1 **Chemical Abrasion: The Mechanics of Zircon Dissolution**

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9   **Abstract**

10   Chemical abrasion is a technique that combines laboratory annealing and partial
11   dissolution in hydrofluoric acid (HF) to selectively remove radiation-damaged portions
12   of zircon crystals prior to U-Pb isotopic analysis, and it is applied ubiquitously to zircon
13   prior to U-Pb isotope dilution thermal ionization mass spectrometry (ID-TIMS). The
14   mechanics of zircon dissolution in HF and the impact of different leaching conditions
15   on the zircon structure, however, are poorly resolved. We present a microstructural
16   investigation that integrates microscale X-ray computed tomography (μCT), scanning
17   electron microscopy, and Raman spectroscopy to evaluate zircon dissolution in HF. We
18   show that μCT is an effective tool for imaging metamictization and complex dissolution
19   networks in three dimensions. We find that most grains do not dissolve predominantly
20   from rim-to-core. Acid frequently reaches crystal interiors via fracture networks
21   spatially associated with radiation damage zoning and inclusions to dissolve higher U
22   zones, material in the vicinity of fractures, and some inclusions. Other acid paths to
23   crystal cores include the dissolution of surface-reaching inclusions and the percolation
24   of acid across zones with high defect densities. In highly crystalline samples dissolution
25   is crystallographically-controlled with dissolution proceeding almost exclusively along
26   the *c*-axis. Increasing the leaching temperature from 180 °C to 210 °C results in deeper
27   etching textures, wider acid paths, more complex internal dissolution networks, and
28   greater volume losses. We discuss the implications of our findings for zircon ID-TIMS
29   U-Pb geochronology and paired trace element analyses, radiation damage annealing
30   models, and for using μCT for imaging radiation damage zoning for (U-Th)/He
31   thermochronology.

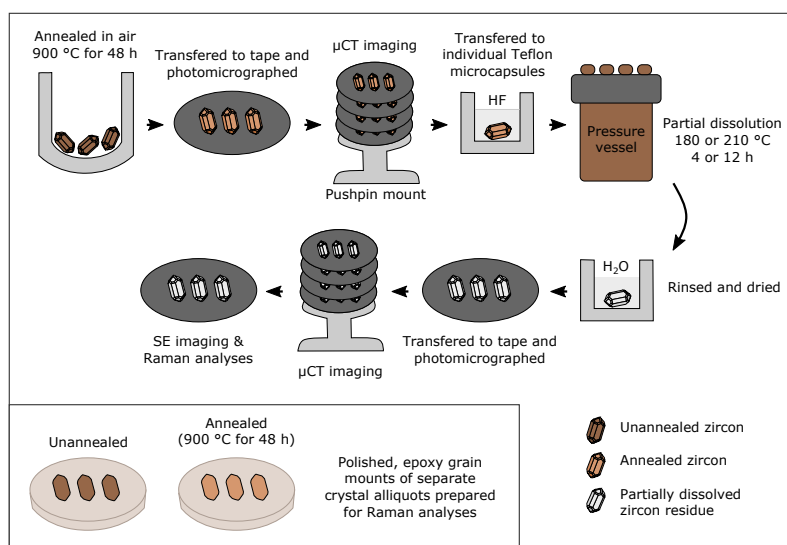
1 Introduction

Zircon U-Pb dating by isotope dilution thermal ionization mass spectrometry (ID-TIMS) produces high-precision dates that the Earth science community depends on to calibrate geologic time (Bowring and Schmidtz, 2003; Schoene, 2014). Zircon crystals affected by radiation damage – caused by alpha recoil events in the ^{238}U, ^{235}U, and ^{232}Th decay series and the spontaneous fission of ^{238}U (Holland and Gottfried 1955; Weber et al., 1990; Murakami et al., 1991; Meldrum et al. 1998; Trachenko et al., 2002; Ewing et al., 2003) – can lose radiogenic Pb by diffusion, leaching, or recrystallization compromising the accuracy of U-Pb ages (Mezger, 1997; Nasdala et al., 1998; Geisler et al., 2002). Pb-loss can sometimes be identified graphically on a concordia diagram when there is a mismatch between the ^{238}U/^{206}Pb and the ^{235}U/^{207}Pb isotopic clocks, but sometimes discordia lines closely track concordia making Pb-loss difficult to detect, thereby complicating age interpretations from zircon datasets (Mezger, 1997; Schoene, 2014).

Chemical abrasion, a technique that combines laboratory annealing to induce partial structural recovery and leaching in hydrofluoric acid (HF) to selectively remove soluble, radiation-damaged portions of crystals prior to U-Pb isotopic analysis, revolutionized the field's ability to date zircon crystals affected by open system behavior (Mundil et al., 2004; Mattinson, 2005; 2011). Still, many chemically abraded U-Pb zircon datasets exhibit anomalously young, concordant dates that are often attributed to residual Pb-loss (Davydov et al., 2010; Schoene et al., 2010a; Schmidtz and Davydov, 2012; Meyers et al., 2012). Undetected residual Pb-loss can potentially bias critical geologic interpretations such as correlations between terrestrial flood volcanism and biotic crises where ~100 ka precision and accuracy matter (Schoene et al., 2010a), or other correlated biostratigraphic and radioisotopic calibrations constructed to study key climate transitions in Earth history (Schmidtz and Davydov, 2012). This ongoing challenge has recently prompted the ID-TIMS U-Pb community to more closely evaluate how different chemical abrasion protocols – which can vary considerably both within and between individual laboratories – affect geochronological results (Huyskens et al., 2016; Widmann et al., 2019).

Despite the near-universal acceptance of chemical abrasion, the mechanics of zircon dissolution during acid digestion are poorly understood, and several outstanding questions remain. Do most zircon crystals predominantly dissolve from rim to core? How does acid reach crystal interiors to dissolve metamict zones? Does partial dissolution effectively remove all mineral and melt inclusions? How does changing the temperature and duration of leaching affect the zircon structure? It is not unreasonable to assume that a zircon grain predominantly dissolves from rim to core, since crystal rims are often enriched in actinides and radiation damage relative to crystal cores

71 (Mattison, 2005; 2011). However, acid has been observed to reach grain interiors
72 presumably via either pre-existing fractures or soluble radiation damage networks
73 formed by interconnected fission or alpha recoil tracks, much like how natural fluids
74 are thought to leach radiogenic Pb from grain interiors (Mundil et al., 2004; Mattinson,
75 2005; 2011). Despite some qualitative observations, none of these hypotheses have been
76 rigorously tested nor leveraged to gain a mechanistic understanding of the annealing
77 and leaching process.
78
79 A basic understanding of the microstructural processes that occur during partial
80 dissolution in HF acid is needed to improve Pb-loss mitigation efforts and ensure the
81 accuracy of high-precision ID-TIMS zircon U-Pb dates. In this study, we present the first
82 three-dimensional (3D) view of zircon dissolution based on microscale X-ray computed
83 tomography data (μCT) acquired before and after leaching in HF. We evaluate both
84 zircon crystals with different radiation damage levels as well as different leaching
85 conditions (180 °C vs. 210 °C, 4 h vs. 12 h). These data are paired with secondary
86 electron images of etched grain surfaces and Raman spectral data used to characterize
87 radiation damage and track changes in zircon crystallinity. In addition to achieving
88 valuable new insights into the mechanics of zircon dissolution, our μCT data reveal
89 exciting opportunities for quickly and non-destructively imaging radiation damage
90 zoning in zircon in 3D which has broader implications for zircon chronology.
91
92 **2 Methods**
93
94 **2.1 Samples**
95
96 Our study focuses on four zircon samples (AS3, SAM-47, KR18-04, and BOM2A) that
97 together span nearly the full radiation damage spectrum. AS3 is an intermediate-to-
98 high damage sample from the Mesoproterozoic Duluth Complex anorthositic series,
99 emplaced during the North American Midcontinent Rift (Paces and Miller, 1993;
100 Schmitz et al., 2003; Takehara et al., 2018; Swanson-Hysell et al., 2020). The sample of
101 AS3 used in this study is the same as that studied by Takehara et al. (2018) ~~which was~~
102 collected from the same locality as that of Paces and Miller (1993) (92°09′32.4″,
103 46°45′43.4″). AS3 crystals are coarse-grained, orange to orangish-brown, and fractured.
104 Most grains are tabular prisms or anhedral shards and many show evidence of
105 hydrothermal alteration (Takehara et al., 2018). SAM-47 is an intermediate-to-high
106 damage Archean sample from the Corunna Downs granitoid complex of the Pilbara
107 Craton (89°59′55.97″, 100°08′2.38″). Grains are euhedral, brown, and translucent. KR18-
108 04 is an intermediate-to-low damage sample from a Neoproterozoic rhyolite body
109 associated with the glaciolacustrine Konnarock Formation of Virginia, USA
110 (MacLennan et al., 2020) (36°41'47.95", 81°24'22.08"). Grains are small, transparent, pink-

111 orange and prismatic. BOM2A is our lowest-damage sample from a Paleocene trachyte
112 dike in Mumbai, India associated with rifting following the main phase of Deccan Traps
113 volcanism (Basu et al., 2020). Crystals are small, transparent, colorless, and prismatic.
114
115 Aliquots of unannealed and annealed (900 °C for 48hr) grains from each of the four
116 zircon samples were ~~set aside at the start of the study,~~ mounted, polished, and
117 characterized using Raman spectroscopy to quantify the degree of radiation damage
118 ~~present in each sample,~~ as key bands in the zircon Raman spectrum broaden
119 predictably with increasing damage (Nasdala et al., 2001; Palenik et al., 2003; Váczi and
120 Nasdala, 2017). Annealed grain mounts were also imaged using optical microscopy,
121 cathodoluminescence (CL) ~~imaging,~~ and/or backscattered electron (BSE) ~~imaging~~ to
122 characterize growth textures ~~for each sample~~ (Fig. 1).
123

124
125 Figure 1: Summary of our experimental workflow.

2.2 Workflow for partial dissolution experiments

127
128 A diagram depicting our experimental workflow is presented in Fig. 1. ~~Separate~~
129 aliquots of the four zircon samples were annealed in quartz crucibles in air at 900 °C for
130 48 hours in a box furnace. Annealed grains were mounted on sticky tape (~6 mm
131 diameter circles fashioned using a hole punch) and imaged using optical microscopy.
132 The ~~four~~ sticky tape mounts were then stacked on top of a pushpin and loosely secured
133 with tape for μCT imaging (Cooperdock et al., 2016,). After imaging, grains were
134 removed from the sticky tape and transferred to ~~individual~~ Teflon microcapsules for
135 leaching in concentrated HF in a Parr Instrument Company pressure digestion vessel at
136 180 °C or 210 °C for a duration of 4 or 12 h. The chosen temperatures bracket the range

137 commonly used for chemical abrasion by the ID-TIMS U-Pb community (Huyskens et
138 al., 2016; Widmann et al., 2019). Leaching durations were selected based on a sample's
139 initial radiation damage content. Most intermediate-to-high damage zircon crystals
140 (AS3 and SAM-47) were chemically abraded at shorter durations to ensure that intact
141 zircon residues remained (as opposed to dust), although one subset of AS3 grains were
142 leached at 180 °C for the full 12 h. The intermediate-to-low damage samples (KR18-04
143 and BOM2A) maintained structural integrity over longer leaching durations, so grains
144 were leached for the full 12 h period commonly used for chemical abrasion.
145
146 After partial dissolution, residues – the portions of zircon crystals that survive chemical
147 abrasion – were rinsed in Milli-Q water, dried down, and carefully transferred to fresh
148 sticky tape. Mounted residues were then re-imaged using optical microscopy and μCT
149 to generate a "before" and "after" imagery dataset. Microphotographs of annealed
150 grains and chemically abraded zircon residues are presented in Fig. 2. Following μCT,
151 residue mounts were carbon coated, and secondary electron (SE) images of residue
152 surfaces were acquired using a scanning electron microscope (SEM). Raman spectra
153 were measured for a subset of zircon residues to characterize samples' crystallinities.
154

○ SAM-47 Zr30   ○ SAM-47 Zr30, 210 °C for 4 h
○ BOM2A Zr31   ○ BOM2A Zr31, 210 °C for 12 h

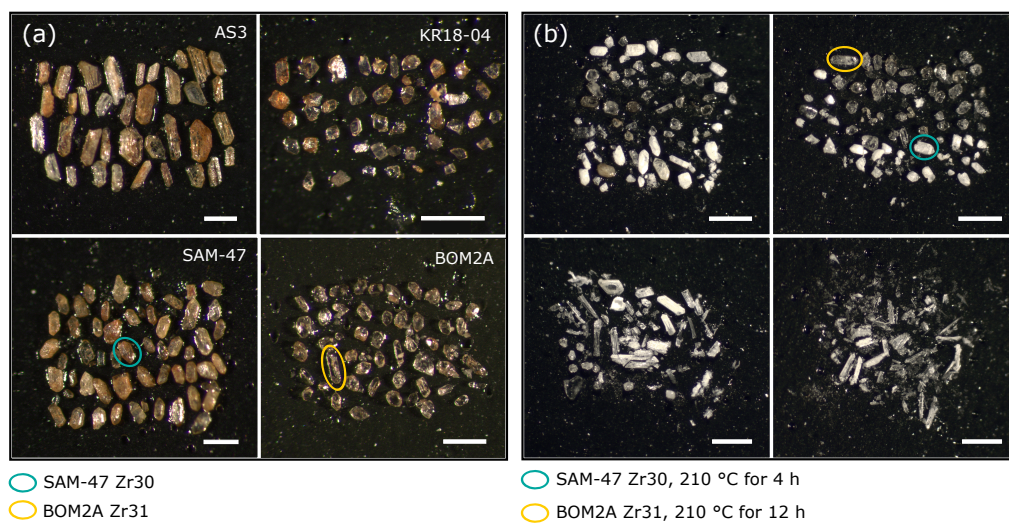



Figure 2: Photomicrographs of zircon crystals mounted on tape for μCT imaging. **(a)**
Photomicrograph of annealed grains prior to chemical abrasion **(b)** Photomicrograph of chemically
abraded zircon residues. Each tape mount in this image has a mixture of different zircon samples
treated at different leaching conditions.

155
156
157

2.3 Instrumentation and analyses

Chemical abrasion was carried out using equipment and clean lab space at Princeton University. CL and BSE ~~electron~~ images of polished mounts were acquired using the XL30 FEG SEM at the PRISM Imaging and Analysis Center at Princeton University equipped with a mini-Gatan CL detector and a semiconductor BSE detector. Most images were acquired using a 10 kV accelerating voltage, 10 mm working distance, and spot size. SE images of chemically abraded zircon residues were captured using the Quanta FEG 200 Environmental-SEM also at the PRISM Imaging and Analysis Center. This system is equipped with a Schottky field emission gun and Everhart-Thornley secondary electron detector. SE images were acquired using low vacuum mode (~0.4 to 0.8 Torr) to minimize charging due to sample topography. Scans used a 10 kV accelerating voltage, 10 to 10.5 mm working distance, and spot size 4 or 5.

All X-ray computed tomography data were collected at the High-Resolution X-ray Computed Tomography Facility at the University of Texas at Austin using a Zeiss Xradia 620 Versa. Measurements were made with X-rays set to 120 kV and 15 W and prefiltered with the LE3 filter. For each scan 2401 views were obtained over a 360° rotation at 4 s per view on the 4x detector. 16-bit TIFF images were reconstructed at 1.62 μm/voxel, using a beam hardening correction setting of 1.8 in the Xradia Reconstructor software. All 2D and 3D visualizations presented were rendered using Object Research Systems (ORS) Dragonfly software.

Raman spectra were acquired using the Horiba LabRAM Evolution Raman spectrometer in the High-Pressure Mineral Physics Laboratory at Princeton University. This confocal system is equipped with 532 nm and 632.81 nm diode lasers and a thermoelectrically cooled CCD detector. The instrument was calibrated daily using the silicon 520.7 cm^{-1} Raman band and the automated protocol implemented within the Horiba Scientific LabSpec6 software. Additionally, a quartz reference spectrum was acquired daily to verify the accuracy of measured peak positions. All measurements were made using an 1800 g/mm grating, a 100 μm slit, and a 400 to 100 μm confocal pin hole. This setup has a spectral resolution better than 2 cm^{-1} and a spatial resolution of ~2 μm. Polynomial background subtractions and Gaussian-Lorentzian peak fits were made using LabSpec6 software. Peak widths have estimated uncertainties on the order of 10% (2σ) based on tests of measurement and peak fit reproducibility. All reported peak widths (full width at half maximum, FWHM) have been corrected for instrumental broadening following the approach of Váczi (2014).

3 Results

3.1 Images of polished grain mounts

SEM and reflected light images of annealed AS3 and SAM-47 grains are presented in
Fig. 3. CL images of AS3 grains reveal broad oscillatory or convoluted compositional
zoning patterns with evidence of hydrothermal alteration. Many crystals are finely
fractured, and some have large melt inclusions that are commonly oriented parallel to
the *c*-axis. Some fractures and alteration zones are observed to cross-cut compositional
zones. SAM-47 crystals were not CL luminescent. Reflected light images acquired under
the Raman microscope, however, show that most grains have fine-scale concentric
growth zoning. BSE images reveal that some crystals are finely fractured and host
inclusions. Many of these inclusions are cross-cut by fractures. SEM images of annealed
KR18-04 and BOM2A zircon grains are presented in Fig. 4. Both samples have ~~typical~~
~~magmatic~~ growth patterns including some oscillatory zoning and some faint, broad

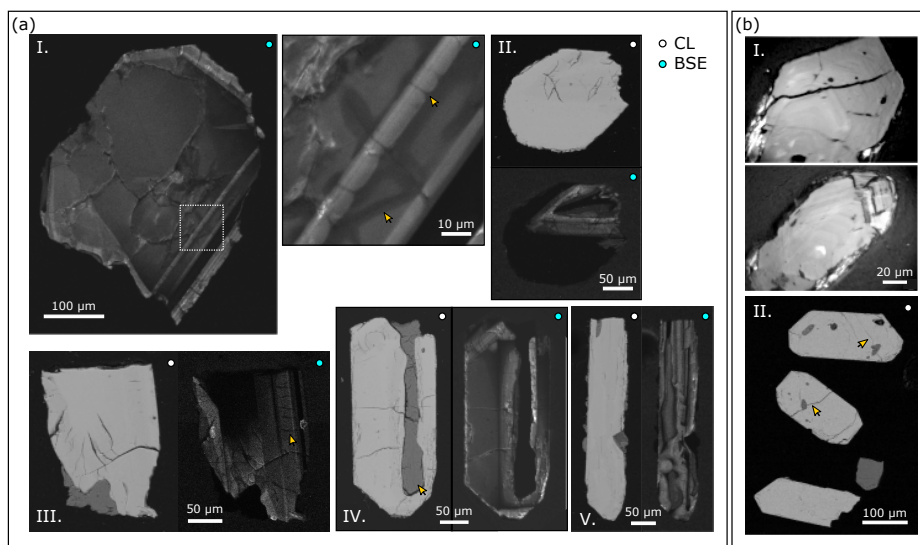



Figure 3: Representative images of annealed AS3 and SAM-47 zircon that have not been treated
by chemical abrasion. **(a)** SEM images of annealed AS3 zircon. I. A zircon with simple growth
zoning. Arrows highlight dark hydrothermal alteration zones associated with fine-scale
fractures. Some fractures cross-cut compositional zones. II. Zircon with an unfractured metamict
rim and a fractured core. III. Zircon with row of fractures that cross-cuts a compositional zone.
IV. Zircon with a large melt inclusion oriented parallel to the c-axis. V. Zircon with convolute
growth zoning. **(b)** Representative images of annealed SAM-47 zircon. I. Reflected light images
showing fine-scale concentric growth zoning. II. BSE images showing that some grains are finely
fractured. Some of these fractures pass though mineral inclusions (arrows).

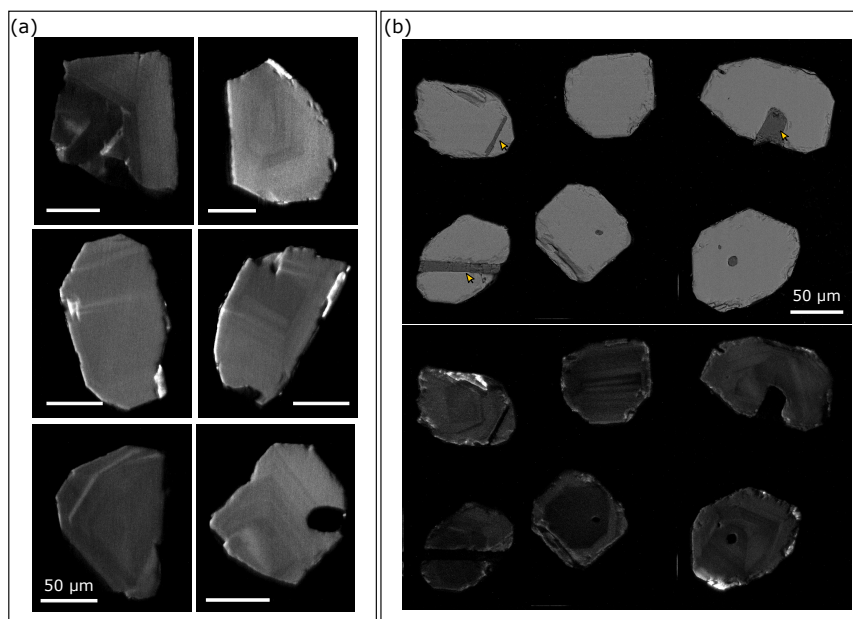



Figure 4: Representative images of annealed KR18-04 and BOM2A zircon that have not been treated by chemical abrasion. **(a)** CL images of annealed KR18-04 zircon with typical magmatic growth patterns. All scall bars are 50 μm. **(b)** Representative BSE (top) and CL (bottom) images of annealed BOM2A zircon showing typical magmatic growth zoning. Arrows highlight the frequent occurrence of apatite inclusions.

211   zones. Fractures are rare. BOM2A crystals frequently have needle-like apatite

212   inclusions, many of which are surface reaching.

213

214   **3.2 Raman spectroscopy**

215

216   **3.2.1 Polished grain mounts**

217

218   Key bands in the zircon Raman spectrum – most notably the $v_3(SiO_4)$ Si-O asymmetric

219   stretching band near ~1008 cm^{-1} and the external E_g mode near ~357 cm^{-1} – broaden and

220   shift to lower frequencies with increasing radiation damage (Nasdala et al. 1995, Zhang

221   et al. 2000, Nasdala et al. 2001, Anderson et al. 2020a, Härtel et al. 2021). Measured

222    $v_3(SiO_4)$ and E_g peak widths and positions are reported in Table S1. We derive alpha

223   dose estimates (α/g) for each sample using the calibration presented by Váczi and

224   Nasdala (2017) for the $v_3(SiO_4)$ peak width.

225

226   Raman data for unannealed AS3 and SAM-47 indicate intermediate-to-high degrees of

227   radiation damage with strong inter- and intra-crystalline variations (Fig. 5a). Estimated

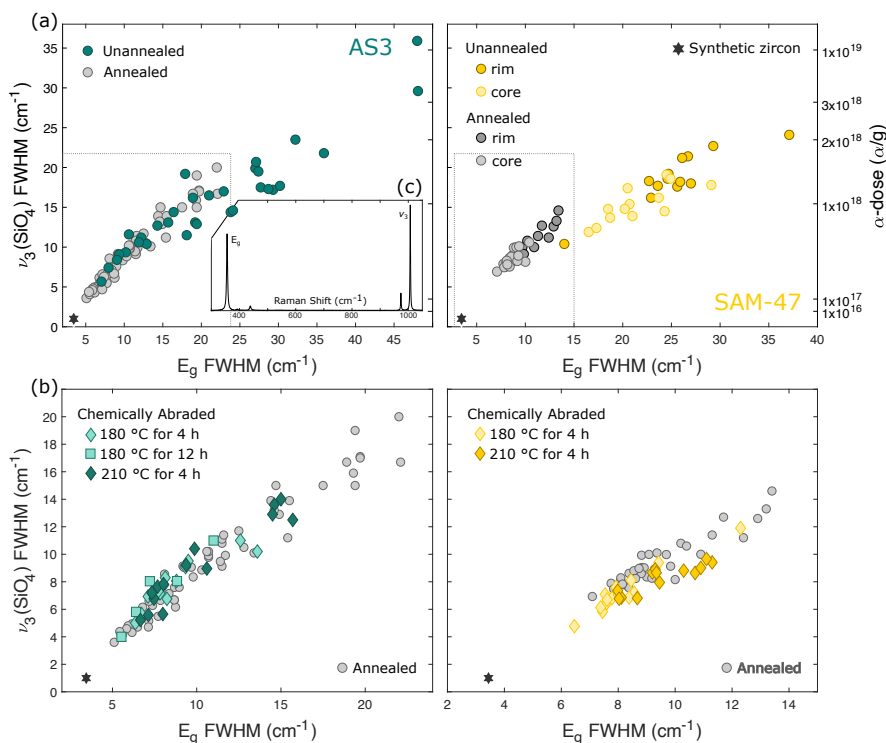



Figure 5: Raman $v_3(SiO_4)$ and E_g peak width data for intermediate-to-high damage samples AS3 (left) and SAM-47 (right). **(a)** Results for unannealed and annealed (900 °C for 48 hour) zircon samples. Alpha dose estimates for unannealed zircon samples derived from $v_3(SiO_4)$ peak width measurements are shown on the right y-axis (Váczi and Nasdala, 2017). Gray boxes mark the plot area presented in (b). **(b)** Results for annealed zircon samples and chemically abraded zircon residues. **(c)** Representative spectrum of synthetic zircon with peak assignments.

228 alpha doses for AS3 range from ~2×10^{17} α/g to >1×10^{19} α/g (the saturation value for
229 Raman-derived damage estimates). CL black regions that yielded anomalous zircon
230 spectra with fluorescent artifacts indicative of altered material were excluded from
231 radiation damage estimates. Estimated alpha doses for unannealed SAM-47 samples
232 range from ~6×10^{17} to 2×10^{18} α/g. Crystal rims in SAM-47 samples have
233 accumulated more radiation damage than crystal cores, indicating that rims are
234 enriched in actinides relative to cores. Alpha dose estimates for both AS3 and SAM-47
235 span above and below the estimated alpha dose threshold assigned to fission track
236 percolation 1.9×10^{18} α/g (Ketcham et al., 2013). This threshold also corresponds to key
237 transitions in zircon material properties including density (Holland and Gottfried, 1955;
238 Murakami et al., 1991; Ewing et al., 2003). Unannealed KR18-04 and BOM2A zircon
239 samples have low-to-intermediate levels of radiation damage and a lesser degree of
240 radiation damage zoning (Fig. 6a). Estimated alpha doses range from ~5×10^{16} to 7×10^{17}

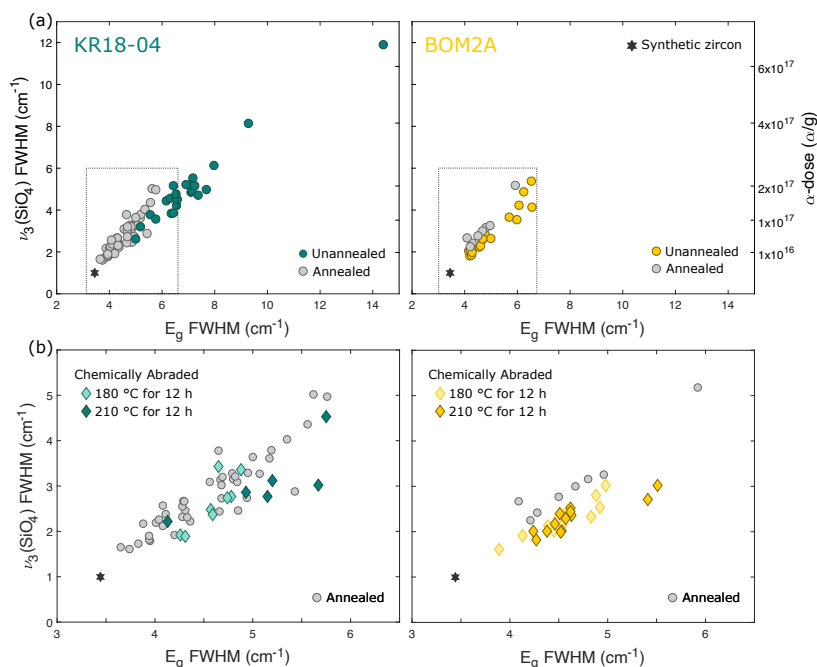



Figure 6: Raman $v_3(SiO_4)$ and E_g peak width data for lower damage samples KR18-04 (left) and BOM2A (right). **(a)** Results for unannealed and annealed (900 °C for 48 hour) zircon samples. Alpha dose estimates for unannealed zircon samples derived from $v_3(SiO_4)$ peak width measurements are shown on the right y-axis (Váczi and Nasdala, 2017). Gray boxes mark the plot area presented in (b). **(b)** Results for annealed zircon samples and chemically abraded zircon residues.

241   α/g and ~6×10^{15} to 2×10^{17} α/g for the two samples, respectively, well below the 1.9×10^{18}
242   α/g threshold.

243

244   Compared to their unannealed counterparts, $v_3(SiO_4)$ and E_g peak widths in annealed
245   AS3, SAM-47, and KR18-04 samples are narrower, consistent with the partial annealing
246   of radiation damage (Fig. 5a and Fig. 6a) (Zhang et al., 2000; Geisler et al., 2002; Ginster
247   et al., 2019; Härtel et al., 2021). $v_3(SiO_4)$ and E_g peak width ranges for each sample have
248   also narrowed, implying that annealing has decreased the magnitude of inter- and
249   intra-crystalline variations in radiation damage. Annealing seems to have had minimal
250   effect on the crystallinity of low-damage BOM2A. We note that none of the samples
251   have achieved complete structural recovery after annealing at 900 °C for 48 h, since all
252   measured peak widths are broader than that of synthetic zircon.

253

254   We note that relationship between the $v_3(SiO_4)$ and E_g peak widths is steeper after
255   annealing in each of the four samples, since the two Raman peaks have different
256   temperature sensitivities (Härtel et al., 2021). This observation suggests that laboratory

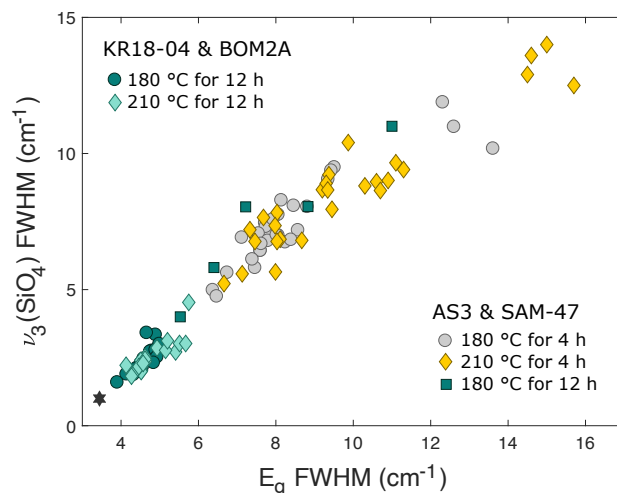



Figure 7: Raman v_3(SiO$_4$) and E_g peak width results for all chemically abraded zircon residues.

257   annealing is not simply the inverse of radiation damage accumulation. As such, we
258   caution against using the Váczi and Nasdala (2017) calibration to derive alpha dose
259   estimates from v_3(SiO$_4$) peak widths for annealed or chemically abraded samples and
260   omit alpha dose axes from Figures 5b and 6b.
261
262   **3.2.2 Chemically abraded zircon residues**
263
264   Raman v_3(SiO$_4$) and E_g peak width measurements for chemically abraded zircon
265   residues are shown in Fig. 5b and Fig. 6b. The broadest peaks for AS3, SAM-47, KR18-
266   04, and BOM2A residues are narrower than that of their annealed but unleached
267   counterparts. This pattern is most evident in the two higher damage samples, indicating
268   that HF leaching has dissolved the most damaged zircon material in each sample. The
269   two lower damage samples, however, each have only one annealed datapoint with a
270   broader v_3(SiO$_4$) and E_g peak. We interpret this to suggest that small differences in
271   radiation damage in crystals with low initial alpha doses does not have a significant
272   impact on which portions of a grain dissolve.
273
274   Notably, SAM-47 and BOM2A residues each have at least one data point with a
275   narrower v_3(SiO$_4$) and E_g peak width than their solely annealed counterparts suggesting
276   that some residues have a higher degree of crystallinity. Further, we find that the
277   residue datapoints for these two samples largely plot below (at lower v_3 for a given E_g)
278   the annealed datapoints indicating a change in the relationship between the v_3(SiO$_4$) and
279   E_g peaks. Taken together, these observations could suggest that additional structural
280   recovery occurs in some zircon samples during HF leaching even after dry annealing at
281   significantly higher temperatures.

282

283 In Fig. 7 we compile Raman results for the four zircon samples to evaluate the effects of
284 different partial dissolution conditions on the crystallinity of zircon residues. The
285 spread in datapoints for AS3 residues leached at 180 °C for 12 h (all SAM-47 zircons
286 disintegrated after 12 h) is shifted toward narrower values compared to AS3 and SAM-
287 47 residues leached at either 180 °C or 210 °C for 4 h. This could imply that increasing
288 the duration of the leaching step results in a more crystalline zircon residue due to the
289 progressive dissolution of higher damage domains. We note, however, that only a small
290 number of AS3 crystals survived 12 h of chemical abrasion, and only a small number of
291 Raman analyses were made. We recommend further study to better evaluate this
292 possibility. Somewhat surprisingly, we do not find leaching temperature to have a
293 significant effect on the crystallinity of zircon residues; AS3 and SAM-47 samples
294 leached for 4 h at 180 °C or 210 °C have residues with broadly similar peak width
295 distributions, as do KR18-04 and BOM2A samples leached for 12 h at 180 °C or 210 °C.
296 This could potentially reflect a small n-problem. We find that AS3 residues leached at
297 180 °C for 12 h have universally broader peak widths compared to KR18-04 and
298 BOM2A residues treated under the same leaching conditions. These results stress that a
299 sample's initial radiation damage content profoundly affects the crystallinity of a
300 sample's residue.

301

302 **3.3 Imaging textures before and after partial dissolution**

303

304 **3.3.1 AS3**

305

306 The accumulation of radiation damage decreases the density of zircon by 17% from ~4.7
307 to 3.9 g/cm³ with the most rapid density change occurring over an alpha dose interval of
308 ~1×10^{18} to ~4×10^{18} α/g (Holland and Gottfried, 1955; Murakami et al., 1991; Ewing et al.,
309 2003; Nasdala et al., 2004). Raman data for unannealed AS3 grains indicates that these
310 samples have alpha doses spanning above and below this interval. Lower density
311 materials attenuate X-rays less, so metamict zones should appear darker in grayscale
312 μCT image slices than crystalline zircon. Indeed, we find that some AS3 crystals exhibit
313 density zoning (Fig. 8), indicating that annealing at 900 °C for 48 hr does not
314 significantly increase zircon density in strongly metamict material. As evidenced by our
315 SE images and discussed further below, μCT does not capture radiation damage zoning
316 that does not result in a strong density contrast such as variations in radiation damage
317 below the ~1×10^{18} α/g threshold.
318

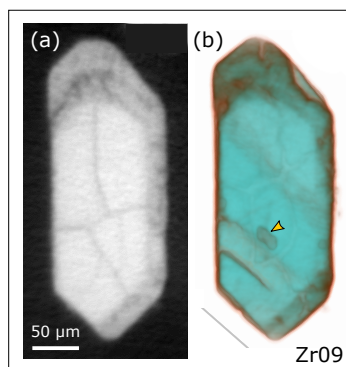



Figure 8: µCT images of a zircon with density zoning. **(a)** 2D µCT image slice of an annealed – but not leached – AS3 zircon crystal with a dark, low-density rim interpreted as metamict and a light, crystalline, and fractured core. **(b)** Semi-transparent 3D rendering of the µCT data for the same grain. High-density zircon is teal, and lower-density material is orange-brown. The arrow marks an ~~interior~~ inclusion. The faint stripes are surface indents of surficial inclusions not shown.

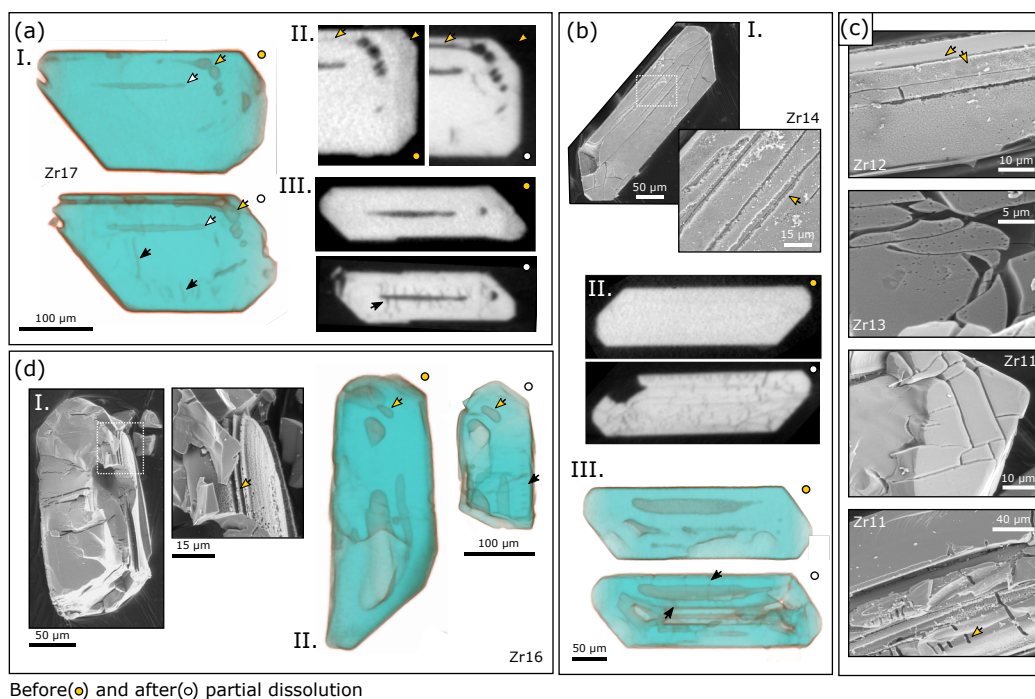
319 Images of annealed and chemically abraded AS3 grains are presented in Figures 9, 10,
320 11, S1, and S2. Each figure shows results for one of the three leaching conditions – 180
321 °C for 4 h, 210 °C for 4 h, and 180 °C for 12 h –, respectively. Here we briefly summarize
322 key observations. We refer the reader to the figure captions for additional context.
323
324 Damaged zircon is intrinsically more soluble in HF than crystalline zircon. µCT images
325 show that low-density metamict rims and interior zones are removed early in the
326 leaching process at relatively low temperatures (180 °C for 4 h). SE images also
327 document the removal of ==fine-scale== ~~compositional~~ zones early in the leaching process.
328
329 Etching ~~in SE images~~ reflect the removal of ~~soluble~~ crystal defects including defects
330 related to partially-annealed radiation damage, dislocations, low-angle grain
331 boundaries, and intrinsic point defects. For spatial reference, fission tracks are ~16.7 µm
332 and alpha recoil tracks (clusters of alpha recoil tracks stemming from a single decay
333 chain) average ~125 nm in length prior to annealing (Ewing et al., 2003; Jonckheere,
334 2003). In SE images, low damage ~~compositional~~ zones have smooth surfaces, whereas
335 higher damage zones have pitted or sponge-like surfaces due to the etching of closely
336 spaced radiation damage defects (Fig. 9c and Fig. 10aI). Etch pits and radiation damage
337 zoning textures are not observed in µCT images due to the dataset's lower spatial
338 resolution (1.62 µm voxels).
339
340 The ~~geometric~~ shape of individual etch pits on a grain's surface – such as the diamond
341 or pyramid-like appearance of many pits – is independent of the nature of the defect
342 (Jonckheere and Van den ==h==aute, 1996; Jonckheere et al., 2005; 2022). The pit's surface

Before(○) and after(○) partial dissolution

Figure 9: SE and μCT images of AS3 grains pre- and post-chemical abrasion (yellow dots and white dots, respectively) at 180 °C for 4 h. **(a)** I. Semi-transparent 3D renderings of μCT data for Zr17 showing melt inclusions removed by partial dissolution (yellow and white arrows) and newly visible fractures (black arrows). II. 2D μCT image slices showing the removal of a metamict rim and interior compositional zone. III. 2D μCT cross section of the melt inclusion marked by white arrows in I. Newly visible radial fractures have developed along the length of the melt inclusion (black arrow). **(b)** I. SE images of Zr14 showing the widening of fractures on the grain surface. II. 2D μCT image slices showing a fracture network after partial dissolution. III. 3D rendering of μCT data showing radial fractures (black arrows) around large melt inclusions removed by partial dissolution. **(c)** SE images of zircon residues illustrating the contrast between a smooth, low damage surface and a higher damage pitted surface (Zr12), curved acid paths and small etch pits (Zr13), blocky fractures (Zr11 top), and dumbbell-like dissolution features (Zr11 bottom). **(d)** I. SE images of Zr16 showing the removal of ~~fine-scale compositional~~ zones. II. 3D rendering of μCT data ~~with~~ showing the removal of large melt inclusions (yellow arrows), the formation of a parallel fracture sequence (black arrow), and significant volume loss likely due to breakage along the grain center where there are two giant melt inclusions.

343 symmetry instead reflects the mineral's crystallography. Zircon dissolution in HF is
344 anisotropic, so the shape of etch pits also varies with crystallographic orientation
345 (Gleadow et al., 1976; Yamada et al., 1995). As such, while individual diamond-shaped
346 etch pits closely resemble SE images of etched fission tracks ~~presented by others for~~
347 zircon, apatite, monazite, and titanite (e.g., Jones et al., 2022), these could reflect other
348 defect types such as lattice dislocations; if the surficial etch pit has overtaken the initial

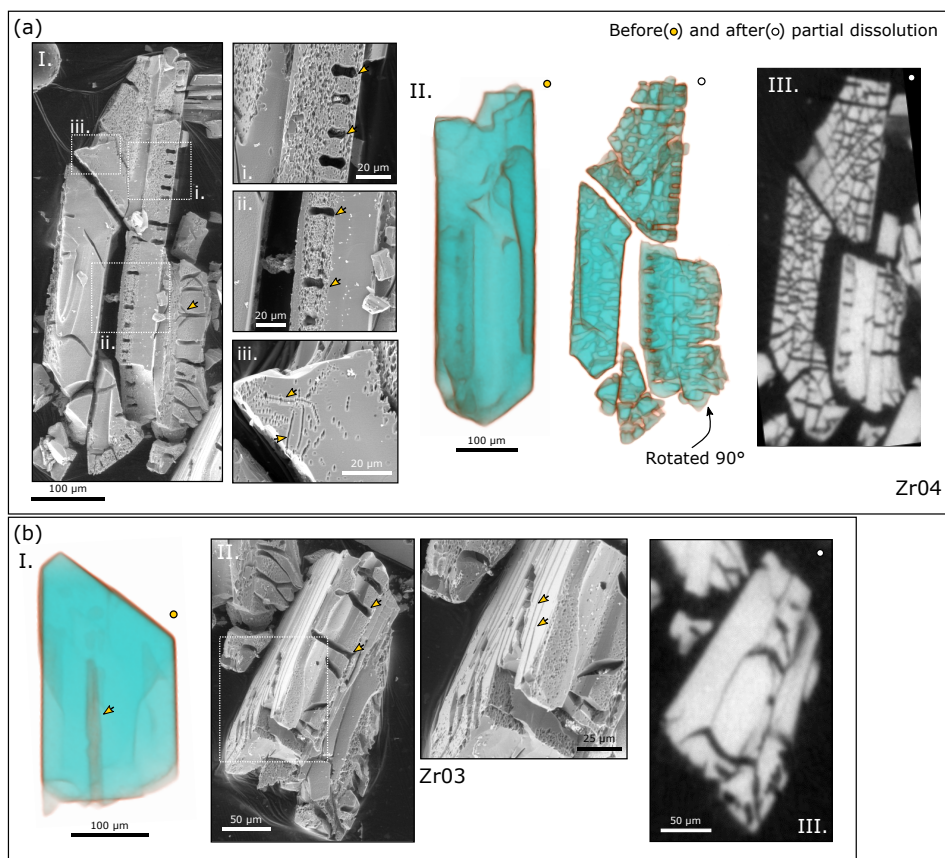



Figure 10: SE and µCT images of AS3 grains pre- and post-chemical abrasion at 210 °C for 4 h. **(a)** I. SE images of Zr04, a large crystal broken into four pieces. The rotated piece marked with a yellow arrow shows a ~~nice~~ cross-section of the grain interior. The arrow highlights an example of a branching channel. The higher magnification images show that these channels correlate with dumbbell features that cross-cut ~~compositional~~ zones of relatively low (i) or high (ii) radiation damage. iii shows etch pit arrays likely indicative of dislocations loops or low-angle grain boundaries. II. 3D rendering of the µCT data shows the development of a complex dissolution network in the crystal's interior. III. 2D µCT image slice showing that the intensive fracturing observed in 3D is restricted to narrow plane within the crystal. **(b)** I. Semi-transparent 3D rendering of µCT data for Zr03 showing a large melt inclusion. II. SE images show elongated, channel-like dumbbells (low magnification) and the apparent removal of fine-scale compositional zones (high magnification). III. 2D µCT image slice showing wide acid paths in the grain interior.

349   fission track channel beneath the surface it is impossible to tell. Most fission tracks
350   likely annealed during our pre-leach 900 °C annealing step (e.g., Yamada et al. 1995),
351   although some etch pits could reflect fission tracks that were pre-etched geologically
352   prior to chemical abrasion. Given the limited abundance, larger size, and spacing of the

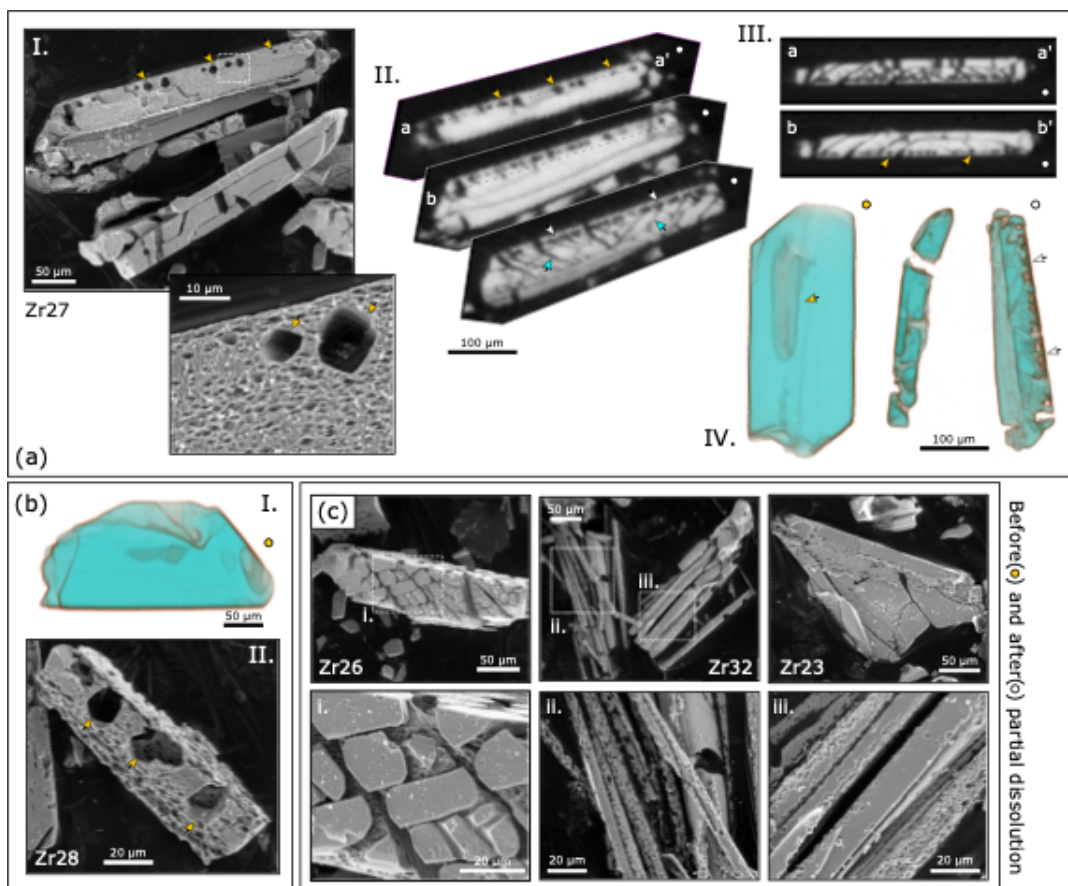
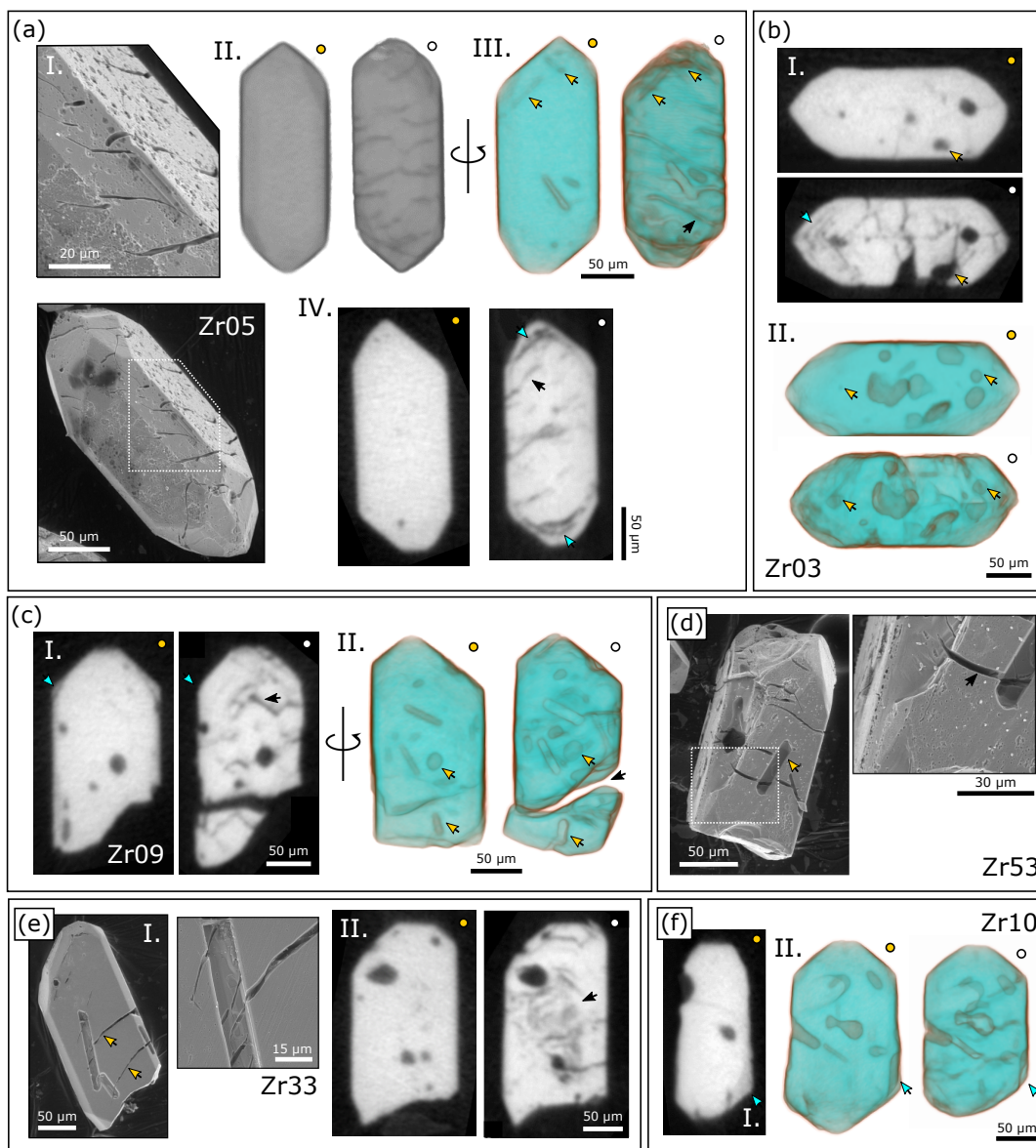



Figure 11. SE and µCT images of AS3 pre- and post-chemical abrasion at 180 °C for 12 h. **(a)** I. SE images of sample Zr27 showing a row of dumbbells along the length of the zircon crystal. The higher magnification SE image shows a sponge-like surface texture. II. A series of 2D µCT image slices progressively stepping down to view structures beneath the crystal's surface. The yellow arrows highlight the same dumbbell features marked on the SE image in I. The teal arrows highlight fractures, many of which radiate from dumbbell features. The white arrows mark another series of dumbbells on the bottom side of the crystal. III. Cross-sectional 2D µCT image slices of a-a' and b-b' as labeled in II. White arrows mark second set of dumbbells with a different crystallographic orientation. IV. Semi-transparent 3D rendering of µCT data with arrows highlighting a large melt inclusion. The dissolution of this inclusion likely caused the grain to break into two pieces. The white arrows mark the same row of dumbbells as indicated by the white arrows in II. **(b)** I. Semi-transparent 3D rendering of µCT data for Zr28 ~~prior~~. II. SE image of the husk-like zircon shell with large dumbbell features. **(c)** SE images of zircon residues Zr26, Zr32, and Zr23 showing cobble stone, straw, and lace-like textures.

353   diamond and pyramid-like etch pits, we find them unlikely to reflect etching of

354   partially annealed-alpha recoil tracks. We interpret etch pit arrays that do not correlate

355   with expected compositional zoning patterns (Fig. 10a-iii) to reflect the dissolution of
356   dislocation loops or low-angle grain boundaries.
357
358   Etch textures are more subtle at low temperatures and short leaching durations. At
359   hotter temperatures and longer leaching durations, etched zones have deeper, sponge-
360   like textures indicative of a greater degree of dissolution. At a full 12 h leach, ~~only~~ a
361   heavily dissected crystalline husk, a collection of perforated straw-like zones, or a
362   cobble stone-like residue is sometimes all that remains.
363
364   ~~Geometrical~~ dissolution features ~~that cross-cut compositional zones~~ as highlighted in
365   Fig. 10a and Fig. 11a and hereafter referred to as dumbbells, are a common feature in
366   AS3 zircon residues. Some dumbbells cross-cut zones of relatively high radiation
367   damage, while others cross-cut zones of relatively low radiation damage. All observed
368   dumbbells are oriented parallel to the grain's c-axis. 3D rendering of μCT data reveal
369   that dumbbells are surface expressions of complex, fracture networks restricted to
370   specific ~~compositional~~ zones. The ~~geometrical~~ shape of dumbbells and the branching,
371   channel-like appearance of some fractures in SE imag~~ing~~, indicate that these fracture
372   networks are focal points for crystallographically-controlled dissolution. Aside from
373   dumbbells, we note that fractures ~~in general~~ are a common feature in both SE and μCT
374   images of leached grains.
375
376   ~~Excitingly,~~ our μCT dataset also generates new insights into the fate of inclusions
377   hosted deep within grain ~~interiors.~~ In μCT image slices, inclusions appear dark with
378   grayscale intensities marginally above that of background (air and tape) due to their
379   low density and mean atomic number relative to that of zircon. We interpret an
380   inclusion to have been removed if: 1) its gray-scale intensity decreases to that of
381   background, 2) there is a change ~~to its~~ size or morphology after leaching, or 3) there is a
382   clear acid path to the inclusion. We find that the majority of inclusions in AS3 appear to
383   dissolve at short leaching durations. Around the largest inclusions, we observe radial
384   fractures in μCT images of leached grains that are not apparent ~~in the before imagery~~
385   ~~dataset.~~
386
387   **3.3.2 SAM-47**
388
389   Images of annealed and chemically abraded SAM-47 grains treated at 180 °C or 210 °C
390   for 4 h are presented in Figures 12, 13, S3, and S4. Like AS3, several annealed SAM-47
391   crystals have density zoning in μCT. In most cases density zoning is in the form of
392   metamict rims, however, we note ~~that~~ one crystal ~~was seen~~ with oscillatory density
393   zoning. This finding is consistent with our Raman data which shows that unannealed
394   SAM-47 samples have alpha doses that span the interval over which density changes

Before(○) and after(○) partial dissolution

395 rapidly occur (Holland and Gottfried, 1955; Murakami et al., 1991; Ewing et al., 2003;
396 Nasdala et al., 2004). Like AS3, we find that low density rims and interior zones are
397 removed by chemical abrasion at low leaching temperatures and duration (180 °C, 4 h).
398
399 SE images of SAM-47 residues treated at 180 °C for 4 h show a range in surface textures
400 (Fig. 12). Some grains have smooth, unetched surfaces while others are more strongly
401 etched. These variations likely reflecting inter-crystalline variations in radiation

Figure 12: SE and µCT images of SAM-47 grains pre- and post-chemical abrasion at 180 °C for 4 h. **(a)** I. SE images of Zr05 showing deep grooves on the grain's surface and a sponge-like etch texture. II. Opaque 3D rendering of µCT data showing that these surface fractures are only apparent after partial dissolution. III. Semi-transparent 3D rendering of µCT data with yellow arrows marking inclusions removed by partial dissolution. IV. 2D µCT image slices highlighting an example of an acid path into the grain interior (black arrow) and the removal of ~~oscillatory compositional~~ zones (teal arrow). **(b)** I. 2D µCT image slices showing the removal of fine-scale oscillatory ~~compositional~~ zones (teal arrow) and a mineral inclusion (yellow arrows) in Zr03. II. Semi-transparent 3D rendering of µCT data with yellow arrows depicting the removal of more mineral inclusions. **(c)** I. 2D µCT image slices of Zr09 showing the removal of a low-density rim (teal arrow) and an acid path into the grain interior (black arrow). II. Semi-transparent 3D rendering of µCT data highlighting the removal of inclusions (yellow arrows) and the formation of a large fracture (black arrow). **(d)** SE images of Zr53 showing crystal-shaped voids interpreted as dissolved surface-reaching inclusions (yellow arrow) and the fractures that crosscut these voids (black arrow). **(e)** SE images of Zr33 ~~again~~ showing fractures cross-cutting inclusions removed by partial dissolution (yellow arrows) and a smooth grain surface. II. 2D µCT image slices showing a convolute pattern of material dissolved from the crystal core. **(f)** I. 2D µCT image slices highlighting a low-density rim on Zr10. II. Semi-transparent 3D rendering of µCT data showing the removal of this rim.

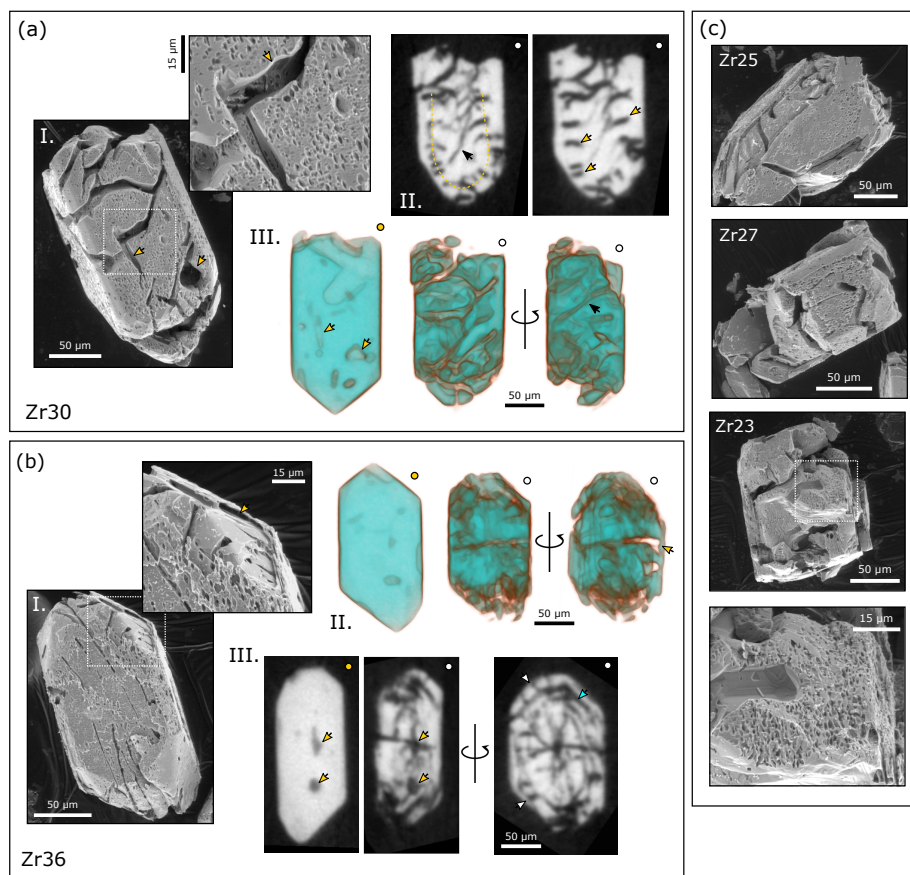
402 damage. Large prismatic voids on grain surfaces indicate that low-intensity chemical
403 abrasion removes surface-reaching inclusions. Most prismatic voids are crosscut by
404 large fractures, while other grains have finer sinuous fracture patterns not associated
405 with surface-reaching inclusions. µCT imaging shows that many most zircon residues
406 treated at 180 °C for 4 h have fractures or acid paths to grain interiors that were not
407 visible in the pre-etching image data. These paths ~~have~~ allowed ~~for~~ the dissolution of
408 inclusions, fine-scale oscillatory zones, and convolute zones from crystal interiors.
409
410 SE images of SAM-47 residues treated at 210 °C for 4 h have deeper, sponge-like etching
411 textures (Fig. 13). Many grains look dog-chewed. Etch pits are larger with diamond-like
412 shapes similar to those observed in AS3 crystals treated at either 210 °C for 4 h or 180 °C
413 for 12 h, and fractures are commonly wider. SE images again show the removal of
414 surface-reaching inclusions, and the shell-like appearance of some residues hints at the
415 removal of interior zones. µCT images of residues treated at 210 °C for 4 h reveal
416 significant dissolution in grain interiors. Oscillatory ~~compositional~~ zones and inclusions
417 have been removed from deep within crystal cores. Acid paths are in general wider and
418 more interconnected, and fractures crosscut where mineral inclusions once were. We
419 also observe fracture patterns similar to the dumbbells observed in AS3 residues. In a
420 visual game of connect-the-dots in a µCT image slice of Zr30 (Fig. 13a-II), dumbbell-like
421 features appear to crosscut what is likely a continuous, oscillatory ~~compositional~~ zone.
422 Other fractures appear to radiate from the dumbbell features. We see dumbbell-like
423 fracture patterns again in sample Zr36 (Fig. 13b-III) where crosscutting fractures

Before(○) and after(○) partial dissolution

Figure 13: SE and μCT images of SAM-47 grains pre- and post-chemical abrasion at 210 °C for 4 h. **(a)** I. SE images of Zr30 showing wide fractures, the removal of mineral inclusions (yellow arrows), and a moderately etched surface. II. 2D μCT image slices highlighting dumbbell-like features (yellow arrows) interpreted to cross-cut what could be a concentric ~~compositional~~ zone (yellow dashed line). The black arrow exhibits how fractures radiate from the dumbbell features. III. Semi-transparent 3D rendering of μCT data. Yellow arrows correlate to those in I. The black arrow highlights how the fractures observed on the surface propagate through the crystal interior. **(b)** I. SE images of Zr36 showing fractures, diamond-shaped etch pits, and the targeted removal of ~~a compositional zone~~ (yellow arrow). II. Semi-transparent 3D rendering of μCT data. The yellow arrow highlights the grain's shell-like appearance because of significant dissolution in the grain's interior. III. 2D μCT image slices showing the removal of mineral inclusions (yellow arrows), oscillatory zones (teal arrow), and dumbbell-like fractures that appear to cross-cut compositional zones (white arrows). **(c)** SE images of dog-chewed zircon residues Zr25, Zr27, and Zr25.

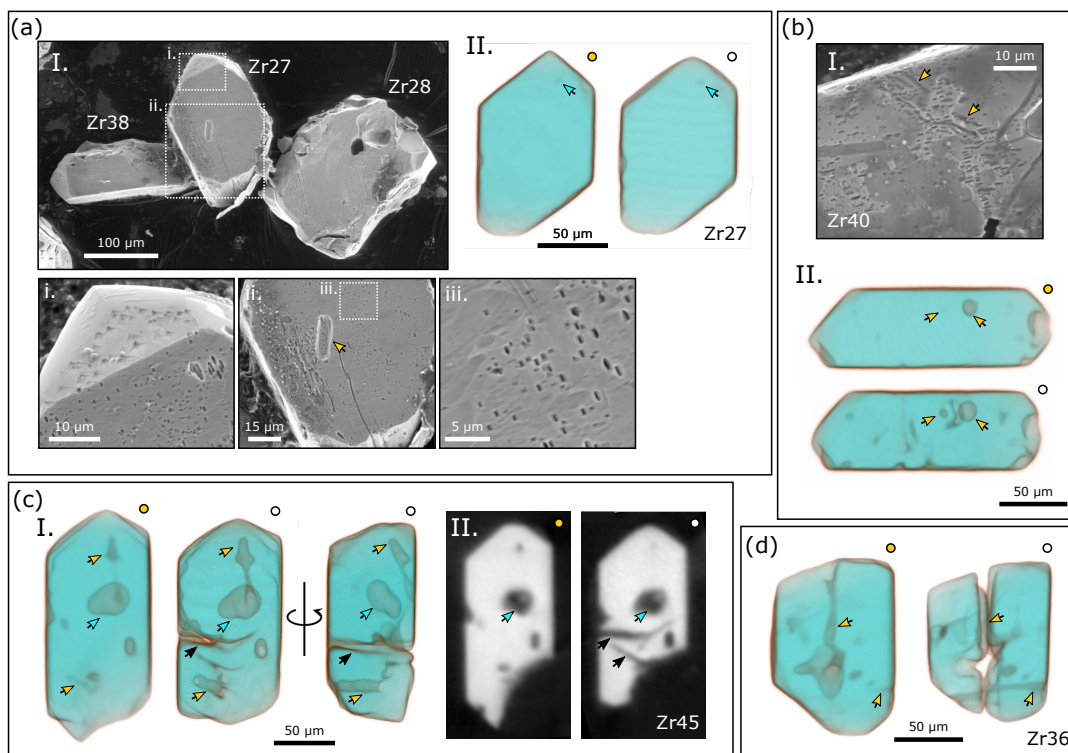
424   connect different oscillatory zones removed by dissolution to one another and to the
425   grain surface.
426
427

Before(●) and after(○) partial dissolution

Figure 14: SE and µCT images of KR18-04 grains pre- and post-chemical abrasion at 180 °C for 12 h. **(a)** I. A low magnification SE image of zircon samples Zr38, Zr27, and Zr28 and higher magnification images of Zr27 showing close up images of rectangular and triangular etch pits and the removal of a surface-reaching inclusion (yellow arrow). II. Semi-transparent 3D rendering of µCT data for Zr27. Arrows highlight an inclusion inferred to have survived partial dissolution. **(b)** I. SE image of Zr40 with linear etch pit arrays likely indicative of dislocations. II. Semi-transparent 3D rendering of µCT data highlighting inclusions that dissolved. **(c)** I. Semi-transparent 3D rendering of µCT data for Zr45. Teal arrows highlight a large inclusion inferred to have survived partial dissolution, while yellow arrows mark inclusions that dissolved. Black arrows mark acid paths. II. 2D µCT image slices. Teal arrows mark the same multi-phase inclusion in I. Black arrows mark acid paths ~~not apparent in the before imagery dataset.~~ **(d)** Semi-transparent 3D rendering of µCT data for Zr36. Yellow arrows highlight surface-reaching inclusions removed by partial dissolution, resulting in a large cavity in the grain's interior.

428

429 **3.3.3 KR18-04**

430

431 Images of annealed and chemically abraded KR18-04 grains treated at 180 °C or 210 °C

432 for 12 h are presented in Fig. 14 and Fig. 15, respectively. SE images of residues treated

433 at 180 °C show intact-grains with mildly etched surfaces (Fig. 14). Etch pits on (100) are

434 small, prismatic, and generally rectangular, while etch pits on other crystal faces are

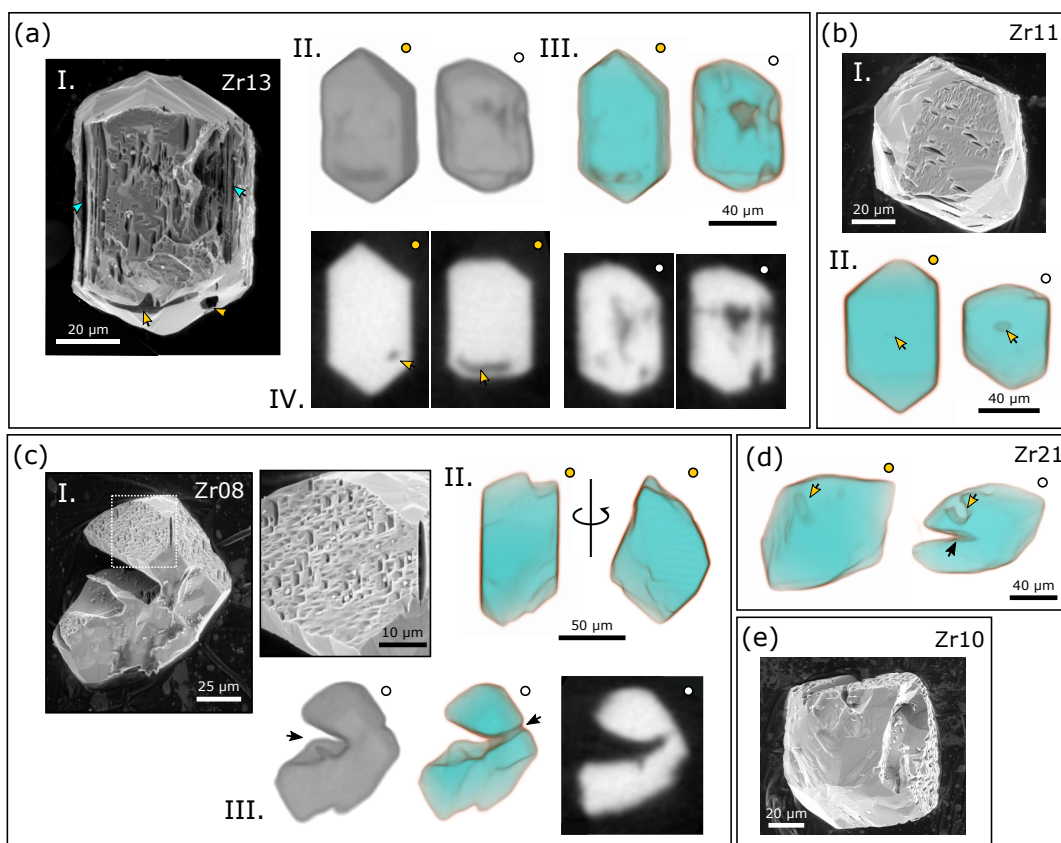
435 more triangular, highlighting that the shape of etch pits ~~are~~ crystallographically

Before(○) and after(○) partial dissolution

Figure 15: SE and μCT images of KR18-04 grains pre- and post-chemical abrasion at 210 °C for 12 h. **(a)** I. SE image of Zr13 showing dissolved inclusions (yellow arrows) and the removal of oscillatory zones (teal arrows). II. Opaque 3D rendering of μCT data. III. Semi-transparent 3D rendering of μCT data. IV. Representative 2D μCT image slices indicate that a significant amount of zircon ~~material~~ was dissolved ~~from~~ the grain's interior. Yellow arrows correlate to those in I. **(b)** I. SE image of Zr11 showing deep etch pits on (100) ~~with the long axes~~ oriented parallel to the crystal's *c*-axis. Etch pits are absent from other crystal faces. II. Semi-transparent 3D rendering of μCT data showing a dissolved inclusion. **(c)** I. SE images of Zr08. High magnification image shows closely spaced and overlapping prismatic etch pits that form a sponge-like texture. II. Semi-transparent 3D rendering of μCT data acquired before partial dissolution. III. Opaque and Semi-transparent μCT 3D renderings and a representative 2D μCT image slice of the sample after partial dissolution. Black arrows highlight acid paths into the grain interior. **(d)** Semi-transparent 3D rendering of μCT data for Zr21. Yellow arrows mark an inclusion that dissolved. The black arrow highlights the acid path that inexplicably cut into the grain interior. **(e)** SE image of Zr10 with deep prismatic etch pits present on some grain surfaces but not others.

436   controlled. Linear etch pit arrays suggest the dissolution of defects related to dislocation
437   loops.

438

439 Large crystal-shaped voids on grain surfaces indicate that surface-reaching inclusions
440 are removed by chemical abrasion. μCT images of residues treated at 180 °C indicate
441 that partial dissolution removes some – but not all – mineral inclusions from crystal
442 interiors. For example, the large multi-phase inclusion in Fig. 14c-I is interpreted to
443 have survived partial dissolution since 1) there is apparent change to the grayscale
444 intensities of either phase relative to that of background, 2) there is no apparent change
445 to the inclusion's size or morphology, and 3) there is no evidence that an acid path has
446 reached the inclusion. ~~We note that beam hardening effects make it challenging to~~
447 ~~identify whether or not smaller inclusions have survived chemical abrasion. In such~~
448 ~~cases, grayscale intensity values cannot be used to identify whether or not an inclusion~~
449 ~~has been removed.~~

450

451 We note that some residues have fractures or acid paths that lack obvious precursors in
452 the before imagery dataset. Qualitatively, before-and-after μCT imagery suggest
453 minimal volume loss and a slight shortening of prismatic grain's c-to-a aspect ratio.

454

455 SE images of residues treated at 210 °C show the removal of fine-scale oscillatory zones
456 and surface-reaching inclusions. Etch pits are well-preserved on some crystal faces
457 including (100) and entirely absent on others. Etch pits are generally larger than those
458 observed in 180 °C residues. Many are deep, rectangular, and well-faceted. The long
459 axes of deep rectangular pits align parallel to the crystallographic *c*-axis, while the long
460 axes of shallower rectangular pits align parallel to the *a*-axis. Etch pit clusters have a
461 sponge-like texture. μCT images of residues treated at 210 °C show that inclusions and
462 zircon material have been dissolved from grain interiors. Some grains have deep
463 ~~carveouts from~~ crystal interiors with no obvious structural precursor in the before
464 imagery dataset. Before-and-after imagery suggest higher volume loss and a
465 pronounced shortening of some grains' aspect ratio.

466

467 **3.3.4 BOM2A**

468

469 Images of annealed and chemically abraded BOM2A grains treated at 180 °C or 210 °C
470 for 12 h are presented in Fig. 16 and Fig. 17, respectively. ~~SE images of r~~esidues treated
471 at 180 °C are largely intact (Fig. 16). Similar to KR18-04 residues leached under the same
472 conditions, etch pits are small and rectangular. Some etch pits are isolated while others
473 are interconnected. Some surfaces have deep voids that penetrate the grain ~~interior~~ but
474 do not correlate with inclusions. μCT images qualitatively suggest minor volume loss
475 with a slight shortening along a crystal's c-axis. Chemical abrasion appears to dissolve
476 surface-reaching inclusions and some – but not all – inclusions from crystal interiors.
477 Some residues have fractures that are spatially associated with inclusions.

478

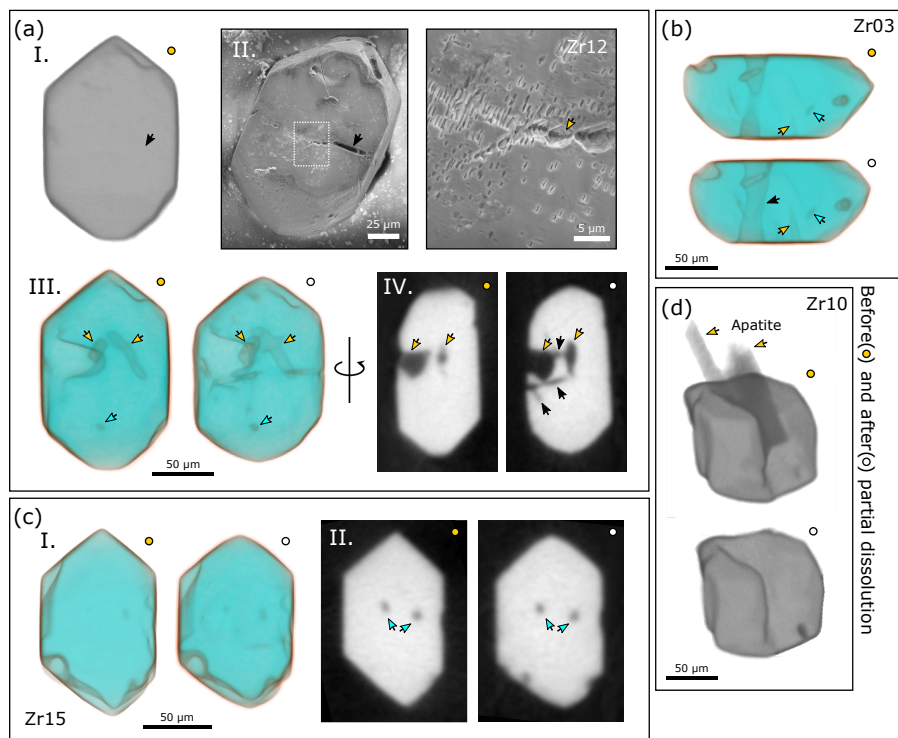



Figure 16. SE and μCT images of BOM2A grains pre- and post-chemical abrasion at 180 °C for 12 h. **(a)** I. Opaque 3D rendering of μCT data for Zr12. II. SE image of grain surface with close up image of clustered and isolated rectangular etch pits. The black arrow points to a void in the crystal perhaps related to a surficial inclusion not apparent in the pre-chemical abrasion dataset, and the yellow arrow highlights another interesting dissolution feature. III. Semi-transparent 3D rendering of μCT data showing inclusions removed by partial dissolution (yellow arrows) and inclusions inferred to have survived (teal arrows). IV. 2D μCT image slices with yellow arrows depicting inclusions dissolved during chemical abrasion and black arrows highlighting acid paths. **(b)** Semi-transparent 3D rendering of μCT data for Zr03 showing inclusions removed by partial dissolution (yellow arrows) and inclusions inferred to have survived (teal arrows). The black arrow highlights an acid path cutting through the crystal interior. **(c)** I. Semi-transparent 3D rendering of μCT data for Zr15 suggesting a slight shortening along the *c*-axis. II. 2D μCT image slices showing inclusions inferred to have survived partial dissolution. **(d)** Opaque 3D rendering of μCT data for Zr10 showing the removal of large, protruding apatite inclusions by partial dissolution.

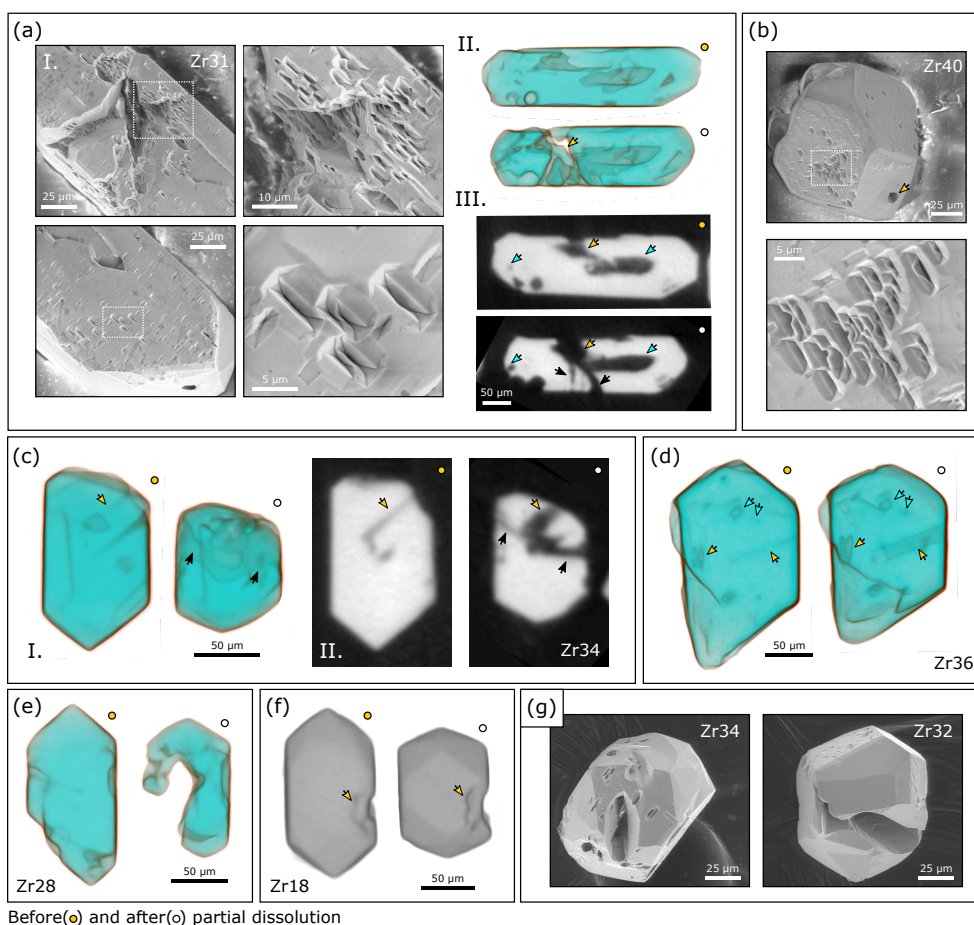
479 SE images of residues treated at 210 °C show etch pits ~~are~~ preserved on some crystal
480 faces but not others suggesting a crystallographic control on etch pit formation or
481 preservation (Fig. 16). Like KR18-04 residues leached under the same conditions, etch
482 pits are larger with well-developed facets. Some are isolated ~~will~~ others interconnect to
483 form acid paths into grain interiors. The long axes of deep, octahedral etch pits on (100)
484 align with the crystal's *c*-axis, while the long axes of shallower etch pits that form
485 perpendicular to the octahedral ones align with the crystal's *a*-axis. Some SE images

Before(o) and after(o) partial dissolution

Figure 17: SE and µCT images of BOM2A grains pre- and post-chemical abrasion at 210 °C for 12 h. **(a)** I. SE images of Zr31 showing deep fractures penetrating the grain's interior. Close up images show well-faceted etch pits on (100) some of which are isolated while~~s~~ others are interconnected. The long axes of deep, ==octahedral etch pits== are oriented parallel to the *c*-axis, whereas the long axes of shallower etch pits are oriented parallel to the *a*-axis. II. Semi-transparent 3D rendering of µCT data again highlighting the development of large fractures. III. 2D µCT image slices. Teal arrows highlight inclusions that were dissolved, the yellow arrow points to a surface-reaching inclusion that acted as an acid path into the grain interior, and the black arrow highlights acid paths not observed in the before imagery dataset. **(b)** SE images of Zr40 that demonstrates how some crystal~~lographic~~ faces are strongly etched while others are pristine. Etch pits are again strongly prismatic and sometimes interconnected. The yellow arrow points to a void where there once was an inclusion. **(c)** I. Semi-transparent 3D rendering of µCT data for Zr34 showing a significant shortening of the crystal's *c*-axis. II. 2D µCT image slices. The yellow arrows highlight surface-reaching inclusions removed by partial dissolution. Black arrows mark acid paths not apparent in the before imagery dataset. **(d)** Semi-transparent 3D rendering of µCT data for Zr36. Teal arrows highlight inclusions inferred to have survived partial dissolution. Yellow arrows highlight inclusions that were dissolved. **(e)** Semi-transparent 3D rendering of µCT data for Zr28 showing significant volume loss from the grain interior. **(f)** Opaque 3D rendering of µCT data for Zr18. Yellow arrows highlight how some topographic features are preserved during partial dissolution despite significant volume loss. Note how crystal facets are better developed after partial dissolution. **(g)** Low magnification SE images of Zr34 and Zr32 showcasing the crystallographic-dependence of surface etching and acid paths that cut deep into grain interiors.

486   show that acid has penetrated deeply into grain interiors forming what look like

caverns. Many of these caverns lack precursors in pre-etching images. µCT images
show that the dissolution of surface-reaching inclusions commonly allows acid into
crystal cores. We find that some of the fractures observed in SE images are spatially
associated with large mineral inclusions. Like the 180 °C leach, we find that leaching at
210 °C removes some – but not all – interior inclusions. Qualitatively, volume loss
~~appears~~ greater at 210 °C, and the *c*-axis is considerably shorter in most crystals after
partial dissolution. Before-and-after images show that some topographic features are
preserved during chemical abrasion. ~~We also find that~~ some residues are more strongly
faceted than they were prior to chemical abrasion.

3.4 Quantifying volume loss and changes to crystal morphology

All quantitative measurements made using the ruler and segmentation functions in
Dragonfly ORS software for samples KR18-04 and BOM2A are presented in
supplementary Tables S2 and S3 and summarized in Fig. 18. We find that leaching at
180 °C for 12 h causes a ~5 to 10 % decrease in the length of a crystal's *c*-axis (Fig. 18a).
Increasing the leaching temperature to 210 °C results in a greater degree of shortening
on the order of ~15 to 30 %. In contrast, the length of a crystal's *a*-axes shows little
(maximum <4 %) to no change after leaching at 180 °C or 210 °C (Fig. 18b).
Consequently, the aspect ratio (c/a) of a crystal decreases during chemical abrasion (Fig.
18c). Note, a 2 % change in a crystal with an initial axis length of 80 µm equates to a
change of 1.6 µm which is approximately the spatial resolution of our µCT dataset (1.62
µm). As such we take ~2 % to be a minimum estimate for our measurement error.

Estimated volume losses are presented in Fig. 18d. ~~Our~~ SE images clearly indicate that
the spatial resolution of our µCT dataset does not adequately capture fine-scale
dissolution features. As such, we consider our volume estimates based on grayscale
segmentation to reflect first-order approximations for minimum volume loss. We find
that chemical abrasion at 180 °C for 12 h dissolves ~5 to 10 % of a grain by volume,
whereas chemical abrasion at 210 °C for 12 h dissolves ~25 to 50 % of a grain by volume.
Although there is considerable overlap between the BOM2A and KR18-04 datasets at
both leaching conditions, KR18-04 values are skewed toward a greater degree of
volume loss than BOM2A. This is likely due to the impact of radiation damage on
zircon solubility; unannealed KR18-04 grains on average have higher initial alpha doses
than unannealed BOM2A grains.

Fig. 18e suggests that there may be a weak correlation in which crystals with aspect
ratio's <2.5 dissolve more readily than crystals with aspect ratio >2.5 amongst samples
leached at 210 °C. This reflects the fact that crystals with lower aspect ratios have a
higher proportion of faster dissolving surfaces. The fact that this correlation is so weak,

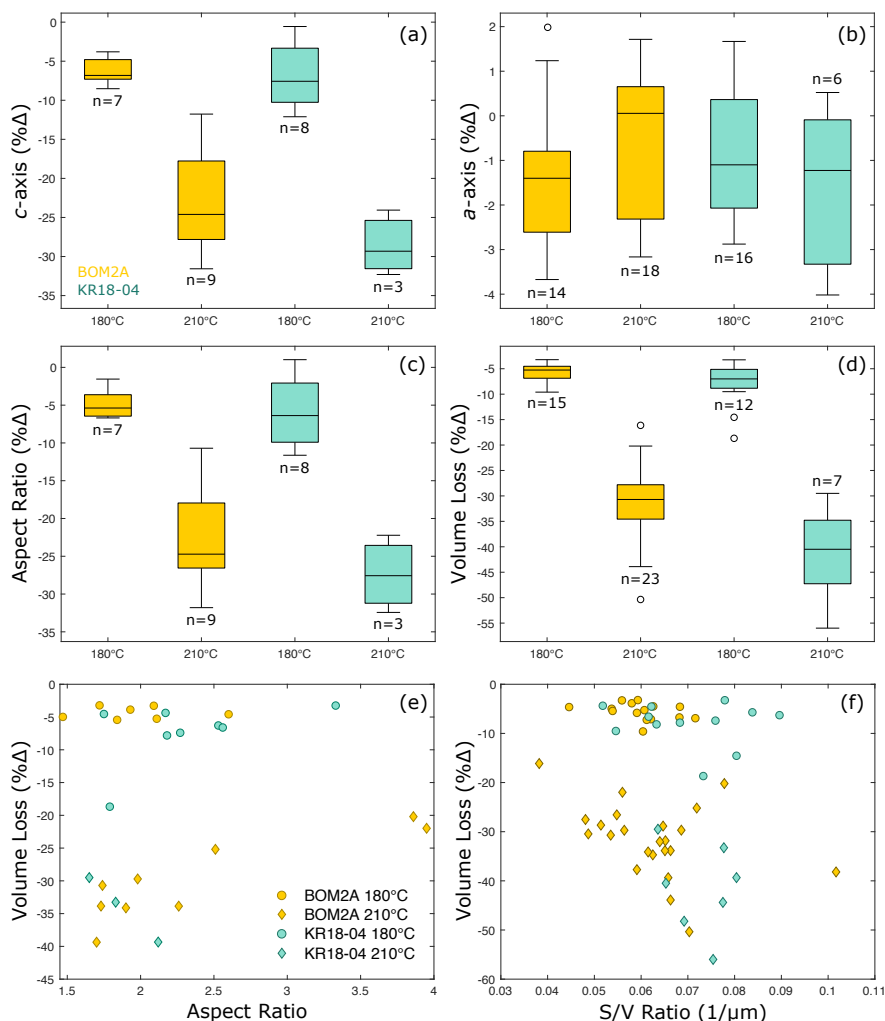



Figure 18: ~~Data p~~lots summarizing crystal morphology, volume, and surface area measurements for KR18-04 and BOM2A. **(a)** Boxplot showing how the length of a grain's *c*-axis changes during chemical abrasion. In all box plots, the central line represents the dataset's median, the box extends to the dataset's 25th and 75th percentiles, the whiskers extend to include the full data range excluding outliers, and circles markers are outliers that exceed the 99% confidence interval. **(b)** Boxplot showing how the length of a grain's *a*-axis changes during chemical abrasion. **(c)** Boxplot showing how a grain's aspect ratio (*c/a*) changes during chemical abrasion. **(d)** Boxplot showing estimated volume loss during chemical abrasion. **(e)** Scatter plot showing the relationship between a grain's initial aspect ratio and estimated volume loss. **(f)** Scatter plot showing the relationship between a grain's initial surface-to-volume ratio and estimated volume loss.

527

528 however, likely indicates that a crystal's bulk radiation damage has a greater control on
529 dissolution than its aspect ratio. The data in this figure, however, clearly stresses that
530 leaching temperature ultimately has more control than aspect ratio on the rate of zircon
531 dissolution. There is also not a clear correlation between a grain's initial surface area-to-
532 volume ratio and volume loss (Fig 18f).

533

534 **4 Discussion**

535

536 **4.1 The Mechanics of Zircon Dissolution**

537

538 **4.1.1 Higher damage grains**

539

540 Except for low-density metamict rims that are removed by low-intensity chemical
541 abrasion (180 °C for 4 h), we find that AS3 and SAM-47 samples – which have initial
542 alpha doses between ~$2\times10^{17}\,\alpha$/g to >$1\times10^{19}\,\alpha$/g – do not predominantly dissolve from
543 rim-to-core. Instead, our results suggest that acid often reaches and dissolves material
544 from grain interiors including inclusions and soluble oscillatory compositional zones
545 with higher degrees of radiation damage (Fig. 9 – Fig. 13) leaving behind a more
546 crystalline zircon residue free of inclusions (Fig. 5).

547

548 In higher damage grains, fractures play a fundamental role in zircon dissolution by
549 providing acid access to crystal interiors. While fractures are common in CL and BSE
550 images of annealed AS3 and SAM-47 grains, fractures are rare in μCT images of
551 annealed grains. We attribute the apparent discrepancy between our SEM and μCT
552 dataset to the difference in spatial resolution between the two imaging methods.
553 Fractures are likely visible in μCT zircon residues because dissolution has widened
554 them beyond the dataset's 1.62 μm spatial resolution (Fig. 9b-I).

555

556 We find that many fractures observed in SE and μCT images of zircon residues are
557 spatially associated with radiation damage zoning (Fig. 10a, Fig. 11a-b, and Fig. 13b).
558 Radial or concentric fracturing related to internal stresses caused by volume expansion
559 of radiation-damaged domains is a common feature in zircon (Chakoumakos et al.,
560 1987; Lee and Tromp, 1995). Fracturing has also been attributed to internal stresses
561 caused by volume reduction due to radiation damage annealing (Geisler et al. 2001a,
562 Geisler et al. 2002). CL images of annealed AS3 samples demonstrate that fractures
563 associated with radiation damage zoning are often present prior to partial dissolution in
564 HF acid (Fig. 3a-I, a-II, and a-III). Some of the fractures observed in CL images of AS3
565 grains show evidence of hydrothermal alteration indicating that they are geological in
566 nature (Fig. 3a-I). We consider it likely, however, that some fractures developed during
567 dry annealing at 900 °C for 48 h or perhaps even during hydrothermal annealing in HF

568   (Geisler et al., 2001b; Geisler et al., 2002). Dual radiation damage accumulation and
569   annealing, fracturing mechanisms best explain why some fractures in zircon residues
570   crosscut zones of relatively high radiation damage while others crosscut zones of
571   relatively low radiation damage (Fig. 10a). Radiation damage zoning fracturing
572   mechanisms also explain why complex fracture networks tend to develop within certain
573   compositional zones (Fig. 10a, Fig. 11a).

575   Fractures are also commonly associated with inclusions. We observe radial fractures
576   around melt inclusions in µCT images of AS3 residues (Fig. 9a-b) and fractures that
577   crosscut mineral inclusions in SE and µCT images of SAM-47 residues (Fig. 12d-e).
578   Similar fractures are also observed in BSE images of annealed SAM-47 grains (Fig. 3b).
579   BSE images of unannealed SAM-47 grains confirm that some of these fractures formed
580   prior to the start of the experiment. We hypothesize, however, that some fractures likely
581   developed during laboratory annealing at 900 °C for 48 h, since zircon and inclusions
582   have different material properties such as coefficients of thermal expansion (e.g.,
583   Subbarao et al., 1990; Hovis et al., 2015). Stress fractures around inclusions have long
584   been used to identify heat treatment in gemstones (Crowningshield and Nassau, 1981;
585   Nassau 1981).

587   While fractures related to radiation damage zoning and inclusions are the major
588   highways providing acid access to crystal interiors, SE images of overlapping etch pits
589   indicate that acid also percolates across regions with high defect densities including
590   zones of higher radiation damage (Fig. 10a, Fig. 11) and regions with dislocation loops
591   (Fig. 10a-iii). Increasing the temperature or duration of acid leaching results in more
592   pronounced and interconnected etching textures on grain surfaces, wider acid paths,
593   and the formation of more complex dissolution networks deep within crystal interiors.

595   **4.1.2 Lower damage grains**

597   The mechanics of zircon dissolution are considerably different for samples KR18-04 and
598   BOM2A. Initial alpha dose estimates for these samples range from ~6×10^{15} to $7\times10^{17}\,\alpha/g$
599   (Fig. 6). Fractures spatially associated with large mineral inclusions in µCT images of
600   chemically abraded residues still play an important role as acid conduits to grain
601   interiors (Fig. 14d, Fig. 16a, Fig. 17a). We again interpret such fractures to most likely
602   form during laboratory annealing at 900 °C for 48 h due to internal stresses caused by
603   differences in coefficients of thermal expansion (Crowningshield and Nassau, 1981;
604   Nassau, 1981; Subbarao et al., 1990; Hovis et al., 2015). Fracturing related to radiation
605   damage zoning, however, does not appear to contribute to zircon dissolution in
606   samples with less radiation damage and more muted intracrystalline variations. In
607

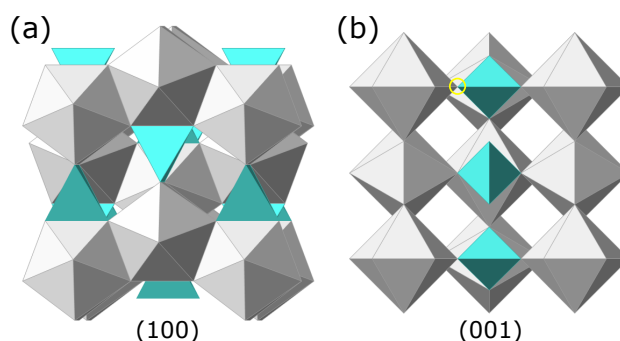



Figure 19: Projections of the zircon crystal structure (Hazen and Finger, 1979; Finch and Hanchar, 2003). ZrO_8 polyhedra are in light gray and SiO_4 tetrahedra are in teal. **(a)** Projection on (100) looking down the *a*-axis. The *c*-axis is vertical to the page, and the a_2-axis is horizontal. **(b)** Projection on (001) looking down the *c*-axis. The yellow circle highlights the corner-sharing bonds between the SiO_4 tetrahedra and the ZrO_8 polyhedra. Projections were rendered using CrystalMaker® software.

608

609   some samples though, ~~results suggest that~~ chemical abrasion ~~does~~ dissolve some

610   soluble concentric zones from crystal interiors (Fig. 15a).

611

612   Other mechanisms by which acid reaches a grain interior~~'s~~ is via the dissolution of

613   surface reaching inclusions (Fig. 14d, 15a, 16d) and the percolation of acid across

614   regions with higher defect densities and overlapping etch pits (Fig. 15, Fig. 16a, Fig. 17a-

615   b). In some samples, chemical abrasion dissolves large volumes from crystal cores

616   without clear structural reasons (Fig. 15c-d, Fig. 17e). This could reflect the dissolution

617   of zones with more radiation damage, but the pattern of material dissolved does not

618   obviously conform with the growth zonation patterns expected for these samples.

619   Combined, these various acid paths lead to the dissolution of some – but not all –

620   interior inclusions.

621

622   Importantly, μCT measurements indicate that dissolution in highly crystalline material

623   is crystallographically-controlled and strongly anisotropic. Most dissolution occurs

624   along the *c*-axis. Etch pits preserved on (100) suggest that dissolution along the *a*-axis is

625   mostly limited to ~~the dissolution of~~ defects that intersect the grain surface. In the (100)

626   and (010) projections of the zircon structure ZrO_8 polyhedra share edges with adjacent

627   ZrO_8 polyhedra and SiO_4 tetrahedra (Fig. ~~20~~) (Hazen and Finger, 1979; Finch and

628   Hanchar, 2003). Whereas in the (001) projection ~~of the zircon structure,~~ ZrO_8 polyhedra

629   share edges with adjacent ZrO_8 polyhedra and *corners* with adjacent SiO_4 tetrahedra.

630   ~~Based on our findings, w~~e infer that the~~se~~ corner sharing bonds ~~in the (001) plane~~ are

631   easier to break during dissolution than the solely edge-sharing bonds ~~in the (100) and~~

632   ~~(010) planes~~ causing faster dissolution along the *c*-axis. Increasing the leaching

633 temperature from 180 °C to 210 °C leads a more significant shortening of a crystal's
634 aspect ratio and greater volume loss. In the absence of acid pathways into crystal
635 interiors, grains with low radiation damage predominantly dissolve from rim-to-core
636 along the crystal's *c*-axis (Fig. 14a, Fig. 15b, and Fig. 16c).

638 Leaching temperature has the strongest control over volume loss in the two samples
639 analyzed. The slight differences between the BOM2A and KR18-04 minimum volume
640 loss estimates suggest that a crystal's bulk radiation damage also plays an important
641 role. Crystal morphology plays a lesser role in that crystals with very high aspect ratios
642 dissolve more slowly than more equant grains. A grain's initial surface-to-volume ratio
643 appears to have no measurable effect on volume loss.

645 **4.2 Implications for ID-TIMS U-Pb geochronology**

647 4.2.1 Zircon U-Pb ages

649 The purpose of chemical abrasion is to remove soluble, radiation-damaged domains
650 prior to U-Pb isotopic analysis to mitigate the ~~negative~~ effects of Pb loss ~~on~~
651 ~~geochronological outcomes~~ (Mattinson et al., 2005; 2011). Recent studies have assessed
652 how different annealing temperatures and partial dissolution conditions affect the U-Pb
653 isotopic and trace element~~al~~ composition of zircon residues (Huyskens et al., 2016;
654 Widmann et al., 2019). The goal of this study is to construct a mechanistic
655 understanding of zircon dissolution and identify possible implications for U-Pb dating
656 ~~upon which future geochronological and geochemical investigations – such as the~~
657 ~~single-crystal stepwise partial dissolution experiments that are currently underway by~~
658 ~~authors AJM and BS – can build.~~

660 ~~Magmatic~~ crystallization of zircon occurs over a period of time within a magma
661 chamber. As such, zircon cores are intrinsically older than zircon rims. A rim-to-core
662 model for zircon dissolution implicitly suggests that dissolving more zircon during
663 chemical abrasion by either increasing the temperature or duration of leaching will
664 remove a greater portion of a crystal's rim and bias its U-Pb date toward an older value.
665 This is especially concerning for geochronological studies of volcanic rocks where the
666 youngest U-Pb date or population of dates is often taken to represent the age of a
667 volcanic eruption.

669 Our results suggest that most zircon crystals with intermediate-to-high levels of
670 radiation damage do not predominantly dissolve from rim-to-core. While increasing the
671 intensity of chemical abrasion leads to textures indicative of greater volume loss, much
672 of that added loss is from the dissolution of interior zones as opposed to the progressive

673   dissolution of crystal rims. Consequently, a typical U-Pb analysis of a zircon residue is
674   more likely to reflect the dissolution of soluble high U zones irrespective of age
675   variation within single grains. In addition to high U zones, inclusions and zircon
676   material surrounding fractures are also dissolved. As such, U-Pb analyses of zircon
677   residues with initial intermediate-to-high radiation damage are more likely to broadly
678   reflect mixed core-rim ages.

680   Some lower damage grains do predominantly dissolve from rim-to-core along a
681   crystal's *c*-axis. This is most apparent in samples leached at 210 °C for 12 h. Growth
682   zones along *c* are often broader than growth zones along *a*, so a volumetrically greater
683   portion of younger domains are likely removed due to *c*-preferential dissolution;
684   however, since rim material on (100) is preserved due to limited dissolution along *a*,
685   there remains a mixed core-rim age component. Further, our analysis suggests that
686   zircon material is commonly dissolved from crystal interiors in lower damage grains.
687   As such, whether hot leaching causes residue ages to be biased toward older values is
688   likely to depend on crystal-dependent factors such as the number, size, and distribution
689   of mineral inclusions, the distribution of higher U domains, and pre-existing fractures.

691   In regard to lower damage grains, another point to consider is that our Raman results
692   for chemically abraded zircon residues suggest that small differences in initial alpha
693   doses in low damage grains do not appear to dramatically affect which portions of a
694   grain dissolve. This observation evokes an important question – why does chemical
695   abrasion work to mitigate Pb loss in young, low~~er~~ damage samples? Perhaps the even
696   more fundamental question is – why does Pb loss occur in highly crystalline grains?
697   Further work is needed to address these outstanding questions.

699   In most samples regardless of initial damage content, ~~we find that~~ chemical abrasion at
700   210 °C is more effective at mining out soluble zones from crystal interiors. Based on our
701   mechanistic blueprint, we predict that hotter leaching temperatures are thus more likely
702   to better mitigate Pb-loss in geochronological datasets. An important caveat, however,
703   is that hot leaching may not be appropriate for all samples. Our μCT volume estimates
704   indicate that even in low-to-intermediate damage grains 12 h of partial dissolution at
705   210 °C can dissolve ~25 to 50% of a grain. This means a substantial portion of radiogenic
706   Pb is lost prior to U-Pb isotopic analysis of the zircon residue lowering the precision of
707   the analysis. This is potentially problematic for young or low-U samples. Even greater
708   volume losses are expected for higher damage grains. More U-Pb isotopic investigations
709   of different chemical abrasion protocols – such as single-crystal stepwise partial
710   dissolution experiments – are needed to find the correct balance between removing
711   domains affected by Pb-loss while preserving enough closed-system material for high-
712   precision geochronological analysis.

713

714   On a secondary note, our study shows that in addition to radiation damage other

715   intrinsic defects such as dislocations are also preferentially dissolved by chemical

716   abrasion. Atom probe studies have shown that dislocation loops can sequester

717   radiogenic Pb and other incompatible trace elements redistributed during shock,

718   metamorphism, or deformation (Reddy et al. 2016, Peterman et al. 2016; 2019).

719   Removing sequestered radiogenic Pb from dislocations by HF leaching should in theory

720   increase U-Pb discordance. However, as radiation damaged domains affected by Pb loss

721   are also dissolved during one-step chemical abrasion, leaching likely leads to a net

722   decrease in U-Pb discordance of the dated residue. Early efforts at stepwise chemical

723   abrasion, however, do suggest that partial dissolution can leach some radiogenic Pb

724   from undigested zircon residues in in unannealed grains – perhaps from dislocations –

725   leading to unwanted U and Pb elemental and Pb isotopic fractionation in early leaching

726   steps (Davis and Krogh, 2000; Mattinson, 2005).

727

728   4.2.2 Inclusions and zircon trace element analyses

729

730   Integrating chemical abrasion ID-TIMS U-Pb dates with trace element analyses (TEA) of

731   the same volume of dissolved zircon can provide important information about

732   petrogenetic processes (Schoene et al. 2010b). Incompatible trace elements such as

733   common Pb, LREEs, Fe, Al, Ca, and Mn can be introduced during metamictization or

734   hydrothermal alteration (Geisler et al., 2001b; Takehara et al., 2018). Our data ~~suggest~~

735   that damaged zones are readily dissolved during chemical abrasion, and thus should

736   not affect TEA of zircon residues. The integrative TEA approach, however, broadly

737   assumes that inclusions are also dissolved during chemical abrasion, such that the final

738   volume analyzed is zircon as opposed to a zircon-inclusion mixture. A zircon-inclusion

739   mixture would likely result in anomalous trace element concentrations and – if

740   inclusions are Pb-bearing – ~~artificially~~ high common Pb contents which ~~can~~ affect the

741   precision of the U-Pb analysis (Bell et al. 2019). While geochronologists endeavor to

742   select inclusion-free grains, this is not possible for all zircon samples. Further, not all

743   inclusions can be identified optically with a standard binocular picking scope ~~and~~

744   ~~excluded from consideration~~.

745

746   The fate of inclusions during chemical abrasion has never been rigorously investigated.

747   Our data suggest that inclusions are readily dissolved in grains with intermediate-to-

748   high radiation damage densities due to the development of stress fractures that form

749   presumably during laboratory annealing at 900 °C. These findings strongly emphasize

750   that the annealing step of chemical abrasion is important not just for minimizing

751   leaching-induced elemental and isotopic fractionation (Mattinson, 2005; 2011), but also

752   for building acid paths into grain interiors for to dissolve inclusions. In lower damage

753 grains, fracturing can remove large inclusions during partial dissolution, but some
754 inclusions – especially small ones armored by highly crystalline zircon – can survive 12
755 h of chemical abrasion at 210 °C. ~~As such, some lower-damage residues may be~~
756 ~~susceptible to inclusion contamination.~~ Increasing the leaching temperature from 180 °C
757 to 210 ° ~~seems to~~ improve the likelihood that inclusions will be removed, but it does not
758 guarantee it. All surface-reaching inclusions, however, are dissolved at the tested
759 leaching conditions.
760
761 **4.3 Implications for radiation damage annealing models**
762
763 Previous annealing studies (Zhang et al., 2000; Geisler et al., 2001a; Ginster et al., 2019;
764 Härtel et al., 2021; Ende et al., 2021) and the Raman analyses presented here
765 demonstrate that heating in air at 900 °C for 48 hours anneals a significant fraction of
766 radiation damage in zircon crystals with intermediate-to-high ~~initial~~ radiation damage.
767 The change in the relationship between the widths of the $v_3(SiO_4)$ and E_g peaks (Fig. 5a
768 and Fig. 6a), however, suggest that annealing or radiation damage is not simply the
769 inverse of damage accumulation – i.e. bounding environments in zircon partially
770 annealed by dry laboratory heating are different than bounding environments in zircon
771 affected only by damage accumulation. Given this observation, we caution that an
772 equivalent $v_3(SiO_4)$ peak width – or derived alpha dose estimate – for an annealed grain
773 and for a grain affected only by damage accumulation is unlikely to reflect equivalent
774 damage states which has important implications for the use of Raman-based annealing
775 models (Ginster et al., 2019).
776
777 There is also an apparent change in the relationship between the widths of the $v_3(SiO_4)$
778 and E_g peak after partial dissolution in HF acid in some samples, and a small number of
779 Raman analyses ~~for~~ chemically abraded residues are more crystalline than their
780 annealed counter parts (Fig. 5b and Fig. 6b). Taken together, we interpret these
781 observations to suggest that some radiation damage is annealed hydrothermally during
782 HF leaching in some samples. This is somewhat surprising given how much hotter the
783 earlier dry-annealing step is compared to the partial dissolution temperature (180 or 210
784 °C). Nonetheless, Widman and colleagues (2019) report similar findings in their study
785 of chemically abraded Plešovice zircon; some of their chemically abraded zircon
786 residues also had more crystalline Raman signatures than zircon fragments that were
787 dry-annealed only.
788
789 Together these studies contribute to a large body of experimental evidence that
790 indicates that radiation damage in zircon partially anneals at low temperatures under
791 hydrothermal conditions on short, laboratory timescales (Rizvanova et al. 2000; Geisler
792 et al. 2001b, 2002, 2003). Annealing as well as other recrystallization reactions in zircon

793 are likely catalyzed by hydrogen diffusion and ionic exchange reactions between zircon
794 and other soluble cations (Petit et al. 1989, Geisler et al. 2001b, Takehara et al. 2018). As
795 such, the extent to which radiation damage anneals in wet geological environments –
796 and how deeply wet annealing effects extend into crystal interiors – likely depends on a
797 combination of heating temperature, heating duration, and the composition of
798 hydrothermal fluids (Geisler et al. 2001b, 2002).
799
800 The kinetics of dry verses wet annealing clearly differ as evidenced by their discrepant
801 temperature sensitivities and hypothesized mechanistic processes. Given the prevalence
802 of fluids in geological environments, it could be argued that geological annealing of
803 radiation damage in zircon most often occurs under hydrothermal conditions.
804 However, most radiation damage annealing models are based on dry annealing kinetics
805 that may poorly approximate geological conditions (Zhang et al. 2000, Geisler et al.
806 2001a, Yamada et al. 2007, Ginster et al. 2019, Härtel et al. 2021). Some of these models
807 are embedded in thermal modeling programs and used to interpret time-temperature
808 histories from complex zircon fission track and (U-Th)/He datasets (Guenthner et al.
809 2013, Guenthner 2021). As such, quantifying zircon radiation damage annealing kinetics
810 under hydrothermal conditions could help to improve interpretations of deep-time low-
811 temperature thermochronology datasets. Wet annealing studies would likely also
812 advance our understanding of how Pb is lost from the zircon crystal structure in
813 geological environments. This knowledge could potentially be used to tailor chemical
814 abrasion protocols to improve U-Pb ~~geochronological outcomes~~ for zircon crystals
815 affected by one or more episodes of hydrothermal annealing.
816
817 **4.4 Imaging radiation damage zoning: Implications for (U-Th)/He thermochronology**

818 The accumulation of radiation damage in zircon has a profound impact on He diffusion
819 kinetics and applications of ~~deep-time~~ zircon (U-Th)/He thermochronology (Guenthner
820 et al. 2013; Cherniak, 2019; Anderson et al. 2017; 2020b). While cathodoluminescence
821 imaging and Raman 2D spectral mapping have previously been used to either
822 qualitatively or quantitatively characterize the distribution of radiation damage in
823 polished zircon grains prior to laser ablation zircon (U-Th)/He analyses (Danišík et al.,
824 2017; Anderson et al., 2017; 2020a), finding a method for rapid and non-destructive 3D
825 characterization of strong radiation damage zoning in unpolished grains for single-
826 crystal zircon (U-Th)/He dating has remained elusive. μCT offers ~~an exciting new~~ way
827 to quickly screen zircon grains for strong radiation damage zoning prior to (U-Th)/He
828 analysis. Strongly zoned grains could either be excluded from datasets or corrections
829 could be applied to account for expected intracrystalline variations in He diffusivity.
830 μCT data can also be used to identify ~~mineral phases or~~ inclusions and intergrowths
831 that might impact He systematics (Cooperdock et al., 2016; Cooperdock and Stockli,

832   2018; Cooperdock et al. 2022), and improve alpha ejection corrections by generating
833   more robust surface area-to-volume estimates (Cooperdock et al., 2019) ~~and providing~~
834   ~~key insights into compositional zoning~~.

5 Conclusions

836   ~~Here we present results for a~~ microstructural investigation – X-ray micro-computed
837   tomography (μCT), scanning electron microscopy, and Raman spectroscopy data – of
838   zircon crystals before and after chemical abrasion ~~that~~ yield new insights into the
839   mechanics of zircon dissolution ~~during~~ HF ~~digestion~~. Selected samples have a range of
840   accumulated alpha doses that cover nearly the full radiation damage spectrum. ~~SE~~
841   ~~images of~~ chemically abraded zircon residues ~~show that~~ high-U oscillatory zones,
842   radiation damage defects, and other intrinsic defects such as lattice dislocations are
843   preferentially dissolved during acid digestion. In high~~er~~ damage materials etch pits
844   generally have diamond-like shapes that closely resemble etched fission tracks. At
845   longer leaching durations and in more crystalline zircon samples, etch pit morphology
846   becomes increasingly prismatic due to crystallographically-controlled dissolution. The
847   interconnectivity of etch pits in SE images demonstrates how acid can percolate across
848   regions with high defect densities. Dumbbell features that crosscut radiation damage
849   zones ~~in some SE images~~ highlight the important role ~~that~~ fracturing related to
850   radiation damage accumulation and/or annealing ~~plays in the dissection of higher~~
851   ~~damage grains. SE images of zircon residues also show that~~ fractures commonly
852   crosscut voids where inclusions once were.

853   We pair our surface texture catalog with μCT images of the same grains acquired before
854   and after chemical abrasion to understand the effects of HF leaching on crystal cores.
855   ~~We find that t~~he density contrast between crystalline and metamict zircon is apparent in
856   μCT images, making μCT an effective tool for the rapid – and non-destructive –
857   imaging of strong radiation damage zoning in zircon ~~in 3D. We find that m~~ost zircon
858   crystals, especially high~~er~~ damage grains, do not dissolve predominantly from rim-to-
859   core. Low-density rims and interior zones visible in μCT images are dissolved during
860   low intensity chemical abrasion. However, leaching also removes oscillatory zones,
861   material around fractures, and some inclusions from crystal cores. The main
862   mechanisms by which acid reaches grain interiors is via fracturing due to internal
863   stresses caused by radiation damage zoning and inclusions and dissolved surface-
864   reaching inclusions. While many fractures formed geologically, we hypothesize that dry
865   laboratory annealing at 900 °C prior to HF leaching likely contributes to fracture
866   development, making dry annealing a critical step of the chemical abrasion process.
867   Increasing the leaching temperature from 180 °C to 210 °C or increasing the leaching

868 duration leads to the development of more extensive dissolution networks in higher
869 damage grains.

870 More crystalline zircon samples lack fracturing related to radiation damage zoning.
871 Acid still, however, reaches the interior of many crystals via the other acid paths
872 described. Some but not all mineral inclusions are removed after 12 h of chemical
873 abrasion. μCT measurements show that dissolution in lower damage grains is strongly
874 anisotropic. Most dissolution occurs along the crystallographic *c*-axis with minimal
875 dissolution ~~occurring~~ along *a*. Even in low~~er~~ damage grains, bulk radiation damage
876 appears to be the major factor controlling the degree of volume loss during partial
877 dissolution. Increasing the leaching temperature from 180 °C to 210 °C leads to an up to
878 ~40 % increase in volume loss in the lower-damage grains analyzed.

879 We broadly discuss potential implications for applications of ID-TIMS U-Pb
880 geochronology. Since most crystals analyzed do not follow a simple rim-to-core
881 dissolution pattern, we expect that most U-Pb analyses of zircon residues reflect mixed
882 core-rim age components. Chemical abrasion at 210 °C appears to more effectively mine
883 out soluble zones from crystal interiors, however increasing the leaching temperature
884 210 °C also results in higher volume losses that could result in lower-precision U-Pb
885 analyses. More ID-TIMS U-Pb data – such as single crystal step-wise degassing
886 experiments conducted using different leaching conditions – are needed to identify the
887 best balance between removal of damaged material compromised by Pb loss and
888 removal of excess closed-system material. Since some inclusions appear to survive 12 h
889 of chemical abrasion in low~~er~~ damage samples, trace element analyses of highly
890 crystalline zircon should be evaluated for possible inclusion contamination.

891 Raman analyses of annealed grains suggest that dry annealing is not the inverse of
892 radiation damage accumulation. Further, Raman data for chemically abraded zircon
893 residues presents additional evidence that some radiation damage anneals
894 hydrothermally at low temperatures (180 °C to 210 °C) which has important
895 implications for the usefulness of current Raman-based dry radiation damage annealing
896 models. We also suggest the μCT imaging could be a useful tool for studying the effects
897 of radiation damage zoning on He diffusion in 3D and for applications of deep-time
898 zircon (U-Th)/He thermochronology.

899 **Supplement.** The supplement to this article is available online at:

900 **Author Contributions.** AJM designed and conducted the experiments. All authors
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902 and manuscript.

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