



# Iceland is not a magmatic analog for the Hadean: Evidence from the zircon record



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## ABSTRACT

Tangible evidence of Earth's earliest (Hadean; >4.0 Ga) crust, and the processes and materials that contributed to its formation, exists almost entirely in a record of detrital zircon from Jack Hills, Western Australia, and a few other locations. Iceland, with its thick, juvenile, basaltic crust and relatively abundant silicic rocks, is considered a potential modern analog for the Hadean magmatic environment where >4 Ga zircon formed. We present the first extensive dataset for Icelandic zircon, with trace element and oxygen isotope compositions from samples that span the island's history and full range of tectonic settings. This statistically robust zircon-based comparison between Iceland and the early Earth reveals distinctions in chemistry that suggest fundamental differences in magmatic environments. Whereas the  $\delta^{18}\text{O}$  signature of Hadean zircons generally exceed that of zircons equilibrated with mantle-derived magma ( $85\% \geq 5.3\text{‰}$ ; median  $6\text{‰}$ ), almost all Icelandic zircons are characterized by a “light” oxygen signature ( $98\% \leq 5.3\text{‰}$ ; median  $3\text{‰}$ ). Deviations from “juvenile” oxygen values indicate that many Hadean zircons and almost all Icelandic zircons grew from magmas with substantial contributions from materials that had interacted with surface waters. In the Hadean case, the interaction occurred at low temperatures, while in Iceland, it was a high-temperature interaction. Icelandic and Hadean zircons are also distinct in their Ti concentrations (Icelandic median concentration 12 ppm, Hadean median 5 ppm). Titanium in zircon correlates positively with temperature of crystallization, and this difference in median Ti concentration suggests a temperature difference of at least  $50^\circ\text{C}$ . Other differences in trace elements compositions are consistent with the interpretation that Icelandic and Hadean zircons grew in magmas with very different origins and histories (e.g., the heavy rare earth element Yb is almost an order of magnitude higher in Icelandic zircon). A comparison with elemental data for Phanerozoic zircon from different environments demonstrates that the Hadean population is unusually depleted in Ti, but otherwise similar to zircons from continental arc settings. Zircons from Iceland, and from modern evolving rift environments where oceanic lithosphere and upwelling asthenosphere are replacing continental lithosphere, are compositionally intermediate between mid-ocean ridge and continental arc zircon populations. The elemental distinctions are consistent with fractionation of zircon-bearing magmas under hotter and drier conditions in Icelandic, mid-ocean ridge, and evolving rift environments and cooler and wetter conditions in arc and, especially, Hadean environments.

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## 1. Introduction

Iceland is Earth's largest oceanic island, atop one of Earth's largest oceanic plateaus (Thordarson and Hoskuldsson, 2002), a product of voluminous magma production at the junction of a hotspot and an actively-spreading mid-ocean ridge (Vink, 1984; Thordarson and Larsen, 2007). With only 2% of Earth's mid-ocean

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ridge system subaerially exposed (Wright et al., 2012), Iceland's remarkably thick crust (averaging 25 km, reaching 40 km; Bjarnason, 2008) provides rare subaerial access to young oceanic crust. The basalts that comprise the majority of the Icelandic plateau are interpreted to have been derived from both depleted (MORB-like) and enriched (OIB-like) mantle (e.g., Sigmarsson and Steinthórs-son, 2007).

Approximately 10% of the rocks exposed at the surface of Iceland are silicic, making the island host to the greatest known concentration of silicic rock in the modern ocean (Jonasson, 2007). This abundance of silicic material, coupled with the unusual thickness of the crust, hints at juvenile continental nucleation and permanent crust construction in an oceanic environment (Kröner and Layer, 1992; Cloos, 1993). This phenomenon has not been recognized elsewhere in the recent geologic record, but it is often postulated that Iceland is a modern analogue for ancient crustal construction (e.g., Hadean Earth: Galer and Goldstein, 1991; Valley et al., 2002; Martin and Sigmarsson, 2005; early Earth: Taylor and McLennan, 1985; Marsh et al., 1991; Sigmarsson et al., 1991; Gunnarsson et al., 1998; Bindeman et al., 2012; Reimink et al., 2014; cf. Harrison et al., 2008; Hopkins et al., 2008; Harrison 2009, 2013), and that a better understanding of Icelandic felsic magma petrogenesis will clarify the origins of Earth's earliest continental crust (cf. Maas et al., 1992).

There are a number of similarities between Iceland and what is envisioned for the Hadean crust-building setting that suggest petrogenetic parallels. Both are or were (presumably) dominantly mafic environments with thickened crust, elevated geothermal gradients and magma production rates, and silicic components generated in the absence of significant pre-existing felsic material (e.g., Rapp et al., 1991; Condie and Pease, 2008; Martin et al., 2008; Bindeman et al., 2012). These features we recognize in Iceland from direct observation and interpretation; our direct knowledge of the Hadean comes from zircon, the only tangible evidence that remains of crust older than 4 billion years (e.g., Mojzsis et al., 2001; Wilde et al., 2001; Valley et al., 2002; Harrison et al., 2008; Hopkins et al., 2008), with the possible exception of the Nuvvuagittuq lava sequence in Quebec (O'Neil et al., 2011, 2012; Turner et al., 2014; cf. Cates et al., 2013). Evaluating the Hadean–Iceland analogy therefore requires a comparison of zircon from the two settings, but very few data have been reported for Icelandic zircon (Carley et al., 2011; Martin et al., 2011; Siler, 2011; Bindeman et al., 2012; Padilla, 2011). In this paper, we present a greatly expanded study of zircon in Iceland as a basis for comparison with the Hadean record, providing a powerful test of the “Iceland as a Hadean analogue” hypothesis.

## 2. Materials and methods

### 2.1. Icelandic samples and mineral separation

Icelandic zircons analyzed in this study were collected from eight volcanic localities (pumice, lava, near-surface subvolcanics); six intrusions; eight modern river sediments; and three sedimentary rock units. Sample names, geographic locations, and number of zircon analyses per sample are tabulated in Table 1. As demonstrated by Fig. 1, samples were collected with the intention to survey the diversity of ages, locations and tectonic environments that exist in subaerial Iceland, in an attempt to fully capture compositional and petrogenetic diversity in this dynamic setting. Data are presented for individual samples in the supplemental materials. In the body of this comparison-based paper, however, we present zircons from these diverse samples as one representative Icelandic population just as we treat zircons from the Hadean as one representative zircon population.

### 2.2. Analytical methods

We separated zircons from samples using standard crushing, sieving, density (water and heavy liquid), magnetic, and hand-picking techniques. Once zircons were separated from their host, we mounted them in epoxy and polished them to expose grain interiors. Grain interiors were imaged by cathodoluminescence (CL) using the JEOL JSM 5600 scanning electron microscope (SEM) at the Microanalysis Center shared by the US Geological Survey and Stanford University or the Tescan Vega 3 LM Variable Pressure SEM at Vanderbilt University. We used reflected light and CL images to strategically place high-precision, high-resolution, oxygen and trace element analytical spots.

We measured oxygen isotope ratios with high spatial resolution using the CAMECA ims1270 microprobe at UCLA-NSF facilities and a  $\text{Cs}^+$  beam with a diameter of approximately 15  $\mu\text{m}$  and sputter depth of approximately 1  $\mu\text{m}$ , following methods described by Trail et al. (2007). In total, we analyzed 653 spots over five analytical sessions (see Appendix A for specifics: Reduced O Data). Instrumental mass fractionation was determined using analyses of R33 standard zircons (5.5‰; Black et al., 2005) that were mounted in close spatial proximity to our grains. The standard deviation of R33 in each mount was also used as an estimate for the uncertainty of individual spot analyses on unknowns. Oxygen data are reported as  $\delta^{18}\text{O}$  permil (‰) values, calculated relative to Vienna Mean Standard Ocean Water (VSMOW; Baertschi, 1976). Results can be found in Section 3.1.1 and Fig. 2, with more complete data tabulated in Appendix A (Reduced O Data; Oct. 2011 O unreddened; April 2012 O unreddened; Jan. 2013 O unreddened; May 2013 O unreddened; Aug. 2013 O unreddened).

We measured trace element concentrations with high spatial resolution using the Sensitive High Resolution Ion Microprobe, Reverse Geometry (SHRIMP-RG) and an  $\sim 1.5\text{--}2.5$  nA  $\text{O}_2^-$  beam with a diameter of  $\sim 15$   $\mu\text{m}$  and sputter depth of approximately 1  $\mu\text{m}$  at the Stanford-USGS Microanalytical Facility. In total, we analyzed 671 spots over the course of six analytical sessions (see Appendix A “Iceland SHRIMP TE Data” for specifics; Appendix A also includes 150 trace element analyses from Carley et al., 2011). Trace element abundances were calculated relative to those on in-house standard MAD (Barth and Wooden, 2010). We typically used methods following those described in Mazdab and Wooden (2006), Claiborne et al. (2006, 2010b) and Barth and Wooden (2010). In a small subset of the dataset (refer to Appendix A “Iceland SHRIMP TE Data” for sample specifics), a limited set of trace elements was measured simultaneously with the U–Pb age routine.

Trace element compositions are presented in Section 3.1.3 and Fig. 3 (Ti); Section 3.1.3 and Figs. 4 and 5 (Rare Earth Elements: REEs); Section 3.1.4 and Fig. 6 (Y, Yb, Hf, U). Appendix A (Iceland SHRIMP TE Data) contains the full data set.

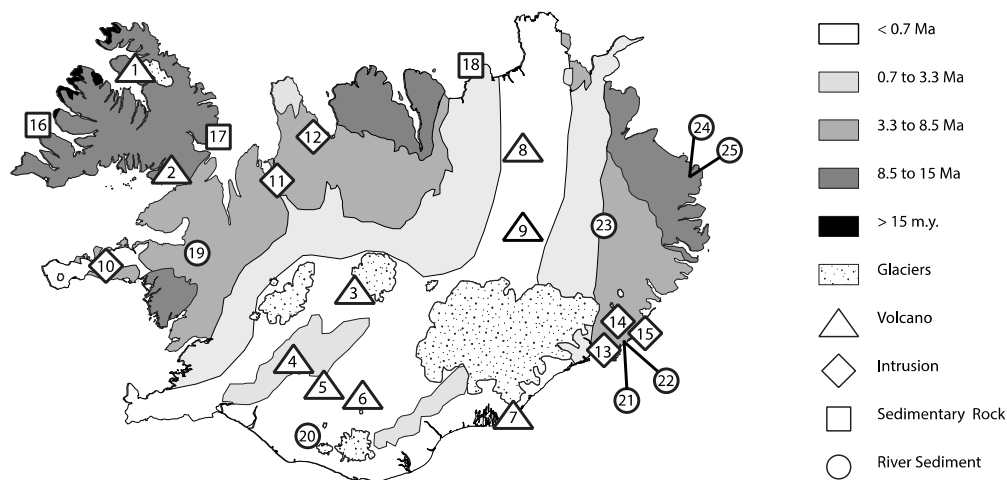
### 2.3. Data compilations from literature

Hadean data used in this comparison (Figs. 2–9) are from published literature (Maas et al., 1992; Mojzsis et al., 2001; Peck et al., 2001; Wilde et al., 2001; Cavosie et al., 2004, 2005, 2006; Crowley et al., 2005; Watson and Harrison, 2005; Pidgeon and Nemchin, 2006; Valley et al., 2006; Trail et al., 2007, 2011; Harrison and Schmitt, 2007; Harrison et al., 2008; Fu et al., 2008; Kemp et al., 2010; Bell et al., 2011; Nemchin et al., 2006). We compiled data for zircon grains with ages reported to be  $\geq 4$  Ga. The Hadean data compilation, along with supplementary information (publication, sample location and description, temperature-to-Ti calculation, etc.), can be found in Appendix A (Hadean Ti Compilation; Hadean O Compilation; Hadean TE Compilation).

**Table 1**

An overview of samples used in the creation of the Icelandic zircon dataset.

System name	Sample type	Map number	Sample name	Location (coordinates) <sup>a</sup>	TE analyses	O analyses
Hrafnfjörður	Volcanic	1	KK-24	27W 552230, 7279551 <sup>b</sup>	14	12
Króksfjörður	Volcanic	2	IKK	27W 455836, 7264252	9	8
Kerlingarfjöll	Volcanic	3	IEKIM	27W 580732, 7169302	3	0
			IEKIT	27W 576956, 7169439	18	7
Stóra-Laxa	Volcanic	4	IEFS-1a	27W 535438, 7109774	27	25
Hekla	Volcanic	5	IHB	27W 558938, 7106903 <sup>b</sup>	26 <sup>c</sup>	43 <sup>d</sup>
Torfajökull	Volcanic	6	IETR	27W 576365, 7095290	19	38
			5A03	Unavailable	33 <sup>c</sup>	0
			3A03	Unavailable	19 <sup>c</sup>	0
			ITHn	27W 584358, 7093649 <sup>b</sup>	16 <sup>c</sup>	0
			ITN	27W 595113, 7099846 <sup>b</sup>	17 <sup>c</sup>	9
			Lauf	Unavailable	0	18 <sup>d</sup>
Öræfajökull	Volcanic	7	IOHn	28W 420478, 7086216 <sup>b</sup>	23 <sup>c</sup>	16
Krafla	Volcanic	8	IEKG-1a	28W 410640, 7292179	30	25
Askja	Volcanic	9	IC45	28W 419661, 7214591 <sup>b</sup>	16 <sup>c</sup>	27 <sup>d</sup>
Snæfellsness-Knörr	Intrusive	10	IISK	27W 383104, 7191705	20	24
Viðidalsfjall	Intrusive	11	IIM	27W 521634, 7256525	23	23
Laxárdalsfjöll	Intrusive	12	LS-11	27W 439559, 7348977	19	36
Vesturhorn	Intrusive	13	IIV	28W 500765, 7126998	13	15
Slaufrudalur	Intrusive	14	IISlau	28W 498493, 7132374	5	5
Austurhorn	Intrusive	15	Mafic	28W 522402, 7142368	34 <sup>e</sup>	18
			AIC-G			
			Silicic	28W 524122, 7146308	84 <sup>e</sup>	62
			AIC-NS			
			Hval-1a	28W 523914, 7146660	0	22 <sup>d</sup>
Selardalur	Sed. Rock	16	IXSd-1	26W 635504, 7296772	17	13
Husavíkurkleif	Sed. Rock	17	IXH	27W 470820, 7280239	22	27
Tjörnes	Sed. Rock	18	IXT	28W 397693, 7334527	27	30
Midá	River Sed.	19	ISM <sub>i</sub>	28W 464561, 7211545 <sup>b</sup>	48	23
Markarfljót	River Sed.	20	ISM	27W 552381, 7059713 <sup>b</sup>	52	33
Fjardarsá	River Sed.	21	ISFjar	28W 500225, 7131316 <sup>b</sup>	39	17
Jökulsá í Lóni	River Sed.	22	ISJL	28W 505478, 7144079 <sup>b</sup>	57	18
Lagarfljót	River Sed.	23	ISLF	28W 506732, 7216451	25	43
Storaá	River Sed.	24	ISS	28W 561363, 7260665	31	39
Krossá-Kækjudalsá	River Sed.	25	ISKK	28W 553667, 7260140	33	83

<sup>a</sup> All coordinates are UTM, datum WGS 1984 unless otherwise indicated.<sup>b</sup> Coordinates presented as UTM, datum Hjørsey 1955.<sup>c</sup> Trace element data published in Carley et al. (2011); included here to create a more comprehensive Icelandic dataset.<sup>d</sup> Oxygen data published in Bindeman et al. (2012).<sup>e</sup> Trace element data presented in Padilla (2011).

**Fig. 1.** Schematic map of Iceland showing ages of strata (modified from Thordarson and Hoskuldsson, 2002) and sample lithologies and locations for this study. *Volcanic Samples:* [1] Hrafnfjörður; [2] Króksfjörður; [3] Kerlingarfjöll; [4] Stóra-Laxa; [5] Hekla; [6] Torfajökull; [7] Öræfajökull; [8] Krafla; [9] Askja. *Intrusive Samples:* [10] Snæfellsness-Knörr; [11] Viðidalsfjall; [12] Laxárdalsfjöll; [13] Vesturhorn; [14] Slaufrudalur; [15] Austurhorn. *Sedimentary Rock Samples:* [16] Selardalur; [17] Husavíkurkleif; [18] Tjörnes. *River Sediment Samples:* [19] Midá; [20] Markarfljót; [21] Fjardarsá; [22] Jökulsá í Lóni; [23] Lagarfljót; [24] Storaá; [25] Krossá-Kækjudalsá.

We have also compiled a database of zircon trace element compositions from (1) mid-ocean ridge basalt (MORB; Grimes et al., 2007, 2009; Cavosie et al., 2009); (2) a continental hotspot (post-caldera rhyolites, Yellowstone caldera, USA: Stelten et al., 2013); (3) continental arcs (Aucanquilcha volcanic cluster [Ti only]: Walker et al., 2010; Mount Saint Helens volcano, USA: Claiborne

et al., 2010a; Claiborne, 2011; Flanagan, 2009; South Sister volcano, USA: Stelten and Cooper, 2012; detrital zircons from the McCoy Mountain formation, USA: Barth et al., 2013); and (4) rifts that are evolving from continental to oceanic, where continental lithosphere is being replaced by ascending asthenosphere and newly-formed oceanic lithosphere (hereafter referred to as “evolv-

ing rifts,” with examples from Alid, Eritrea: Lowenstern et al., 1997, 2006; Flanagan et al., 2010, and Salton Sea Trough, CA: Schmitt and Vazquez, 2006; Schmitt et al., 2013). These data are used as standards of comparison for the Icelandic and Hadean datasets (Sections 3.2.1–3.2.3; Figs. 7, 8, 9).

Zircon trace element analyses for the global comparison (which we compiled from published literature) were all collected using the SHRIMP-RG, and calibrated to in-house standard MAD. The Hadean data, however, represent a variety of analytical sources and calibration standards. Thus, analytical biases may exist between the SHRIMP-RG data and the Hadean sets. Furthermore, Hadean zircons may have undergone alteration over the course of the last >4.0 Ga. We therefore exercise caution when conducting the data comparison. Because light rare earth element (LREE) concentrations in zircon are the most susceptible to substantial modification during alteration (relative to heavy REEs; HREEs), we exclude them from our comparisons. We place great confidence in the HREEs, which are most abundant, easiest to measure accurately and precisely, and least susceptible to alteration. We are confident that observations and conclusions based on HREE concentrations are reflections of zircon compositions and not the product of alteration or analytical bias.

#### 2.4. Treatment of Ti-in-zircon data

Watson and Harrison (2005) demonstrated a close correlation between Ti content of zircon and crystallization temperature, and presented an initial calibration of a Ti-in-zircon geothermometer. Ferry and Watson (2007) subsequently calibrated the geothermometer to take into account the influence of activities of SiO<sub>2</sub> and TiO<sub>2</sub>. Many papers on Hadean zircon report only Ti-in-zircon temperatures rather than concentrations (e.g., Watson and Harrison, 2005; Valley et al., 2006; Trail et al., 2007, 2011; Harrison et al., 2008; Bell et al., 2011). In these cases, we recast temperature data as Ti concentrations, using the appropriate equations (Watson and Harrison, 2005; Ferry and Watson, 2007) and unit TiO<sub>2</sub> and SiO<sub>2</sub> activities as in the published papers; the specifics of our temperature-to-titanium conversions can be found in Appendix A (Hadean Ti Compilation).

As the Hadean (and many Icelandic) samples are detrital, we cannot confidently constrain activities of TiO<sub>2</sub> and SiO<sub>2</sub>. This uncertainty, along with inconsistencies in approach to estimating activities in different studies, makes direct comparison of calculated Ti-in-zircon temperatures problematic. We therefore simply compare Ti concentrations in this paper (Sections 3.1.3 and 3.2.1; Figs. 3 and 7). To make conservative, semiquantitative, comparisons of temperatures between Hadean and Icelandic zircons, we use the Ferry and Watson (2007) equation and assign activities of unity for SiO<sub>2</sub> and TiO<sub>2</sub>, unless otherwise indicated in the text. Given the many issues that affect the calculation of Ti in zircon temperatures, it should be stressed that all absolute temperature values are model dependent and should be treated as estimates of a probable temperature range.

### 3. Results and discussion

#### 3.1. Comparing Hadean and Icelandic zircon populations

##### 3.1.1. Oxygen isotopes

We collected 653 new oxygen isotope measurements in Icelandic zircons, and supplement our new dataset with 100 oxygen isotope measurements previously reported by Bindeman et al. (2012). Together, these analyses yield a mean  $\delta^{18}\text{O}$  value of +3.0‰ (1 s.d. = 1.3‰) and a median of +3.2‰. Ninety percent of the analyses fall between +0.2‰ and +4.7‰ (the 5th and 95th percentiles of the dataset, respectively). Outliers extend down to

−2.3‰ and up to +7.8‰. The lowest 5% of the dataset is composed almost exclusively of zircons from the Torfajökull central volcano (19 of 38 analyses) and a small intrusion that we call Snæfellsness-Knórr on the Snæfellsness Peninsula (18 of 38 analyses). The highest 5% comprises zircons from multiple intrusions, lavas and tephra, and sands and sandstones from across the island.

Ninety percent of the 352 reported Hadean  $\delta^{18}\text{O}$  values fall between 4.6‰ and 7.5‰ (Mojzsis et al., 2001; Peck et al., 2001; Wilde et al., 2001; Cavosie et al., 2005, 2006; Trail et al., 2007, 2011; Harrison et al., 2008; Bell et al., 2011; Nemchin et al., 2006), with outliers extending from 2.9‰ (Trail et al., 2007) to 10.5‰ (Trail et al., 2007). This dataset has both a mean and median of 6.1‰ (1 s.d. = 0.9‰). Although 64% of the Icelandic oxygen dataset overlaps with the Hadean, with values  $\geq 2.9\%$ , the difference in distribution of values between the two populations is striking. As shown in Fig. 2, the Icelandic zircon population is highly depleted in  $^{18}\text{O}$  relative to the Hadean.

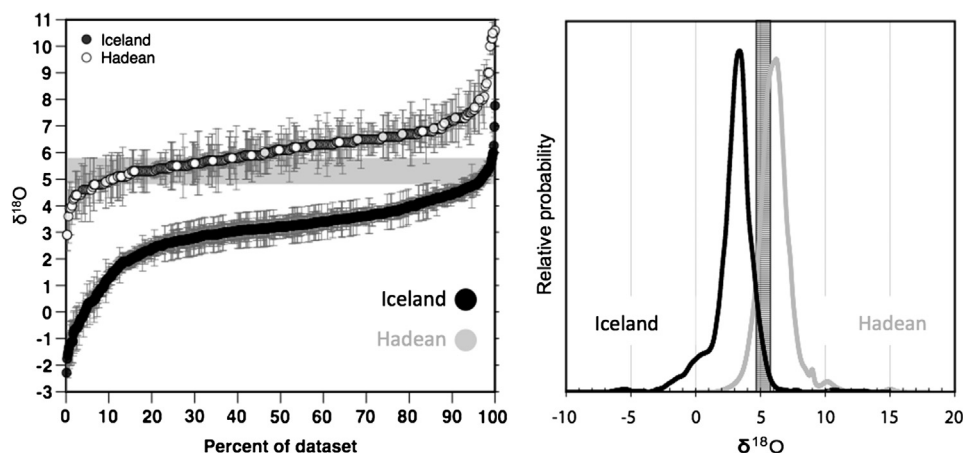
The generally accepted range of  $\delta^{18}\text{O}$  values for zircons derived from a closed-system mantle-derived melt ( $5.3 \pm 0.6\%$ ; Valley, 2003; cf.  $5.3 \pm 0.8\%$  and  $5.2 \pm 0.5\%$  for mid ocean ridge zircons, reported by Cavosie et al., 2009 and Grimes et al., 2011) creates an effective boundary between the two populations (Fig. 2). Of 763 in situ analyses of oxygen in Icelandic zircon, 750 (98%) analyses fall below 5.3‰; while only 54 of 352 (15%) published Hadean analyses fall below 5.3‰.

Deviation of  $\delta^{18}\text{O}$  away from 5.3‰ is evidence that neither Icelandic zircons, nor most (i.e., 283 of 355) Hadean zircons, grew in closed-system mantle-derived melts. Instead, the deviation suggests that both the ancient and the Icelandic zircons grew in magmas whose sources (or major assimilants) were influenced by meteoric water or seawater. However, this is where the similarities end; the fact that the Icelandic oxygen isotope signatures are low in  $\delta^{18}\text{O}$  and the Hadean is high suggests that the source material and the processes at work were distinctly different.

In order to elevate  $^{18}\text{O}$  relative to  $^{16}\text{O}$  in magmas and zircons that crystallize from them, source material (or major assimilant) must have undergone low temperature alteration by sea or meteoric water. For example, at 50 °C,  $\Delta^{18}\text{O}_{\text{Ab-H}_2\text{O}}$  fractionation is  $\sim 20\%$  (Matsuhisa et al., 1979; Ab is used as a proxy for silicic rock). Therefore, any normal  $\delta^{18}\text{O}$  rock (i.e.  $\sim$ mantle value, +6‰) will be shifted upward even by typically low- $\delta^{18}\text{O}$  Icelandic meteoric water (that is, if the water is heavier than −14‰). Strong low-temperature fractionation results in high  $\delta^{18}\text{O}$  in the solid products of such a reaction; that is, minerals formed or chemically modified during weathering or sedimentary processes, or low temperature hydrothermal exchange. Conversely, to decrease  $\delta^{18}\text{O}$  in magmas and zircons, the source material (or major assimilant) must undergo high temperature alteration by low- $\delta^{18}\text{O}$  surface water (sea or meteoric). This reduction is most effective if alteration temperatures exceed  $\sim 250\text{--}350\text{ }^\circ\text{C}$ , where fractionation ( $\Delta^{18}\text{O}_{\text{Ab-H}_2\text{O}}$ ) is less than 6‰. At still higher temperatures, fractionation becomes minimal and the solid products more closely reflect the low- $\delta^{18}\text{O}$  composition of the surface waters that induced alteration.

It appears that the distinction in  $\delta^{18}\text{O}$  indicates substantial differences between petrogenesis of zircon-bearing Hadean and Icelandic magmas. However, it is conceivable that these differences are less fundamental than they appear. We propose three possibilities that may explain the differences in  $\delta^{18}\text{O}$  observed between Hadean and Icelandic zircons:

1. The difference reflects general changes in the oxygen isotopic composition of the mantle or surface waters through time (i.e., higher values in the Hadean).
2. The universal depletion of  $^{18}\text{O}$  in Icelandic zircon is the consequence of an unusual, low  $\delta^{18}\text{O}$  mantle source for Icelandic magmas, not of an otherwise distinctive petrogenetic process.



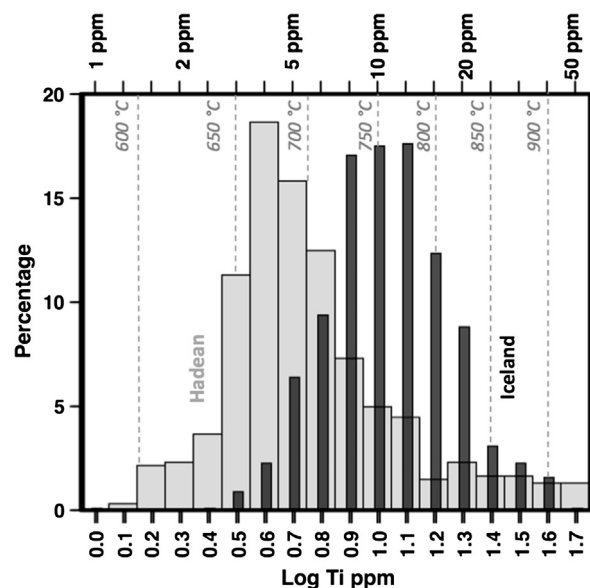
**Fig. 2.** (Left): Icelandic ( $n = 763$ ) and Hadean ( $n = 352$ ) zircon  $\delta^{18}\text{O}$  values, with analytical uncertainties. See Appendices (Reduced O data and Hadean O compilation) for detail. Icelandic and Hadean oxygen datasets were sorted in order of increasing value before plotting. (Right): Probability density plots of Icelandic (black) and Hadean (white) zircon  $\delta^{18}\text{O}$  values. In both left and right panels, the estimated range of  $\delta^{18}\text{O}$  for zircon equilibrated with mantle-derived magmas ( $5.3 \pm 0.6\text{‰}$ , Valley, 2003; cf. mid-ocean ridge zircons,  $5.3 \pm 0.8\text{‰}$  and  $5.2 \pm 0.5\text{‰}$ , reported by Cavosie et al., 2009 and Grimes et al., 2011, respectively) is indicated by the gray bar.

3. Iceland's near-polar environment, with resulting low- $\delta^{18}\text{O}$  surface water, greatly amplifies the isotopic influence of relatively modest contributions from hydrothermally altered rock.

The first possibility suggested above—substantially higher oxygen isotope ratio for typical mantle or seawater in ancient Earth—has no basis in data for either modern or ancient rocks (e.g., Burdett et al., 1990; Valley et al., 2005).

The second possibility—a mantle source beneath Iceland that is anomalously low in  $\delta^{18}\text{O}$ —has indeed been suggested, but it has only been seriously applied to basalts (e.g., Muehlenbachs et al., 1974; Skovgaard et al., 2001; MacLennan et al., 2003; Burnard and Harrison, 2005; Macpherson et al., 2005; Thirlwall et al., 2006). However, analyses of olivine phenocrysts, including those from low  $\delta^{18}\text{O}$  basalts, invariably return normal  $\delta^{18}\text{O}$  values (Bindeman et al., 2008). This suggests that the Icelandic plume is normal in  $\delta^{18}\text{O}$  and that the basalts acquire their low- $\delta^{18}\text{O}$  in the crust. Furthermore, even the strongest proponents of a low- $\delta^{18}\text{O}$  mantle plume suggest values no lower than  $\sim 4\text{‰}$  (Thirlwall et al., 2006). Generation of silicic magmas through fractional crystallization of such basalts would yield silicic magmas and zircons only slightly below typical mantle values ( $5.3 \pm 0.6\text{‰}$ ; Valley, 2003). Generation of silicic magmas through partial melting of the unaltered equivalents of such basalts would yield the same result. While our zircon dataset includes values consistent with this origin, they are in the minority (cf. Bindeman et al., 2008, 2012).

The final explanation for the  $^{18}\text{O}$ -depleted signature of Icelandic zircon—hydrothermal alteration by glacial-climate, extremely-low  $\delta^{18}\text{O}$  surface water—is not supported either by our dataset or by measured and estimated past values of Icelandic waters. Our analyzed zircons span the past  $\sim 15$  m.y. of Icelandic history, a period that encompasses climate ranging from warm-temperate through cooling to full glaciation (e.g., Thordarson and Hoskuldsson, 2002). More specifically, 182 of the 763 oxygen analyses considered here are from systems that were active  $>8.5$  Ma (Fig. 1), from a time when Iceland's climate was warm (e.g., Denk et al., 2011) and presumably surface waters did not have unusually low  $\delta^{18}\text{O}$ . Despite this, no systematic change in  $\delta^{18}\text{O}$  is observed through time (refer to the map in Fig. 1, as well as system-specific data in Appendix A: Reduced O data). These oldest Icelandic zircons have an average (and median)  $\delta^{18}\text{O}$  of  $3.2\text{‰}$ , compared to an average of  $3.0\text{‰}$  (median  $3.2\text{‰}$ ) for zircons from systems  $<8.5$  Ma, and an average of  $2.4\text{‰}$  (median of  $2.3\text{‰}$ ) for the young, active volcanoes in this dataset (Askja, Krafla, Örfajökull, Kerlingarfjöll, Torfajökull, Hekla). Modest variability is consistent with the muting effect of



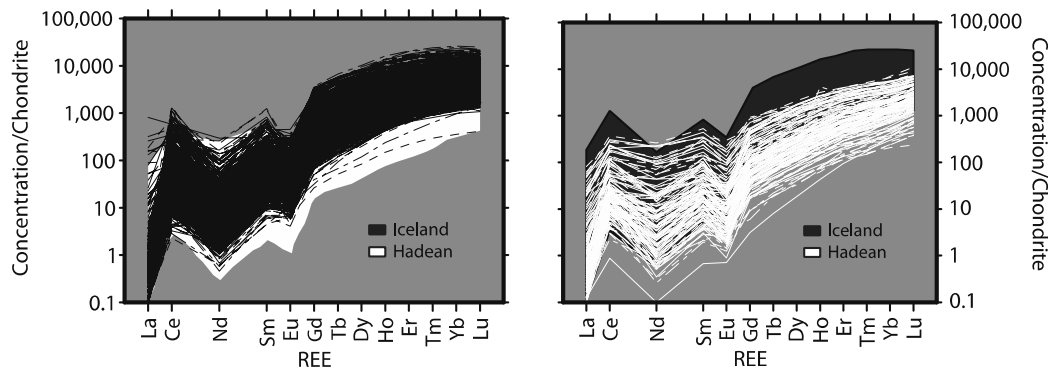
**Fig. 3.** Histograms depicting distribution of Ti in Hadean ( $n = 600$ ) and Icelandic ( $n = 820$ ) zircon populations. Log Ti ppm labels (x-axis) are placed at the start of each bin; for reference, Ti concentrations (ppm) are shown above the top x-axis. We only present Ti concentrations up to 50 ppm, but percentages are calculated using full data set (see Appendices: Iceland SHRIMP TE data and Hadean Ti compilation). Estimated temperatures, provided as a general reference, are calculated using the methods of Ferry and Watson (2007) and Ti and Si activities of 1.0. These estimates represent minimum temperatures.

maritime location on  $\delta^{18}\text{O}$  of Icelandic surface waters and absence of evidence for extremely low  $\delta^{18}\text{O}$  meteoric waters in Iceland's past (cf. Bindeman et al., 2006). Thus, we argue that the strong signature of the contribution of hydrothermally altered material to zircon-bearing silicic magma is not simply a reflection of the altering fluids having unusually low  $\delta^{18}\text{O}$ .

### 3.1.2. Titanium concentrations

As with oxygen isotopic compositions, Ti concentrations divide Hadean and Icelandic zircons into two overlapping but distinct populations (Fig. 3). The Icelandic population (mean Ti: 13.6 ppm, median: 11.9 ppm) is shifted towards higher Ti concentrations than the Hadean (mean: 7.1 ppm, median: 5.4 ppm).

The distinct distributions of Hadean and Icelandic Ti concentrations imply a noteworthy difference between the histories of the magmas from which the two populations of zircons grew. As



**Fig. 4.** Chondrite-normalized rare earth element (REE) patterns in Hadean ( $n = 167$ ) and Icelandic ( $n = 781$ ) zircons. In the left panel, individual Icelandic analyses are presented on top of a field representing typical Hadean compositions (outliers excluded when the field was drawn; <1% of analyses). In the right panel, individual Hadean data points taken from the literature are plotted on top of a field representing typical Icelandic compositions (outliers excluded when the field was drawn; <1% of analyses). Chondrite values are from [McDonough and Sun \(1995\)](#).

the Hadean (and many Icelandic) samples are detrital, we cannot tightly constrain activities of  $\text{TiO}_2$  and  $\text{SiO}_2$ , and we acknowledge that there will be significant uncertainty in any quantitative estimates of temperature. In any case, Icelandic Ti concentrations that are roughly twice as high as those of Hadean zircons require either: (1) systematically higher temperatures during growth of Icelandic compared to Hadean zircons; (2)  $a_{\text{TiO}_2}$  that is far higher in Icelandic magmas or  $a_{\text{SiO}_2}$  that is far lower; or (3) both. Consider the following examples. If we assume  $a_{\text{TiO}_2}$  and  $a_{\text{SiO}_2}$  of unity, the median calculated Icelandic growth temperature ( $\text{Ti} = 12$  ppm) is  $763^\circ\text{C}$ ; the average for the Hadean ( $\text{Ti} = 5$  ppm), calculated using the same activities, is  $685^\circ\text{C}$ . Assuming  $a_{\text{TiO}_2} = 0.5$  and  $a_{\text{SiO}_2} = 1$ , the Icelandic median is  $835^\circ\text{C}$  and the Hadean is  $746^\circ\text{C}$ . To make the average temperatures match,  $a_{\text{TiO}_2}$  would have to be far lower (approximately half of the Icelandic value) in the Hadean magmas, or  $a_{\text{SiO}_2}$  would have to be much higher (a factor of almost 2). Much higher  $a_{\text{TiO}_2}$  for Icelandic magmas is very unlikely: it has been argued that  $a_{\text{TiO}_2}$  in melts from which Hadean zircons crystallized was relatively high ( $\geq 0.6$ ; e.g. [Harrison, 2009](#), in part on the basis of rutile inclusions in some zircon crystals). There is also no reason to believe that  $a_{\text{SiO}_2}$  is especially low in zircon-bearing magmas from Iceland (whole-rock analyses of our zircon-bearing samples approach or exceed 70 wt.%  $\text{SiO}_2$ , and glass when present invariably exceeds 70 wt.%). We therefore suggest that growth of Hadean zircons did indeed take place at much lower temperatures than growth of Icelandic zircons.

### 3.1.3. Rare earth elements (REEs)

Chondrite-normalized REE patterns for Icelandic zircons are generally typical of those reported from igneous rocks ([Fig. 4](#)): heavy (H) REEs are extremely enriched relative to light (L) REEs, and positive Ce and negative Eu anomalies are ubiquitous. Similar trends are observed for the Hadean dataset and the range of LREEs is similar, but there is one noteworthy distinction: HREE concentrations are much lower in Hadean zircons (see lower overall HREEs in [Fig. 4](#) and clear distinction in Yb in [Fig. 5](#)). Ytterbium concentrations in Hadean zircons range from  $\sim 55$ –840 ppm (excluding lowest and highest 5%) for the Hadean zircons, with a median of 240 ppm; the Icelandic Yb concentrations are much higher, spanning a range from  $\sim 240$ –2100 ppm with a median of 820 ppm.

The ratio Gd/Sm effectively distinguishes Icelandic from Hadean zircon populations ([Fig. 5](#)). The range of Gd/Sm for the Hadean (excluding the lowest and highest 5%) is  $\sim 2$ –8; for Iceland, it is  $\sim 7$ –11. For a given Sm concentration, the Gd/Sm of Iceland is consistently higher; at  $\sim 8$  ppm Sm, the Gd/Sm of the Hadean ranges from  $\sim 2$ –6, while for Iceland the Gd/Sm ranges from  $\sim 7$ –11.

Another ratio that highlights distinctions between the Icelandic and Hadean zircon populations is Gd/Yb. Excluding what appear

to be outliers in the Hadean dataset, Icelandic and Hadean zircons overlap considerably but define distinct, coherent groups in plots of Gd/Yb vs REE concentrations (e.g. [Fig. 5](#)(bottom panels)). The median Hadean Gd/Yb is 0.07, whereas that of Icelandic zircon is 0.12. The minimum (5th percentile) value of the Hadean cluster is also substantially lower at 0.03, compared to 0.07 for Iceland.

Europium anomalies are similar for Hadean and Icelandic zircons, ranging from negligible ( $\sim 0.95$ ) to below 0.10 ([Fig. 5](#)). The greatest anomalies are more extreme in Icelandic zircons than in Hadean (0.03 vs 0.06), but these are in grains that are far richer in REEs than any from the Hadean. At similar Yb concentrations, there is no discernible difference in Eu/Eu\*.

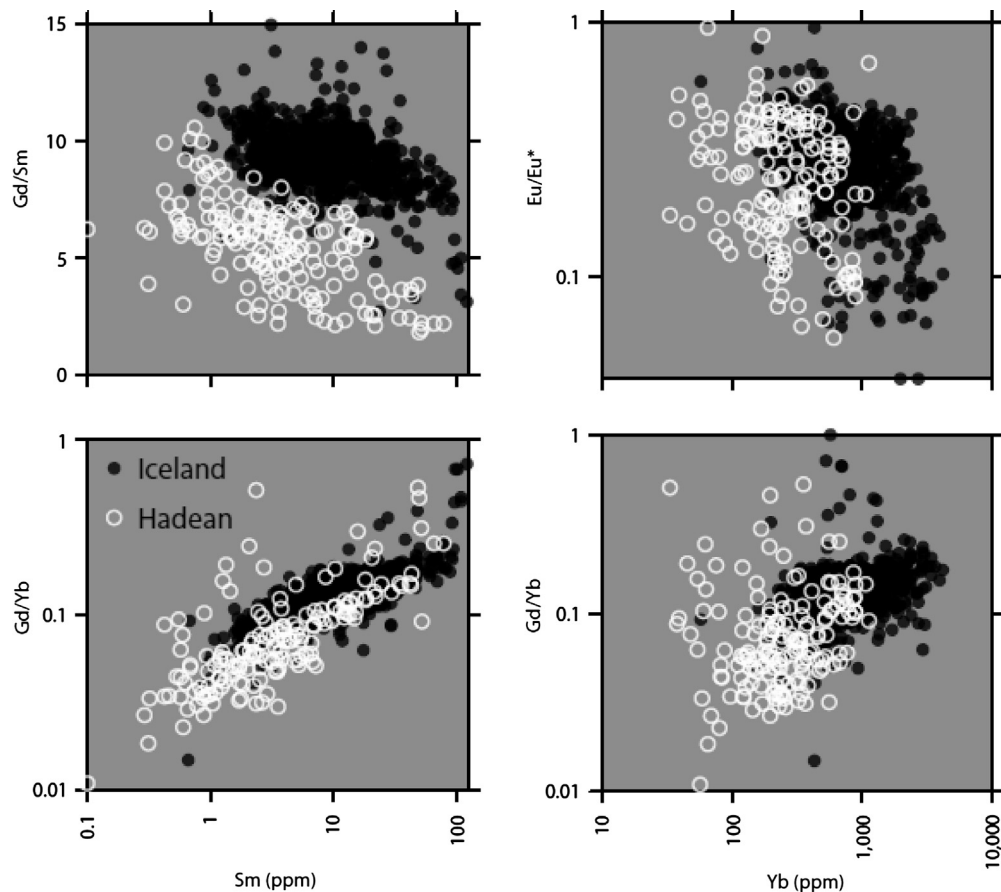
### 3.1.4. Trace element discrimination

[Grimes et al. \(2007\)](#) demonstrated that zircons that have crystallized from magmas in continental and oceanic settings could generally be distinguished based on concentrations of Yb, U, Y and Hf. We plot our Icelandic and Hadean zircon data sets on the diagrams that they developed in [Fig. 6](#).

On a plot of Yb vs U ([Fig. 6a](#)), the Icelandic zircon population defines a narrow field that parallels the continental–oceanic boundary established by [Grimes et al. \(2007\)](#); the Icelandic data lie close to the oceanic boundary, but almost exclusively within the continental field (higher U/Yb than oceanic zircon). Hadean zircons are also exclusively “continental,” but in a less well-defined field that stretches much farther from the boundary into the continental field (lower Yb for a given U concentration for the Hadean vs. Iceland). Ytterbium concentrations are substantially higher in Icelandic zircons ( $\sim 150$  ppm to  $\sim 4000$  ppm) than in Hadean zircons ( $\sim 30$  ppm to  $\sim 1000$ ). Icelandic zircons have U contents that span a far broader range—almost three orders of magnitude, from  $\sim 20$  ppm to  $\sim 3000$  ppm—than Hadean, which have U concentrations that span only a little more than an order of magnitude, from  $\sim 40$  ppm to  $\sim 700$  ppm. It is possible that difference at the upper end of the ranges is the result of high-U zircons from the Hadean being lost as a consequence of metamictization and subsequent mechanical and chemical breakdown during the last  $>4$  Ga. Regardless, Hadean zircons clearly range to compositions not seen in Iceland, notably in terms of their low Y, Yb and HREEs in general, higher average U/Yb and negative U/Yb vs Y trend, and higher Hf ([Fig. 6](#)). Hadean zircons all plot well within established continental fields in [Fig. 6](#), whereas Icelandic zircons tend to plot on the continental side of the oceanic–continental boundary and extend slightly into the oceanic field.

### 3.1.5. Discrimination by combined oxygen isotopes and trace elements

Combining oxygen isotopic composition with selected trace elements and trace element ratios (e.g. Ti, Yb, Gd/Sm; [Fig. 7](#)) permits



**Fig. 5.** Comparison of Icelandic ( $n = 781$ ) and Hadean ( $n = 167$ ) HREEs (Yb) and MREEs (Sm, Gd) concentrations and ratios, and Eu anomalies.

almost complete distinction of analyzed Hadean ( $n = 60$  for Ti and 95 for REEs) from Icelandic ( $n = 384$ ) zircon populations. Less than 5% of Icelandic zircons with paired trace elements and O isotope analyses lie within the Hadean compositional range on such plots. While this does not prove the absence of magmas produced by Iceland-like petrogenetic conditions during the Hadean, it strongly supports the contention that such conditions are exceedingly rare, as indicated by  $>4$  Ga zircons that have been identified to date.

### 3.2. Hadean and Icelandic zircon trace element compositions in a global context

As noted in the previous sections, oxygen isotopes and trace element compositions reveal significant differences between Icelandic and Hadean zircon populations: most notably, Icelandic zircons have much lower  $\delta^{18}\text{O}$  and higher Ti concentrations (suggesting higher crystallization temperatures) and are more strongly enriched in HREEs. In this section, we assess how trace element compositions of both zircon populations compare to those from other Phanerozoic magmatic-tectonic settings.

In the following sections and figures we compare the Ti concentrations (Fig. 7), and discriminatory elemental concentrations and ratios (Gd/Yb, Sm, Yb; Fig. 8 [cf. Fig. 5] and U, U/Yb, Y, Hf; Fig. 9 [cf. Fig. 6]) of Icelandic and Hadean zircons to zircons within our global database (see Section 2.3). Chondrite-normalized REE patterns (for zircon and available bulk-rock examples) are presented in Appendix A (see figure file).

#### 3.2.1. Titanium

Zircons from different environments have widely varying distributions of Ti concentration, from narrow to broad and simple to complex (Fig. 8), but distinctions between Ti-rich and -poorer

populations are evident (see Global TE Data and Global Ti Table in Appendix A for more detail). Median concentrations, less susceptible to the effects of outliers than means, reflect these differences best: MORB (15 ppm) and Iceland (12 ppm) are distinctly higher, Yellowstone, continental-oceanic rifts, and continental arcs (8 ppm) have intermediate values, and Hadean Ti concentrations (5 ppm) are demonstrably lower than the other populations. This comparison further highlights the disparity between Icelandic and Hadean zircon.

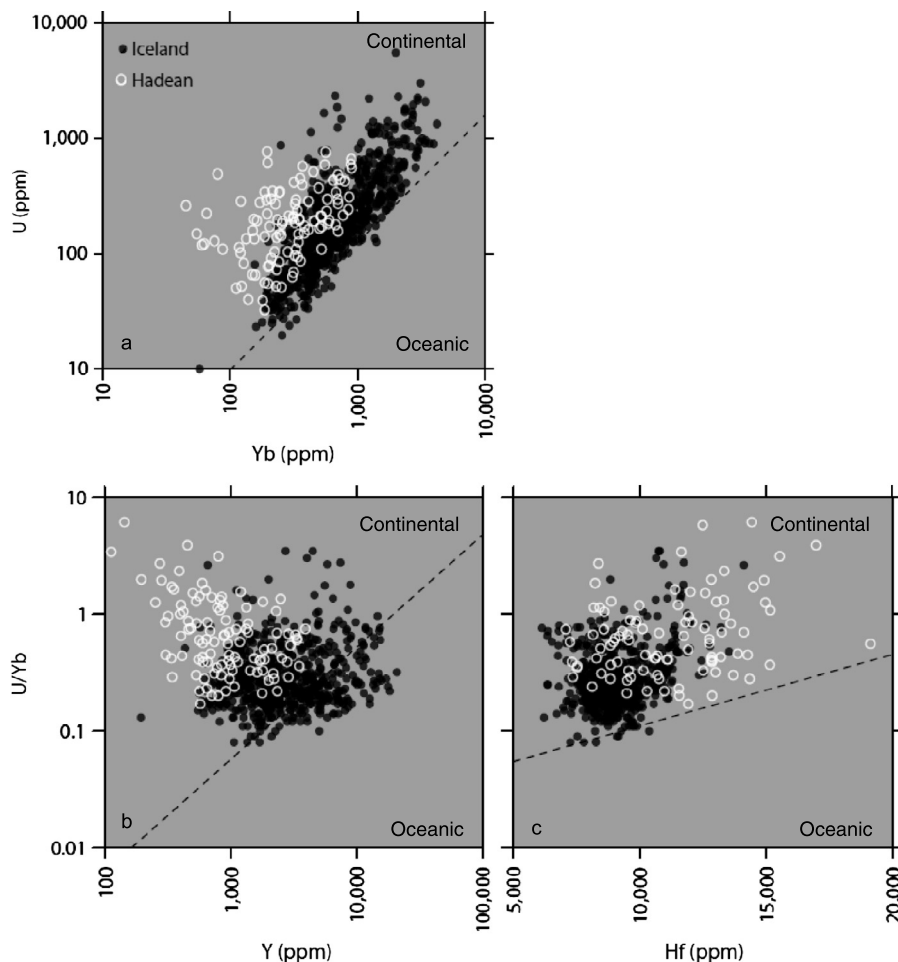
#### 3.2.2. Rare earth elements (REEs)

The Gd/Yb ratio discussed in Section 3.1.3 and Fig. 5 highlights differences in our global zircon database (Fig. 9). Most notable is the observation that zircons from both the Hadean and Phanerozoic continental arcs are quite variable in Gd/Yb, ranging downward to values not observed in other environments. Iceland, evolving rifts and MORB extend to very high Yb concentrations (up to  $\sim 6000$ – $10,000$  ppm), while the Hadean, continental arcs and the continental hotspot are less enriched (maxima near 1000 ppm).

Chondrite-normalized REE plots comparing Iceland and Hadean zircons to those from the global dataset are compiled in Appendix A (see figure file), along with a chondrite-normalized REEs plot for Icelandic felsic rocks and well-established global rock compositions (primitive mantle, E-MORB, N-MORB, OIB, Andean arc rocks). These plots confirm that REE compositions in zircons do indeed reflect differences in magma compositions (as expected), giving confidence that our zircons are robust, and telling us what we should expect when whole-rock compositions are known.

#### 3.2.3. Trace element discrimination

Trace element compositions of zircons from our global database, when plotted in Grimes et al. (2007) discrimination diagrams,



**Fig. 6.** Comparison of Icelandic ( $n = 700$ ) and Hadean ( $n = 108$ ) trace element compositions on discrimination diagrams in the style of Grimes et al. (2007). Dashed lines delineate “continental” (above the line) and “oceanic” (MORB) compositional fields. a: Yb (ppm) vs U (ppm); b: Y (ppm) vs U/Yb; c: Hf (ppm) vs U/Yb.

define similar fields to those initially shown by those authors (Fig. 10). Most but not all MORB zircons fall in their “oceanic crust fields” on U/Yb vs Y and Hf and U vs Yb diagrams, and almost 100% of Hadean, continental arc, and continental hotspot (Yellowstone) zircons lie above the defining boundaries of Grimes et al. (2007), within the continental field (Fig. 10). The Hadean and continental arc fields are almost indistinguishable; particularly in U/Yb vs. Y space, with low Y values and a negative correlation typifying the U/Yb vs. Y space.

Icelandic and continental–oceanic rift zircons are mostly within the continental fields, but a few analyses (notably, Salton Sea zircons in the plot of Y vs U/Yb; see figure file in Appendix A) extend into the “oceanic” field. Thus, Icelandic and evolving-rift zircons define a field that overlaps with but is clearly intermediate between the more continental populations (arcs, Yellowstone, Hadean) and MORB.

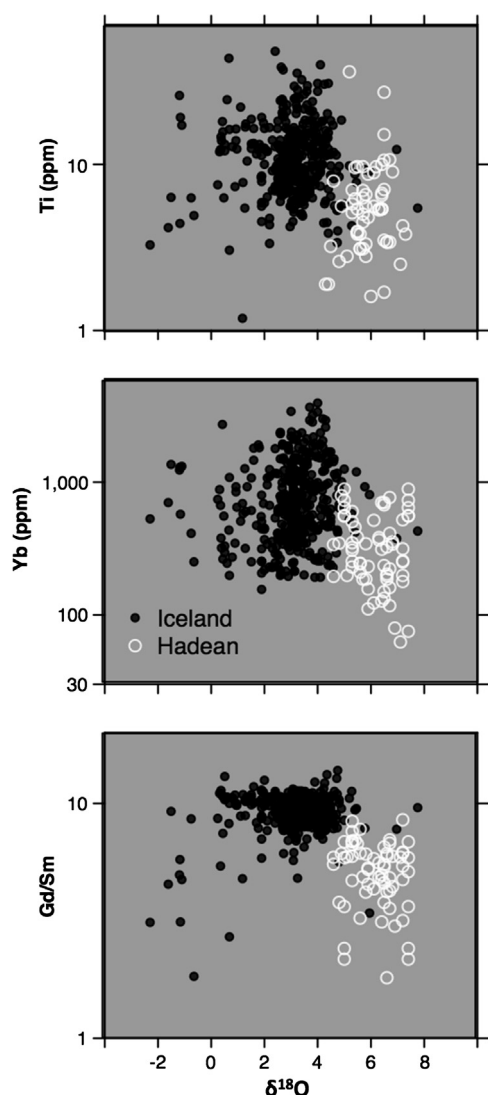
### 3.3. Elemental contrasts: possible petrogenetic implications

It is plausible that the mantle from which Hadean magmas were ultimately derived was essentially primordial (undepleted). If this were the case, zircons will reflect the significant elemental differences between the Hadean mantle and the mantle from which modern Icelandic and other magmas are derived. However, the distinguishing characteristics of Hadean zircon—low MREEs and HREEs, Ti, and U—cannot be explained by derivation from a less depleted mantle source. We therefore conclude that the compositions of zircon-bearing Hadean magmas differed fundamentally

from zircon-bearing Icelandic magmas, and that the petrogenetic processes that yielded the Hadean zircon signature had little to do with a unique mantle composition. We therefore include them below in a discussion to consider general petrogenetic implications of the compositions of zircon from different settings.

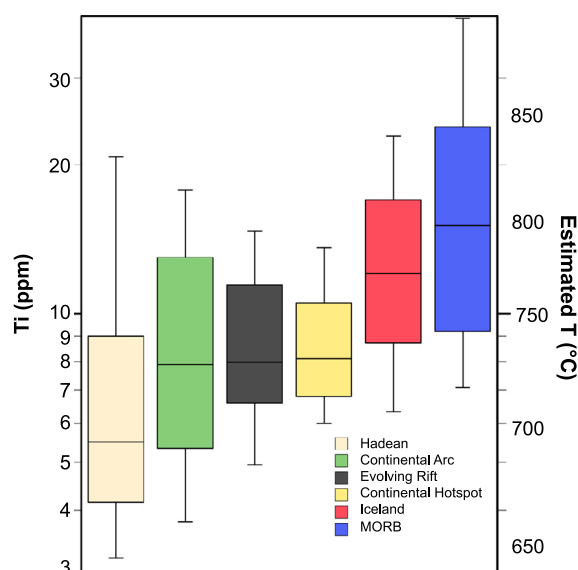
Zircons from settings where there is no subduction influence and little or no continental lithosphere—those from Iceland, as well as MORB and evolving continental–oceanic rift settings—are distinct in composition from those from Phanerozoic arcs and even more so from Hadean zircons. The former group is most notably distinguished by higher Ti (in Icelandic and MORB zircons) and middle to heavy REE concentrations. This probably reflects differences that relate to magma genesis and evolution in the contrasting Phanerozoic settings: hotter, drier magmas in juvenile rift and plume environments, cooler and wetter magmas in subduction environments. This leads directly to the higher Ti in zircons from rift/plume settings.

Trace element abundances evolve very differently in the contrasting settings as a consequence of the different coexisting crystalline assemblages and resulting differences in trace element partitioning (e.g. Bachmann et al., 2005; Rollinson, 1993). The REEs and Y are incompatible with major minerals that coexist with higher-T melts (olivine, pyroxenes, feldspar, mostly plagioclase, oxides  $\pm$  quartz; except where clinopyroxene is unusually abundant); thus, silicic melts produced by the extensive fractionation of these minerals will have high concentrations of these elements. In contrast, amphibole and REE-rich accessories commonly join the crystalline assemblage in cooler, wetter magmas in subduc-



**Fig. 7.** Discriminating between Icelandic ( $n = 384$ ) and Hadean ( $n = 60$  for Ti, 95 for Gd, Sm and Yb) zircon populations using oxygen isotopes and trace elements. Paired Ti and O Hadean data comes from [Trail et al. \(2007, 2011\)](#) and [Harrison et al. \(2008\)](#). Paired O and REE data comes from [Peck et al. \(2001\)](#), [Wilde et al. \(2001\)](#), and [Cavosie et al. \(2006\)](#).

tion environments; therefore MREEs, HREEs, and in some cases LREEs are low in silicic melts. Saturation in key accessory minerals is insensitive to water content of melts all other compositional parameters being equal. Therefore, they appear earlier relative to major silicates in cool wet magmas compared to in hot dry magmas (e.g. [Watson and Harrison, 1983](#); [Harrison and Watson, 1984](#); [Boehnke et al., 2013](#)). This distinction is consistent with the contrasts in elemental compositions of Phanerozoic silicic magmas from different tectonic environments (e.g. [Pearce et al., 1984](#)). By implication, Hadean zircon compositions suggest magmas that were dramatically different from those of modern Iceland. The zircon-saturated Hadean magmas were likely similar to but perhaps even cooler and wetter than modern subduction zone magmas ([Harrison, 2009, 2013](#)), as opposed to magmas produced by fractional crystallization of MORB-like basalt (as proposed by [Coogan and Hinton, 2006](#)). To carry the interpretation further, these compositions also refute the hypothesis that the magmas from which Hadean zircon grew were products of impact melting (a finding that supports the conclusions of [Darling et al., 2009](#) and [Wielicki et al., 2012](#)).



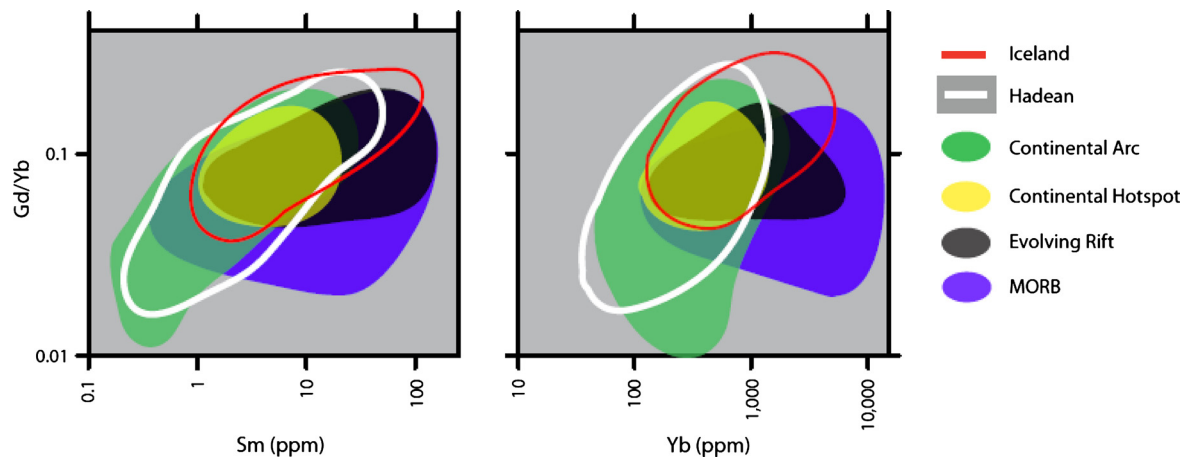
**Fig. 8.** Comparison of Ti-in-zircon distributions of global zircon populations. Whiskers extend to the 10th and the 90th percentile. The lower boundary of each box represents the 25th percentile and the upper boundary represents the 75th percentile (i.e., box represents middle 50% of zircon compositions for each population). The line bisecting each box represents the median composition of the population. Calculations were made with complete datasets, capped at 100 ppm (all published values above 100 ppm were assumed to be from analytical spots that overlapped inclusions or Ti-rich cracks). Y axis is log-scale, values presented in ppm. Compiled data are as follows: MORB ( $n = 404$ ; [Grimes et al., 2007, 2009](#); [Cavosie et al., 2009](#)); continental hotspot ( $n = 152$ ; [Yellowstone: Stelten et al., 2013](#)); continental arc ( $n = 817$ ; [Aucanquilcha: Walker et al., 2010](#); [Mount Saint Helens: Claiborne et al., 2010a; Claiborne, 2011; Flanagan, 2009](#); [Three Sisters: Stelten and Cooper, 2012](#); [McCoy Mountain Complex detrital: Barth et al., 2013](#)); continental-oceanic rift ( $n = 158$ ; [Alid: Lowenstern et al., 2006, 1997; Flanagan et al., 2010](#); [Salton Sea: Schmitt and Vazquez, 2006; Schmitt et al., 2013](#)). Iceland and Hadean as in [Fig. 3](#).

#### 4. Conclusions

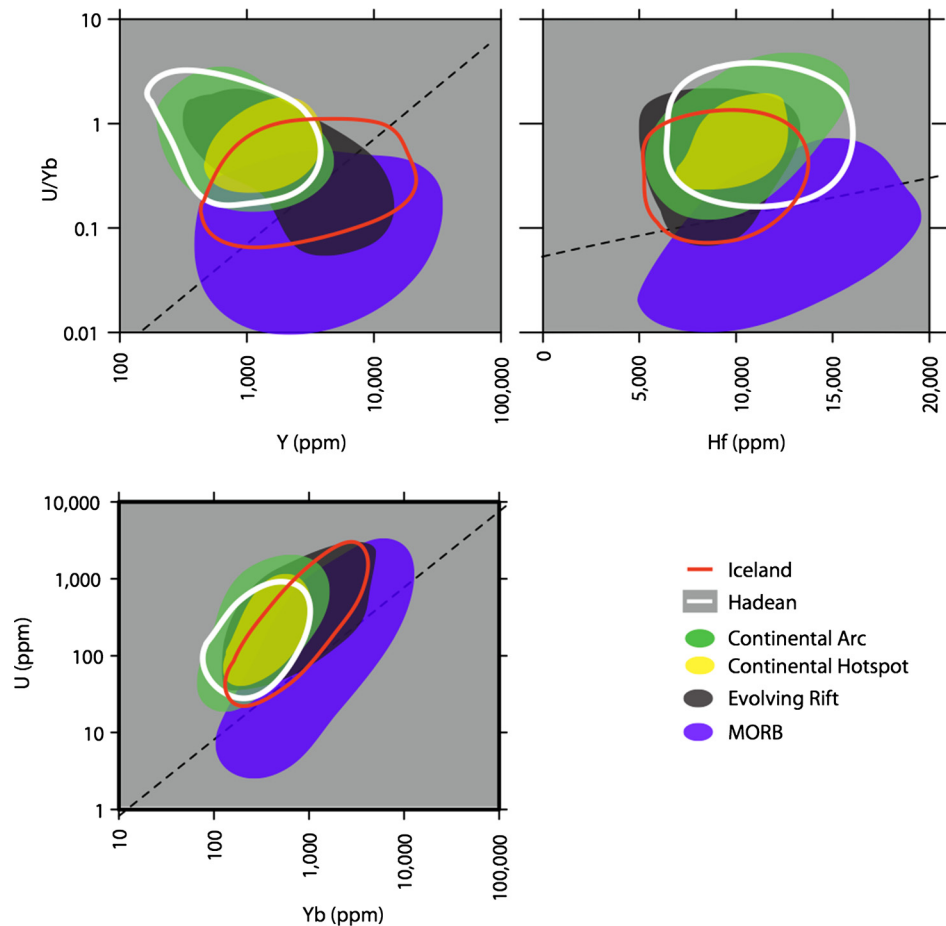
Zircon provides the only concrete record of the Hadean that is available to geoscientists today. Therefore, inferences about the Hadean are best built upon comparisons with zircon from well-constrained modern environments. In this paper, we have presented a new data set for the elemental and oxygen isotopic compositions of Icelandic zircon, compared these data with those that have been published for Hadean zircon, and finally compared both of those data sets to elemental data for zircon from other well-established Phanerozoic environments.

The  $\delta^{18}\text{O}$  signatures of Icelandic and Hadean zircon populations are dramatically different. Almost all ( $\sim 98\%$ ) analyzed Icelandic zircons have  $\delta^{18}\text{O}$  below the expected mantle value of  $\sim 5.3\text{‰}$ , whereas only 15% of Hadean zircons fall below this value. The mean and median for Iceland zircon is  $\sim 3\text{‰}$ , in contrast to  $\sim 6\text{‰}$  for Hadean zircon. This dichotomy strongly suggests an important difference in source materials for melts from which the zircons grew. The low  $\delta^{18}\text{O}$  of Icelandic zircon appears to require that the source material, or a volumetrically very important contaminant, of silicic magmas in Iceland is crustal material that has been hydrothermally altered by surface waters (e.g., [Bindeman et al., 2012](#)). In contrast, there is little evidence for appreciable contributions from such material to the Hadean magmas from which zircon grew. The range of  $\delta^{18}\text{O}$  of Hadean zircon is more compatible with normal mantle and minor sedimentary contributors, similar to Phanerozoic continental and island arc magmas ([Harrison, 2009](#)).

Concentrations of Ti clearly distinguish Icelandic (median 12 ppm) from Hadean (median 5 ppm) zircons. This suggests a substantially higher-temperature magmatic growth environment



**Fig. 9.** A global comparison of Gd/Yb (MREE/HREE) in analyzed zircon. Fields were drawn using the following datasets: MORB ( $n = 309$ ; Grimes et al., 2007; Cavoie et al., 2009); continental hotspot ( $n = 153$ ; Yellowstone: Stelten et al., 2013); continental arc ( $n = 944$ ; Mount Saint Helens: Claiborne, 2011; Flanagan, 2009; Three Sisters: Stelten and Cooper, 2012; McCoy Mountain Complex detrital: Barth et al., 2013); continental-oceanic rift ( $n = 147$ ; Alid: Lowenstern et al., 2006, 1997; Flanagan et al., 2010; Salton Sea: Schmitt and Vazquez, 2006; Schmitt et al., 2013). Iceland and Hadean are as in Fig. 5. Fields were drawn excluding <10% of data points (outliers) for each population. Figures with individual data points (including outliers excluded here) can be found in Appendix A (see figure file).



**Fig. 10.** Trace element discrimination diagrams in the style of Grimes et al. (2007). Fields were drawn using the same datasets as in Fig. 9 (some minor variability in  $n$  values, see Appendix A (Global TE data) for specifics). Fewer than 10% of data points (outliers) were excluded from each population when drawing fields. Figures with individual data points (including outliers excluded here) can be found in Appendix A (see figure file). Top left: Y (ppm) vs (U/Yb); Top right: Hf (ppm) vs (U/Yb); Bottom: Yb (ppm) vs U (ppm).

for Icelandic than for Hadean zircons, probably by 50–100 °C. Among populations that we have compiled for this investigation (see Fig. 8), only MORB zircon matches or exceeds Ti in Icelandic zircon. Hadean zircon, in contrast, has generally lower Ti than any of the other populations, implying unusually low-temperature silicic magmatism (Harrison, 2013).

Other trace elements provide informative comparisons among Icelandic and Hadean zircons and zircons from other environments. In REEs, Hf, U, and ratios of these elements, Hadean zircons are closely aligned with continental zircons (arc, and in part with a continental hotspot [Yellowstone]), whereas Icelandic zircons are generally intermediate in composition between continental and

MORB zircons. Iceland, MORB, and Yellowstone zircons share distinctly higher HREE concentrations than arc and Hadean zircons; Iceland and Yellowstone have higher U/HREE than MORB and lower ratios than continental arcs and the Hadean.

The comparisons presented in this paper support the following conclusions:

- (1) The environment in which silicic magmas are generated in Iceland is distinctly different from that in which Hadean zircon-bearing magmas were generated.
- (2) Magmatic environments in which Hadean zircon grew appear to have more in common with Phanerozoic continental settings than with Iceland or more typical mid-ocean ridge environments.
- (3) Elemental compositions of Icelandic zircon occupy a distinct field, overlapping with both continental and oceanic zircon. The Icelandic field roughly coincides with that of modern rifts where continental lithosphere is being replaced by upwelling asthenosphere and new oceanic lithosphere.
- (4) The high Ti and middle and heavy REEs of Icelandic, MORB, and evolving rifts (in M-HREEs, less-so in Ti) stand in contrast to lower Ti and M-HREEs in arc settings. The lower concentrations of these key elements are probably a consequence of cooler and wetter magmas in arc settings. Following this reasoning, Hadean zircons may reflect even cooler and wetter magmatism than Phanerozoic arcs.

## Acknowledgements

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## Appendix A. Supplementary material

Supplementary material related to this article can be found online at <http://dx.doi.org/10.1016/j.epsl.2014.08.015>.

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