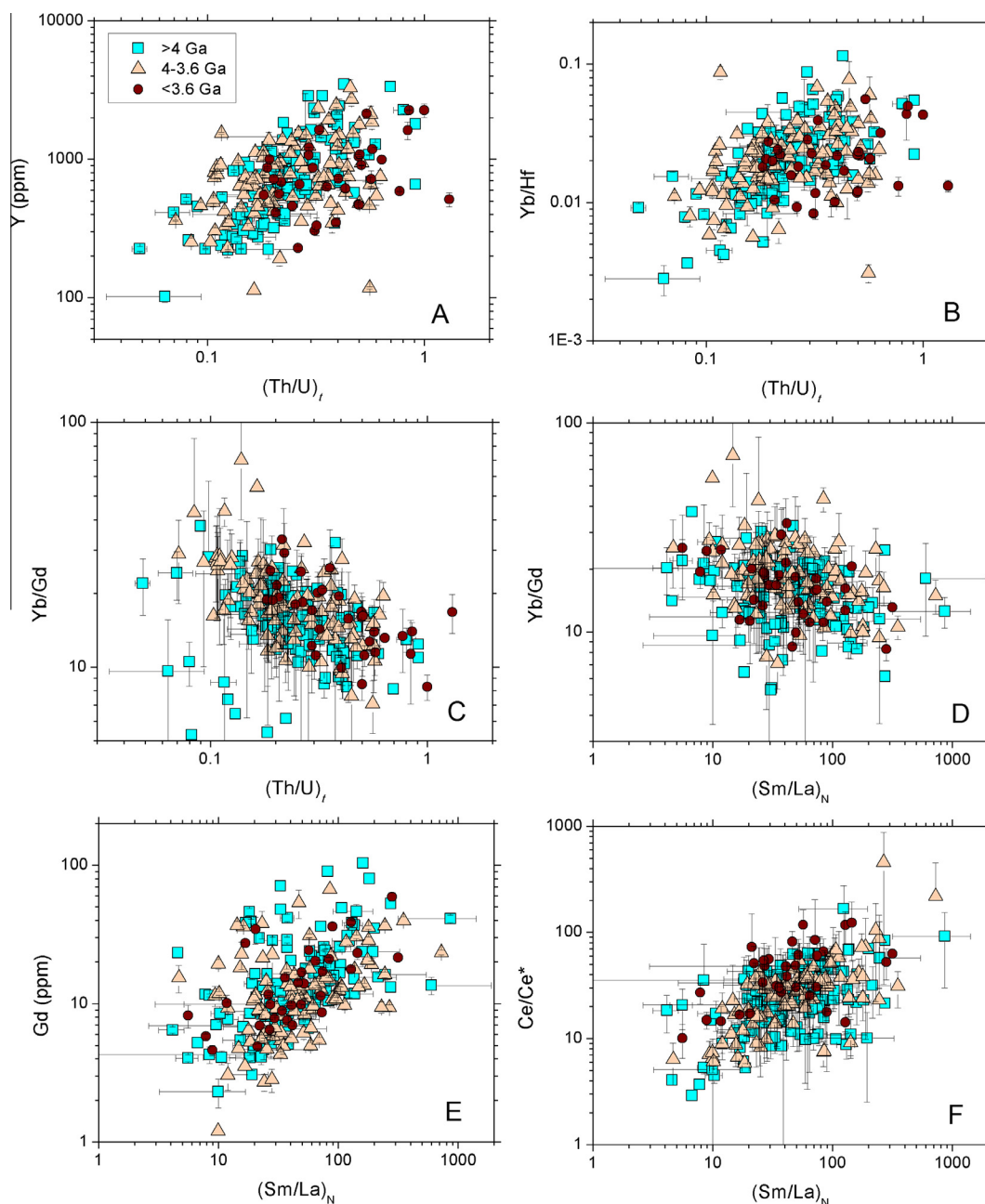


Fig. 11. Trace element variations among the primary dataset, grouped by age category. (A) Y vs. $(\text{Th}/\text{U})_i$; (B) Yb/Hf vs. $(\text{Th}/\text{U})_i$; (C) Yb/Gd vs. $(\text{Th}/\text{U})_i$; (D) Yb/Gd vs. $(\text{Sm}/\text{La})_N$; (E) Gd vs. $(\text{Sm}/\text{La})_N$; (F) Ce/Ce* vs. $(\text{Sm}/\text{La})_N$.

to either magmatic compositional evolution or variations in source materials (e.g., Claiborne et al., 2010; Barth et al., 2013).

Although the causes of all primary trace chemistry variations among Jack Hills zircons are not entirely clear (and in some cases may remain somewhat obscure due to the unknown diversity of source rocks), the LREE-I permits better constraints on the ranges of primary trace element contents and ratios. This is especially useful for identifying minority components of the Jack Hills population which might otherwise be overlooked as contamination. For example, although high apparent T^{Xln} were

previously known to be a contamination effect (Harrison and Schmitt, 2007), the cutoff between primary high-temperature zircons and contamination effects was unclear. Using the LREE-I we have shown that although almost all apparent T^{Xln} above $\sim 850^\circ\text{C}$ appear to be associated with alteration, the minority of zircons with $800\text{--}850^\circ\text{C}$ T^{Xln} are probably recording primary Ti contents and may represent a minority high-temperature provenance (Fig. 8A). The f_{O_2} calculated for the zircons using the Ce/Ce* method of Trail et al. (2011) shows a range from several log units above FMQ to several log units below (Fig. 6D), similar to their initial dataset for the Hadean zircons. Among zircons with

primary chemistry, LREE flatness varies over several orders of magnitude, and its covariance with several other trace element quantities among otherwise primary-seeming Jack Hills zircons (Fig. 11D–F), distinct from its behavior among altered samples, suggests that magmatic zircon exhibits characteristic Sm/La variations likely related to fractionation of phases such as amphibole or sphene, as mentioned above which may be suitable for petrologic or provenance purposes. An additional concern is that Ce/Ce* serves as an f_{O_2} proxy (Trail et al., 2011), such that the correlation of Sm/La with Ce/Ce* (Fig. 11F) brings up the question of whether Sm/La correlates with actual melt f_{O_2} or whether the Ce/Ce* is potentially affected by REE fractionation as well as by f_{O_2} .

5.4. Implications for zircon trace element studies

Despite their ancient formation (between 3.0 and nearly 4.4 Ga) and long history of metamorphism in their host conglomerate, most non-metamict Jack Hills zircons do not show clear signs of chemical alteration and appear to preserve their primary chemistry. The LREE-I is a good indicator for fluid-related alteration, especially along some cracks and in metamict regions, and provides a method to also identify alteration in analyses with poor microstructural documentation. Altered Jack Hills zircons can with a few exceptions be explained by mineralization with known secondary phases, made clearer using the LREE-I classification scheme. Some variations thus revealed in the chemistry of altered samples by host zircon age could suggest changing conditions of alteration with time.

It is unclear whether the LREE-I cutoff values we adopt here are universal or specific to the Jack Hills zircons. Application of an LREE-I cutoff of 30 to other zircon populations may not be justified and identifying covariation of trace chemistry in specific populations should override our recommendation. Zircon populations undergoing hydrothermal alteration in fluids of differing composition, or contaminated by differing secondary mineral assemblages, may show correlations distinct from those at Jack Hills. The LREE-I will also be appropriate in many cases of non-hydrous contamination, given the generally high LREE/HREE slope in most crustal materials which could serve as potential contaminants (e.g., glass inclusions). As extraterrestrial zircons become increasingly important in our study of the solar system (e.g., Hopkins and Mojzsis, 2015), they may also show such anhydrous contamination effects suitable for screening by the LREE-I. The LREE-I is more efficient than Sm/La or LREE contents alone at identifying contamination and hydrothermal alteration, and can form the basis for quality filtering of detrital zircon trace element data for provenance determination and other purposes.

This study is based on ion microprobe analyses for which small, shallow analysis pits allow identification of spot placement versus cracks in the vast majority of cases by later electron imaging. Since many crack-overlapping analyses show no evidence for chemical alteration, rejecting analyses on cracks will reject the majority of altered samples but also a substantial amount of primary chemical data. However, for other techniques microstructural

information may be less clear or nonexistent. Deep laser ablation pits may destroy visual indicators for alteration under the surface of the analyzed zircon. In this case, application of the LREE-I cycle by cycle may help to identify secondary chemistry from now-obliterated features. Similarly, solution ICP-MS analysis, as in the TIMS-TEA method (Schoene et al., 2010), links trace element contents to TIMS U–Pb ages for dissolved volumes of zircon, destroying contextual information. The LREE-I can assist in identifying alteration in these cases as well. Better filters to eliminate the effects of contamination will lead to better understanding the true range of variation of REE and other trace elements in zircon. This is a crucial first step for better developing this controversial but potentially rich source of information on zircon formation and the chemistry of host magmas.

6. CONCLUSIONS

Jack Hills zircons exhibit varying degrees of chemical alteration and secondary mineralization, although most non-metamict zircons have probably not experienced bulk chemical change except along cracks. We introduce the Light Rare Earth Element Index for recognizing contamination by exchange with external fluids or secondary mineralization, or $LREE-I = Dy/Nd + Dy/Sm$. Among Jack Hills zircons, low LREE-I (<30) indicates alteration and the quantity shows correlations with several known alteration features (high P, Ti, Fe, REE + Y), and provides better identification of altered samples than use of Sm/La or specific LREE concentrations alone. Better identification of the alteration features helps in identifying causes of alteration and contamination, which in Jack Hills zircons is consistent with the secondary phases known to fill cracks. Analysis spots in regions with altered CL zoning do not show distinct trace element chemistry relative to magmatically zoned regions and display similar correlations among trace element quantities, suggesting that these CL patterns were not imparted by chemical exchange with the environment. Primary trace element contents and ratios among the zircons exhibit potential signatures of variations in source magma chemistry and mineral fractionation. Better identification of primary ranges in chemistry may help identify specific provenances in the future, and better identification of alteration features may help to identify some aspects of the post-crystallization history of out-of-context zircons.

ACKNOWLEDGMENTS

Most of the new oxygen isotope analyses presented in this study were conducted by Haibo Zou at UCLA. We thank Axel Schmitt and Rita Economos for help with our other ion microprobe analyses. Comments by associate editor Alexander Nemchin and two anonymous reviewers greatly improved the manuscript. The ion microprobe facility at UCLA is partially supported by a grant from the Instrumentation and Facilities Program, Division of Earth Sciences, NSF (EAR-1339051). This research was supported by a Simons Collaboration on the Origins of Life Postdoctoral Fellowship (293529) to E.A.B. and an NSF grant (EAR-0948724) to T.M.H.

APPENDIX A. SUPPLEMENTARY DATA

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.gca.2016.07.016>.

REFERENCES

- Amelin Y., Lee D.-C., Halliday A. N. and Pidgeon R. T. (1999) Nature of the earth's earliest crust from hafnium isotopes in single detrital zircons. *Nature* **399**, 252–255.
- Anders E. and Grevesse N. (1989) Abundances of the elements: meteoritic and solar. *Geochim. Cosmochim. Acta* **53**, 197–214.
- Barth A. P., Wooden J. L., Jacobson C. E. and Economos R. C. (2013) Detrital zircon as a proxy for tracking the magmatic arc system: the California arc example. *Geology* **41**, 223–226.
- Bell E. A. and Harrison T. M. (2013) Post-Hadean transitions in Jack Hills zircon provenance: a signal of the Late Heavy Bombardment? *Earth Planet. Sci. Lett.* **364**, 1–11.
- Bell E. A., Harrison T. M., McCulloch M. T. and Young E. D. (2011) Early Archean crustal evolution of the Jack Hills Zircon source terrane inferred from Lu–Hf, $^{207}\text{Pb}/^{206}\text{Pb}$, and $\delta^{18}\text{O}$ systematics of Jack Hills zircons. *Geochim. Cosmochim. Acta* **75**, 4816–4829.
- Bell E. A., Harrison T. M., Kohl I. E. and Young E. D. (2014) Eoarchean crustal evolution of the Jack Hills zircon source and loss of Hadean crust. *Geochim. Cosmochim. Acta* **146**, 27–42.
- Bell E. A., Boehnke P., Harrison T. M. and Mao W. L. (2015a) Potentially biogenic carbon preserved in a 4.1 Ga zircon. *Proc. Natl. Acad. Sci.* **112**, 14518–14521.
- Bell E. A., Boehnke P., Hopkins-Wielicki M. D. and Harrison T. M. (2015b) Distinguishing primary and secondary inclusion assemblages in Jack Hills zircons. *Lithos* **234–235**, 15–26.
- Belousova E. A., Griffin W. L., O'Reilly S. Y. and Fisher N. I. (2002) Igneous zircon: trace element composition as an indicator of source rock type. *Contrib. Miner. Petrol.* **143**, 602–622.
- Caro G., Bennett V. C., Bourdon B., Harrison T. M., von Quadt A., Mojzsis S. J. and Harris J. W. (2008) Application of precise $^{142}\text{Nd}/^{144}\text{Nd}$ of small samples to inclusions in diamonds (Finch, South Africa) and Hadean zircons (Jack Hills, Western Australia). *Chem. Geol.* **247**, 253–265.
- Cavosie A. J., Wilde S. A., Liu D., Weiblen P. W. and Valley J. W. (2004) Internal zoning and U–Th–Pb chemistry of Jack Hills detrital zircons: a mineral record of early Archean to Mesoproterozoic (4348–1576 Ma) magmatism. *Precamb. Res.* **135**, 251–279.
- Cavosie A. J., Valley J. W., Wilde S. A. and E.I.M.F. (2005) Magmatic $\delta^{18}\text{O}$ in 4400–3900 Ma detrital zircons: a record of the alteration and recycling of crust in the Early Archean. *Earth Planet. Sci. Lett.* **235**, 663–681.
- Cavosie A. J., Valley J. W., Wilde S. A. and E.I.M.F. (2006) Correlated microanalysis of zircon: trace element, $\delta^{18}\text{O}$, and U–Th–Pb isotopic constraints on the igneous origin of complex >3900 Ma detrital grains. *Geochim. Cosmochim. Acta* **70**, 5601–5616.
- Claiborne L. L., Miller C. F. and Wooden J. L. (2010) Trace element composition of igneous zircon: a thermal and compositional record of the accumulation and evolution of a large silicic batholith, Spirit Mountain, Nevada. *Contrib. Mineral. Petrol.* **160**, 511–531.
- Compston W. and Pidgeon R. T. (1986) Jack Hills, evidence of more very old detrital zircons in Western Australia. *Nature* **321**, 766–769.
- Coogan L. A. and Hinton R. W. (2006) Do the trace elements compositions of detrital zircons require Hadean continental crust? *Geology* **34**, 633–636.
- Corfu F., Hanchar J.M., Hoskin P.W.O., Kinny P. (2003). Atlas of zircon textures. In *Zircon. Reviews in Mineralogy* (eds. J. M. Hanchar, P. W. O. Hoskin). **53**, pp. 469–500.
- Crowley J. L., Myers J. S., Sylvester P. J. and Cox R. A. (2005) Detrital zircon from the Jack Hills and Mount Narryer, Western Australia: evidence for diverse >4.0 Ga source rocks. *J. Geol.* **113**, 239–63.
- De Hoog J. C. M., Lissenberg C. J., Brooker R. A., Hinton R., Trail D. and Hellebrand E. (2014) Hydrogen incorporation and charge balance in natural zircon. *Geochim. Cosmochim. Acta* **141**, 472–486.
- Ferry J. M. and Watson E. B. (2007) New thermodynamic models and revised calibrations for the Ti-in-zircon and Zr-in-rutile thermometers. *Contrib. Miner. Petrol.* **154**, 429–437.
- Finch R.J., Hanchar J.M. (2003). Structure and chemistry of zircon and zircon-group minerals. In *Zircon. Reviews in Mineralogy and Geochemistry* (eds. J. M. Hanchar, P. W. O. Hoskin). **53**, pp. 1–25.
- Fletcher I. R., Rosman K. J. R. and Libby W. G. (1988) Sm–Nd, Pb–Pb and Rb–Sr geochronology of the manred complex, Mount Narryer, Western Australia. *Precamb. Res.* **38**, 343–354.
- Geisler T., Pidgeon R. T., Kurtz R., Bronswijk W. V. and Schleicher H. (2003a) Experimental hydrothermal alteration of partially metamict zircon. *Am. Mineral.* **88**, 1496–1513.
- Geisler T., Rashwan A. A., Rahn M. K. W., Poller U., Zwingmann H., Pidgeon R. T., Schleicher H. and Tomaschek F. (2003b) Low-temperature hydrothermal alteration of natural metamict zircons from the Eastern Desert, Egypt. *Mineral. Mag.* **67**, 485–508.
- Gieré R. (1996) Formation of rare earth minerals in hydrothermal systems. In *Rare Earth Minerals: Chemistry, origin and ore deposits* (eds. A. P. Jones, F. Wall and C. T. Williams). Chapman and Hall, London, UK, pp. 105–150.
- Grimes C. B., John B. E., Kelemen P. B., Mazdab F. K., Wooden J. L., Cheadle M. J., Hanghoj K. and Schwartz J. J. (2007) Trace element chemistry of zircons from oceanic crust: a method for distinguishing detrital zircon provenance. *Geology* **35**, 643–646.
- Harrison T. M. (2009) The Hadean crust: evidence from > 4 Ga zircons. *Ann. Rev. Earth Planet. Sci.* **37**, 479–505.
- Harrison T. M. and Schmitt A. K. (2007) High sensitivity mapping of Ti distributions in Hadean zircons. *Earth Planet. Sci. Lett.* **261**, 9–19.
- Harrison T. M., Blichert-Toft J., Müller W., Albareda F., Holden P. and Mojzsis S. J. (2005) Heterogeneous Hadean hafnium: evidence of continental crust by 4.4–4.5 Ga. *Science* **310**, 1947–1950.
- Harrison T. M., Schmitt A. K., McCulloch M. T. and Lovera O. M. (2008) Early (≥ 4.5 Ga) formation of terrestrial crust: Lu–Hf, $\delta^{18}\text{O}$, and Ti thermometry results for Hadean zircons. *Earth Planet. Sci. Lett.* **268**, 476–86.
- Holden P., Lanc P., Ireland T. R., Harrison T. M., Foster J. J. and Bruce Z. (2009) Mass-spectrometric mining of Hadean zircons by automated SHRIMP multi-collector and single-collector U/Pb zircon age dating: the first 100,000 grains. *Int. J. Mass Spectrom.* **286**, 53–63.
- Hopkins M. D. and Mojzsis S. J. (2015) A protracted timeline for lunar bombardment from mineral chemistry, Ti thermometry and U–Pb geochronology of Apollo 14 melt breccia zircons. *Contrib. Miner. Petrol.* **169**, 1–18.

- Hopkins M., Harrison T. M. and Manning C. E. (2008) Low heat flow inferred from >4 Gyr zircons suggests Hadean plate boundary interactions. *Nature* **456**, 493–496.
- Hopkins M., Harrison T. M. and Manning C. E. (2010) Constraints on Hadean geodynamics from mineral inclusions in >4 Ga zircons. *Earth Planet. Sci. Lett.* **298**, 367–376.
- Hoskin P. W. O. (2005) Trace-element composition of hydrothermal zircon and the alteration of Hadean zircon from the Jack Hills, Australia. *Geochim. Cosmochim. Acta* **69**, 637–648.
- Hoskin P. W. O. and Black L. P. (2000) Metamorphic zircon formation by solid-state recrystallization of protolith igneous zircon. *J. Metamorph. Geol.* **18**, 423–439.
- Hoskin P. W. O. and Ireland T. R. (2000) Rare earth element chemistry of zircon and its use as a provenance indicator. *Geology* **28**, 627–630.
- Hoskin P.W.O., Schaltegger U. (2003) The composition of zircon and igneous and metamorphic petrogenesis. In *Zircon. Reviews in Mineralogy and Geochemistry* (eds. J. M. Hanchar, P. W. O. Hoskin). **53**, pp. 343–385.
- Hoskin P. W. O., Kinny P. D., Wyborn B. and Chappell B. W. (2000) Identifying accessory mineral saturation during differentiation of granitoid magmas: an integrated approach. *J. Petrol.* **41**, 1365–1396.
- Kemp A. I. S., Wilde S. A., Hawkesworth C. J., Coath C. D., Nemchin A., Pidgeon R. T., Vervoort J. D. and DuFrane S. A. (2010) Hadean crustal evolution revisited: new constraints from Pb–Hf isotope systematics of the Jack Hills zircons. *Earth Planet. Sci. Lett.* **296**, 45–56.
- Maas R., Kinny P. D., Williams I. S., Froude D. O. and Compston W. (1992) The Earth's oldest known crust: a geochronological and geochemical study of 3900–4200 Ma old detrital zircons from Mt. Narryer and Jack Hills, Western Australia. *Geochim. Cosmochim. Acta* **56**, 1281–1300.
- Mezger K. and Krogstad E. J. (1997) Interpretation of discordant U–Pb zircon ages: an evaluation. *J. Metamorph. Geol.* **15**, 127–140.
- Mojzsis S. J., Harrison T. M. and Pidgeon R. T. (2001) Oxygen-isotope evidence from ancient zircons for liquid water at the Earth's surface 4300 Myr ago. *Nature* **409**, 178–181.
- Mojzsis S. J., Devaraju T. C. and Newton R. C. (2003) Ion microprobe U–Pb age determinations on zircon from the late Archean granulite facies transition zone of southern India. *J. Geol.* **111**, 407–425.
- Myers J. S. (1988a) Early archaean narryer gneiss complex, yilgarn craton, Western Australia. *Precamb. Res.* **38**, 297–307.
- Myers J. S. (1988b) Oldest known terrestrial anorthosite at Mount Narryer, Western Australia. *Precamb. Res.* **38**, 309–323.
- Paces J. B. and Miller J. D. (1993) Precise U–Pb ages of duluth complex and related mafic intrusions, northeastern Minnesota: geochronological insights into physical, petrogenetic, and paleomagnetic and tectonomagnetic processes associated with the 1.1 Ga mid-continent rift system. *J. Geophys. Res.* **98**, 13997–14013.
- Peck W. H., Valley J. W., Wilde S. A. and Graham C. M. (2001) Oxygen isotope ratios and rare earth elements in 3.3–4.4 Ga zircons: ion microprobe evidence for high $\delta^{18}\text{O}$ continental crust and oceans in the Early Archean. *Geochim. Cosmochim. Acta* **65**, 4215–4299.
- Pidgeon R. T. (2014) Zircon radiation damage ages. *Chem. Geol.* **367**, 13–22.
- Rasmussen B., Fletcher I. R., Muhling J. R. and Wilde S. A. (2010) In situ U–Th–Pb geochronology of monazite and xenotime from the Jack Hills belt: implications for the age of deposition and metamorphism of Hadean zircons. *Precamb. Res.* **180**, 26–46.
- Rasmussen B., Fletcher I. R., Muhling J. R., Gregory C. J. and Wilde S. A. (2011) Metamorphic replacement of mineral inclusions in detrital zircon from Jack Hills, Australia: implications for the Hadean Earth. *Geology* **39**, 1143–1146.
- Rudnick R. L. and Gao S. (2003) Composition of the continental crust. *Treatise on Geochemistry* **3**, 1–64.
- Schoene B., Laskoczy C., Schaltegger U. and Günther D. (2010) A new method integrating high-precision U–Pb geochronology with zircon trace element analysis (U–Pb TIMS-TEA). *Geochim. Cosmochim. Acta* **74**, 7144–7159.
- Spaggiari C. V., Pidgeon R. T. and Wilde S. A. (2007) The Jack Hills greenstone belt, Western Australia Part 2: lithological relationships and implications for the deposition of ≥ 4.0 Ga detrital zircons. *Precamb. Res.* **155**, 261–286.
- Tarduno J. A., Cottrell R. D., Davis W. J., Nimmo F. and Bono R. K. (2015) A Hadean to Paleoproterozoic geodynamo recorded by single zircon crystals. *Science* **349**, 521–524.
- Trail D., Mojzsis S. J., Harrison T. M., Schmitt A. K., Watson E. B. and Young E. D. (2007) Constraints on Hadean zircon protoliths from oxygen isotopes, REEs and Ti-thermometry. *Geochim. Geophys. Geosyst.* **8**, Q06014.
- Trail D., Watson E. B. and Tailby N. D. (2011) The oxidation state of Hadean magmas and implications for early Earth's atmosphere. *Nature* **480**, 79–82.
- Valley J. W. (2003) Oxygen isotopes in zircon. *Rev. Mineral. Geochem.* **53**, 343–385.
- Vavra G., Schmid R. and Gebauer D. (1999) Internal morphology, habit and U–Th–Pb microanalysis of amphibolite-to-granulite facies zircons: geochronology of the Ivrea Zone (Southern Alps). *Contrib. Miner. Petrol.* **34**, 380–404.
- Watson E. B. and Cherniak D. J. (1997) Oxygen diffusion in zircon. *Earth Planet. Sci. Lett.* **148**, 527–544.
- Watson E. B. and Harrison T. M. (2005) Zircon thermometer reveals minimum melting conditions on earliest Earth. *Science* **308**, 841–844.
- Weiss B. P., Maloof A. C., Tailby N., Ramezani J., Fu R. R., Hanus V., Trail D., Watson E. B., Harrison T. M., Bowring S. A., Kirschvink J. L., Swanson-Hysell N. L. and Coe R. S. (2015) Pervasive remagnetization of detrital zircon host rocks in the Jack Hills, Western Australia and implications for records of the early geodynamo. *Earth Planet. Sci. Lett.* **430**, 115–128.
- Wiedenbeck M., Hanchar J. M., Peck W. H., Sylvester P., Valley J., Whitehouse M., Kronz A., Morishita Y., Nasdala L., Fiebig J., Franchi I., Girard J.-P., Greenwood R. C., Hinton R., Kita N., Mason P. R. D., Norman M., Ogasawara M., Piccoli P. M., Rhede D., Satoh H., Schulz-Dobrick B., Skår O., Spicuzza M. J., Terada K., Tindle A., Togashi S., Vennemann T., Xie Q. and Zheng Y. F. (2004) Further characterisation of the 91500 zircon crystal. *Geostand. Geoanal. Res.* **28**, 9–39.
- Wielicki M. T., Harrison T. M. and Schmitt A. K. (2012) Geochemical signatures and magmatic stability of impact produced zircons. *Earth Planet. Sci. Lett.* **321–322**, 20–31.
- Wilde S. A. (2010) Proterozoic volcanism in the Jack Hills Belt, Western Australia: some implications and consequences for the World's oldest zircon population. *Precamb. Res.* **183**, 9–24.
- Yang W. B., Niu H. C., Shan Q., Sun W. D., Zhang H., Li N. B., Jiang Y. H. and Yu X. Y. (2014) Geochemistry of magmatic and hydrothermal zircon from the highly evolved Baerzhe alkaline granite: implications for Zr–REE–Nb mineralization. *Miner. Deposita* **49**, 451–470.

Associate editor: Alexander Nemchin