A novel approach to identifying mantle-equilibrated zircon by using trace element chemistry

Ziqin Ni¹, Ricardo Arevalo Jr.¹, Philip Piccoli², and Barry L Reno³

¹University of Maryland, College Park ²University of Maryland ³Northern Territory Geological Survey

November 24, 2022

Abstract

One of the requirements for inferring local mantle redox states via zircon Ce/Ce* oxybarometry and Ti-in-zircon thermometry is to select mantle-equilibrated zircon (i.e., unaltered magmatic zircon without interaction to hydrosphere). Traditional protocols for identifying mantle-equilibrated zircon require a comprehensive examination of whole rock geochemistry in addition to zircon morphology, texture, and trace element and isotopic measurements to obtain information for zircon saturation context, source melt petrogenesis, and post-magmatic history. This study proposes a simple filter scheme for selecting mantle-equilibrated zircon using trace element systematics alone (P, Ti, Y, Nb, REE, Hf, Th, U). A total of 13 filtering criteria are synthesized from previous studies based on simulations, experiments, and compiled global datasets, all of which help to provide geological context and ultimately constrain the inferred melt redox state from three perspectives: (1) mineral inclusions; (2) source melt petrogenesis; and, (3) zircon saturation context. The filter scheme presented here, which is based on detailed classifications of zircon morphology/texture and host rock compositions of 2317 zircon analyses from 30 independent references, is shown to distinguish non-magmatic zircon (Group III), magmatic zircon with significant inclusions and/or sourced from highly enriched source melt (Group II), and mantle-equilibrated zircon (Group I). A case study of Group I mantle-equilibrated zircon from Greenland suggests that their respective mantle source has reached FMQ -0.5 since ca. 2950 Ma. Future applications of this filter scheme include studies of out-of-context detrital and/or xenocrystic zircon.

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9			
10	¹ University of Maryland, College Park, MD, 21401		
11	² Northern Territory Geological Survey, Darwin, NT, 0800		
12 13	Corresponding author: Ziqin Ni (zni@umd.edu)		
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15 16 17 18	 Key Points: Zircon Ce/Ce* oxybarometry Ti-in-zircon thermometry Mantle oxygen fugacity 		
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26 in-zircon thermometry is to select mantle-equilibrated zircon (i.e., unaltered magmatic zircon without

27 interaction to hydrosphere). Traditional protocols for identifying mantle-equilibrated zircon require

28 comprehensive examination of whole rock geochemistry in addition to zircon morphology, texture, and 29 trace element and isotopic measurements to obtain information for zircon saturation context, source melt

30 petrogenesis, and post-magmatic history. This study proposes a simple filter scheme for selecting mantle-

31 equilibrated zircon using trace element systematics alone (P, Ti, Y, Nb, REE, Hf, Th, U). A total of 13

32 filtering criteria are synthesized from previous studies based on simulations, experiments, and compiled

33 global datasets, all of which help to provide geological context and ultimately constrain the inferred melt

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35 saturation context. The filter scheme presented here, which is based on detailed classifications of zircon 36 morphology/texture and host rock compositions of 2317 zircon analyses from 30 independent references,

is shown to distinguish non-magmatic zircon (Group III), magmatic zircon with significant inclusions

38 and/or sourced from highly enriched source melt (Group II), and mantle-equilibrated zircon (Group I). A

39 case study of Group I mantle-equilibrated zircon from Greenland suggests that their respective mantle

40 source has reached Δ FMQ -0.5 since ca. 2950 Ma. Future applications of this filter scheme include

41 studies of out-of-context detrital and/or xenocrystic zircon.

42

43 Plain Language Summary

44 Zircon is a robust accessory mineral commonly found in many rock types. The Ce/Ce* and Ti content in 45 zircon provide valuable insights about the redox states of local magmatic environment from which it

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49 comprehensive examinations of zircon and their host rock (i.e., whole rock geochemistry, zircon

50 morphology, texture, and trace element and isotopic measurements) in order to obtain information for

50 morphology, texture, and trace element and isotopic measurements) in order to obtain information for 51 zircon saturation context, source melt petrogenesis, and post-magmatic history. This study, however,

52 presents a simple filter scheme that facilitates the selections of mantle-equilibrated zircon and provides

53 quick insights about zircon petrogenesis using trace element systematics alone (P, Ti, Y, Nb, REE, Hf, Th,

54 Û).

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60 **1. Introduction**

61 Zircon ($ZrSiO_4$) is a robust accessory mineral commonly found in many rock types, capable of surviving

62 multiple igneous or metamorphic events, weathering and transport, hydrothermal alteration, etc. In the

63 zircon crystal lattice, VIIIZr⁴⁺ may be exchanged for a range of incompatible trace elements, such as large 64

ion lithophile elements (LILE; e.g., U and Th) and high field strength elements (HFSE; e.g., Hf and rare 65 earth elements, REE). Due to low modal abundances, the fractionation of zircon has a little effect on the

66 bulk melt composition (major oxides, e.g., SiO_2) and magmatic environment (e.g., oxygen fugacity,

67 temperature). Consequently, zircon trace element and isotope systematics can provide valuable insights

68 about the local magmatic environment from which it crystallized. For example, studies of zircon

69 chemistry have been used to infer: melt crystallization temperatures based on Ti concentrations in zircon

70 (e.g., Watson and Harrison, 2005; Ferry and Watson, 2007; Fu et al., 2008; Siégel et al., 2018); the timing

71 of crystallization and/or metamorphism from U-Th-Pb radiometric dating (e.g., Zheng et al., 2004;

72 Tichomirowa et al., 2013); the provenance of source material from concentrations of LILEs and HFSEs

73 (e.g., Hoskin and Ireland, 2000; Belousova et al., 2002; Grimes et al., 2007, 2015; Chapman et al., 2016);

74 and, the degree of crustal assimilation in magmatic systems based on coupled O-Hf isotopes (e.g., 75 Hawkesworth and Kemp, 2006; Trail et al., 2007; Page et al., 2007; Cavosie et al., 2009; Spencer et al.,

76

2017).

77 Of particular importance, magmatic oxygen fugacity (or fO_2) has been inferred from the abundances of

78 multivalent elements, namely Ce (3+, 4+) and Eu (2+, 3+), relative to other monovalent REE (3+ only).

79 In zircon, REE^{3+} can replace Zr^{4+} in a coupled substitution with additional cations (e.g., P^{5+}) to balance

80 charge. The compatibilities of trivalent REE in zircon increase systematically from La to Lu due to

81 progressively smaller ionic radii with increasing atomic number (commonly termed the lanthanide 82 contraction; Figure 1). However, under oxidizing conditions, a greater proportion of Ce is present as the

83 higher Ce⁴⁺ valence state, resulting in preferential incorporation into the zircon structure (relative to Ce³⁺)

due to its smaller ionic size and equivalent charge to Zr^{4+} . This substitution bias results in a "positive 84

85 spike" of Ce relative to nearby trivalent elements La and Pr in normalized composition diagrams,

enabling the quantification of a Ce anomaly as: $Ce/Ce^* = Ce_N/\sqrt{La_N \times Pr_N}$. In comparison, under 86

reducing conditions, a greater proportion of Eu takes on the lower Eu^{2+} valence state. Because Eu^{2+} is too 87

88 large to fit into the zircon structure without incurring significant lattice strain, Eu exhibits a "negative

89 trough" relative to neighboring trivalent Sm and Gd, defining a Eu anomaly as: $Eu/Eu^* = Eu_N/Eu^*$

90 $\sqrt{\mathrm{Sm}_{\mathrm{N}} \times \mathrm{Gd}_{\mathrm{N}}}$.

91 Magmatic fO₂, as recorded by accessory zircon, is an important control on elemental behavior, such as

92 solubility (e.g., soluble Fe^{2+} versus insoluble Fe^{3+}), mobility (e.g., mobile UO_4^+ versus immobile U^{4+}),

93 chemical affinity (e.g., siderophile S at low fO_2 versus lithophile S at high fO_2), and compatibility (e.g.,

compatible Eu^{2+} versus incompatible Eu^{3+} in plagioclase). Understanding the oxygen fugacity of the 94

95 upper mantle in the early Earth is particularly valuable for quantitatively describing processes associated

96 with planetary differentiation (e.g., Frost et al., 2008; Frost and McCammon, 2008; Yang et al., 2014) and

97 the evolution of atmospheric composition (e.g., Kump et al., 2001, Trail et al., 2011; Lee et al., 2014).

98 Consequently, Ce/Ce* (and to a lesser extent Eu/Eu*) preserved in zircon may provide powerful insights

99 into the composition and dynamics of the Earth's deep interior and surface in the geological past.

100



102 Figure 1. Schematic chondrite normalized pattern of REE in zircon. Ce/Ce* and Eu/Eu* are calculated as

103 $Ce_N/\sqrt{La_N \times Pr_N}$ and $Eu_N/\sqrt{Sm_N \times Gd_N}$ respectively, where the subscript N indicates trace element

104 values normalized to CI chondrites (McDonough and Sun, 1995). As the oxygen fugacity of the system

105 increases (darker shade of gray), Ce/Ce* is expected to increase whereas Eu/Eu* is expected to decrease.

106 The majority of terrestrial magmatic zircon will have both positive Ce/Ce* and negative Eu/Eu*.

107 <u>1.1 Quantitative zircon Ce/Ce* oxybarometry and Ti-in-zircon thermometry</u>

108 Experimental studies demonstrate a variety of empirical relationships between fO_2 in silicate melts and

109 Ce/Ce* recorded in zircon (Trail et al., 2011 & 2012; Burnham and Berry, 2012; Smythe and Brenan,

110 2015 & 2016). In general, such relationships are most sensitive to the alumina and water concentration of 111 the melt, and to a lesser degree the temperature of the melt when the system reaches zircon saturation. As

such, experimentally-calibrated Ce/Ce* oxybarometry and Ti-in-zircon thermometry are often applied

113 together to provide a streamlined estimation of melt redox state, which are often reported as orders of

magnitude deviations from the fO_2 of mineral assemblage fayalite-magnetite-quartz (FMQ) at a specific

115 temperature, i.e., Δ FMQ (Chou, 1978).

116 Multiple studies have attempted to constrain zircon Ce/Ce* in different environments, such as anhydrous

117 peralkaline melts at high temperature (i.e., 1300 °C; Burnham and Berry, 2012). However, such

118 conditions are less likely to precipitate appreciable amount of zircon due to high zircon solubilities but

119 low Zr availability in mafic magmas (Watson and Harrison, 1983; Boehnke et al., 2013; Shao et al., 2019).

120 Statistically, the majority of natural zircon crystallizes in hydrous alumina-saturated melts (i.e.,

determined by the molar ratio of $Al_2O_3/(Na_2O + K_2O)$, or A/NK > 1) at relatively lower temperatures (e.g.,

- 122 ~800 °C). Therefore, the empirical relationship that most universally describes Ce partitioning behavior in
- 123 natural zircon is from Trail et al. (2012),

124
$$\ln\left(\frac{Ce}{Ce^*}\right)_{CHUR} = (0.1156 \pm 0.0050) \times \ln(fO_2) + \frac{13860 \pm 708}{T(K)} - (6.125 \pm 0.484)$$
 Eqn (1),

125 where the experiments were conducted at 10 kbar and 800 - 1300 °C with 2 to 10 wt% H₂O (Trail et al., 2012).

- 127 The zircon crystallization temperature T in Eqn (1) can be inferred from the Ti concentration in zircon
- 128 following the quantitative relationship below (Ferry and Watson, 2007):

129
$$log(Ti in zircon ppm) = (5.711 \pm 0.072) - \frac{4800\pm86}{T(K)} - log(a_{SiO_2}) + log(a_{TiO_2})$$
 Eqn (2).

- 130 The activity of $SiO_2(a_{SiO_2})$ and $TiO_2(a_{TiO_2})$ are dimensionless quantity that describes the chemical
- 131 potential of SiO₂ and TiO₂ of the system relative to quartz and rutile, respectively. In the literature, the
- 132 value of a_{SiO_2} is commonly assumed to be unity as zircon most commonly crystallizes from melt that is
- 133 close to quartz saturation (Ferry and Watson, 2007). The value of a_{TiO_2} in silicic melts at appropriate
- 134 magmatic temperature is typically between 0.6 and 1, and it can be estimated based on the crystallization
- 135 of mineral phases at equilibrium with zircon, such as rutile $(a_{TiO_2}=1)$, and ilmenite and/or titanite $(a_{TiO_2}=1)$
- 136 0.6) (Watson et al, 2006; Ferry and Watson, 2007). In applications to quartz-free crustal rocks and/or
- detrital zircon with limited or no geological context, the uncertainty in a_{SiO_2} and a_{TiO_2} will impose only
- 138 limited effects on calculated temperatures. For example, assuming $a_{SiO_2} = 1$ and $a_{TiO_2} = 1$ yields an
- 139 uncertainty of up to 70 °C uncertainty in calculated temperature (Ferry and Watson, 2007).

140 **1.2 Advantages and limitations of zircon geochemical proxies**

- 141 The greatest promise of coupled Ce/Ce* oxybarometry and Ti-in-zircon thermometry is the streamlined
- estimation of melt redox state; theoretically, any zircon crystal of magmatic origin (even out-of-context
 detrital and xenocrystic samples) can provide an independent evaluation of melt dynamics, requiring only
- a limited set of chemical measurements. However, the direct application of these methods to magmatic
- 145 zircon can generate an unrealistic spread in calculated melt redox states that extends below conditions
- 146 expected at the core mantle boundary ($\Delta FMQ < -4$; McCammon, 2005) to those found in the modern
- 147 atmosphere ($\Delta FMQ > +10$; McCammon, 2005). This wide range of inferred redox states recorded by
- 148 zircon can be explained by: (1) melt contributions from multiple sources (mantle magmas, assimilated
- 149 crustal rock, etc.); (2) dynamic growth conditions (disequilibrium crystallization, mineral decomposition
- 150 during metamorphism, etc.); and/or (3) modification of zircon trace element concentration via post-
- 151 magmatic processes (subsolidus crystallization, hydrothermal alteration, etc.). These dynamic geological
- processes can diversify the composition of source melt, and change trace element signatures in zircon
- syn- and/or post- zircon saturation. As a result, a zircon may be described by a characteristic confidence
- 154 level that it has retained information about the mantle (including local redox state).
- Historical applications of Ce/Ce* oxybarometry in zircon have focused on reporting melt redox states of mantle-equilibrated zircon as a way to constrain the inferred fO₂ variation observed in natural systems. Mantle-equilibrated zircon refer to unaltered magmatic zircon that crystallized from source melt without interaction with the hydrosphere and/or assimilation of exogenous materials (e.g., sediments, crustal materials). Evaluation of zircon mantle-equilibration state traditionally requires a number of analytical protocols including (but not limited to):
- determination of whole rock chemistry to estimate the source melt composition, calculate
 apparent zircon/melt partition coefficient for Ce, infer the crystallization behavior (equilibrium)
 versus disequilibrium) and growth environment of zircon;
- petrographic examination and/or chemical mapping (e.g., via back-scattered electron (BSE) or cathodoluminescence (CL) imaging) to characterize zircon morphology and texture, identify

- mineral or fluid inclusions, evaluate intragranular and intergranular chemical and isotopic
 variation based on zoning, and infer petrogenetic history (Corfu et al., 2003; reference therein);
- measurement of isotopes in individual zircon crystal. For example, U-Pb dating to understand the population of zircon saturation in host rock, and oxygen isotopes to screen zircon that crystallized from source melt with negligible interaction to hydrosphere, and within the mantle-equilibration zone ($\delta^{18}0$ 5.3 ± 0.3 ‰, 2sd) (Valley et al, 1998); and,
- chemical filtering to exclude zircon that carry trace element signatures indicative of mineral
 inclusions (e.g., apatite, etc.; Bell et al., 2019) and non-magmatic features (i.e., hydrothermal and
 metamorphic zircon; Hoskin & Black, 2002; Hoskin, 2005).

175 These requirements are often necessary to obtain a thorough understanding of zircon saturation conditions,

176 constrain statistical variances, and add confidence to inferred melt redox states. For instance, the

application of these methods has enabled the demonstration that mantle-equilibrated zircon center around

the FMQ buffer (e.g., Trail et al., 2011). However, such strict protocols also reduce the size of viable data

179 sets and ultimately undermine the capability/advantage of the method by requiring extensive analyses that

180 may not be feasible given financial (cost), programmatic (time), and/or logistical (sample mass)

181 limitations. For example, in situ measurements of oxygen isotope in zircon require Secondary Ion Mass

182 Spectrometry (SIMS), which are not only expensive but also demand a critical mass of zircon for in situ

183 analysis (Valley, 2003).

184 **<u>1.3 Purpose of this study</u>**

185 The purpose of this study is to establish a multidimensional filter scheme that facilitates the determination

186 of mantle source oxygen fugacity from magmatic zircon based only on a narrow range of trace element

187 systematics, without reducing the accuracy of inferred fO_2 estimates. Instead of relying on extensive

188 contextual observations (e.g., petrography, whole rock compositions, and oxygen isotope ratios), trace

189 element abundances and dynamics are used to isolate zircon that have experienced diverse geological 190 processes (e.g., inclusions, subsolidus crystallization, crystallized from melt with potential interaction to

190 processes (e.g., inclusions, subsolidus crystallization, crystallized from melt with potential interaction to 191 hydrosphere etc.), so that the combined filters can screen effectively for mantle-equilibrated zircon

191 (Figure 2). The selectivity of these chemical criteria is evaluated objectively by applying the methods

developed here to robust, publicly available zircon databases. Zircon with the greatest compositional

similarity to the canonical trace element chemistry of mantle-equilibrated zircon should theoretically have

195 the highest probability of recording (and preserving the signature of) the local mantle redox state.



Figure 2. A comparison diagram between traditional approach and this study at screening mantle-equilibrated zircon.

199 <u>2. Zircon data compilation and preparation</u>

200 In order to evaluate the effectiveness of the filtering criteria proposed here, we compiled a zircon dataset

201 that includes samples from a wide geographical and age distribution. The data were compiled from

202 independent 30 references that measured the following trace element concentrations: P, Ti, Y, Nb, REE,

203 Hf, Th, U (see Supplementary Material I and dataset references below). Zircon entries without trace

204 element concentrations listed, or with values below detection limits, are not used in this study. The dataset

205 used in this study contains data for 2173 individual zircon analyses.

206 To investigate the relationship between host rock and zircon trace element systematics, each zircon entry

was labelled with silica content and A/NK values of their host rocks, and further classified based on the

208 type of their host rock (i.e., igneous, metamorphic, detrital, carbonatite, kimberlite, and mineral deposits).
209 The origin of each individual zircon was deduced from BSE and CL imaging (i.e., magmatic, magmatic)

The origin of each individual zircon was deduced from BSE and CL imaging (i.e., magmatic, magmatic 210 with inclusion, magmatic with metamorphic rims, magmatic with hydrothermal rims, metamorphic,

hydrothermal, metamict). The classification was left as blank if no host rock or contextual information

was provided in the literature. Such detailed classification and labelling facilitate the validation of the

trace element systematics summarized from simulations, experiments and measurements in the literature

summarized in section 3, and further demonstrate the sensitivity of the proposed filtering scheme in

sections 4 and 5.

- 216 The Ce/Ce*, Ti-in-zircon temperature, and melt redox state were calculated for all 2173 zircon entries
- 217 compiled here using Eqn (1) and (2), assuming unity a_{SiO_2} and a_{TiO_2} respectively. By propagating errors
- associated with Ti-in-zircon temperature (\pm 70 °C; Ferry and Watson) and 5% (2sd) analytical uncertainty
- 219 on REE measurement, the uncertainty for reported Δ FMQ value here is about $\pm 2 \log$ units.

220 <u>3. Trace element systematics of zircon</u>

As mentioned in section 1.2, the variance of inferred melt redox state derived from Ce/Ce* in zircon can

be attributed to three categories: (1) mineral inclusions; (2) source melt petrogenesis; and (3) saturation context of zircon. The trace element systematics of zircon associated with these processes have been

223 context of zircon. The trace element systematics of zircon associated with these processes have been 224 explored independently in previous studies via simulations, experiments, and global datasets, which are

- 224 explored independently in previous studies via simulations, experiments, a
- summarized below as foundations for selecting filtering criteria.

226 <u>3.1 Mineral inclusions in zircon</u>

227 Mineral inclusions are common in igneous zircon. Some inclusions act as nucleation sites for crystallizing

- 228 zircon crystals in melt (i.e., primary inclusion); others, however, are alteration or exsolution features
- 229 reflecting post-magmatic processing (e.g., hydrothermal alteration, metamorphism, exsolution features)
- 230 (i.e., secondary inclusion). The scale of such intragranular heterogeneity varies from visible micron-sized
- inclusions to nanoscale trace element enrichment zones (Corfu et al., 2003; Anderson et al., 2008;
- Hofmann et al., 2014; Bell et al., 2015). Therefore, sampling of inclusion phases and/or local enrichment zones cannot be completely avoided even with high-resolution petrographic imaging. Spatially resolved
- 233 zones cannot be completely avoided even with high-resolution petrographic imaging. Spatially resolved 234 analytical techniques that characterize exceedingly small sample volumes (e.g., Secondary Ion Mass
- 235 Spectrometry, SIMS) are particularly susceptible to disproportionate sampling of trace amounts of
- inclusions or nanoscale enrichments; the chemical signatures of localized features may be artificially
- amplified by individual spot analyses.
- 238 Based on this study, measurements of zircon plagued by primary and secondary inclusions can lead to up
- to 15 orders of magnitude variation in inferred melt redox states, as such phases may inflate estimated Ti-
- in-zircon temperatures (e.g., via excess Ti derived from titanite and magnetite) and/or attenuate the
 magnitude of observed Ce/Ce* anomalies (e.g., via overprinting REE signatures). Simple two-component
- magnitude of observed Ce/Ce^{**} anomalies (e.g., via overprinting REE signatures). Simple two-component mixing between a variety of phases commonly included in zircon (i.e., apatite, titanite, allanite, xenotime,
- and monazite) and the most primitive zircon grain from the case study reviewed in Section 5.2 (see below)
- 244 demonstrates that as little as 0.0001 wt % of monazite and allanite inclusions will reduce Ce/Ce* by more
- than 80%. Interestingly, 0.5 wt % of inclusions enriched in light REE will overprint the Ce/Ce* signature
- completely (Figure 3).
- 247 Therefore, due to the high sensitivity of Ce/Ce* oxybarometry to mineral inclusions and the potential
- risks of sampling them, filtering magmatic zircon for such based on diagnostic chemical trademarks is
- 249 one of the most important steps for constraining variation in inferred melt redox states.
- 250





Figure 3. Mixing models between zircon and potential inclusions across a range of mixing proportions demonstrates the sensitivity of Ce/Ce* to chemical overprinting. The REE concentration of unadulterated zircon is modeled after sample 524994 Zircon 76, the most primitive zircon grain from the case study reviewed in Section 5.2. The average REE concentration of apatite is from Zhong et al. (2018a), and the compositions of the other phases (xenotime, monazite, titanite, allanite) are from Bea et al. (1996; see Supplementary Material II). The insets describe the relationship between Ce/Ce* and the mixing ratio of inclusions.

259 Historical criteria for filtering hydrothermal zircon include Ce/Ce^* , La concentration, $(Sm/La)_N$, and light

rare earth element index (LREE_I), calculated as the concentrations of Dy/Nd+Dy/Sm. Based on

petrographically predetermined magmatic and hydrothermal zircon, filtering schemes previously proposed in literature targeting the selection unaltered magmatic zircon are Ce/Ce* \leq 100, La between

proposed in literature targeting the selection unaltered magmatic zircon are Ce/Ce^{*} \leq 100, La between 0.002 to 0.5 ppm, (Sm/La)_N between 30 to 1000, and LREE_I > 60 (Hoskins 2005; Bell et al., 2019).

Because Ce/Ce* is one of the input parameters for calculating oxygen fugacity via Eqn (1), the range of

265 Ce/Ce* is especially important for accurately determining melt redox state. The traditional upper

boundary Ce/Ce* ≤ 100 is adopted as a filter for magmatic zircon because Ce/Ce* >100 is approximately

267 equivalent to an unrealistic magmatic environment as oxidized as modern atmosphere ($\Delta FMQ > +10$;

268 McCammon, 2005). The lower boundary of Ce/Ce*, however, cannot be directly inferred because it

269 varies with the amount of REE in the melt, as well as the mixing ratio of inclusions in the sample.

- 270 Therefore, instead of setting a lower boundary of Ce/Ce*, the other three parameters, La concentration,
- 271 (Sm/La)_N, and LREE_I, are used to change the fraction of inclusions within zircon.

Figure 4 shows the sensitivity of La concentration, (Sm/La)_N, and LREE_I for filtering mineral inclusions

- of different mixing ratio to zircon. La < 0.1 ppm is the most sensitive parameter that is able to filter out
- 274 zircon with mineral inclusions as low as 0.0001 wt%, but such sensitivity is reduced by up to three orders 275 of magnitude if La < 0.5 ppm is used instead. Similarly, $(Sm/La)_N > 100$ is able to discern 0.0001 wt%
- 275 of magintude in La < 0.5 ppin is used instead. Similarly, $(Sin/La)_N > 100$ is able to discern 0.0001 wt% 276 monazite and allanite, but relaxing the requirement to $(Sm/La)_N > 30$ masks up to 0.2 wt% of xenotime,
- which can attenuate Ce/Ce* by 80 %. Although LREE_I is the least sensitive parameter among these
- three, it is important to use an additional La-independent criterion to monitor inclusions because the
- analytical uncertainties of La measurements in zircon may be high due to analytical limits of detection.
- 280 Further, because trace element concentrations of each mineral inclusion vary over two orders of
- 281 magnitudes in natural samples, multidimensional criteria can increase the filtering power and reduce the
- 282 probability of detecting inclusions.
- 283 Therefore, the boundaries of current filtering scheme are updated to identify samples with the highest
- probabilities of reflecting unaltered mantle-equilibrated magmatic zircon: La concentration between 0.1
- and 0.002 ppm, $(\text{Sm/La})_{\text{N}}$ between 100 and 1000, and LREE_I > 60. In addition, Ce/Ce* \leq 100 is
- adopted to distinguish magmatic zircon.

287



Figure 4. A sensitivity comparison between all three inclusion indicators: La concentration; $(Sm/La)_N$; and, LREE_I as a function of mixing ratio (%). The shaded areas represent regions that will be selected (or accepted) by the filter scheme.

292 **<u>3.2 Source melt petrogenesis</u>**

293 Zircon starts to crystallize when the Zr availability in the system (e.g., source melt) is greater than or

294 equal to the zircon saturation content. Zircon saturation content, or the minimum Zr concentration

required to precipitate zircon in the melt, tends to decrease with an increasing degrees of melt

polymerization and/or decreasing magma temperature (Boehnke et al., 2013; Hanchar and Watson, 2003).

For example, the zircon saturation content in basaltic magma is about 2000 to 30000 ppmw Zr (Shao et al.,

298 2019) but reduces to ~100 ppmw in silicic magma (Watson, 1979). The availability of Zr in melt,

however, is constrained and remains relatively constant; for example, the average Zr content in global

300 mid ocean ridge basalt (e.g., ~100 ppmw; e.g., Arevalo and McDonough, 2010) is similar to the

- 301 composition of the bulk continental crust (~130 ppmw Zr; e.g., Rudnick, 1995). Despite similar Zr
- availability, the zircon saturation contents of these two systems are dramatically different because melt
- 303 polymerization serves as a dominant control, and prevents the crystallization of zircon in mantle-derived
- 304 magma unless the source melt interacts with metasomatic fluids or assimilates felsic materials (e.g., 305 marine sediments, slab-derived melt, or crusts). In fact, the source melts of most zircon in ultramafic
- 306 and/or mafic host rocks in compiled dataset are often interpreted as melt products of metasomatized
- 307 mantle-wedge, or contaminated mantle-derived melt that mixed with slab-derived fluids or crustal
- 308 materials during ascent (e.g., Janoušek et al 2019; Robinson et al., 2015; Tichomirowa et al., 2012; Sun et
- al., 2018; Vilalva et al., 2019, etc.). Because fluids and surface materials have undergone various low
- 310 temperature processes (chemical and mechanical weather, erosion, etc.) and commonly possess enriched
- 311 incompatible trace element abundances, assimilation of these materials can easily overprint the inherited
- 312 fO₂ signatures from the original mantle source.
- 313 Historical studies of source melt petrogenesis focus on whole rock geochemistry and isotopic
- measurements of zircon crystals (e.g., Robinson et al., 2015; Liang et al, 2018; Janoušek et al., 2019).
- 315 Specifically, whole rock geochemistry provides insights about the provenance and composition of the
- 316 source melt, and oxygen and Hf isotopes of zircon track the interaction to metasomatic fluids and the
- 317 contribution of felsic materials. In this study, instead of relying on whole rock or detailed isotopic
- analyses, previously developed trace element proxies are used to infer the formation and composition of
- 319 source melt.

320 **<u>3.2.1 Source melts from igneous sources: P \leq 750 ppm and (REE+Y)/P molar ratio > 1</u>**

321 Zircon is commonly found in granitic systems, but felsic melt can derive from both igneous sources (I-

322 type granite, alumina-saturated metaluminous melt) and sedimentary sources (S-type granite, alumina-

323 oversaturated peraluminous melt). Generation of melt from a sedimentary protolith implies little to

- nothing about mantle redox conditions, so zircon from S-type granitoids provide less insight into the deep
- 325 Earth compared to mantle-equilibrated zircon.
- 326 Zircon P concentration provides a gauge to identify the type of granitic protolith. The average P
- 327 concentration of global MORB is ~600 ppmw (Arevalo Jr. and McDonough, 2010). Due to its
- 328 incompatibility to most major minerals, the P concentration of a melt may increase as the magma
- 329 differentiates until apatite precipitates. Apatite (Ca₅(PO₄)₃(OH, Cl, F)) is a common accessory phase that
- 330 crystallizes prior to zircon saturation in metaluminous melt (Lee et al., 2014), but dissolves in
- peraluminous melt as magmatic differentiation continues (Mysen et al., 1997). Despite the insignificant
- 332 difference of bulk rock P_2O_5 concentration between S-type and I-type granites, the saturation and
- 333 dissolution of apatite control the availability of P in residual melts.
- 334 In general, S-type zircon inherit a higher P concentration, whereas only 10 % of I-type zircon have P
- concentration > 750 ppm (Burnham and Berry, 2017). Moreover, coupled substitution between P^{5+} and
- 336 $(\text{REE}, \mathbf{Y})^{3+}$ for Zr^{4+} becomes dominant in melt with a higher P concentration. S-type zircon are observed
- to have a strong linear correlation between the molar ratios for REE+Y and P, whereas I-type zircon are
- observed to have (REE +Y)/P molar ratio > 1. The lack of linear correlation in I-type zircon implies
 preference of additional REE incorporation mechanisms in P-deficient metaluminous melt. In a case study
- by Burnham and Berry (2017), the authors suggest that the combined criteria $P \le 750$ ppm and
- (REE+Y)/P molar ratio > 1 enables the isolation 96% of I-type zircon based on 144 zircon analyses from
- 342 characterized S-type and I-type granites.

- 343 Similar source melt information has been inferred form Eu/Eu* (Wang et al., 2012, see section 3.3.4) and
- 344 Al content in detrital zircon (Trail et al., 2017). Although they are not specifically addressed in these
- sections, they could be considered as alternative criteria for differentiating source of source melt. 345

346 3.2.2 Limited interaction with fluids and surface materials: U/Yb \leq 20 and/or Th/Yb \leq 10

- 347 Partial melting of basaltic systems, especially at arc settings, often involves fluid components and/or more
- 348 felsic lithologies (e.g., marine sediments and continental crust). The degree of such interaction can be
- 349 inferred from U/Nb, Th/Nb ratios in zircon. Fluid immobile Nb fractionates from fluid mobile Th and U
- 350 during low temperature surface weathering, erosion, and/or fluid interaction. Thus, normalization of Th
- 351 and U to Nb can be used as a monitor for mixing with such exogenous materials.
- 352 Based on over 5300 zircon analyses compiled by Grimes et al. (2015)., the zircon formed in arc magmas
- 353 may be distinguished from those derived from mid-ocean ridges and intraplate ocean island by notably
- 354 higher U/Nb >20 and Th/Nb >10, due to the recycling of Th and U enriched sediments and/or
- 355 contribution of U and Th mobilized by hydrous fluid. Therefore, zircon with U/Nb \leq 20 and/or Th/Nb \leq
- 356 10 best represent crystallization from mantle-equilibrated melt without sufficient interaction to surface
- 357 materials and fluids.
- 358 Similar trace element systematics for assessing fluid interaction and felsic material assimilation include
- 359 U/Yb and Th/Yb (Grimes et al., 2007). These proxies could be used interchangeably or considered as
- 360 additional criteria to reaffirm the selection. However, the specific values of these ratios vary if source
- 361 melt originate from variably enriched mantle sources. For example, while low U/Yb ($< \sim 0.1$) appears to
- 362 be diagnostic of zircon from differentiated melt originating from a depleted mantle source, zircon from
- relatively enriched geochemical reservoirs typically carry higher U/Yb ratios (Grimes et al., 2007, Grimes 363
- 364 et al., 2015, Carley et al. 2014). Therefore, while U/Nb and Th/Nb are preferred in this study, multiple
- 365 filtering criteria are encouraged to be used simultaneously.

366 **3.3 Zircon saturation context**

367 As a magma progressively differentiates prior to zircon saturation, the precipitation of major mineral

- 368 phases will continuously change the availability of major elements in the melt, including redox-sensitive
- ratios such as Fe²⁺/Fe³⁺, thereby manipulating the melt redox state. Saturation and/or dissolution of 369 370 accessory phases, such as monazite or xenotime, can control trace element budgets in residual melts, thus
- 371 changing the REE signatures inherited by zircon. In addition, the speed of magma differentiation and
- 372
- oversaturation of trace elements can lead to disequilibrium crystallization of zircon, resulting in observed 373 partitioning behavior that deviate from calibrated relationships (e.g., Eqn (1)). Such magmatic processes
- 374 play significant roles in changing melt redox states and influencing trace element concentrations in zircon.
- 375 Beyond saturation from magmatic melt, zircon can also experience re-equilibration, dissolution, and
- 376 recrystallization in Zr-rich melts sources from the decomposition of Zr-rich mineral phases, or Zr-rich
- 377 metasomatic fluids. In such cases, saturation of non-magmatic zircon will not appropriately record the
- 378 melt redox state via Eqn (1). We employ five chemical filters to monitor for: (1) fractionation of redox-
- 379 sensitive mineral phases and REE-enriched accessory phases; (2) degree of magma differentiation; (3)
- 380 equilibrium crystallization of zircon; and, (4) non-magmatic zircon signatures.

381 3.3.1 Absence of flat HREE pattern: (Lu/Gd)_N between 10 and 74

- 382 The partitioning of heavy REE (HREE) zircon is suppressed due to fractionation of garnet prior to or
- 383 contemporaneous with zircon crystallization, leading to a characteristic flat HREE pattern (or a "plateau")
- 384 in the zircon. More problematic, the fractionation of garnet can alter the melt redox state by up to 6 orders
- of magnitude in arc settings (Tang et al., 2018), as Fe^{2+} is more compatible in garnet, leaving behind 385 residual melt with a disproportionate concentration of Fe³⁺. Because Fe serves as a major control on local 386
- fO_2 , an increase in Fe^{3+/} Σ Fe in the residual melt (as promoted by fractionation of garnet) could effectively 387
- oxidize the system, consequently changing the Ce^{4+}/Ce^{3+} ratio in the melt relative to the original mantle 388
- 389 setting. In addition, flat HREE patterns may also be imparted by metamorphic processes. Under high-
- 390 temperature and high-pressure environments where garnet is stable, partial melting or decomposition of
- 391 Zr-rich mineral phases (e.g., titanite) can contribute Zr, leading to subsolidus crystallization of zircon.
- 392 Similarly, zircon in mantle-derived host rocks devoid of garnet (i.e., kimberlite, carbonatite) can also have 393 flat HREE pattern due to incomplete melting of garnet in mantle source region (Hoskin and Schaltegger,
- 394 2003; Rubatto, 2017). Saturation of zircon in mantle-derived melt is thermodynamically hindered unless
- 395 it is aided by a large amount of metasomatic fluids or slab-derived felsic melt. Therefore, zircon with flat
- 396 HREE pattern often associate fractionation of garnet in melt, metamorphic origin of zircon, or
- 397 disequilibrium crystallization in mantle-derived host rock, so they imply little about the local magmatic
- 398 environment.
- Experimental results show that $D_{Lu}^{Zircon/Melt}/D_{Gd}^{Zircon/Melt}$ in hydrous granitic melt is approximately 15 at 800°C and 20 kbar, typical conditions for subduction zone or thickened oceanic crust, but the value of this 399
- 400
- 401 ratio diminishes to 11 in the presence of garnet (Rubatto and Hermann, 2007). During high temperature
- metamorphism in the lower crust (<900C, 7 kbar), $D_{Lu}^{Zircon/Garnet}/D_{Gd}^{Zircon/Garnet}$ further approaches unity (Taylor et al., 2015). This agrees with the empirical observations that mantle-affinity zircon (co-402
- 403
- 404 presence of garnet) have $(Lu/Gd)_N$ ranging from 1~10, metamorphic zircon with $(Lu/Gd)_N$ approaching 1
- 405 (Kelly and Harley, 2005; Whitehouse and Platt, 2003), whereas typical granitic zircon have $(Lu/Gd)_N$
- 406 ranging from 16-74 (Hoskin and Schaltegger, 2003). The formation of metamorphic zircon from garnet
- 407 break-down during magma ascent also leads to a greater enrichment of HREE compared to magmatic
- 408 zircon (Rubatto, 2002; El-Bialy and Ali, 2013). Therefore, magmatic zircon without coexistence of garnet
- 409 tends to have $(Lu/Gd)_N$ between 10 and 74.

410 3.3.2 Avoiding fractionation of accessory phases: Th/U ratio between 0.2 and 4

- 411 Prior to or during zircon saturation, crystallization of Th-enriched phases (e.g., monazite and thorite)
- 412 and/or U-enriched phases (e.g., coffinite, uraninite, or monazite) induces local heterogeneity of Th and U
- 413 in the melt, enhancing observed Th/U variances in cogenetic magmatic zircon. Such heterogeneity can be
- 414 further augmented via post-magmatic processes, such as hydrothermal alteration, metamorphism, and/or
- 415 low temperature weathering. Hydrothermal fluids may mobilize, redistribute, or precipitate Th-rich and
- U-rich inclusions along cracks, or promote mass loss of U by oxidizing U^{4+} to form fluid mobile UO_4^{2-} . 416
- 417 Metamorphism, decomposition, and crystallization of Th- and U-rich accessary phases can also incur
- 418 spatial variations in Th and U concentration in melts, facilitating the dissolution and disequilibrium
- 419 growth of zircon (Xiang et al., 2011). As a result, zircon with extreme values of Th/U are often associated
- 420 with significant inclusion/fractionation of accessory phases, disequilibrium crystallization, and non-
- 421 magmatic origins.
- 422 Based on 10,693 magmatic zircon analyses compiled in Kirkland et al. (2015), zircon Th/U ratios range
- 423 from near 0 up to 19.8, with a median of 0.65 and a positive skewness of 6.7. Although metamorphic
- 424 zircon exhibit a similar spread in Th/U, a greater percentage of metamorphic zircon have Th/U < 0.1
- 425 (Yakymchuk et al., 2018). Historically, Th/U < 0.1 was used as filtering tool for metamorphic zircon, but

- 426 even zircon in ultrahigh temperature metamorphic assemblage (> 900 °C) can exhibit Th/U > 0.1,
- 427 reinforcing the complexity of Th/U systematics (Kelly and Harley, 2005).
- 428 The large variance in Th/U recorded by natural zircon may be attributed to reasons mentioned above.
- 429 However, the effects of each of these controls on Th/U ratios have not been fully characterized. Therefore,
- 430 the Th/U ratio of the mantle is used to identify zircon that have preserved the native mantle signature.
- Assuming Th/U in the mantle varies between 0.2 to 4 (Wipperfurth et al., 2018), our dataset implies
- 432 greater than 89% of zircon fall within this range (Figure 5).



434



437 **<u>3.3.3 Constraining differentiation and metasomatism: Hf concentration: 5,000-13,000 ppmw</u></u>**

438 As HFSE, Hf and Zr are both highly incompatible in most mineral phases, so the Hf and Zr concentration 439 in melt increases significantly as magma differentiates. Zircon, as one of the primary carriers of Hf in

in melt increases significantly as magma differentiates. Zircon, as one of the primary carriers of Hf in
 magmatic systems, readily incorporates Hf into its crystal lattice due to the same valence states and

similar ionic radii to Zr^{4+} (Wang et al., 2010). Therefore, the Zr/Hf ratio in zircon remains relatively

- 441 similar folic radii to Zi⁻ (wang et al., 2010). Therefore, the Zi/Ti rado in Zicon remains relatively 442 constant in granitic magma unless metasomatism and/or crystallization of Hf-enriched accessary phases
- 443 (e.g., hafnon) fractionate Zr/Hf.

444 According to 2201 zircon electron microprobe analyses complied in Wang et al. (2010), the Zr/Hf

signatures recorded by granitic zircon range from 5 to 100, showing a nearly normal distribution with a

446 mean, median, and mode of 39. Zircon from pegmatite or highly evolved rocks tend to have Zr/Hf closer

to 20 (Linnen and Keppler, 2002; Pupin, 2000). Interactions with a fluid phase will reduce Zr/Hf ratio in

448 zircon, resulting in enrichment and positive correlation between Hf and Rb (Linnen and Keppler, 2002).

- 449 By assuming an average Zr concentration in zircon based on stoichiometry, a Zr/Hf ratio between 39 (the
- 450 mean/median/mode of granitic zircon) and 100 (the max value observed in the same data set; Wang et al.,
- 451 2010) equates to 5,000 to 13,000 ppmw Hf in magmatic zircon. Approximately 85% of the data compiled
- 452 in this study fall within this compositional range. Notably, zircon with Hf > 13,000 ppmw commonly
- 453 exhibit higher La contents, corroborating a potential metasomatic influence and/or precipitation of LREE-
- 454 enriched mineral phases.

455 <u>3.3.4 Equilibrated crystallization of zircon from silicic melt: Eu/Eu*: 0.1 - 0.6</u>

- 456 Besides Ce, Eu is another REE that has two valence states, Eu^{2+} and Eu^{3+} ; Eu^{2+} is strongly incompatible in
- the zircon structure due to the large ionic size and required coupled substitution in zircon structure.
- 458 Therefore, the Eu/Eu* ratios in zircon rarely exceed one, unless zircon saturates in disequilibrium
- 459 conditions (Hoskin and Schaltegger, 2003; Trail et al., 2012).
- 460 The relationship between Eu/Eu* and Hf depicts a continuum of magma differentiation that connects
- zircon from mantle-derived melts (i.e., carbonatite and kimberlite) to silicic melt (i.e., igneous rocks;
- Figure 6). Majority of zircon in carbonatite and kimberlite are observed to have low Hf concentration and
- 463 Eu/Eu* > 1, supporting hypothesis that saturation of zircon in mantle-derived melt is thermodynamically
- unfavorable. However, as magma sufficiently evolves, zircon inherits a higher concentration of Hf and
 lower Eu/Eu*; for example, the majority of igneous zircon from this study have Eu/Eu* < 0.6 (Figure 6).
- lower Eu/Eu*; for example, the majority of igneous zircon from this study have Eu/Eu* < 0.6 (Figure 6).
 The distribution of Eu/Eu* broadly correlates to types of parental magma. Zircon from I type granitoid
- has a distinctive lower $En/Eu^* \le 1$ than zircon from S- and A-type granitoid (Wang et al., 2012; Sawaki
- 468 et al., 2017). Therefore, mantle-equilibrated zircon is expected to have Eu/Eu* between 0.1 to 0.6.





470



473 <u>3.3.5 Crystallization temperature for magmatic zircon: Ti concentration: 2 - 24 ppm</u>

474 The onset temperature of zircon saturation is controlled by the compatibility of Zr in major mineral

475 phases as they precipitate from a melt, and the starting Zr concentration of the system. By assuming a

476 highly incompatible behavior of Zr in the phases that first crystallize from a basaltic magma ($D_{Zr} \le 0.01$)

477 and a 100 ppmw initial Zr concentration, zircon is expected to saturate starting at 850 °C based on
478 simulation of magma differentiation (Lee et al., 2014; Nandedkar et al., 2014; Borisov, 2019). The actual

478 simulation of magina differentiation (Lee et al., 2014, Nandedkar et al., 2014, Bonsov, 2019). The actual 479 zircon saturation temperature of 11,705 igneous zircon is estimated to be ~800 to 600 °C, based on their

- 480 Ti concentration and melt composition parameter M (i.e., the cation ratio of $(Na + K + 2Ca) / (Al \cdot Si)$ of
- 481 the melt/whole rock) (Samperton et al., 2017; Siégel et al., 2018).
- 482 The majority of zircon data compiled in this study has Ti-in-zircon temperatures between 710 and 810 °C,
- 483 which converges to the crystallization temperature range suggested by the simulations described above,
- 484 600 to 850 °C as well as in literatures (Figure 7; Harrison et al., 2007; Fu et al., 2008). Therefore, by
- 485 assuming unity a_{SiO_2} and a_{TiO_2} in Ti-in-zircon thermometry, we constrained the Ti concentration in
- 486 magmatic zircon between 2 and 24 ppm, corresponding to zircon saturation temperature between 600 °C
- 487 to 850 °C respectively.

488



490 **Figure 7.** Density plot of Ti-in-zircon temperatures determined from the zircon data set compiled here, 491 categorized by host rock type. The area under each curve has a cumulative probability of 1.

492 **4.** A proposed scoring system to gauge confidence

Based on the discussion above, a total of 13 filtering criteria are summarized, all of which help to limit
 external interferences and artificial variances in inferred redox states from three perspectives:

495	(1) Mineral inclusions in zircon:
100	T 0.000 0.1

- 496 La concentration: 0.002 0.1 ppm
- 497 $(Sm/La)_N$ between 100 and 1000

498	$LREE_I > 60$
499	(2) Source melt petrogenesis:
500	$U/Nb \le 20$
501	$Th/Nb \le 10$
502	$P \le 750$ ppmw and (REE+Y)/P molar ratio > 1
503	(3) Zircon saturation context:
504	$Ce/Ce^* \le 100$
505	$(Lu/Gd)_N$ between 10 and 76
506	Hf concentration between 5000 and 13000 ppm
507	Th/U ratio between 0.2 and 4
508	Eu/Eu* between 0.1 to 0.6
509	Ti concentration between 2 to 24 ppm

- 510 These criteria may be translated into a numeric scheme by employing a binary scoring system. A zircon
- 511 will score 1 for each criterion it satisfies in Categories (2) and (3); if the zircon falls outside the
- 512 predefined range, it receives a score of 0 for that proxy. However, because inclusion phases have
- 513 extraordinary control on both Ce/Ce* and Ti-in-zircon temperatures, the criteria outlined in Category (1)
- are given a 2x weight factor; that is to say, a zircon will receive a score of 2 for each criterion it satisfies
- 515 in Category (1). If the zircon falls outside the predefined range, it receives a score of 0 for that Category
- 516 (1) proxy. For example, a zircon entry that satisfies all criteria except that its U/Nb > 20, La 517
- 517 concentration > 0.1 ppmw, and $(Lu/Gd)_N < 10$ ppmw will have a total score of 11 (Figure 8).
- 518 The total score estimates the similarity of a given zircon entry to a mantle-equilibrated zircon. Zircon with
- 519 the high scores are most likely to represent mantle-equilibrated zircon, whereas zircon with low scores
- 520 have a reduced probability of preserving the identities of their respective mantle sources. Samples with
- 521 the highest confidence of reflecting mantle-equilibrated zircon will have a maximum score of 15 (i.e.,
- 522 satisfying all criteria).



- 524 Figure 8. An example of calculating the score of zircon that satisfy all criteria except that its U/Nb > 20,
- 525 La concentration > 0.1 ppmw, and $(Lu/Gd)_N < 10$.

526 <u>5. Discussion</u>

- 527 The scores for all 2173 zircon entries compiled here cover the entire scoring range from 1 to 15 (Figure 9).
- 528 Application of Hoskin's differentiation diagrams suggest that most low score zircon are derived from
- 529 hydrothermal sources, whereas high score zircon cluster within the magmatic domain (Figure 10). In
- general, the zircon population with the highest scores converge at melt redox states near the FMQ region.
 Based on the distributions of scores, the zircon may be divided into three groups, as described further
- 531 Based on the distributions of 532 below (Figure 11a).

533 <u>5.1 Variation in inferred fO₂ due to magmatic and post-magmatic processes</u>

Group III zircon have scores ≤ 7 with a median oxygen fugacity Δ FMQ -5.6 \pm 5.1 (\pm median absolute deviation; Fig. 11a). Consequently, these samples are interpreted to represent non-magmatic zircon. The

- 536 median absolute deviation is calculated as the median of the absolute distances of each data value to the
- median of whole sample set; compared to standard deviations, this value is less affected by outliers and
- 538 better represents statistical dispersion within dataset. Group III zircon generally yield Ce/Ce* approaching
- 539 unity but surprisingly high Ti-in-zircon temperatures (>1000 °C), highlighting unusual trace element
- 540 characteristics (Figure 9). Group III zircon represent >75 % of zircon from metamorphic rocks and > 90%
- 541 from carbonatites (Figure 11b). According to the textures and morphologies of these samples provided in
- their source references, zircon with unity Ce/Ce* and high temperature often associates with metamict,
- 543 hydrothermal, and metamorphic zircon, which validate that Group III zircon represent non-magmatic
- 544 origin (Figure 12).

Group II zircon have scores from 8 to 13 with a median oxygen fugacity Δ FMQ -0.3 ± 4.8. They mostly represent zircon with mineral inclusions and zircon that crystallized from parental magma that interacted with hydrous fluids and/or crustal materials. Group II zircon have Ti-in-zircon temperature 620 to 850 °C, in agreement with experiments and simulations of magmatic zircon crystallization temperature. However, their Ce/Ce* ranges over three orders of magnitudes (Figure 9). Hoskin discriminant diagrams suggest the majority of Group II zircon extend from the magmatic zone towards hydrothermal signatures (Figure 10).

- 551 Such a trend implies that Group II zircon may have had magmatic origins but fluid alteration and/or
- 552 metamorphism conditions induced post-magmatic trace element diffusion, mineral exsolution, or
- 553 inclusions that attenuated Ce/Ce* and diminish the original magmatic fingerprint.
- 554 Group II includes nearly all zircon derived from kimberlites, detrital zircon in sedimentary rocks (i.e., 555 siltstone), and ~40% zircon from igneous rocks (Figure 11b). According to the specific examples in this
- sitistone), and ~40% zircon from igneous rocks (Figure 11b). According to the specific examples in study, zircon in kimberlite is identified as xenocryst with a source melt of mafic composition
- 557 (Kostrovitsky et al., 2016), and detrital zircon in siltstone is crystalized from a melt of A-type granitoid or
- a mixture of felsic and mafic melt (Paulsen et al., 2017). Therefore, despite the range of host rock
- 559 compositions, most of Group II zircon have a magmatic origin. Petrographic examination via BSE and
- 560 CL images suggest most Group II samples have magmatic textures but with inclusions or secondary
- recrystallization features, likely resulting from hydrothermal fluids or metamorphism (Figure 12).

562	Group I zircon have scores from 14 to 15, meaning they have the highest confidence level of
563	representing mantle-equilibrated zircon. The most noticeable differences between Group I and II zircon

are the reduced variations in temperature and Ce/Ce*, and by extension inferred melt redox state (Figure11a).

566 The majority of Group I zircon are from the rhyolitic Mesa Falls Tuff (MFT) at Yellowstone volcanic 567 field (Rivera et al., 2016). The physical conditions and mechanisms of generating silicic magma at 568 Yellowstone are hotly debated topics because cyclic caldera collapse, magma mixing, and crustal 569 assimilation often overprint and complicate the signatures of minerals and magma (Bindeman and Valley, 570 2001; Wotzlaw et al., 2015). As a result, Yellowstone zircon often inherit heterogeneous oxygen isotopic 571 compositions and trace element concentrations across zones that reflect variations in melt conditions as a 572 function of time. Based on detailed petrographic observation, trace element composition, and U-Pb dating, 573 Rivera et al. (2016) identified 4 Chemical Domains in MFT zircon that represent distinctive magma 574 conditions; in general, Domains 1 and 2 represent magma mixing from hydrothermally altered crust (characterized by statistically distinct δ^{18}) below mantle field); Domain 3 represents the oldest pristine 575 magma in the zircon core; and, Domain 4 represents magma with significant fractionation. Out of >400 576 577 zircon analyses, this filter scheme has successfully avoided all zircon from Domains 1, 2, and 4, and only 578 picked up zircon from Domain 3, sourced from the most primitive melt. Similarly, other Group I zircon 579 include magmatic cores from Cu-Zn deposits (Zhu et al, 2017), detrital zircon in siltstone (Paulsen, 2017), 580 and magmatic zircon from Yellowstone rhyolite (Colon et al., 2015). Although there are no oxygen 581 isotopes for selected zircon grains as corroborative validation for their mantle-equilibrated source melt, all 582 of these references have: (1) observed multistage growth of zircon and preservation of magmatic texture 583 for some zircon; and, (2) highlighted the likelihood of maintaining mantle-equilibrated source melt based

- 584 on Hf and oxygen isotopes on limited zircon grains and whole rock.
- 585 Accordingly, this filter scheme has demonstrated the capacity to isolate non-magmatic zircon (Group III
- 586 zircon), magmatic zircon with inclusions or enriched source melt sources (Group II zircon), and mantle-
- equilibrated zircon (Group I). Based on the Group I zircon population from the compiled zircon dataset interrogated here, we infer a local mantle redox state of ΔFMQ 2.56 \pm 0.90 (n= 17). This result overlaps
- with upper mantle redox values $\Delta FMQ \pm 2$ via Fe³⁺/ Σ Fe on spinel peridotites (Frost and McCammon,
- 590 2008). Such variation could be a true variation of natural melt redox state, or due to uncertainty of trace
- 591 element measurements. The main sources of uncertainty of this inferred redox state are: (1) unfiltered
- inclusions; (2) variable source melt sources and compositions (and potential magma mixing); (3) extreme
- 593 fractional crystallization; (4) analytical uncertainty in trace element measurements; and, (5) inaccuracy of
- the melt redox state calculation (Eqn. 1).

595



Figure 9. Application of the proposed filter scheme and scoring system to the zircon dataset compiled here (n = 2173). In general, the large spread in observed Ce/Ce* may be attributed to distinct sources of source melts, magmatic differentiation prior to zircon saturation, and/or mineral inclusions in trace element measurements. The black dotted and solid lines represent $\Delta FMQ \pm 2$, and blue dashed lines represent ΔFMQ of a single Ce/Ce* value at different Ti-in-zircon temperatures.



Figure 10. Distribution of the compiled zircon data set within the pre-established magmatic and hydrothermal fields proposed by Hoskin (2005).



Figure 11. (a) Boxplots of zircon populations for each score. Based on the median and variance of inferred melt redox states, these populations may be divided into three groups: Group I (score 14 to 15),



types within each group (the percentage represents the proportion of all zircon that fall within each group).

610



611

612 **Figure 12.** Plot of Ce/Ce* and temperature in zircon as a function of morphology and textures. The 613 texture of each individual zircon was deduced from BSE and CL imaging from source references (see 614 Supplementary Material I for more details). The black dotted and solid lines represent ΔFMQ ± 2 .

615 5.2 Application: a case study of TTG zircon from Greenland

- 616 A case study of 76 zircon from three Tonalite-Trondhjemite-Granodiorite (TTG) rock samples (524994,
- 617 524906, 524907) in Greenland is considered here using the filter scheme described above. The trace
- 618 elements in each sample were measured via laser ablation inductively coupled plasma mass spectrometry
- 619 (LA-ICPMS; see Supplementary Material III). After calculating inferred oxygen fugacity (via Ce/Ce*)
- 620 and Ti-in-zircon temperatures using Eqn (1) and (2), assuming unity for a_{SiO_2} and a_{TiO_2} , the score of each
- 621 zircon grain was determined (Figure 13).



Figure 13. Application of the filter scheme proposed here to a case study of TTG zircon from three
independent samples (524906, 524907, 524994) from Greenland (see Supplementary Material II for
location). (a) Inferred melt redox state as a function of temperature. (b) Distribution of zircon by group.

627 According to the distribution of scores, most zircon in these three Greenland rock samples may be

- 628 characterized as Group III, suggesting a non-magmatic origin (Figure 13b). However, the presence of all
- three classes of zircon (Groups I, II, and III) implies a multi-stage zircon saturation in the host rocks.
 Although a few zircon in 524994 retained their magmatic signatures (Group I samples), the majority has
- 631 experienced significant degrees of hydrothermal alterations and/or metamorphism that led to either
- 632 recrystallization as non-magmatic zircon (Group III) or intermediate degrees of modification (Group II).
- 633 By using the trace element composition of the highest score zircon grain (the most likely mantle-
- equilibrated candidate), we infer a local melt redox state of ΔFMQ -0.5 ca. 2950 Ma. Again, such result
- agrees with the inferred redox state of upper mantle redox via other proxies ($\Delta FMQ \pm 2$, Frost and
- 636 McCammon, (2008)), which imply the validity of assuming unity a_{SiO_2} and a_{TiO_2} to estimate Ti-in-zircon
- 637 temperature of mantle-equilibrated zircon.
- 638 In summary, this filter scheme not only provides quick insights about of zircon saturation, petrogenesis of 639 zircon textures and morphology, and source melt conditions, but also accelerates research by prioritizing
- magmatic zircon crystals that are least likely to be contaminated, or chemically overprinted. Other
- 641 obvious applications of this filter scheme include studies of both out-of-context and in-context zircon,
- 642 providing a quick guideline for directing more comprehensive and lab-intensive whole rock, imaging, and
- 643 isotopic investigations.

644 <u>6. Conclusions</u>

- 645 We have established a simple filter scheme for selecting of mantle-equilibrated zircon using only trace
- 646 element systematics (P, Ti, Y, Nb, REE, Hf, Th, U) as a way to circumvent more extensive analytical
- 647 meausrements/techniques when time, access to lab facilities, and financial resources are limited. This 648 filter scheme has demonstrated the capability of isolating non-magmatic zircon (Group III scores \leq 7),
- 648 filter scheme has demonstrated the capability of isolating non-magmatic zircon (Group III scores \leq 7), 649 magmatic zircon with inclusions or derived from enriched source melt (Group II scores between 8 and 13),
- and mantle-equilibrated zircon (Group I score ≥ 14). The causes of variation in inferred redox states
- 651 Include: (1) unfiltered inclusions; (2) distinct source melt sources and potential magma mixing; (3)
- variable degrees of magma differentiation; (4) analytical uncertainty in trace element measurements; and,
- 653 (5) inaccuracy of the melt redox state calculation. Despite these uncertainties, mantle-disequilibrated
- control to the studies of the studie
- rocks analysis, and oxygen isotopes), enabling the derivation of local mantle oxygen fugacity from trace
- element measurements alone. The selected mantle-equilibrated zircon from a case study of Greenland
- 657 TTG zircon using this filter scheme implicate a mantle source Δ FMQ -0.5 ca. 2950 Ma.
- 658 Although this filter scheme cannot provide zircon analysis as thorough as more comprehensive protocols,
- 659 it provides quick insights about petrogenesis of zircon, including zircon saturation, textures, and
- morphology, and source melt conditions. The filtering criteria also accelerate research by prioritizing
- magmatic zircon crystals that are least likely to be chemically overprinted. Future applications of this
- 662 filter scheme extend to studies of out-of-context and in-context zircon.

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1026 Acknowledgments

This study was financially supported by the NASA grant (80NSSC18K1612). Special thanks are
given to my parents, professors, and groupmates for their guidance and unconditional supports
on this study. Thank you, Dr. Dustin Trail for his kind encouragements. The compiled dataset

- 1030 was acquired from 30 previously published works, which are listed in the supporting information
- 1031 file (supplementary file 1). The self-collected Greenland dataset was submitted to Earthchem
- 1032 (under review) and also accessible in the supporting information (supplementary file 2).