

STEPWISE CHEMICAL ABRASION ID-TIMS-TEA OF MICROFRACTURED HADEAN ZIRCON

PREPRINT, COMPILED JUNE 13, 2019

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ABSTRACT

The Hadean Jack Hills zircons represent the oldest known terrestrial material, providing a unique and truly direct record of Hadean Earth history. This zircon population has been extensively studied via high spatial resolution, high throughput *in situ* isotopic and elemental analysis techniques such as secondary ionization mass spectrometry (SIMS), but not by comparatively destructive, high-temporal-precision (<0.05% two-sigma) thermal ionization mass spectrometry (TIMS). In order to better understand the lead loss and alteration history of terrestrial Hadean zircons, we conduct stepwise chemical abrasion isotope dilution thermal ionization mass spectrometry with trace element analysis (CA-ID-TIMS-TEA) on manually microfractured Hadean Jack Hills zircon fragments previously dated by SIMS. We conducted three successive HF leaching steps on each individual zircon fragment, followed by column chromatography to isolate U-Pb and trace element fractions. Following isotopic and elemental analysis, the result is an independent age and trace element composition for each leachate of each zircon fragment. We observe ~50 Myr of age heterogeneity in concordant residues from a single zircon grain, along with a protracted history of post-Hadean Pb-loss with at least two modes circa ~0 and 2-4 Ga. Meanwhile, step-wise leachate trace element chemistry reveals enrichments of light rare earth elements, uranium, thorium, and radiogenic lead in early leached domains relative to the zircon residue. In addition to confirming the efficacy of the *LREE-I* alteration index and providing new insight into the mechanism of chemical abrasion, the interpretation and reconciliation of these results suggests that Pb-loss is largely driven by low-temperature aqueous recrystallization, and that regional thermal events may act to halt – not initiate – Pb-loss from metamict domains in the Hadean Jack Hills zircons.

1 INTRODUCTION

Terrestrial zircons with U-Pb ages in excess of 4 Ga were first fortuitously discovered in the Paleoproterozoic Mt. Narryer quartzite by Froude et al. [1], and subsequently in greater abundance by Compston and Pidgeon [2] in a quartz pebble metaconglomerate at the Jack Hills – both in the Narryer Gneiss Complex of the Yilgarn Craton, western Australia. Zircons with Hadean (> 4 Ga) ²⁰⁷Pb/²⁰⁶Pb ages have subsequently been reported from most other continents including North America [3, 4, 5], South America [6, 7], Eurasia [8, 9, 10, 11], India [12], and Africa [13], suggesting a widely distributed occurrence of zircon-bearing crust by at least the late Hadean. Nonetheless, both the antiquity [14] and quantity [15] of Hadean zircon from the Jack Hills far exceeds that yet analyzed from any other locality; as such, the Jack Hills zircon record predominates our understanding of the Hadean Eon on Earth.

While the interpretation of petrologic and geochemical data derived from Hadean zircons can be difficult, many constraints have been interpreted to suggest a relatively temperate Hadean eon, featuring liquid water and continental crust [16, 17, 18]. Hadean Jack Hills zircons display oxygen isotope compositions enriched in ¹⁸O relative to the mantle, suggesting a parental magma that incorporated silicates which have interacted with liquid water [19, 20, 21, 22]. Unlike lunar and meteoritic zircon [23], Jack Hills Hadean zircons display positive Ce anomaly

lies [24, 25], suggesting conditions sufficiently oxidized to produce Ce⁴⁺, perhaps associated with magmatic water. Although magma Ti activity is not perfectly constrained for detrital zircons (except in a handful of zircons containing apparently primary rutile inclusions), observed Ti-in-zircon temperatures of ~680 C are most consistent with a parental magma produced by water-saturated eutectic melting of pelitic sediment [26, 17]. The same Hadean zircons display felsic inclusion suites including some phases such as apatite, biotite, hornblende, and alkali feldspar [27, 28, 29] that are not abundant or not reported in the host quartzite [30] but are ubiquitous components of granitic magmas. Compounding the above constraints, higher mantle potential temperatures in the Hadean imply lower zirconium abundances for a given magma SiO₂, increasing the difficulty of saturating zircon and increasing the volume of felsic crust required to crystallize a given volume of zircon [31]. If correct, such a relatively uniformitarian Hadean would appear plausibly consistent with independent evidence for subduction-driven flux melting since at least 3.85 Ga [32]. Nonetheless, a large proportion of the Archean geological community would strongly dispute such views [33, 34], and controversy regarding the nature and origin of Earth's earliest crust is likely to persist. Consequently, much remains to be learned from the terrestrial Hadean zircon record.

To date, the study of the Jack Hills zircons has proceeded in tandem with the development of high throughput, minimally

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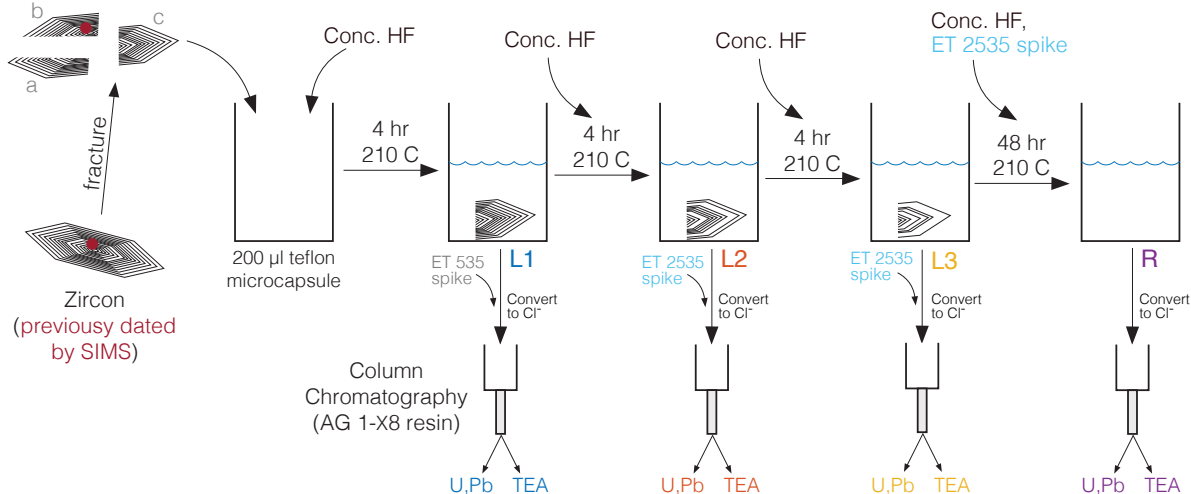


Figure 1: Schematic illustration of the step leaching methodology employed in this study. U, Pb fractions separated by column chromatography for each leachate of each zircon fragment were analyzed on an IsotopX Phoenix 62 Thermal Ionization Mass Spectrometer, while TEA solutions were analyzed for trace element concentration on a Thermo Element 2 ICPMS at Princeton University.

destructive *in situ* analytical techniques such as Secondary Ion Mass Spectrometry (SIMS) [1, 2, 15]. While the high spatial precision and high throughput of these techniques has been critical to the study of the Jack Hills zircons, technical (matrix effects, mass and elemental fractionation) and mathematical (counting statistics) constraints frequently impose an effective tradeoff between spatial and temporal precision.

Consequently, while Hadean $^{207}\text{Pb}/^{206}\text{Pb}$ ages are frequently resolved to the $\pm 0.5\%$ level, there is a limit to the extent to which the concordance of the independent $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{235}\text{U}$ chronometers (and thus our confidence that a measured age reflects closed-system behavior) can be established with *in situ* methods. Such limitations are particularly relevant when attempting to distinguish early open-system behavior (i.e., early Pb-loss or Pb-gain), which will move samples nearly parallel to Concordia [35]. Early Pb-remobilization during Archean ultra-high-temperature (UHT) metamorphism has been observed in at least one case to produce spurious apparent Hadean $^{207}\text{Pb}/^{206}\text{Pb}$ ages in Eoarchean zircons from UHT granulites of the Napier Complex, Enderby Land, Antarctica [36, 37]. However, such extreme effects have been ruled out in the Jack Hills zircons [14] which do not appear to have undergone greater than greenschist facies metamorphism [38]. Even so, early Pb mobility – particularly Pb loss – has often been considered as a limitation when interpreting Hadean zircon Hf isotope systematics [39, 40, 41]

While originally requiring multi-grain zircon aliquots some eight orders of magnitude larger than a typical SIMS ablation pit, the average mass of sample used in a bulk isotope dilution TIMS U-Pb analysis has decreased by more than five orders of magnitude between 1975 and 2010. Over the the same period, temporal precision has improved by over an order of magnitude, all due to improvements in analytical techniques and instrumentation [42]. In total, we may now expect to obtain $< 0.05\%$ relative temporal precision and accuracy on a single $< 1\ \mu\text{g}$ fragment of Hadean zircon, providing a precise and accurate test of closed-system behavior through concordance.

To improve the likelihood of analyzing closed-system material, zircon fragments intended for ID-TIMS may be first treated with chemical abrasion, which has been observed to selectively dissolve damaged domains likely to have undergone Pb-loss [43, 44]. While twelve hours of chemical abrasion in concentrated HF at 210 °C is frequently presumed to effectively mitigate Pb-loss in zircon, the underlying mechanism and the kinetics of this process remain poorly understood. Moreover, since previously published TIMS ages for Jack Hills Hadean zircons [45] predate the advent of chemical abrasion, it was unknown whether such Hadean zircons could survive the full standard 12 hr / 210 °C chemical abrasion procedure. Conducting chemical abrasion in a stepwise manner, where intermediate leachates are extracted and retained for analysis, eliminates this risk. By combining such *stepwise* chemical abrasion with TIMS-TEA, we may obtain matched trace-element and geochronological data for each subsequent chemical abrasion step of each analyzed zircon fragment. While time-consuming, such an analytical procedure has the potential to provide insight into both the geologic history of Jack Hills Hadean zircon and the efficacy of chemical abrasion.

2 METHODS

Here we apply stepwise CA-ID-TIMS-TEA (chemical abrasion, isotope dilution, thermal ionization mass spectrometry with trace element analysis) to sub-grain fragments of Jack Hills zircons. Since only some three percent of Jack Hills zircons have ages > 4.0 Ga [17], Jack Hills zircons with late Hadean ($\sim 4.0 - 4.1$ Ga) SIMS ages were selected from epoxy mounts previously characterized by *in situ* techniques at UCLA (Table S1). A total of 23 epoxy mounted half-zircons were selected for TIMS analysis at Princeton University, of which 14 were further dissected into two to five fragments each by microfracturing with a tungsten carbide point, resulting in a grand total of 54 sub-grain zircon fragments.

123 To prepare for chemical abrasion [43], each zircon fragment
124 was individually loaded into a separate quartz crucible and an-
125 nealed for 48 hours at 900 °C. Annealed zircons were trans-
126 ferred to 3 ml Savillex perfluoroacetate (PFA) beakers and
127 moved to a class 1000 cleanroom where they were rinsed with
128 MilliQ ultrapure water, transferred to 200 μ l Savillex PFA mi-
129 crocapsules, and rinsed with ultrapure HCl. Subsequent analyt-
130 ical steps were conducted in the cleanroom using class 10 clean
131 hoods, ultrapure reagents distilled in a Savillex DST-1000 sub-
132 boiling still (blank-checked to ensure common Pb concentra-
133 tions less than 0.1 pg/g), and PFA labware cleaned by heating
134 with alternating ultrapure acids for periods of months to years.

135 In the first analytical campaign, 36 zircon fragments in sepa-
136 rate microcapsules were loaded into two teflon-lined Parr pres-
137 sure dissolution vessels with ultrapure hydrofluoric acid (100
138 μ l 29 M HF plus 15 μ l 3 M HNO₃ per microcapsule, with 5
139 ml moat HF) and chemically abraded in two steps of six hours
140 at 210 °C. In the second analytical campaign, the remaining
141 18 zircon fragments were chemically abraded in a single Parr
142 vessel in three steps of four hours, as illustrated in Figure 1.
143 Between each leaching step, all supernatant acid was extracted,
144 spiked, and retained for analysis (comprising the L1, L2, and
145 L3 leachates). Subsequently, the surviving zircon residue was
146 thoroughly rinsed with H₂O, HCl, HNO₃, and HF, before fi-
147 nally dissolving any surviving zircon over 48 hours at 210 °C
148 with ultrapure HF (as during abrasion) and a measured quantity
149 of isotope dilution tracer. The EARTHTIME ²⁰⁵Pb-²³³U-²³⁵U
150 “ET535” tracer [46, 47] was used for all L1 analyses, while the
151 EARTHTIME ²⁰²Pb-²⁰⁵Pb-²³³U-²³⁵U double-spike “ET2535”
152 was used for the more critical L2, L3, and residue analyses.

153 After chemical abrasion and dissolution, each of the resulting
154 54 dissolved zircon residues and 126 leachates was evaporated
155 to dryness, converted to chlorides by heating with ultrapure 6
156 M HCl, evaporated a second time, and redissolved in ultrapure
157 3 M HCl to prepare for ion chromatography. For each sam-
158 ple, a small PTFE column was loaded with 50 μ l of chloride
159 form Eichrom AG1-X8 anion exchange resin (200-400 mesh),
160 cleaned alternately with H₂O and 6 M HCl, and conditioned
161 with 3.1 M HCl. Following the separation procedure of Krogh
162 [48] with the modifications of Schoene et al. [49], samples were
163 loaded and trace elements eluted in 3 M HCl followed by Pb
164 elution in 6 M HCl and U elution in H₂O. Eluted U-Pb sepa-
165 rates were evaporated to dryness with \sim 2 μ l 0.03 M H₃PO₄ and
166 stored for analysis.

167 Isotopic and trace element analyses of the resulting separates
168 were conducted in 2015-2016 at Princeton University. Evap-
169 orated U-Pb separates were loaded (U and Pb together) onto
170 zone-refined rhenium filaments with \sim 2 μ l silica gel emitter
171 [50] for analysis by IsotopX Phoenix 62 TIMS. Thermal ion-
172 ization mass spectrometry and data reduction procedures were
173 equivalent to those of Schoene et al. [51], with Pb collected by
174 peak-hopping on a Daly detector, correcting for a detector dead-
175 time of 43.5 ns as determined by repeated analyses of NBS 982
176 reference material. Where beam intensity allowed, U was col-
177 lected by static multicollection on Faraday cups with 10¹² Ω
178 amplifiers; otherwise, U was collected by peak-hopping on a
179 Daly detector, correcting for 37.5 ns deadtime as established
180 by repeated analyses of CRM U500. During TIMS analysis,
181 two fragments were identified as contamination introduced dur-

ing single-fragment annealing, and rejected. Isotopic data was
processed and analytical uncertainty propagated using Tripoli
and U-Pb Redux [52, 53], using a ²³⁸U/²³⁵U ratio of 137.818
 \pm 0.045 (two-sigma) [54]. Trace element separates were subse-
quently analyzed on a Thermo Scientific Element 2 ICPMS fol-
lowing the procedure of Schoene et al. [49], with zircon trace
element abundances normalized to 496000 ppm Zr in zircon.
Finally, zircon U and Th concentrations were calculated using
the zircon Th/U ratio determined from Pb isotopic composition,
the ICPMS-derived Th concentrations, and ID-TIMS U and Pb
masses. The resulting elemental and isotopic data are tabulated
in Tables S1 and S2; all analytical uncertainties are reported as
two-sigma unless otherwise noted.

3 RESULTS

The Concordia diagrams of Figure 2 reveal a highly hetero-
geneous age population, including four concordant Hadean
residues with ²⁰⁷Pb/²⁰⁶Pb dates ranging from 4142.30 \pm 0.63
to 4004.20 \pm 0.51 Ma (excluding tracer and decay constant un-
certainty), a wide range of variably discordant L2-L3 leachates,
and a distinct, highly discordant population of L1 leachates.
Three of the four concordant Hadean zircon residues are de-
rived from a single grain, RSES58 z6.10, which also yielded
three concordant L3 leachates and a single concordant L2
leachate (all Hadean), as highlighted in Figure 2C. These con-
cordant ages from different fragments of a single zircon crys-
tal span some 70 Myr. As may be expected from Mattinson
[43] and the success of CA-TIMS over the subsequent
decade, leachates are typically more discordant than residues.
L1 leachates in particular are markedly more discordant than
other analyses, forming a broad array trending towards a lower
intercept at the origin (Figure 2A), as might result from zero-
age Pb-loss. Four leachate analyses – all of them L2 leachates
– yield negatively discordant ages.

Zircon residues are observed in Figure 3A to be systemati-
cally (with only one imprecise exception) older than their re-
spective leachates in ²⁰⁷Pb/²⁰⁶Pb space, even at low discordance.
For a given zircon fragment, L1-L3 leachates are found to
have ²⁰⁷Pb/²⁰⁶Pb ages some 10s to 100s of Myr younger than
residues, with the age gap between corresponding leachates
and residues increasing with leachate discordance. In particu-
lar, since modern U or Pb remobilization (e.g., Pb-loss without
additional isotopic fractionation) has no effect on ²⁰⁷Pb/²⁰⁶Pb
ages, systematic age gaps between residues and leachates in
²⁰⁷Pb/²⁰⁶Pb space are most readily attributed to ancient, not re-
cent, Pb-loss.

Using the TIMS-TEA methodology of Schoene et al. [49], we
are able to combine trace element and isotopic analyses on the
exact same volume of zircon, allowing us to consider the chem-
ical characteristics of zircons that have undergone open-system
behavior. We observe that both discordance and leaching ex-
tent are strongly correlated with bulk chemistry. In particular,
L1 leachates are identifiable by their low Zr content as a propor-
tion of measured cations, as well as their extreme discordance.
As observed in Figure 3B, Zr represents less than 90% of the
observed cation budget by mass in L1 leachate analyses, sug-
gesting that the material removed in L1 leaching steps is not
stoichiometric zircon; in later leaching steps, chemistry evolves
towards that of the pure zircon residue. Meanwhile, as seen in

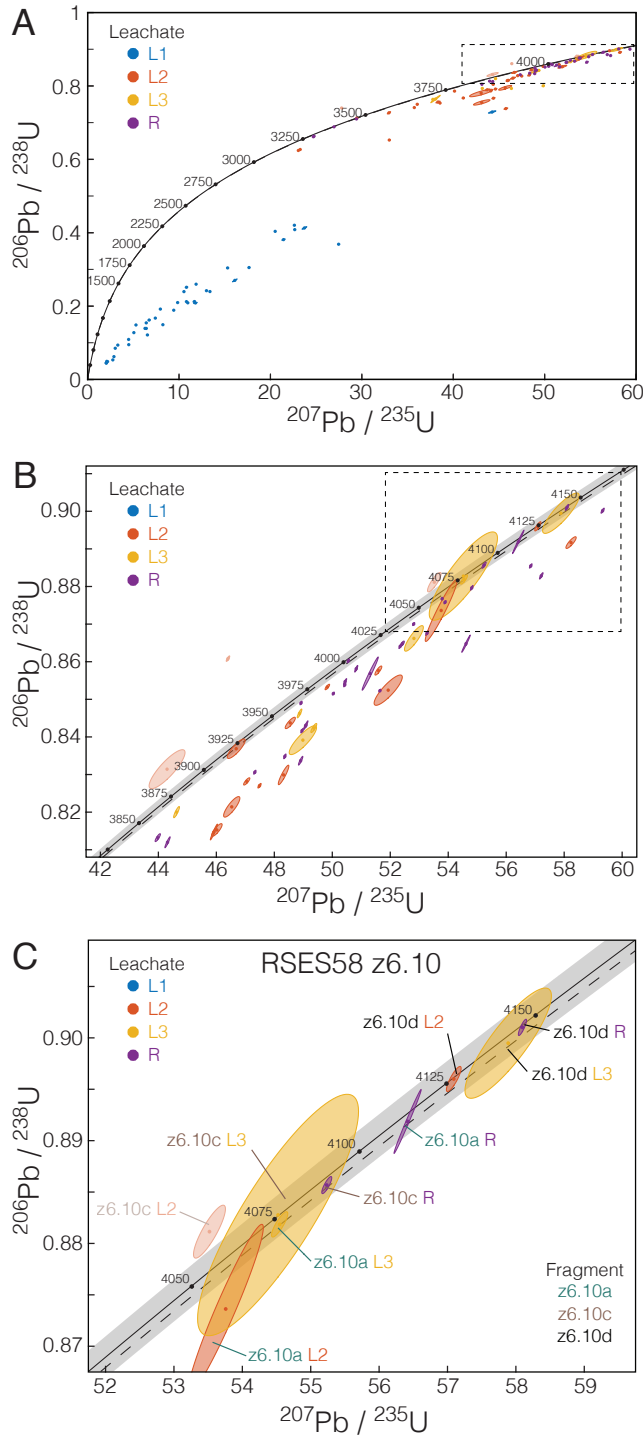


Figure 2: CA-ID-TIMS ages for Jack Hills zircon by fragment and leaching step, in Wetherill [35] concordia space. A: Full range, including recent Pb-loss array in L1 leachates. B: Hadean-Eoarchean inset, emphasizing complexity of the Hadean record suggesting early lead loss and protracted crystallization history. C: Concordant fragments and leachates of zircon RSES58 z6.10, illustrating ~50 Myr age heterogeneity between concordant residues of zircon fragments from the same polished half-zircon. At this scale, the uncertainty in the $\lambda_{U-238}/\lambda_{U-235}$ decay constant ratio that defines Concordia becomes important; here the solid Concordia line and grey two-sigma error envelope reflects the values of Jaffey et al. [55], while the dashed line reflects those of Schoene et al. [56]. All dates plotted along the Concordia line are in Ma.

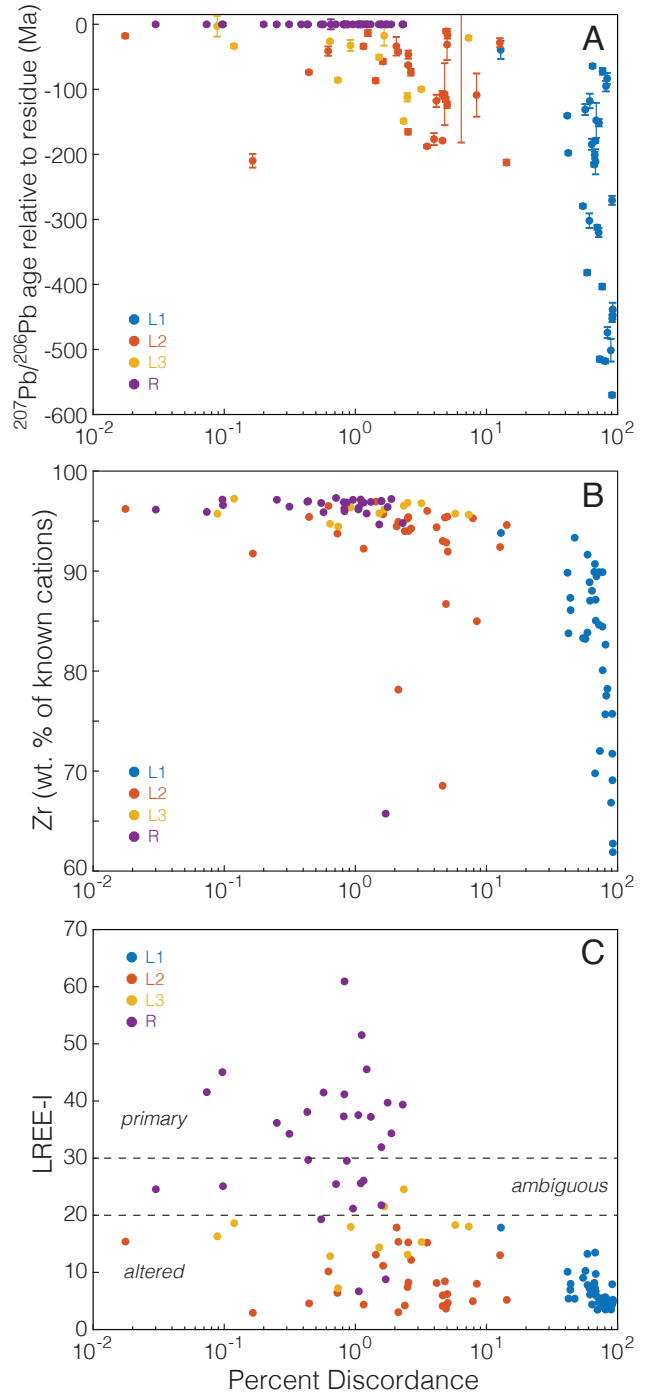


Figure 3: A: Age of each leachate relative to its associated residue (if any) plotted as a function of percent discordance. Age offset increases with discordance, but may reach ~100 Myr even for leachates of similar discordance to their residue. B: Abundance of Zr relative to total measured cation concentration as a function of measured discordance. L1 leachates are distinguished by their high discordance and low Zr proportion. C: The light rare earth alteration index ($LREE-I = Dy/Nd + Dy/Sm$) of Bell et al. [25, 57] plotted as a function of measured discordance. High $LREE-I$ in TEA measurements accurately distinguishes primary zircon residues from leachates.

240 Figure 3C, leachates are reliably resolved from pristine residues
241 by the light rare earth index $LREE-I$ of Bell et al. [25, 57]. Re-
242 assuringly, all L1 and L2 leachates fall in the "altered" field
243 defined by Bell et al. [25] ($LREE-I < 20$), while the "primary"
244 ($LREE-I > 30$) field contains only residues; the remaining anal-
245 yses fall in the "ambiguous" field of $LREE-I$ between 20 and 30
246 comprise residues and L3 leachates.

247 On an element-by-element basis, we observe a distinct pat-
248 tern of trace element enrichment in leachates relative to zircon
249 residues (Figure 4). L1 leachates display LREE concentrations
250 up to a factor of 25 higher than their corresponding residues,
251 along with smaller enrichments in MREE. The discordant L1
252 leachates are also highly radiogenic, with over ten times the Pb^*
253 of pristine zircon residue. Consistent with Pb-loss, this radio-
254 genic lead excess is outpaced by the extreme Th ($\sim 30 \times$ residue)
255 and U ($\sim 50 \times$ residue) concentrations of the same leachates. On
256 the same basis, L2 leachates display comparatively muted en-
257 richments in REE, U, Th, and Pb^* , while L3 leachates dis-
258 play significant enrichments only in LREE.

259 A comparison of TIMS and SIMS $^{207}Pb/^{206}Pb$ ages in Figure 5
260 reveals that, for leachates and discordant residues, SIMS ages
261 (typically targeted on low-U cores) are generally older than
262 TIMS ages on fragments of the same grains. Discordant TIMS
263 analyses, especially including early leachates, are likely access-
264 ing damaged open-system domains that were excluded from the
265 analyzed SIMS spot. Indeed, depending on the scale of spatial
266 heterogeneity in U-Pb discordance, smaller analytical volumes
267 may be less likely to mix closed- and open-system domains,
268 leading to increased median concordance as a statistical conse-
269 quence of smaller analytical volume. However, as seen in Fig-
270 ure 5, TIMS and SIMS $^{207}Pb/^{206}Pb$ ages are in relatively good
271 agreement for concordant residues surviving the full 12 hours
272 of chemical abrasion.

273 4 DISCUSSION

274 4.1 Chemical Abrasion and U-Pb geochronology

275 Open-system behavior is arguably the foremost complicating
276 factor in radioisotopic geochronology. With two independent
277 decay chains proceeding at different rates, the U-Pb system in
278 principle allows us to track open-system behavior with discor-
279 dance, and in some cases to even determine the age of Pb-loss.
280 For zircon, chemical abrasion has been observed to remove
281 damaged domains that have undergone lead loss, and is now
282 widely applied [43, 44, 60, 42]. However, the same combina-
283 tion of annealing and acid leaching has not been entirely suc-
284 cessful in other minerals: monazite responds poorly to anneal-
285 ing [61], while baddeleyite (ZrO_2) displays complicated behav-
286 ior upon abrasion despite its chemical similarity to zircon [62].

287 Even more puzzling, modern (zero-age) Pb loss is ubiquitous
288 in zircon [63, 64, 65, 66] and to a lesser degree baddeleyite
289 [67, 68, 62], even when it is not observed in other minerals
290 such as monazite [64] and sphene [66] from the same sample.
291 Despite some early suggestions, laboratory handling has been
292 largely ruled out as a source of such zero-age Pb-loss [64];
293 much to the contrary, laboratory acid treatment reproducibly
294 *decreases* normal discordance both in zircon and other miner-
295 als [43, 62, 61]. Even in unannealed zircon, where leaching
296 may induce unwanted isotopic fractionation, leachates are con-

297 sistently more discordant than residues [69, 70, 60]. Clearly,
298 fully understanding these phenomena is central to the reliabil-
299 ity of chemically abraded zircon U-Pb ages.

300 Consistent with literature expectations [43, 60], chemical abra-
301 sion is remarkably successful at removing Jack Hills zircon
302 domains that have undergone open system processes: concor-
303 dance consistently increases with increasing leaching extent
304 (Figures 2, 3). Components removed in the first four hours
305 (L1) are observed to cluster in an array near the origin in Fig-
306 ure 2, suggesting they have previously undergone near zero-
307 age Pb loss. Chemically, these components are not stoichio-
308 metric zircon, with zirconium representing less than 90% of
309 the cation mass budget. Instead, we suggest that both highly
310 metamict (amorphous) [e.g., 71, 72] zircon, as well as inclu-
311 sions and crack-filling precipitates of other less durable miner-
312 als, are rapidly dissolved and removed within these first four
313 hours of chemical abrasion. The geochemistry of material re-
314 moved during subsequent abrasion steps is markedly closer to
315 that of pristine zircon, though still detectably altered accord-
316 ing to the $LREE-I$ alteration index of Bell et al. [25, 57]. Con-
317 sequently, we suggest that this material removed in the later
318 hours of chemical abrasion corresponds to variably radiation-
319 damaged, altered zircon that may have been partially annealed
320 or recrystallized.

321 To better understand the age of open-system behavior affect-
322 ing discordant leachate fractions, in Figure 6A we estimate the
323 vector of Pb-loss removed by a single leaching step by plot-
324 ting discordia arrays defined by sequential analysis pairs for
325 the same fragment. Ordered by leaching step in Concordia
326 space, the lower intercept age of Pb-loss removed by chemical
327 abrasion steadily increases with leaching extent. In particular,
328 two modes are observed: near zero-age lower intercepts corre-
329 sponding to L1 leaching steps, and broadly Archean lower in-
330 tercepts corresponding to later leaching steps (Figure 6B). This
331 trend, along with the relatively pristine zircon chemistry of later
332 leaching steps, may be explained by considering that zircon do-
333 mains which have undergone ancient but *not* recent lead loss
334 must have been subsequently partially annealed or recrystal-
335 lized. Such domains would consequently be more resistant to
336 chemical abrasion than their fully metamict counterparts, and
337 thus preferentially accessed only in the later stages of chemical
338 abrasion.

339 These results, in the context of other recent observations, sup-
340 port the conclusion of Black [64] that zero-age lead loss in zir-
341 con results from aqueous processes associated with exposure
342 and incipient weathering. The Jack Hills zircons have not been
343 affected by any recent tectonothermal disturbances [59, 58],
344 and (according to lithium zonation) have never been metamor-
345 phosed above greenschist facies [38] – yet they still display per-
346 vasive recent and ancient lead loss. In contrast to the terres-
347 trial Jack Hills zircons dated here, Lunar zircons of equivalent
348 antiquity display little to no Pb-loss even in leachates [73] de-
349 spite potential exposure to shock metamorphism [74]; one of
350 the clearest distinguishing factors to explain this discrepancy is
351 the complete absence of water on the moon.

352 While diffusion of most cations (including U and Pb) in zircon
353 is extraordinary slow [75], disordered, partially metamict zir-
354 con has long been known to be susceptible to aqueous alteration
355 via recrystallization – on laboratory timescales at hydrothermal

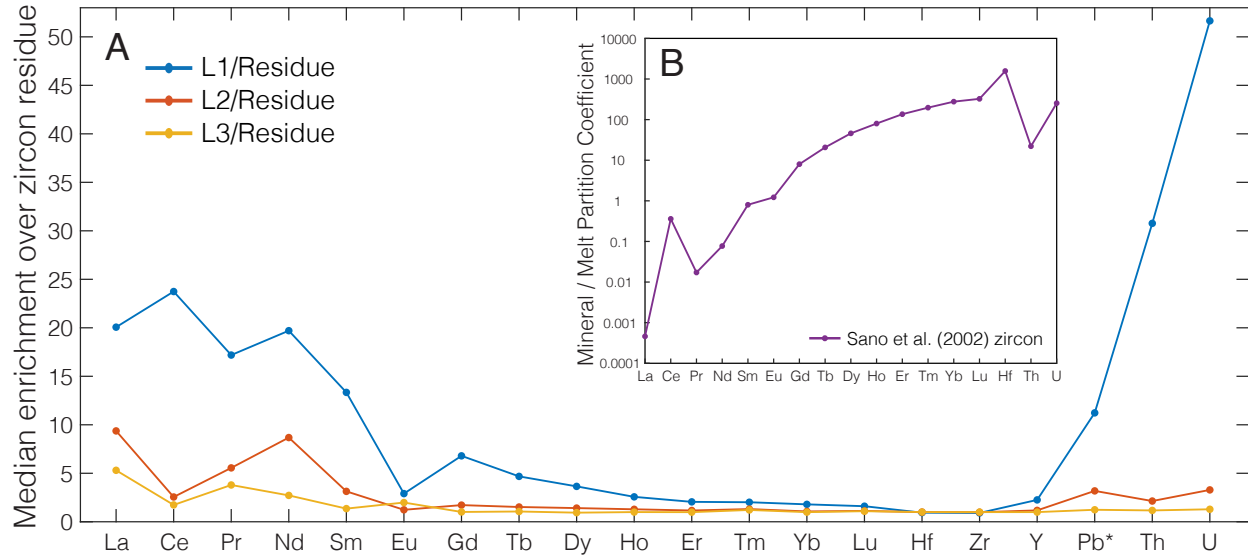


Figure 4: A: Chemical abrasion systematically removes zircon domains rich in LREE, Th, U, and radiogenic Pb. This pattern suggests the preferential removal of zones which have undergone radiation damage and metamictation due to high Th, U content, leaving them vulnerable both to geological open-system behaviour (lead loss) and dissolution during chemical abrasion. Negative Eu anomaly and MREE enrichment in L1 leachates may suggest the importance of coupled substitution in the initial formation of high Th, U domains. B: Typical zircon / melt partition coefficients: with the exception of U and Th, the elements that are least abundant in natural zircon display the highest enrichments in L1 leachates

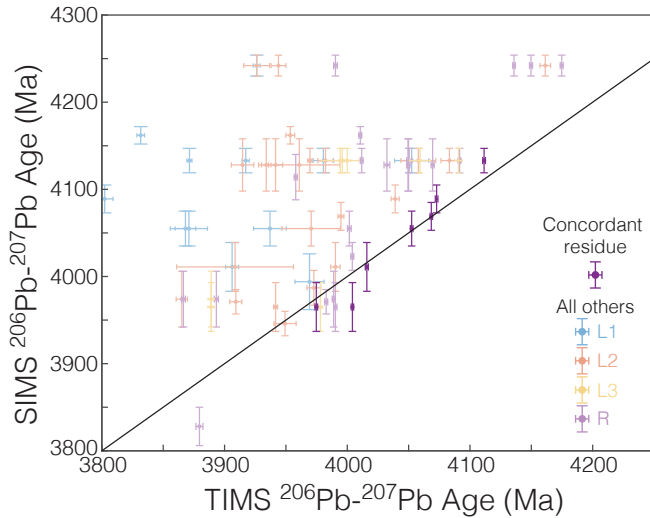


Figure 5: Two-variable cross plot of SIMS spot ages and TIMS $^{207}\text{Pb}/^{206}\text{Pb}$ ages for each fragment and leachate. Concordant residues (bold) plot along the 1:1 line, while others plot above. Horizontal data arrays result from one SIMS spot age per grain plotted against up to four TIMS ages per fragment, with multiple fragments per grain.

temperatures [76, 77, 78, 79, 80], and over longer timescales even at ambient temperatures [63, 64, 81, 82]. There is no reason to expect other accessory minerals such as monazite or sphene to be immune from analogous recrystallization processes [83, 84]. Instead, we suggest that partial resetting of zircon and baddeleyite during aqueous recrystallization may simply reflect the extreme incompatibility of Pb in the zircon (and baddeleyite) crystal under natural conditions [85]. In this context the comparative immunity of higher-Pb_c minerals like mon-

azite and sphene to such exposure-related resetting may simply reflect *closed-system* aqueous recrystallization enabled by their higher tolerance for Pb²⁺ substitution. Exposure-associated aqueous recrystallization may thus satisfactorily explain both the ubiquity of young Pb-loss in terrestrial zircon and baddeleyite, as well as its absence in monazite and sphene.

Why, then, does chemical abrasion succeed for zircon but not baddeleyite? When heated above ~800 °C at atmospheric pressure, metamict zircon decomposes into microcrystalline ZrO₂ and SiO₂, the latter of which is partially volatilized [86, 87]. This process is evidently sensitive to the crystallinity and surface area of the zircon in question, and forms the basis for the whole-grain direct evaporation technique of Kober [88], which, while limited to unspiked $^{207}\text{Pb}/^{206}\text{Pb}$ ages, may resolve zircon domains with different Pb-loss histories in a manner reminiscent of chemical abrasion. Notably, baddeleyite is dramatically more acid-soluble than zircon under laboratory conditions [62]. By converting metamict zircon to quantitatively acid-soluble ZrO₂ crystallites, low-pressure high-temperature (LPHT) annealing prepares zircons for acid leaching. The high temperature at which this conversion occurs and the subsequent quantitative dissolution of ZrO₂ crystallites may explain why isotopic fractionation and reverse discordance are rare in chemical abrasion with annealed zircon but can be significant when acid leaching baddeleyite [62], monazite [61], or un-annealed zircon [70]. Since baddeleyite is already ZrO₂, there is no way to preferentially increase the solubility of damaged domains by annealing, and thus no way to avoid isotopic fractionation, as observed by Rioux et al. [62], during incomplete hydrothermal dissolution.

Critically, since low-temperature aqueous recrystallization products appear to remain rather poorly crystalline (featuring microlites, nanopores, and residual amorphous zones [79, 80,

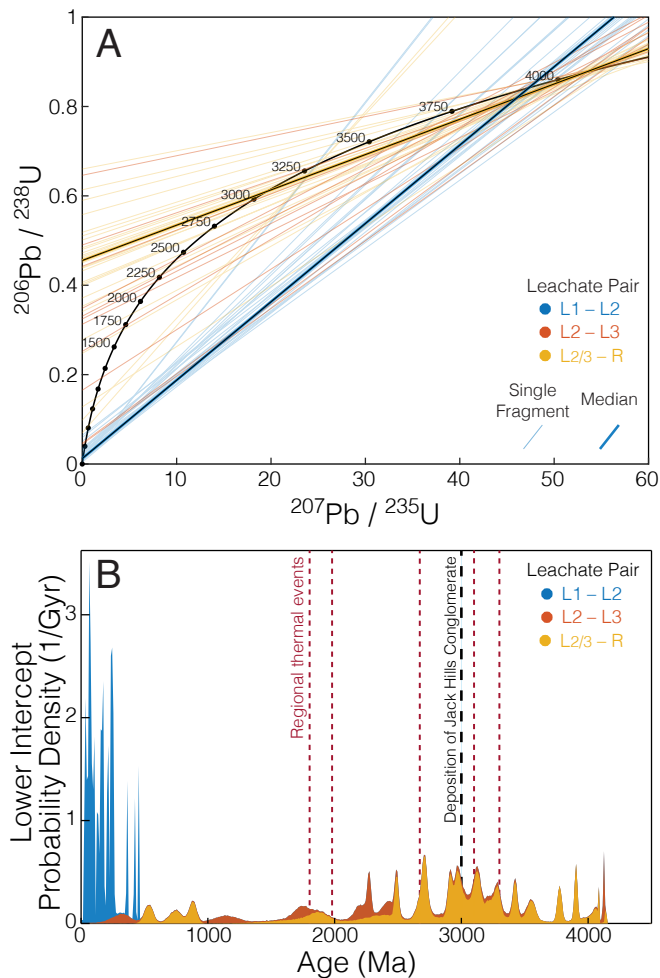


Figure 6: A: Discordia arrays defined by pairs of successive leachate and residue analyses from the same zircon fragment, illustrating slope and Concordia intercepts of each array. B: Probability density plot of the lower intercepts of each leachate-pair discordia array from (A) with the Concordia curve, plotted along with the nominal dates of known regional thermal events after Spaggiari [58] and the approximate depositional age of the Jack Hills metaconglomerate [59]. Arrays defined by L1-L2 leachate pairs have lower intercepts near 0 to 0.5 Ga, while L2-R and (where three leaching steps were conducted) L3-R pairs define arrays with much older – largely Archean – lower intercepts

82, 89)), we may expect that partially metamict zircon that has undergone exposure-associated aqueous Pb-loss and recrystallization remains susceptible to oxide decomposition during LPHT annealing. If this interpretation is correct, the absence of isotopic fractionation during chemical abrasion of zircon may depend more upon the decomposition of radiation-damaged zircon during annealing than on the direct acid-solubility of metamict zircon.

4.2 Geological History of Hadean Jack Hills Zircons

Despite the limited metamorphic grade of the Jack Hills conglomerate [59, 58, 38], All zircon fragments we analyzed show clear chemical signs of alteration in leachate fractions, with enrichments in LREE, U, and Th – corresponding to low *LREE-I* in the "altered" field of Bell et al. [25, 57]. In L1 leachates,

which also display relatively low Zr cation proportions, the extreme enrichments in LREE, U, and Th may be attributed in part to inclusions or crack-filling secondary minerals. The more modest enrichments in L2 and L3 leachates are more likely attributable to partially metamict zircon. This latter case leads unavoidably to some ambiguity regarding the origin of the atypical chemistry of these leachates: if certain zones in a given zircon are preferentially metamict, they must have crystallized with particularly high U and Th concentrations. However, since magmatic zircon has not been observed to crystallize with high LREE, we may assume these contaminants were added at or near the time that Pb was lost from the metamict source domains of L2 and L3 leachates. Fortunately, the two independent decay chains of the U-Pb system allow us to estimate the timing of this alteration.

While highly heterogeneous, the lower intercepts of leachate pairs may be crudely divided between two modes: one modern and one Archean (Figure 6). The complete decoupling of the major L1-L2 Pb-loss mode from any known regional metamorphic events in the Narryer terrane is consistent with the hypothesis that this represents aqueous recrystallization during modern exposure and weathering. In this context, it may be significant that the lower intercepts of L2/3 - R pairs broadly scatter around the estimated depositional age of the Jack Hills quartzite, with a mean lower intercept of 3050 Ma.

While the discordia arrays defined by successive leaching steps are subject to substantial interpretive uncertainty (and need not be geologically meaningful considering the possibility of time-transgressive Pb-loss), it is nonetheless apparent from Figure 6 that L2 and L3 domains do not appear to have been heavily influenced by the same zero-age Pb-loss process seen in L1 domains – suggesting that such domains are not as metamict as they once were. Consequently, it appears that either ancient low-grade metamorphic events or prolonged burial may have acted to partially anneal these domains, locking in ancient Pb-loss. In other words, regional metamorphic events in the Narryer terrane appear, if anything, to halt – not initiate – Pb loss. Subaerial exposure and aqueous weathering – not metamorphism – may explain modern and ancient open-system behavior in the Jack Hills zircons. Such a model parsimoniously reconciles the complicated multiple-Pb-loss history of the Jack Hills zircons (e.g., Figure 2) with their relative lack [38] of high-grade metamorphism.

Finally, concordant Jack Hills zircon residues that have survived chemical abrasion still display dramatic age heterogeneity, with a 50 Ma range observed between different fragments of the same zircon, as seen in Figure 2C. While chemical abrasion may imperfectly or incompletely remove domains that have undergone ancient open-system behavior, any modern U or Pb loss or addition would occur along a markedly steeper line in $^{206}\text{Pb}/^{238}\text{U} - ^{207}\text{Pb}/^{235}\text{U}$ space, and thus cannot explain the observed age heterogeneity in RSES58 z6.10. Nonetheless, due to the minimal curvature of Concordia over this age range, we cannot rule out early (>4 Ga) open-system behavior as a cause of this dispersion, even with ID-TIMS precision on the <0.05% level. Considering the infeasibility of high-temperature diffusive daughter loss without dissolution and recrystallization below zircon saturation temperature [90, 75, 91, 31], we are left with two endmember scenarios to explain the observed age het-

471 erogeneity in RSES58 z6.10: (1) high temperature overgrowth,
472 and (2) low temperature recrystallization. The former suggests
473 repeated magmatic or orogenic events within the Hadean; the
474 latter likely requires the presence of liquid water.

475 5 CONCLUSIONS

476 Stepwise CA-ID-TIMS-TEA analyses confirm the Hadean
477 SIMS ages of Jack Hills zircon fragments, while providing in-
478 sight into both the geological history of open-system behavior
479 in the Jack Hills zircons and the operation and effectiveness of
480 the zircon chemical abrasion procedure of Mattinson [43]. Jack
481 Hills zircon residues and leachates exhibit complex discordance
482 suggesting at least two recorded modes of post-Hadean Pb-loss,
483 as well as at least one episode of Hadean recrystallization or
484 overgrowth. Concordant Hadean residues reveal 50 Myr of age
485 heterogeneity in the fragments of RSES 58 z6.10, suggesting
486 this single zircon may have experienced multiple episodes of
487 magmatism within the Hadean.

488 Most Pb-loss in the Hadean Jack Hills zircons studied here
489 substantially post-dates the Hadean, with episodes focused
490 around ~0 and ~3 Ga – potentially ameliorating some concerns
491 about the impact of Pb-loss on the Hadean Hf isotope record.
492 Moreover, such Pb-loss does not appear to be driven by high-
493 temperature metamorphism; on the contrary, regional metamor-
494 phic events of the Narryer terrane appear to correlate with the
495 partial *annealing* of ancient radiation damage, halting and lock-
496 ing in evidence of ancient Pb-loss in L3 and L2 – but not L1 –
497 domains. Instead, following Stern et al. [63] and Black [64], we
498 propose that Pb-loss in metamict zircon domains is frequently
499 a result of low temperature aqueous recrystallization associated
500 with weathering and subaerial exposure.

501 While small-scale aqueous recrystallization might well be en-
502 visioned as a closed-system process for many minerals, we
503 further propose that the extreme incompatibility of Pb in zir-
504 con and baddeleyite ensures that Pb is excluded during aque-
505 ous recrystallization. Hence, zero-age Pb-loss is apparent in
506 zircon and baddeleyite even when it is absent in, e.g., coexist-
507 ing sphene or monazite. Considering the central role of water
508 in this mechanism of Pb-loss, this hypothesis may explain the
509 ubiquity of recent Pb-loss in terrestrial – but not Lunar – zircon.

510 Our isotopic and trace element results are consistent with the
511 prior expectation that chemical abrasion [43] effectively re-
512 moves zircon domains that have undergone partial open-system
513 behavior, including both metamict zircon and contaminating
514 inclusions. Over the course of twelve hours of HF leaching,
515 leachate chemistry evolves from U, Th, and LREE-enriched to-
516 wards normal zircon, and from discordant to concordant. While
517 the first (L1) leachates are the most radiogenic, they are also
518 the most discordant, and reflect the youngest Pb-loss (Figure 6).
519 The cation proportion of Zr is diminished only in L1 leachates,
520 suggesting most inclusions are removed in the first four hours of
521 chemical abrasion. Meanwhile, elevated U and Th contents in
522 leachates are consistent with the hypothesis that chemical abra-
523 sion preferentially removes the same metamict domains that are
524 susceptible to Pb-loss through aqueous recrystallization. We
525 further note that the conversion of partially metamict zircon to
526 dramatically more acid-soluble baddeleyite during LPHT an-
527 nealing may explain why it is only for zircon that chemical

abrasion is successful in removing open-system domains with-
out significant isotopic fractionation.

Finally, we find that the *LREE-I* alteration index of Bell et al.
[25, 57] accurately identifies non-primary geochemistry in dis-
cordant leachates. In particular, these results demonstrate that
the trace element ratio cutoffs defined by Bell et al. [25] to iden-
tify alteration via SIMS are also applicable to trace element
concentrations determined by ICP-MS in the TIMS-TEA [49]
workflow. Consequently, we hypothesize that screening *in situ*
analyses by *LREE-I* on a cycle-by-cycle basis (with, e.g., split
stream techniques) may allow *in situ* U-Pb analyses to reject the
same altered domains that are removed by chemical abrasion in
CA-TIMS.

All code and data is available at
<https://github.com/brenhinkeller/JackHillsTIMS-TEA>

6 ACKNOWLEDGEMENTS

Thanks to Kyle M. Samperton for valuable discussion. C.B.K. was
supported in part by the U.S. Department of Energy under contract
DE-FG02-97ER25308.

REFERENCES

- [1] Derek O Froude, Trevor R Ireland, Peter D Kinny, Ian S Williams, William Compston, Ian R Williams, and John S Myers. Ion microprobe identification of 4,100–4,200 Myr-old terrestrial zircons. *Nature*, 304(5927):616, August 1983.
- [2] William Compston and Robert T Pidgeon. Jack Hills, evidence of more very old detrital zircons in Western Australia. *Nature*, 321(6072):766–769, June 1986.
- [3] Samuel A Bowring and Ian S Williams. Priscoan (4.00–4.03 Ga) orthogneisses from northwestern Canada. *Contributions to Mineralogy and Petrology*, 134(1):3–16, January 1999.
- [4] Stephen J Mojzsis and T Mark Harrison. Establishment of a 3.83-Ga magmatic age for the Akilia tonalite (southern West Greenland). 202(3-4):563–576, September 2002.
- [5] Tsuyoshi Iizuka, Kenji Horie, Tsuyoshi Komiya, Shigenori Maruyama, Takafumi Hirata, Hiroshi Hidaka, and Brian F Windley. 4.2 Ga zircon xenocryst in an Acasta gneiss from northwestern Canada: Evidence for early continental crust. *Geology*, 34(4):245–248, April 2006.
- [6] Serge Nadeau, Wei Chen, Jimmy Reece, Deokumar Lachhman, Randy Ault, Maria Telma Lins Faraco, Lêda Maria Fraga, Nelson Joaquim Reis, and Léandro Menezes Betiollo. Guyana: the Lost Hadean crust of South America? *Brazilian Journal of Geology*, 43(4):601–606, December 2013.
- [7] Jean-Louis Paquette, J S F Barbosa, S Rohais, S C P Cruz, P Goncalves, J J Peucat, A B M Leal, M Santos-Pinto, and Hervé Martin. The geological roots of South America: 4.1 Ga and 3.7 Ga zircon crystals discovered in N.E. Brazil and N.W. Argentina. *Precambrian Research*, 271:49–55, December 2015.
- [8] HongLiang Wang, Liang Chen, Yong Sun, Xiaoming Liu, XueYi Xu, JuanLu Chen, Hong Zhang, and ChunRong Diwu. 4.1 Ga xenocrystal zircon from Ordovician volcanic rocks in western part of North Qinling Orogenic Belt. *Chinese Science Bulletin*, 52(21):3002–3010, 2007.
- [9] Ji Duo, ChunQi Wen, JianCi Guo, XiaoPing Fan, and XiaoWen Li. 4.1 Ga old detrital zircon in western Tibet of China. *Chinese Science Bulletin*, 52(1):23–26, 2007.

- 584 [10] YaJun Xu, YuanSheng Du, HongWei Huang, ZhiQiang Huang, 645
 585 LiSha Hu, YanHui Zhu, and WenChao Yu. Detrital zircon of 4.1 646
 586 Ga in South China. *Chinese Science Bulletin*, 57(33):4356–4362, 647
 587 2012. 648
- 588 [11] Guang-Fu Xing, Xiao-Lei Wang, Yusheng Wan, Zhi-Hong Chen, 649
 589 Yang Jiang, Kouki Kitajima, Takayuki Ushikubo, and Phillip Go- 650
 590 pon. Diversity in early crustal evolution: 4100 Ma zircons in 651
 591 the Cathaysia Block of southern China. *Scientific Reports*, 4(1): 652
 592 5143, June 2014. 653
- 593 [12] Scott R Miller, Paul A Mueller, Joseph G Meert, George D Ka- 654
 594 menov, Anthony F Pivarunas, Anup K Sinha, and Manoj K Pan- 655
 595 dit. Detrital Zircons Reveal Evidence of Hadean Crust in the 656
 596 Singhbhum Craton, India. *The Journal of Geology*, 126(5):541– 657
 597 552, June 2018. 658
- 598 [13] Benjamin L Byerly, Donald R Lowe, Nadja Drabon, Matthew A 659
 599 Coble, Dale H Burns, and Gary R Byerly. Hadean zircon from a 660
 600 3.3 Ga sandstone, Barberton greenstone belt, South Africa. *Ge- 661
 601 ology*, 46(11):967–970, September 2018. 662
- 602 [14] John W Valley, Aaron J Cavosie, Takayuki Ushikubo, and D A 663
 603 Reinhard. Hadean age for a post-magma-ocean zircon confirmed 664
 604 by atom-probe tomography. *Nature Geoscience*, 7:219–223, 665
 605 March 2014. 666
- 606 [15] Peter Holden, Peter Lanc, Trevor R Ireland, T Mark HARRI- 667
 607 son, John J Foster, and Zane Bruce. Mass-spectrometric min- 668
 608 ing of Hadean zircons by automated SHRIMP multi-collector 669
 609 and single-collector U/Pb zircon age dating: The first 100,000 670
 610 grains. *International Journal of Mass Spectrometry*, 286(2-3): 671
 611 53–63, June 2009. 672
- 612 [16] Aaron J Cavosie, John W Valley, and Simon A Wilde. Chapter 673
 613 2.5 The Oldest Terrestrial Mineral Record: A Review of 4400 674
 614 to 4000 Ma Detrital Zircons from Jack Hills, Western Australia. 675
 615 Elsevier, 2007. 676
- 616 [17] T Mark Harrison. The Hadean Crust: Evidence from 4 Ga Zir- 677
 617 cons. *Annual Review of Earth and Planetary Sciences*, 37(1): 678
 618 479–505, May 2009. 679
- 619 [18] T Mark Harrison, Elizabeth A Bell, and Patrick Boehnke. 680
 620 Hadean Zircon Petrochronology. *Reviews in Mineralogy and 681
 621 Geochemistry*, 83(1):329–363, February 2017. 682
- 622 [19] Stephen J Mojzsis, T Mark Harrison, and Robert T Pidgeon. 683
 623 Oxygen-isotope evidence from ancient zircons for liquid water 684
 624 at the Earth’s surface 4,300 Myr ago. *Nature*, 409(6817):178– 685
 625 181, January 2001. 686
- 626 [20] Simon A Wilde, John W Valley, William H Peck, and Colin M 687
 627 Graham. Evidence from detrital zircons for the existence of con- 688
 628 tinental crust and oceans on the Earth 4.4 Gyr ago. *Nature*, 409 689
 629 (6817):175–178, January 2001. 690
- 630 [21] Aaron J Cavosie, John W Valley, Simon A Wilde, and E I M F. 691
 631 Magmatic $\delta^{18}\text{O}$ in 4400–3900 Ma detrital zircons: A record of 692
 632 the alteration and recycling of crust in the Early Archean. *Earth 693
 633 and Planetary Science Letters*, 235(3-4):663–681, July 2005. 694
- 634 [22] Dustin Trail, Stephen J Mojzsis, T Mark Harrison, Axel K 695
 635 Schmitt, E Bruce Watson, and Edward D Young. Constraints on 696
 636 Hadean zircon protoliths from oxygen isotopes, Ti-thermometry, 697
 637 and rare earth elements. *Geochemistry Geophysics Geosystems*, 698
 638 8(6):1–22, June 2007. 699
- 639 [23] Paul W O Hoskin. The Composition of Zircon and Igneous and 700
 640 Metamorphic Petrogenesis. *Reviews in Mineralogy and Geo- 701
 641 chemistry*, 53(1):27–62, January 2003. 702
- 642 [24] Dustin Trail, E Bruce Watson, and Nicholas D Tailby. The oxida- 703
 643 tion state of Hadean magmas and implications for early Earth’s 704
 644 atmosphere. *Nature*, 480(7375):79–82, November 2011. 705
- [25] Elizabeth A Bell, Patrick Boehnke, and T Mark Harrison. Re- 645
 covering the primary geochemistry of Jack Hills zircons through 646
 quantitative estimates of chemical alteration. *Geochimica et Cos- 647
 mochimica Acta*, 191:187–202, October 2016. 648
- [26] E Bruce Watson. Zircon Thermometer Reveals Minimum Melt- 649
 ing Conditions on Earliest Earth. *Science*, 308(5723):841–844, 650
 May 2005. 651
- [27] Roland Maas, Peter D Kinny, Ian S Williams, Derek O Froude, 652
 and William Compston. The Earth’s oldest known crust: A 653
 geochronological and geochemical study of 3900–4200 Ma old 654
 detrital zircons from Mt. Narryer and Jack Hills, Western Aus- 655
 tralia. *Geochimica et Cosmochimica Acta*, 56(3):1281–1300, 656
 March 1992. 657
- [28] Michelle D Hopkins, T Mark Harrison, and Craig E Manning. 658
 Constraints on Hadean geodynamics from mineral inclusions in 659
 >4 Ga zircons. 298(3-4):367–376, October 2010. 660
- [29] Elizabeth A Bell, Patrick Boehnke, Michelle D Hopkins- 661
 Wielicki, and T Mark Harrison. Distinguishing primary and sec- 662
 ondary inclusion assemblages in Jack Hills zircons. *Lithos*, 234- 663
 235:15–26, October 2015. 664
- [30] John S Myers. Early archaean narryer gneiss complex, Yilgarn 665
 Craton, Western Australia. *Precambrian Research*, 38(4):297– 666
 307, April 1988. 667
- [31] C Brenhin Keller, Patrick Boehnke, and Blair Schoene. Temporal 668
 variation in relative zircon abundance throughout Earth history. 669
Geochemical Perspectives Letters, 3:179–189, April 2017. 670
- [32] C Brenhin Keller and Blair Schoene. Plate tectonics and conti- 671
 nental basaltic geochemistry throughout Earth history. *Earth and 672
 Planetary Science Letters*, 481:290–304, January 2018. 673
- [33] Kent C Condie. A planet in transition: The onset of plate tecton- 674
 ics on Earth between 3 and 2 Ga? *Geoscience Frontiers*, 9(1): 675
 51–60, January 2018. 676
- [34] Jean H Bédard. Stagnant lids and mantle overturns: Implications 677
 for Archaean tectonics, magmagenesis, crustal growth, mantle 678
 evolution, and the start of plate tectonics. *Geoscience Frontiers*, 679
 9(1):19–49, January 2018. 680
- [35] George W Wetherill. Discordant uranium-lead ages, I. *Transac- 681
 tions, American Geophysical Union*, 37(3):320–326, 1956. 682
- [36] Monika A Kusiak, Martin J Whitehouse, Simon A Wilde, 683
 Daniel J Dunkley, Martina Menneken, Alexander A Nemchin, 684
 and Chris Clark. Changes in zircon chemistry during Archean 685
 UHT metamorphism in the Napier Complex, Antarctica. *Ameri- 686
 can Journal of Science*, 313(9):933–967, November 2013. 687
- [37] Nigel M Kelly and Simon L Harley. An integrated microtextur- 688
 al and chemical approach to zircon geochronology: refining the 689
 Archaean history of the Napier Complex, east Antarctica. *Con- 690
 tributions to Mineralogy and Petrology*, 149(1):57–84, February 691
 2005. 692
- [38] Dustin Trail, Daniele J Cherniak, E Bruce Watson, T Mark HARRI- 693
 son, Benjamin P Weiss, and Ian Szumila. Li zoning in zircon as 694
 a potential geospeedometer and peak temperature indicator. *Con- 695
 tributions to Mineralogy and Petrology*, 171(25):1–15, February 696
 2016. 697
- [39] Martin Guitreau and Janne Blichert-Toft. Implications of discor- 698
 dant U–Pb ages on Hf isotope studies of detrital zircons. *Chemi- 699
 cal Geology*, 385:17–25, October 2014. 700
- [40] Elizabeth A Bell, T Mark Harrison, Issaku E Kohl, and Edward D 701
 Young. Eoarchean crustal evolution of the Jack Hills zircon 702
 source and loss of Hadean crust. *Geochimica et Cosmochimica 703
 Acta*, 146:27–42, December 2014. 704

- 705 [41] Martin J Whitehouse, Alexander A Nemchin, and Robert T Pidgeon. What can Hadean detrital zircon really tell us? A critical
706 evaluation of their geochronology with implications for the inter-
707 pretation of oxygen and hafnium isotopes. *Gondwana Research*, 51:78–91, November 2017. 709
- 710 [42] Blair Schoene. U–Th–Pb Geochronology. In Roberta L Rudnick, editor, *Treatise on Geochemistry*, pages 341–378. Elsevier, 2014. 711
- 712 [43] James M Mattinson. Zircon U–Pb chemical abrasion (“CA-
713 TIMS”) method: Combined annealing and multi-step partial
714 dissolution analysis for improved precision and accuracy of zircon
715 ages. *Chemical Geology*, 220(1-2):47–66, July 2005.
- 716 [44] Roland Mundil, Kenneth R Ludwig, Ian Metcalfe, and Paul R
717 Renne. Age and Timing of the Permian Mass Extinctions: U/Pb
718 Dating of Closed-System Zircons. *Science*, 305(5691):1760–
719 1763, September 2004.
- 720 [45] Yuri Amelin, Der-Chuen Lee, Alex N Halliday, and Robert T
721 Pidgeon. Nature of the Earth’s earliest crust from hafnium iso-
722 topes in single detrital zircons. *Nature*, 399(6733):252–255, May
723 1999.
- 724 [46] Daniel J Condon, Blair Schoene, Noah M McLean, Samuel A
725 Bowring, and Randall R Parrish. Metrology and traceability of
726 U–Pb isotope dilution geochronology (EARTHTIME Tracer Cal-
727 ibration Part I). *Geochimica et Cosmochimica Acta*, 164:464–
728 480, September 2015.
- 729 [47] Noah M McLean, Daniel J Condon, Blair Schoene, and
730 Samuel A Bowring. Evaluating uncertainties in the calibration
731 of isotopic reference materials and multi-element isotopic trac-
732 ers (EARTHTIME Tracer Calibration Part II). *Geochimica et*
733 *Cosmochimica Acta*, 164:481–501, September 2015.
- 734 [48] T E Krogh. A low-contamination method for hydrothermal de-
735 composition of zircon and extraction of U and Pb for isotopic age
736 determinations. *Geochimica et Cosmochimica Acta*, 37:485–494,
737 March 1973.
- 738 [49] Blair Schoene, Christopher Latkoczy, Urs Schaltegger, and
739 Detlef Günther. A new method integrating high-precision U–Pb
740 geochronology with zircon trace element analysis (U–Pb TIMS-
741 TEA). *Geochimica et Cosmochimica Acta*, 74(24):7144–7159,
742 December 2010.
- 743 [50] H Gerstenberger and G Haase. A highly effective emitter sub-
744 stance for mass spectrometric Pb isotope ratio determinations.
745 *Chemical Geology*, 136(3-4):309–312, April 1997.
- 746 [51] Blair Schoene, Kyle M Samperton, Michael P Eddy, Gerta Keller,
747 Thierry Adatte, Samuel A Bowring, S F R Khadri, and B Gertsch.
748 U–Pb geochronology of the Deccan Traps and relation to the end-
749 Cretaceous mass extinction. *Science*, 347(6218):182–184, Jan-
750 uary 2015.
- 751 [52] Noah M McLean, Jim F Bowring, and Samuel A Bowring. An
752 algorithm for U–Pb isotope dilution data reduction and uncer-
753 tainty propagation - McLean - 2011 - *Geochemistry, Geophysics,*
754 *Geosystems* - Wiley Online Library. *Geochemistry Geophysics*
755 *Geosystems*, 12(6):1–12, June 2011.
- 756 [53] Jim F Bowring and Noah M McLean. Engineering cyber infras-
757 tructure for U–Pb geochronology: Tripoli and U–Pb Redux. *Geo-*
758 *chemistry Geophysics Geosystems*, 12(6):1–19, June 2011.
- 759 [54] Joe Hiess, Daniel J Condon, Noah M McLean, and Stephen R
760 Noble. 238U/235U Systematics in Terrestrial Uranium-Bearing
761 Minerals. *Science*, 335(6076):1610–1614, March 2012.
- 762 [55] A H Jaffey, K F Flynn, L E Glendenin, and W C Bentley. Preci-
763 sion Measurement of Half-Lives and Specific Activities of 235U
764 and 238U. *Physical Review C*, 4(5):1889–1906, November 1971.
- [56] Blair Schoene, James L Crowley, Daniel J Condon, Mark D
Schmitz, and Samuel A Bowring. Reassessing the uranium
decay constants for geochronology using ID-TIMS U–Pb data.
Geochimica et Cosmochimica Acta, 70(2):426–445, January
2006.
- [57] Elizabeth A Bell, Patrick Boehnke, Melanie Barboni, and T Mark
Harrison. Tracking chemical alteration in magmatic zircon using
rare earth element abundances. *Chemical Geology*, 510:56–71,
April 2019.
- [58] Catherine V Spaggiari. The Jack Hills greenstone belt, Western
Australia: Part 1: Structural and tectonic evolution over >1.5 Ga.
Precambrian Research, 155:204–228, January 2007.
- [59] Catherine V Spaggiari. The Jack Hills greenstone belt, West-
ern Australia: Part 2: Lithological relationships and implications
for the deposition of ≥ 4.0 Ga detrital zircons. *Precambrian Re-*
search, 155(3-4):261–286, January 2007.
- [60] James M Mattinson. Extending the Krogh legacy: development
of the CA–TIMS method for zircon U–Pb geochronology This arti-
cle is one of a series of papers published in this Special Issue on
the theme of Geochronology in honour of Tom Krogh. *Canadian*
Journal of Earth Sciences, 48(2):95–105, January 2011.
- [61] Emily M Peterman, James M Mattinson, and Bradley R Hacker.
Multi-step TIMS and CA-TIMS monazite U–Pb geochronology.
Chemical Geology, 312-313:58–73, June 2012.
- [62] Matthew Rioux, Samuel Bowring, Frank Dudás, and Richard
Hanson. Characterizing the U–Pb systematics of baddeleyite
through chemical abrasion: application of multi-step digestion
methods to baddeleyite geochronology. *Contributions to Miner-*
alogy and Petrology, 160(5):777–801, March 2010.
- [63] T W Stern, S S Goldich, and M F Newell. Effects of weathering
on the UPb ages of zircon from the Morton Gneiss, Minnesota. 1
(6):369–371, November 1966.
- [64] Lance P Black. Recent Pb loss in zircon: A natural or laboratory-
induced phenomenon? *Chemical Geology: Isotope Geoscience*
section, 65(1):25–33, March 1987.
- [65] Bent T Hansen and Johan D Friderichsen. The influence of re-
cent lead loss on the interpretation of disturbed U–Pb systems
in zircons from igneous rocks in East Greenland. *Lithos*, 23(3):
209–223, August 1989.
- [66] B T Hansen, P O Persson, F Söllner, and A Lindh. The influence
of recent lead loss on the interpretation of disturbed U–Pb sys-
tems in zircons from metamorphic rocks in southwest Sweden.
Lithos, 23(1-2):123–136, June 1989.
- [67] T Reischmann. Precise U/Pb age determination with badde-
leyite (ZrO₂), a case study from the Phalaborwa igneous complex,
South Africa. *South African Journal of Geology*, 98(1):1–4, Jan-
uary 1995.
- [68] Ulf Söderlund, P Jonathan Patchett, Jeffrey D Vervoort, and
Clark E Isachsen. The 176Lu decay constant determined by
Lu–Hf and U–Pb isotope systematics of Precambrian mafic intru-
sions. *Earth and Planetary Science Letters*, 219(3-4):311–324,
March 2004.
- [69] James M Mattinson. A study of complex discordance in zircons
using step-wise dissolution techniques. *Contributions to Miner-*
alogy and Petrology, 116(1-2):117–129, March 1994.
- [70] Donald W Davis and T E Krogh. Preferential dissolution of 234U
and radiogenic Pb from α -recoil-damaged lattice sites in zircon:
implications for thermal histories and Pb isotopic fractionation
in the near surface environment. *Chemical Geology*, 172(1-2):
41–58, February 2001.

- 825 [71] Heinrich D Holland and David Gottfried. The effect of nuclear 886
826 radiation on the structure of zircon. *Acta Crystallographica*, 8 887
827 (6):291–300, June 1955.
- 828 [72] Satoshi Utsunomiya, Chris S Palenik, John W Valley, Aaron J 888
829 Cavosie, Simon A Wilde, and Rodney C Ewing. Nanoscale occur- 889
830 currence of Pb in an Archean zircon. *Geochimica et Cosmochimica 890*
831 *Acta*, 68(22):4679–4686, November 2004. 891
- 832 [73] Melanie Barboni, Patrick Boehnke, C Brenhin Keller, Issaku E 892
833 Kohl, Blair Schoene, Edward D Young, and Kevin D McKeegan. 893
834 Early formation of the Moon 4.51 billion years ago. *Science 894*
835 *Advances*, 3(1):e1602365, January 2017. 895
- 836 [74] Carolyn A Crow, Desmond E Moser, and Kevin D McKeegan. 896
837 Shock metamorphic history of >4 Ga Apollo 14 and 15 zircons. 897
838 *Meteoritics & Planetary Science*, 351:472, August 2018. 898
- 839 [75] Daniele J Cherniak. Diffusion in Zircon. *Reviews in Mineralogy 899*
840 *and Geochemistry*, 53(1):113–143, January 2003. 900
- 841 [76] Robert T Pidgeon, James R O’Neil, and Leon T Silver. Ura- 902
842 nium and Lead Isotopic Stability in a Metamict Zircon under Ex- 903
843 perimental Hydrothermal Conditions. *Science*, 154(3756):1538– 904
844 1540, December 1966.
- 845 [77] Thorsten Geisler, Marcus Ulonska, Helmut Schleicher, Robert T 905
846 Pidgeon, and Wilhelm van Bronswijk. Leaching and differential 906
847 recrystallization of metamict zircon under experimental hy- 907
848 drothermal conditions. *Contributions to Mineralogy and Petrology*, 141(1):53–65, April 2001. 908
- 849 [78] Thorsten Geisler, Robert T Pidgeon, Reinhardt Kurtz, Wilhelm 909
850 van Bronswijk, and Helmut Schleicher. Experimental hydrother- 910
851 mal alteration of partially metamict zircon. *American Mineralogist*, 88(10):1496–1513, October 2003. 911
- 852 [79] Thorsten Geisler, Ming Zhang, and Ekhard K H Salje. Recrys- 912
853 tallization of almost fully amorphous zircon under hydrothermal 913
854 conditions: An infrared spectroscopic study. *Journal of Nuclear 914*
855 *Materials*, 320(3):280–291, August 2003. 915
- 856 [80] Thorsten Geisler, Anne-Magali Seydoux-Guillaume, Michael 916
857 Wiedenbeck, Richard Wirth, Jasper Berndt, Ming Zhang, Bori- 917
858 ana Mihailova, Andrew Putnis, Ekhard K H Salje, and Jochen 918
859 Schlüter. Periodic precipitation pattern formation in hydrother- 919
860 mally treated metamict zircon. *American Mineralogist*, 89(8-9): 920
861 1341–1347, August 2004. 921
- 862 [81] Desmond Tromans. Solubility of crystalline and metamict zircon: 922
863 A thermodynamic analysis. *Journal of Nuclear Materials*, 357(1- 923
864 3):221–233, October 2006. 924
- 865 [82] Simon Delattre, Satoshi Utsunomiya, Rodney C Ewing, Jean- 925
866 Loup Boeglin, Jean-Jacques Braun, Etienne Balan, and Georges 926
867 Calas. Dissolution of radiation-damaged zircon in lateritic soils. 927
868 *American Mineralogist*, 92(11-12):1978–1989, November 2007. 928
- 869 [83] Daniel E Harlov, Richard Wirth, and Callum J Hetherington. 929
870 Fluid-mediated partial alteration in monazite: the role of coupled 930
871 dissolution–reprecipitation in element redistribution and mass 931
872 transfer. *Contributions to Mineralogy and Petrology*, 162(2): 932
873 329–348, December 2010. 933
- 874 [84] Alexander P Gysi, Daniel Harlov, and George D Miron. The 934
875 solubility of monazite (CePO₄), SmPO₄, and GdPO₄ in aqueous 935
876 solutions from 100 to 250 C. *Geochimica et Cosmochimica Acta*, 936
877 242:143–164, December 2018. 937
- 878 [85] E Bruce Watson, D J Cherniak, John M Hanchar, T Mark Harri- 938
879 son, and D A Wark. The incorporation of Pb into zircon. *Chemical 939*
880 *Geology*, 141(1-2):19–31, August 1997. 940
- 881 [86] Lutz Nasdala, Christian L Lengauer, John M Hanchar, Andreas 941
882 Kronz, Richard Wirth, Philippe Blanc, Allen K Kennedy, and 942
883 Anne-Magali Seydoux-Guillaume. Annealing radiation damage 943
884 and the recovery of cathodoluminescence. *Chemical Geology*, 191(1-3):121–140, November 2002. 944
- 885 [87] Tamás Váczi, Lutz Nasdala, Richard Wirth, Mathias Mehofer, 945
886 Eugen Libowitzky, and Tobias Häger. On the breakdown of zir- 946
887 con upon “dry” thermal annealing. *Mineralogy and Petrology*, 97(1-2):129–138, October 2009. 947
- 888 [88] Bernd Kober. Whole-grain evaporation for 207Pb/206Pb-age- 948
889 investigations on single zircons using a double-filament thermal 949
890 ion source. *Contributions to Mineralogy and Petrology*, 93(4): 950
891 482–490, August 1986. 951
- 892 [89] Duncan C Hay, Tim J Dempster, Martin R Lee, and David J 952
893 Brown. Anatomy of a low temperature zircon outgrowth. *Contri- 953*
894 *butions to Mineralogy and Petrology*, 159(1):81–92, June 2009. 954
- 895 [90] Daniele J Cherniak, John M Hanchar, and E Bruce Watson. Diffu- 955
896 sion of tetravalent cations in zircon. *Contributions to Mineralogy 956*
897 *and Petrology*, 127(4):383–390, May 1997. 957
- 898 [91] Patrick Boehnke, E Bruce Watson, Dustin Trail, T Mark Harri- 958
899 son, and Axel K Schmitt. Zircon saturation re-revisited. *Chemical 959*
900 *Geology*, 351:324–334, August 2013. 960