Geochronological and Geochemical Effects of Zircon Chemical Abrasion: Insights from Single-Crystal Stepwise Dissolution Experiments

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Abstract

Chemical abrasion in hydrofluoric acid (HF) is routinely applied to zircon grains prior to U-Pb dating by isotope dilution thermal ionization mass spectrometry (ID-TIMS) to remove radiation-damaged portions of grains affected by Pb loss. Still, many chemically abraded datasets exhibit evidence of residual Pb loss. Here we test how the temperature and duration of chemical abrasion affects zircon U-Pb and trace element systematics in a series of 4-hour, single-crystal stepwise dissolution experiments at 180 °C and 210 °C. Microtextural data for the zircon samples studied is presented in a complementary paper by McKanna et al. (2023). We find that stepwise dissolution at 210 °C is more effective at eliminating U, common Pb (Pb), and light rare earth element (LREE) enriched material affected by open system behavior; reduces the presence of leaching-induced artefacts that manifest as reverse discordance; and produces more consistent and concordant results in zircon from the three rocks studied. We estimate that stepwise dissolution in three 4 h steps is roughly equivalent to a single ~8 h leaching step due to the insulating properties of the PTFE sleeve in the Parr pressure dissolution vessel, whereas traditionally labs utilize a single 12-hour leaching step. To better understand the causes of Pb-loss in zircon, we calculate time-integrated alpha dose estimates for leachates and residues from measured radionuclide concentrations to determine: 1) the alpha dose of the material dissolved at the two leaching conditions, and 2) the apparent minimum alpha dose required for Pb loss to occur: ≥ 6 × 1017 α/g. We conclude that a single 8 h leaching step at 210 °C should yield crystallization ages in the majority of zircon and that this can be used as an effective approach for routine analysis. However, Ultimately, the effectiveness of any chemical abrasion protocol will be sample-dependent. By framing Pb loss and zircon solubility in terms of alpha dose, however, workers can better tailor the chemical abrasion process to specific zircon samples to improve the accuracy and precision of U-Pb results.

1. Introduction

Zircon U-Pb geochronology by isotope dilution thermal ionization mass spectrometry (ID-TIMS) has played a pivotal role in constraining the timing and tempo of processes on Earth from the Hadean to the Pleistocene. Zircon is a remarkable chronometer, in part because crystalline zircon is exceptionally chemically and physically durable. The zircon structure, however, can accumulate radiation damage over time. Radiation damage is principally caused by alpha recoil...
In a seminal study, Mattinson (2005, 2011) – building off the previous findings of Krogh and Davis (1975) and Todt and Büsch (1981) – demonstrated that the most radiation-damaged portions of zircon can be effectively removed by hydrofluoric acid through a series of stepwise dissolution experiments on multi-grain aliquots. He showed that early leaching steps sampled high-U material with discordant U-Pb dates, while later leaching steps sampled low-U residues unaffected by open-system behavior. Mattinson (2005, 2011) further established that partially annealing zircon samples prior to leaching helps to minimize the unwanted isotopic fractionation effects that plagued earlier leaching attempts (Davis & Krogh, 2000; Todt & Büsch, 1981). These experimental findings revolutionized the field of zircon U-Pb geochronology by allowing scientists to attain meaningful geochronological results from previously unusable zircon affected by open-system behavior. Air abrasion – the pre-treatment technique previously used to remove crystal rims (thought to be high in U) and improve U-Pb concordance (Krogh, 1981) was largely abandoned. Today, a variation of Mattison’s approach – termed chemical abrasion – is applied to virtually all zircon grains prior to ID-TIMS U-Pb isotopic analysis. In this variation, zircon crystals are annealed at 800 °C to 1200 °C for 36 h to 60 h and then leached in concentrated HF at 180 °C to 210 °C for 10 h to 18 h prior to dissolution and isotopic analysis (Mundil et al., 2004; Huyskens et al., 2016; Widmann et al., 2019).

The decrease in sample size from multi-grain aliquots to portions of single crystals and the concurrent increase in analytical precision in TIMS over the past half-century (e.g., Schoene, 2014) demands a critical re-evaluation of the chemical abrasion technique and the accuracy of the U-Pb ages that the Earth science community has come to rely on. Many studies have now shown that chemically abraded zircon samples often exhibit residual Pb-loss. This challenge is widely recognized in the ID-TIMS U-Pb community and has prompted new investigations into the effects of different annealing and leaching conditions on geochronological outcomes (Huyskens et al., 2016; Widmann et al., 2019), new statistical approaches for evaluating over-dispersed U-Pb datasets (Keller, 2023), and microstructural studies of chemically abraded zircon (McKanna et al., 2023).

We build on earlier work of Mattinson (2005, 2011) and present a series of new stepwise dissolution experiments performed at the single-crystal scale. We evaluate the effects of stepwise chemical abrasion at 180 °C and 210 °C on zircon U-Pb and trace element systematics.
in three zircon samples – AS3, SAM-47, and KR18-04 – which span a range of crystallization ages, geological settings, and radiation damage densities. These zircons come from the same sample aliquots as studied by McKanna et al. (2023) in their recent microstructural investigation of zircon dissolution which presents a unique opportunity to integrate zircon microtextures, geochronology, and geochemistry.

2. Methods

Zircon samples were annealed in quartz crucibles at 900 °C for 48 h in air in a box furnace prior to the start of the experiments. Annealed grains were mounted in epoxy, polished, and imaged by cathodoluminescence (CL) or backscattered electron (BSE) imaging using a XL30 FEG scanning electron microscope equipped with a mini-Gatan CL detector and a semiconductor BSE detector housed at the PRISM Imaging and Analysis Center at Princeton University. Representative images of AS3, SAM-47, and KR18-04 crystals can be found in McKanna et al. (2023) Fig. 3 and Fig. 4.

The stepwise partial dissolution protocol outlined here is very similar to that of Keller et al., (2019, their Fig. 1). Crystals were plucked from their epoxy mounts, rinsed in 30% HNO₃, and individually transferred to 200 µL PFA microcapsules for partial dissolution in ~100 µL of concentrated HF. Microcapsules were loaded into a PTFE-lined Parr pressure dissolution vessel with 5 mL moat HF and placed in a box oven set to 180 °C or 210 °C for a period of 4 h. At the 4 h mark, the pressure vessel was removed from the oven and placed in front of a fan to cool to room temperature.

The microcapsules were then removed from the pressure vessel and the leachate (the dissolved zircon-HF mixture) from each microcapsule was transferred to a clean 7 mL PFA beaker using a pipette. A fresh, acid-cleaned pipette tip was used for each sample transfer. Approximately 100 µL of 6N HCl was added to the residue (the remaining undissolved zircon) in the microcapsule, and the microcapsule was capped and placed on the hotplate for 1 h. The 6N HCl was then pipetted off the residue and added to the 7 mL PFA beaker with the sample leachate. The residue was then sequentially rinsed in the microcapsule using a pipette with 3N HCl, 6N HCl, 30 % HNO₃, and concentrated HF. These rinses were discarded. About 100 µL of fresh concentrated HF was then added to each residue for the second round of step leaching. In total, samples were partially dissolved in a series of three 4-h leaching steps generating a L1, L2, and L3 leachate for each zircon crystal.

After the L3 leachate was collected, the residue was again rinsed with acid and ~100 µL of fresh HF was added to the microcap. Each residue was spiked with the EARTHTIME ²⁰⁵Pb-²³³U-²³⁵U tracer (Condon et al., 2015; McLean et al., 2015) and dissolved in a Parr pressure dissolution vessel in a box oven at 210 °C for 48 to 60 h. Each leachate was spiked with the same tracer, capped, and placed on the hot plate for the same duration. Both leachates and residues were then dried down on the hot plate. Residues were redissolved in ~100 µL of 6N HCl in the Parr pressure vessel in the box oven at 180 °C overnight, and leachates were redissolved in ~100 µL of 6N HCl on the hot plate overnight. Afterward, all residues and leachates were dried down on
the hot plate and redissolved in 3N HCl in preparation for ion exchange chromatography. This procedure was modified slightly for half the KR18-04 zircon samples step-leached at 210 °C to evaluate whether a protocol change could mitigate unwanted U-Pb elemental fractionation effects as suggested by Mattinson (2005) with the goal of eliminating U-loss caused by the incomplete dissolution of fluoride salts. For these samples, after each HF leach was collected, zircon residues were dried down completely on the hot plate before the addition of ~100 µL of 6N HCl. Microcaps were then transferred back to the Parr pressure vessel and redissolved at 180 °C overnight in the box oven. The 6N HCl liquid was then pipetted off the residue and again added to the sample’s HF leachate in the PFA 7 mL beaker. This procedure was repeated for the L2 and L3 leachates. All other steps remained the same.

PTFE columns were prepared with 50 µL of Eichrom AG1-X8 anion exchange resin, cleaned, and equilibrated. U-Pb ion exchange chemistry followed the protocol established by Krogh (1973) and modified by Schoene et al., (2010) for the collection of trace elements. Combined U and Pb fractions were dried down with trace 0.05 M H3PO4 and loaded onto a zone-refined Re filament with a Si-gel emitter (Gerstenberger & Haase, 1997) for isotopic analysis on one of the two IsotopX Phoenix TIMS at Princeton University. Pb isotopes were measured on either the Daly/photomultiplier detector or ATONA Faraday system (Szymanski and Schoene, 2020), and U isotopes were measured as oxides on Faraday cups with 1012 Ω resistors or on the ATONA Faraday system. Mass fractionation in Pb isotopic analyses was corrected for with factors specific to each detector system, derived from a compilation of in-run values measured in double-spiked samples; for U the correction used the known 233U/235U of the tracer. Tripoli and ET-Redux software (Bowring et al., 2011; McLean et al., 2011) were used for processing isotopic data and error propagation, assuming a sample 238U/235U ratio of 137.818 ± 0.045 (2σ) (Heiss et al., 2012). All reported 206Pb/238U and 207Pb/206Pb dates are calculated using the decay constants of Jaffey et al., (1971) and Th-corrected assuming a magma Th/U ratio of 3.5. Reported uncertainties reflect 2σ analytical uncertainties. Common Pb corrections assume a composition equivalent to the blank.

Major and trace element analyses were made using a Thermo Scientific iCap-Q inductively coupled plasma mass spectrometer (ICPMS) at Princeton University following the procedure developed by Schoene et al., (2010), with analytical parameters described in O’Connor et al., (2022) U concentrations were calculated from Th concentrations measured by ICPMS and the Th/U ratio estimated from radiogenic 208Pb and the 206Pb/238U age assuming concordance between the U-Pb and Th-Pb systems. The percent zircon dissolved is calculated using Zr abundances: (Zr_{step}/Zr_{total}) × 100. LREE-indices (LREE-I) quantify LREE-enrichment in zircon which can reflect chemical alteration or sample contamination. The lower the LREE-I, the higher the LREE-enrichment. LREE-I is calculated as [Dy]/[Nd] + [Dy]/[Sm] following Bell et al., (2016).

3. Background and results

3.1 AS3

3.1.1 Geologic setting and sample description
AS3 zircons are from an anorthosite from the Duluth Complex of northern Minnesota, USA which formed during the Mesoproterozoic North American Midcontinent Rift (92°09'32.4", 46°45'43.4") (Paces & Miller, 1993; Miller et al., 2002; Schmitz et al., 2003; Swanson-Hysell et al., 2019, 2020). The Duluth Complex is a massive layered mafic intrusion. The anorthositic and layered series of the complex were emplaced at ~1096 Ma over a duration <1 m.y. (Swanson-Hysell et al., 2020). The voluminous magmatism that formed the Duluth Complex is attributed to decompression melting due to lithospheric extension occurring atop an upwelling magmatic plume (Swanson-Hysell et al., 2020). Rifting in the region ceased at ~1084 Ma (Swanson-Hysell et al., 2019). Thermochronology data from Minnesota River Valley in southern Minnesota suggest that rocks in the region have sat at near-surface temperature conditions since the Neoproterozoic (Guenthner et al., 2013; McDannell et al., 2022).

The AS3 sample studied is the same as that of Takehara et al., (2018). The rock sample is composed of plagioclase, amphibole, clinopyroxene, and ilmenite with minor K-feldspar, apatite, zircon, and baddeleyite. Partially chloritized amphiboles, altered plagioclase, and zeolite veins indicate that this sample of AS3 has interacted with low-temperature hydrothermal fluids as previously described (Takehara et al., 2018). Zircon grains are large and often have large melt inclusions oriented elongate to the c-axis. Crystals exhibit concentric and convolute zonation patterns, and many grains are hydrothermally altered (McKanna et al., 2023; Takehara et al., 2018). Included and altered grains were included in the experiments to evaluate how well geochemical data traces the dissolution of inclusions and altered material. Raman data indicate that grains have accumulated high radiation damage densities with equivalent alpha doses of $2 \times 10^{17}$ to $1 \times 10^{19}$ α/g with significant intracrystalline variations in radiation damage (McKanna et al., 2023).

### 3.1.2 Previous geochronology

Paces and Miller (1993) presented the first U-Pb geochronological data for AS3 zircon. These authors found that six multi-grain aliquots of air-abraded zircon crystals produced concordant ID-TIMS U-Pb dates and assigned the sample a weighted-mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 1099.1 ± 0.5 Ma (2σ). Schmitz et al., (2003) later conducted additional ID-TIMS U-Pb isotopic analysis on individual air-abraded AS3 zircon. The authors found that several crystals produced discordant dates affected by recent Pb loss. Twelve concordant analyses yielded a concordia age of 1099.1 ± 0.2 Ma (2σ). Eight grains from the same sample were later analyzed by chemical abrasion ID-TIMS by Schoene et al., (2006) producing concordant dates with weighted mean $^{206}\text{Pb}/^{238}\text{U}$ and $^{207}\text{Pb}/^{206}\text{Pb}$ ages of 1095.9 ± 0.2 Ma and 1098.6 ± 0.3 (2σ), respectively. These grains were annealed at 900 °C for 60 h and chemically abraded in an HF-HNO$_3$ mixture at 180 °C for 12 to 14 h. Age differences between these and previous results were attributed by the authors to differences in tracer calibration, which had been redone as part of (Schoene et al., 2006).

Takehara et al., (2018) later demonstrated that zircons from a different sample of AS3 collected from the same sample locality are strongly affected by hydrothermal alteration; sensitive high-resolution ion microprobe (SHRIMP) analyses showed that hydrothermally altered zones...
yielded normally discordant U-Pb analyses, were enriched in incompatible trace elements including LREEs, Ca, Mn, Fe, Al, Li, and K, and depleted in Zr and Si.

Figure 1. U-Pb concordia diagrams for the 180 °C (left) and 210 °C (right) AS3 experiments. (a) All data are depicted except for L1 leachates with Pb*/Pb values < 1. (b) Close up of L2, L3, and R data. (c) Close up of zircon residue data. Ellipses with dashed borders were excluded from the weighted-mean $^{206}$Pb/$^{238}$U age for the 180 °C experiment. All ellipses reflect 2σ analytical uncertainties.
3.1.3 U-Pb and trace element results

ID-TIMS U-Pb results for AS3 samples are presented in Fig. 1, Fig. 2, and Table S1. L1 leachates are younger than zircon residues indicating the dissolution of material strongly affected by Pb loss. L1 leachates have large age uncertainties due to high amounts of Pb. Consequently, many large error ellipses overlap the Concordia curve. L1 leachates with higher radiogenic to common Pb (Pb*/Pb) ratios and better age precision are normally discordant. L2 and L3 leachates are older than L1 leachates and form a discordia line through analyses that are either normally discordant, concordant, or reversely discordant. The upper intercept ages for the discordia lines agree within uncertainty with the weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age for residues treated at 210 °C. The lower intercept ages of the discordia lines are zero-age. Ages for L2 and L3 leachates treated at 180 °C are more widely dispersed than ages for L2 and L3 leachates treated at 210 °C. The 180 °C leachates also have larger uncertainties due to higher Pb contents.

Residues treated at 210 °C form a single, concordant age population with weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 1096.42 ± 0.49 Ma (MSWD = 1.7; Fig. 1) in agreement with previous geochronology (Schoene et al., 2006). U-Pb ages of residues treated at 180 °C are dispersed along Concordia; a cluster of residue analyses agree with the 210 °C result yielding a weighted mean $^{206}\text{Pb}/^{238}\text{U}$ age of 1096.29 ± 0.36 Ma (MSWD = 2.3), but a few analyses are either older or younger. Two of the 180 °C residues are reversely discordant. Weighted-mean $^{207}\text{Pb}/^{206}\text{Pb}$ ages for all leachates and residues agree within uncertainty (Fig. 2). The weighted-mean $^{207}\text{Pb}/^{206}\text{Pb}$ ages obtained for the 180°C and 210 °C residues are 1097.03 ± 0.63 Ma (MSWD = 1.7) and 1096.64 ± 0.96 Ma (MSWD = 0.48), respectively. These dates are slightly younger than previous geochronology (Schoene et al., 2006).
Leachates from the 180 °C experiment are enriched in LREE, Pb, and U relative to zircon residues (Fig. 3, Fig. 4, Fig. 5, and Table S2). LREE enrichment is apparent both in chondrite-normalized REE spider diagrams and in LREE-I values. Sample’s LREE-I and radiogenic to
common Pb ratio ($Pb^*/Pb_c$) are clearly correlated. L1 leachates from the 210 °C dataset are 248

Figure 4. AS3 U-Pb and trace element data for the 180 °C (left) and 210 °C (right) experiments. (a) LREE-I versus percent discordance. The horizontal solid line represents perfect concordance. The vertical dashed line depicts a LREE-I threshold value of 35 below which data is notably more discordant. (b) $^{206}Pb^{/238}U$ date plotted as a function of the radiogenic $Pb^*$ to common Pb ratio. Error bars for the percent discordant and $^{206}Pb^{/238}U$ data reflect propagated 2σ analytical uncertainties. Most error bars are smaller than data markers. (c) The radiogenic $Pb^*$ to common Pb ratio versus the LREE-I showing a positive correlation between the two variables.
similarly enriched in LREE, Pb, and U relative to zircon residues, whereas 210 °C L2 and L3 leachates have compositions comparable to residues.

In the majority of samples, most dissolution occurred in the first leaching step with progressively smaller volumes dissolved in L2 and L3. The median fraction of the zircon mass remaining after L3 for the 180 °C experiment is ~35%, whereas for the 210 °C experiment it is ~30%. Percent Pb* mirrors results for percent zircon dissolved in both experiments.

3.2 SAM-47

3.2.1 Geologic setting and sample description

SAM-47 is an Archean (~3.32 - 3.29 Ga) granodiorite from the Corunna Downs Granitic Complex of the Emu Pools Supersuite in the eastern Pilbara Craton (-21°24′29.01″, 119°46′21.03″)
(Barley and Pickard, 1999; Smithies et al., 2003; Van Kranendonk et al., 2007). The tectonic significance of the dome and keel structures of the eastern Pilbara Craton are a matter of debate, and the region has experienced a multi-phase deformational history (Kloppenburg et al., 2001; MacLennan, 2019; Moore and Webb, 2013). ID-TIMS U-Pb cooling ages for apatite from the Corunna Downs Granitic Complex are ~3.3 Ga which are similar to Ar-Ar ages reported by Kloppenburg (2003). The similarity between the U-Pb and Ar-Ar data suggest rapid cooling through ~460°C following intrusion of the granitoid (MacLennan, 2019). Zircon (U-Th)/He dates for the Owen’s Gully diorite from the Mount Edgar Granitic Complex north of the Corunna Downs range from 677.5 ± 36.3 to 815.5 ± 44.6 Ma in age, suggesting that the eastern craton reached near-surface thermal conditions where radiation damage can accumulate in zircon sometime in the Neoproterozoic (Magee et al., 2017). Low-temperature thermochronology data from elsewhere in the Pilbara craton (the northern, central, and western blocks) suggest that the onset of widespread cooling related to basin-development and unroofing varied regionally starting sometime between ~600 and 300 Ma (Morón et al., 2020). Zircon grains separated from SAM-47 are euhedral, brown, and translucent. Crystals display fine-scale concentric growth zones (McKanna et al., 2023). Rims are enriched in actinides and radiation damage relative to cores. Raman data suggest that grains have accumulated intermediate-to-high radiation damage densities with equivalent alpha doses ranging from 6×10^{17} to 2×10^{18} α/g (McKanna et al., 2023). There is no previous U-Pb geochronology for zircon from this sample, however, Pb loss is common in similarly aged zircon from the Pilbara craton (MacLennan, 2019).

### 3.2.2 U-Pb and trace element results

ID-TIMS U-Pb results for SAM-47 samples are presented in Fig. 2, Fig. 6, and Table S3. L1 leachates from both sample sets are normally discordant resulting in \(^{206}\text{Pb}/^{238}\text{U}\) dates that are >800 Ma. younger than zircon residues, indicating the dissolution of domains strongly affected by Pb-loss. Although systematically older than L1 leachates, L2 and L3 leachates from the 180 °C experiment are normally discordant. Two residues from the 180 °C dataset are concordant and have a weighted-mean \(^{206}\text{Pb}/^{238}\text{U}\) age of 3319.5 ± 1.4 Ma (MSWD = 1.7). The remaining four residues are normally discordant. In contrast to the 180 °C experiment, many of the L2 and L3 leachates from the 210 °C experiment are concordant, and the few normally discordant analyses closely approach Concordia. All 210 °C residues overlap or closely hug Concordia. Three of the concordant residues yield a weighted-mean \(^{206}\text{Pb}/^{238}\text{U}\) age of 3316.1 ± 1.6 Ma (MSWD = 1.0) that is slightly younger than the 180 °C dataset. Upper intercept ages for 180 °C residues, 210 °C residues, as well as 210 °C L2 and L3 leachates all agree within uncertainty and produce robust MSWDs as shown in Fig. 6. The most precise upper and lower intercept ages are 3321.23 +0.78/-0.71 Ma and 751 ± 140 Ma, respectively.

Most \(^{207}\text{Pb}/^{206}\text{Pb}\) dates for L2, L3, and R samples from the 210 °C experiment agree within uncertainty (Fig. 2). The 210 °C residues yield a weighted-mean \(^{207}\text{Pb}/^{206}\text{Pb}\) age of 3321.75 ± 0.63 Ma (MSWD = 0.83) which agrees well with our upper intercept ages. In contrast, \(^{207}\text{Pb}/^{206}\text{Pb}\) dates from the 180 °C dataset are notably younger, indicating the dissolution of domains affected by a Pb loss event that occurred in the distant past. The two concordant 180
°C residue analyses yield a weighted-mean $^{207}\text{Pb}/^{206}\text{Pb}$ age of 3320.90 ± 0.87 (MSWD = 0.050) in agreement with the 210 °C results.

L1, L2, and some L3 leachates from the 180 °C experiment are enriched in LREE and Pb$_c$ relative to zircon residues (Fig. 7, Fig. 8, and Table S4). Some – but not all – leachates from the 180 °C dataset are also marginally enriched in U relative to residues (Fig. 5). The composition of a subset of 180 °C L3 leachates closely approximates that of residues. LREE and Pb$_c$ enrichment is

Figure 6. U-Pb concordia diagrams for the SAM-47 180 °C (left) and 210 °C (right) step-leaching experiments. (a) All data for the 180°C experiment. (b) Close up of the L2, L3, and R 180 °C dataset. (c) Close up of the 180 °C residue data. (d) All data for the 210°C experiment. (e) Stacked plot showing the L2, L3, and R 210 °C datasets. All ellipses reflect 2σ analytical uncertainties. Dashed ellipses are excluded from weighted mean calculations.
also evident in L1 and some L2 leachates from the 210 °C dataset, whereas most L3 leachates have compositions comparable to residues. Although a few leachates from the 210 °C experiment are relatively enriched in U, many have U compositions similar to residues.

Figure 7. Chondrite-normalized REE spider diagrams for the 180 °C (left) and 210 °C (right) SAM-47 experiments comparing results for leachates and residues.
Only 10 to 20% of SAM-47 zircon mass dissolved during step-leaching at 180 °C, leaving 80 to 90% of the zircon residue available for final isotopic analysis. Larger volumes were dissolved during step-leaching at 210 °C. Most dissolution occurred in L1—up to 60% mass loss—with progressively smaller amounts dissolved in L2 and L3. Less than 40% of the zircon residue remained for final digestion. Percent Pb* mirrors results for percent zircon dissolved in both experiments.

Figure 8. SAM-47 U-Pb and trace element data for the 180 °C (left) and 210 °C (right) experiments. (a) LREE-I versus percent discordance. The horizontal solid line represents perfect concordance. The vertical dashed line depicts a LREE-I threshold value of 20 below which data is notably more discordant. (b) $^{206}$Pb/$^{238}$U date plotted as a function of the radiogenic Pb* to common Pb ratio. Error bars for the percent discordant and $^{206}$Pb/$^{238}$U data reflect propagated 2σ analytical uncertainties. Most error bars are smaller than data markers. (c) The radiogenic Pb* to common Pb ratio versus the LREE-I showing a positive correlation between the two variables.
3.3 KR18-04

3.3.1 Geologic setting and sample description

KR18-04 zircons come from a Neoproterozoic rhyolite body associated with the glacilacustrine Konnarock Formation in the Blue Ridge Mountains of Virginia, USA (MacLennan et al., 2020) (36°41'47.95", 81°24'22.08"). The Konnarock Formation is part of a structurally continuous sedimentary sequence deposited in a continental rift environment (Merschat et al., 2014). This sequence unconformably overlies gneisses that are related to the Mesoproterozoic Grenville orogeny. ID-TIMS U-Pb ages for zircon separated from KR18-04 were used to show that glacial sedimentation was occurring at tropical latitudes at ~751 Ma, 30 million years prior to the Sturtian Snowball Earth (MacLennan et al., 2020). The post-depositional history of the region is complex and poorly resolved (Roden, 1991). Zircon fission track dates (Tc = ~205°C) from the Blue Ridge suggest that burial reheating and range in age from ~617 Ma to late Paleozoic dates (Naeser et al., 2016). Zircon (U-Th)/He dates (Tc = ~180 °C for crystalline zircon) from the Blue Ridge are contemporaneous with the late-stages of the Alleghenian orogeny indicating that the zircon He chronometer was fully reset by burial reheating and records synorogenic exhumation (Basler et al., 2021).

The KR18-04 rhyolite is crystal-rich with prominent, dominantly euhedral K-feldspar and quartz phenocrysts (MacLennan et al., 2020). Zircon grains separated from KR18-04 are euhedral, pink-orange, transparent, and minimally included. Grains exhibit concentric zoning in cathodoluminescent images with some faint, broad growth zones (McKanna et al., 2023). Raman data suggest that grains have accumulated low-to-intermediate radiation damage densities with equivalent alpha doses ranging from 5×10^{16} to 2×10^{17} α/g (McKanna et al., 2023).

3.3.2 Previous geochronology

Twelve single-crystal zircon ID-TIMS U-Pb analyses for KR18-04 are presented by MacLennan et al., (2020). Zircon were initially chemically abraded at 185 °C for 12 h. However, since many of these analyses retained significant Pb loss, the intensity of chemical abrasion was increased to 210 °C for up to 14 h for the remaining samples. The twelve reported ^{206}Pb/^{238}U dates – which combine both leaching conditions – range from 753.08 ± 0.33 to 741.21 ± 0.35 Ma. The reported data are statistically over-dispersed for a single population. The authors attribute the spread in ages along Concordia and the one discordant analysis to residual Pb loss (their Fig. S10). The reported eruption age for the sample derived from the eight oldest analyses and determined using a Bayesian Markov Chain Monte Carlo technique is 752.60 ±0.12/-0.65 Ma.

3.3.3 U-Pb and trace element results

ID-TIMS U-Pb results for KR18-04 samples are presented in Fig. 9 and Table S5. L1 leachates from both sample sets are affected by Pb loss; L1 leachates with Pb*/Pb̂ ratios >1 are normally discordant and >150 Ma younger than zircon residues. The lower intercept value for L1 leachates from the 210 °C experiment suggests zero-age Pb-loss. L2 leachates from both
experiments are concordant but appreciably older than zircon residues. The majority of L3 leachates are concordant and younger than L2 leachates. Most L3 leachates are either within 3σ uncertainty of residue dates or slightly older. U-Pb analyses of residue samples from the 180 °C experiment are spread along Concordia from 758.63 to 752.99 Ma. In contrast, residue analyses from the 210 °C experiment form a tight cluster with a weighted mean 206Pb/238U age of 752.49 ± 0.24 Ma (MSWD = 0.95, n=6) in agreement with previous geochronology (MacLennan et al., 2020). This weighted-mean age includes analyses measured on the ATONA which produced more precise U measurements for these low-U zircon. The two 210 °C zircon aliquots that followed slightly different step-leaching protocols as outlined in Methods generated equivalent results.

Figure 9. U-Pb concordia diagrams for the KR18-04 180 °C (left) and 210 °C (right) step-leaching experiments. (a) All data are depicted. (b) Close up of L2, L3, and R data excluding leachates with Pb*/Pb, values < 1. (c) Close up of zircon residues. The weighted mean 206Pb/238U date reported for the 210 °C experiment includes residue data with solid ellipse borders. Ellipses with dashed borders were excluded due to low-quality U measurements. All ellipses reflect 2σ analytical uncertainties.

from the 210 °C experiment form a tight cluster with a weighted mean 206Pb/238U age of 752.49 ± 0.24 Ma (MSWD = 1.1, n=6) in agreement with previous geochronology (MacLennan et al., 2020). This weighted-mean age includes analyses measured on the ATONA which produced more precise U measurements for these low-U zircon. The two 210 °C zircon aliquots that followed slightly different step-leaching protocols as outlined in Methods generated equivalent results.
L1, L2, and some L3 leachates from the 180 °C experiment are enriched in LREEs and Pb relative to zircon residues (Fig. 10, Fig. 11, and Table S6). L1 leachates are also strongly enriched in U, while L2 leachates are mildly enriched in U. L3 leachates have U compositions that are similar to residues (Fig. 5). L1 and some L2 leachates from the 210 °C experiment are enriched in LREEs relative to zircon residues, whereas L3 leachates have REE compositions similar to residues. All 210 °C leachates have low Pb* / Pb ratios compared to residues. L1 leachates are

Figure 10. Chondrite-normalized REE spider diagrams for the 180 °C (left) and 210 °C (right) KR18-04 experiments comparing results for leachates and residues.
strongly enriched in U, while L2 and L3 leachates have U compositions that are similar to residues.

Only ~10 to 15% of KR18-04 zircon mass dissolved during step-leaching at 180 °C, leaving ~85 to 95% of the zircon residue available for final isotopic analysis. At 210 °C, ~10 °C to 30% of the zircon dissolved during step-leaching, resulting in residue volumes of 70 to 90%. Percent Pb* mirrors results for percent zircon dissolved in both experiments.

4. Discussion
4.1 Reverse discordance

Reverse discordance and concordant analyses that are older than the samples’ interpreted crystallization ages are common in the AS3 and KR18-04 datasets but absent in SAM-47. Concordant analyses that are “too old” can result from either minor U loss or Pb* gain, causing datasets to lie along a discordia line that overlies the Concordia curve; for brevity, we will also refer to these analyses as “reversely discordant.” Reverse discordance is most common in L2 and L3 leachates, however, a subset of residues from the AS3 and KR18-04 180 °C experiments
are also reversely discordant. Three L2 leachates for the Hadean zircon analyzed by Keller et al., (2019) are similarly reversely discordant.

Reverse discordance in zircon stepwise dissolution experiments is generally attributed to leaching-induced experimental artefacts. Early step-leaching efforts yielded U-Pb isotopic variations that swung wildly between normally and reversely discordant from step-to-step (Todt and Büsch, 1981). Mattinson (1994, 2011) later attributed this effect to the authors’ specific dissolution and spiking method which caused U and Pb to fractionate between supernate and U-bearing fluoride precipitates. However, later step-leaching experiments using different experimental procedures also exhibited reverse discordance in early leaching steps (Chen et al., 2001; Mattinson, 2005, 2011). Mattinson (2005, 2011) charged that early leaching steps must reflect a mixture of U and Pb from the higher-U dissolved zircon volume plus excess Pb* leached from the lower-U intact zircon residue. Mattinson (2005, 2011) further demonstrated that annealing samples at temperatures between 800 - 1100 °C prior to chemical abrasion helped to minimize – but not eliminate – leaching-induced artefacts.

Reverse discordance is observed naturally in some untreated zircon (Kusiak et al., 2015; Wiemer et al., 2017; Williams et al., 1984). In such cases, reverse discordance is generally attributed to either the internal redistribution of Pb within a crystal or by external factors such as alteration by hydrothermal fluids (Mattinson et al., 1996). Alpha recoil can displace Pb* from the position of its parent radioisotope by ~30 nm (Ewing et al., 2003; Weber, 1990, 1993). In crystals with fine-scale growth zoning, Pb* produced by a U atom within a high-U zone can be implanted into a nearby low-U zone producing a localized occurrence of excess Pb* in the low-U zone (Mattinson et al., 1996). Further, ion imaging and atom probe tomography studies of zircon support the case for nano-to-micro scale Pb redistribution under elevated temperatures and pressures (Kusiak et al., 2015; Peterman et al., 2019, 2021; Reddy et al., 2016). These studies show that unsupported Pb* often forms clusters that are not spatially associated with parent radionuclide growth patterns. However, the exact mechanisms by which Pb* migrates through the zircon structure are poorly understood.

Notably, our SAM-47 zircon does not exhibit reverse discordance suggesting that only some samples are predisposed to leaching-induced artifacts or leaching-exposed natural U-Pb fractionation. A zircon’s U-Pb systematics as revealed by stepwise dissolution must therefore reflect its unique compositional characteristics such as the length-scale and magnitude of radionuclide zonation, the extent of Pb loss, or the sample’s geological history. AS3 is hydrothermally altered, so a component of the reverse discordance observed could potentially reflect the redistribution of Pb isotopes during hydrothermal alteration (Takehara et al., 2018). Why KR18-04 zircon is susceptible to reverse discordance is less clear. Grains appear unaltered and most compositional zones are broad; however, some grains do have thin, high-U zones that could contribute to the internal redistribution of Pb* (McKanna et al., 2023 their Fig. 4 & 15a). Zircon fission track and (U-Th)/He data from Blue Ridge indicate that the region was thermally affected by burial reheating during the late-Paleozoic Alleghenian Orogeny (Naeser et al., 2016; Roden, 1991). Still, there is no evidence that KR18-04 has experienced an extreme high-
temperature deformation event. SAM-47 may lack leaching-induced reverse discordance simply because Pb loss in the sample is so pervasive.

Figure 12. Trace element and Pb isotopic composition of zircon residues plotted against ΔAge as described in text. The gray bar at ΔAge = 0 Ma marks the accepted crystallization age for each zircon sample. The data portrayed is inclusive of residues from both the 180 °C and 210 °C experiments. (a) LREE-I versus the ΔAge. (b) Pb*/Pbc versus the ΔAge. (c) εU versus ΔAge. The arrow in each plot marks the placement of a datapoint from the SAM-47 dataset that plots at ΔAge = -60 Ma.
Regardless of the underpinning causes of reverse discordance, this work and that of Mattinson (2005, 2011) demonstrate that increasing the leaching duration and/or temperature helps to eliminate zircon domains affected by open system behavior. These results also highlight that under-leaching samples can produce over-dispersed U-Pb datasets fraught with geologically meaningless analyses. Without the additional context that the 210 °C experiment provides, a researcher could easily interpret the older concordant dates from the 180 °C KR18-04 dataset, for example, as inheritance or prolonged magmatic residence. We stress, however, that our step-wise experiments are under-leached compared to the normal 12 h leaching step used in most labs (see Section 4.3).

4.2 The strengths and limitations of geochemical tools for identifying open-system behavior

Common Pb and LREEs are incompatible in zircon. Mineral and melt inclusions and hydrothermally altered or metamict zones, however, tend to be enriched in LREEs and common Pb (Bell et al., 2016, 2019). Consequently, geochemical indicators such as a sample’s LREE-index (LREE-I = [Dy]/[Nd] + [Dy]/[Sm]) and Pb*/Pb_c (provided demonstrably low laboratory blanks) are useful tools for identifying contamination, hydrothermal alteration, and metamictization. Indeed, our data show that the two variables are generally positively correlated (Fig. 4C, 8C, and 11B). Another important geochemical indicator is U concentration – or effective U concentration (eU = U + 0.235 × Th) – which is a measure of the relative radiation damage in a sample; zircon crystals or leachates from the same sample with higher eU have more radiation damage than crystals or leachates with lower eU.

These three geochemical indicators are useful tools for evaluating zircon dissolution. In the 180 °C experiments, L1, L2, and some L3 leachates are enriched in LREE, Pb_c, and U relative to zircon residues. Whereas in the 210 °C experiments, L1 and some L2 leachates are enriched in the three variables, however, some L2 and most L3 leachates have compositions similar to residues.

Micro-X-ray computed tomography data presented by McKanna et al., (2023) for AS3 and SAM-47 zircon show that acid readily accesses crystal cores via fractures to dissolve mineral and melt inclusions and strongly metamict zones during L1 at 180 °C and 210 °C. As such, we interpret the LREE, Pb_c, and U enrichment in L1 leachates to reflect the dissolution of inclusions, metamict material, and – in the case of AS3 – hydrothermally altered zones. We attribute LREE, Pb_c, and U enrichments in later leaching steps to the continued dissolution of soluble radiation-damaged or altered domains. KR18-04 zircon grains are more crystalline and typically lack fractures. Consequently, acid only accesses the cores of some grains, and some inclusions armored by highly crystalline material appear to survive twelve hours of chemical abrasion at 180 °C or 210 °C (McKanna et al., 2023). Consequently, LREE and Pb_c enrichment in L2 and L3 leaching steps could reflect later-stage dissolution of inclusions as well as the continued dissolution of radiation-damaged or altered domains.

Comparing leachate and residue chemistry is extremely effective at illuminating the progress of zircon dissolution. However, stepwise chemical abrasion is a time- and labor-intensive process. The overwhelming majority of zircon ID-TIMS U-Pb studies perform single-step chemical...
abrasion and discard the leachate. Only the residue is characterized. In an ideal scenario, geochemical indicators such as those described here could be used to support the inclusion or exclusion of anomalously young (or old) analyses in geochronological interpretations. Fig. 12 shows ΔAge (Ma) of residues plotted as a function of a grain’s LREE-I, Pb*/Pb, or eU. ΔAge is calculated as the difference between a residue’s measured 206Pb/238U date and each sample’s accepted crystallization age. Negative values for ΔAge reflect Pb loss, while positive values indicate reverse discordance.

Unfortunately, there is no clear correlation between either of the three geochemical indicators and ΔAge in the samples analyzed. Instead, the data suggest that relative enrichments in LREE, Pb, and U in residues are not reliable indicators of residual open system behavior. We speculate that the residual zircon affected by open-system behavior is likely volumetrically small compared to the volume of the residual closed-system zircon. Thus, the geochemical signature of the open-system behavior is likely masked by the bulk chemistry of the closed-system residue. Relative enrichments in LREE, Pb, and U in residues are likely useful geochemical indicators only if the residual open-system material is proportionally large.

### 4.3 Leaching temperature and one-step versus stepwise chemical abrasion

Stepwise dissolution at 210 °C outperformed stepwise dissolution at 180 °C for all three zircon samples and produced more consistent, concordant datasets. Leaching at 210 °C dissolved zircon material affected by open-system behavior earlier in the leaching process minimizing the frequency and magnitude of normal and reverse discordance compared to the 180 °C experiments (Figures 1, 2, 6, 7, and 10). The efficacy of the hotter leaching temperature is also evident in zircon geochemistry; leaching at 210 °C more efficiently removed zircon material enriched in U, LREE, and Pb.

Notably, U-Pb results for AS3 and KR18-04 residues treated by stepwise dissolution at 180 °C are markedly worse than previous studies (MacLennan et al., 2020; Schoene et al., 2006). Chemical abrasion of AS3 zircon for 12 to 14 h at 180 °C by Schoene et al., (2006) produced concordant, statistically significant weighted mean U-Pb ages without signs of residual Pb loss or reverse discordance. Those authors used intense frantzing to target unpreferred, diamagnetic zircon, whereas this study included altered grains. While some KR18-04 grains treated at 185 °C for 12 h by (MacLennan et al., 2020) exhibited Pb loss, none of their chemically abraded residues were found to be anomalously old or reversely discordant.

These apparent discrepancies beg the question: is a single 12 h leaching step is equivalent to stepwise dissolution in three 4 h leaching steps? PTFE has a low thermal conductivity making it an effective insulator. To evaluate how temperature in the PTFE-lined Parr pressure dissolution vessel changes with time, a small hole was drilled through the top of an old PTFE liner. The pressure vessel was assembled as normal minus the rupture and corrosion disks. A type-K thermocouple with an insulated wire was threaded through the top of the pressure vessel and into the center of the PTFE liner. The pressure vessel was then placed in a box furnace at 180 °C.
or 210 °C. Temperature was monitored using a Perfect Prime thermocouple thermometer until the temperature in the liner reached equilibrium with the box furnace. The pressure vessel was then removed from the furnace and placed in front of a fan, and temperature was recorded as the pressure vessel cooled to near room temperature. Results indicate that PTFE is indeed a very effective insulator; the interior of the pressure vessel heats and cools slowly (Fig. 13). It takes 90 to 95 minutes for the interior of the pressure vessel to reach within 20 °C of the target temperature and an additional 30 to 35 minutes to reach within 10 °C of the target temperature. The pressure vessel takes ~90 minutes to cool to room temperature once removed from the oven.

Given the heating ramp up and cool down times for the PTFE-lined pressure dissolution vessel, samples spend only ~2 h of the 4 h leaching step within 10 °C of the target temperature. As such, a sample leached for 12 h in three consecutive 4 h steps spends ~6 h within 10 °C of the target temperature. Conversely, a sample leached in a single 12 h step spends ~10 h within 10 °C of the target leaching temperature – ~4 h longer than the step-leached sample. Volume loss estimates for KR18-04 further support this conclusion; estimated volume losses for stepwise chemical abrasion (Figure 5) are generally lower than the estimated volume losses presented by McKanna et al., (2023; their Fig. 18) for zircon from the same sample aliquot that were chemically abraded for a single 12-h step.

On the basis of the 10 °C threshold, we estimate that our dated residues have been leached for a duration equivalent to a single ~8 h leaching step. Given our U-Pb results, we conclude that zircon chemically abraded at 180 °C for a single 8 h step are “undercooked” and will likely...
produce data affected by residual Pb loss and/or leaching-induced artifacts. Zircon samples chemically abraded at 210 °C for a single 8-h leach are more likely to produce geologically meaningful results. Unfortunately, we therefore cannot comment on the efficacy of the routinely practiced 12-hour leaching at 180 °C used in many labs, except to say it is likely more effective than the results for residues we present here.

4.4 The relationships between alpha dose, Pb loss, and zircon dissolution: Moving toward a more predictable model for chemical abrasion

Zircon is an outstanding chronometer because radiogenic Pb is immobile in well crystalline zircon (Cherniak et al., 2009; Cherniak and Watson, 2000). Establishing the alpha dose at which radiogenic Pb can mobilize within the zircon structure would help make Pb loss more predictable. We calculate three different time-integrated alpha doses for each sample using the radionuclide concentrations determined for leachates and residues (Table 1). “Total” alpha dose assumes a damage accumulation interval equivalent to a sample’s crystallization age. This calculation ignores the possibility of radiation damage annealing. “Present day” alpha dose estimates attempt to take geological annealing into account. Radiation damage anneals at temperatures above ~200 to 300 °C on geological timescales (Bernet, 2009; Yamada et al., 2007). The closure temperature for the (U-Th)/He system in crystalline zircon is ~180 °C (Guenthner et al., 2013; Reiners et al., 2004). As such, we use published zircon (U-Th)/He dates or thermal histories derived from zircon (U-Th)/He datasets for the Minnesota River Valley (Guenthner et al., 2013; McDannell et al., 2022), the Eastern Pilbara craton (Magee et al., 2017), and the Virginia Blue Ridge (Basler et al., 2021) to estimate minimum damage accumulation intervals for samples’ “present day” alpha doses. Since zircon (U-Th)/He dates for the Eastern Pilbara craton broadly overlap the lower-intercept U-Pb Concordia age for SAM-47, we take the lower-intercept age as the damage accumulation interval. Chosen intervals for AS3, SAM-47, and KR18-04 are 750 Ma, 751 Ma, and 298 Ma, respectively.

“Present day” alpha dose estimates can also be established independently using Raman spectroscopy, since key bands in the zircon Raman spectrum broaden predictably with

<table>
<thead>
<tr>
<th>Sample</th>
<th>Total Pb Loss</th>
<th>Present Day Pb Loss</th>
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<tr>
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</tr>
<tr>
<td>SAM-47</td>
<td>2×10^18</td>
<td>1×10^19</td>
</tr>
<tr>
<td>KR18-04</td>
<td>1×10^17</td>
<td>1×10^19</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Sample</th>
<th>Present Day</th>
<th>Present Day Pb Loss</th>
</tr>
</thead>
<tbody>
<tr>
<td>AS3</td>
<td>2×10^17</td>
<td>2×10^18</td>
</tr>
<tr>
<td>SAM-47</td>
<td>6×10^17</td>
<td>2×10^18</td>
</tr>
<tr>
<td>KR18-04</td>
<td>5×10^16</td>
<td>7×10^17</td>
</tr>
</tbody>
</table>

1Calculated using measured U and Th concentrations and damage accumulation intervals as described in text.
2Raman-based alpha dose estimates reported by McKanna et al., (2023).
increasing alpha dose (Nasdala et al., 2001; Palenik et al., 2003). “Present day” alpha doses for AS3 and SAM-47 closely match Raman-based alpha doses ($\alpha_r$) determined by McKanna et al., 2023. “Present day” alpha doses for KR18-04 have a similar lower bound but a higher upper bound compared to Raman estimates. Most likely, Raman measurements failed to capture volumetrically small, higher-U domains such as the thin concentric dissolution features evident in secondary electron images of KR18-04 residues (McKanna et al., 2023, their Fig. 15a–I reproduced here in Fig. 16b).

The final calculation estimates alpha dose at the time of Pb loss. Because AS3 and KR18-04 exhibit zero-age Pb-loss discord, “present day” and “Pb loss” alpha doses estimates are equivalent. The Pb-loss discord for SAM-47, however, suggests that Pb loss occurred in the distant geological past at or before 751 ± 140 Ma (Fig. 6C). Therefore, the maximum “Pb loss” damage accumulation interval is the difference between the sample’s upper and lower intercept ages which equates to ~2571 Ma.

Fig. 14 shows the distribution of “Pb loss” alpha dose estimates for all leachates affected by Pb loss. Despite vastly different geological settings and ranges in radiation damage densities, leachates affected by Pb loss exhibit similar alpha dose distributions. The majority have alpha doses that are $\geq 6 \times 10^{17} \alpha/g$. We therefore establish this alpha dose as our best estimate for the threshold above which Pb can mobilize within the zircon structure. Notably, this threshold is somewhat lower than the alpha dose $\geq 1 \times 10^{18} \alpha/g$ at which zircon material properties such as density begin to change (Ewing et al., 2003; Nasdala et al., 2004). However, the $6 \times 10^{17} \alpha/g$ threshold is similar to some estimates for the alpha dose at which helium diffusion kinetics
begin to increase causing the closure temperature for He in zircon to decrease (Anderson et al., 2017, 2020). The mechanism that causes Pb loss – diffusion, leaching, or recrystallization – is not clear.

For the best geochronological outcomes, chemical abrasion should target zircon material with alpha doses $\geq 6 \times 10^{17}$ α/g. Fig. 15 shows “present day” alpha dose estimates for all leachates and residues. In the 180 °C experiments, the median alpha dose decreases with increasing leaching duration consistent with the expected effects of radiation damage on zircon solubility. A majority of residues from the 180 °C and 210 °C experiments have alpha doses $> 6 \times 10^{17}$ α/g suggesting that residues may be affected by residual open system behavior in agreement with our U-Pb isotopic results. Evidently, dissolving zircon with lower alpha doses requires longer leaching durations at 180 °C than achieved in this study, which was equivalent to a single 8-hour leach step. In contrast, the median alpha dose for residues as well as L2 and L3 leachates from the 210 °C experiments have alpha doses below the established threshold. Zircon material with alpha doses $\geq 6 \times 10^{17}$ α/g is thus readily dissolved at short leaching durations at 210 °C.

Framing Pb loss and zircon dissolution in terms of alpha dose better allows the user to tailor their chemical abrasion approach to a specific zircon dataset. Fig. 16 plots alpha dose as a function of time for different U concentrations. As described above, different time intervals can be selected for damage accumulation depending on the calculation’s goal. This figure is a simple visual representation that can help a researcher determine whether or not a sample is likely to be affected by Pb loss. Chemical abrasion is a time-consuming method that is applied to the majority of ID-TIMS U-Pb datasets, but it may be unnecessary for low-alpha dose, inclusion-free zircon. Further, by estimating a sample’s “present day” alpha dose distribution, a user can better predict how readily a sample will dissolve. For example, if a sample has a lot of

Figure 15. Box plot diagram showing present day alpha dose distributions at each step of zircon dissolution. Data includes all A63, SAM-47 and KR18-04 leachates and residues. Alpha dose estimates reflect samples’ present day radiation damage. The gray dashed line highlights our best estimate for the minimum alpha dose required for Pb loss to occur. Each box shows the median value (black bar), the upper and lower quartiles (box), the minimum and maximum values (whiskers), and statistical outliers (plus marks).
accumulated radiation damage like SAM-47, leaching longer than a single 8-h step at 210 °C will likely leave little to no residue for isotopic analysis. Whereas, if a sample has a lower alpha dose like KR18-04, a longer 210 °C leach is unlikely to have a significant effect.

As highlighted in Fig. 16b, perhaps the most persistent challenge when it comes to tailoring chemical abrasion for a specific zircon dataset or even a specific zircon crystal is radionuclide zoning. The spatial distribution of radionuclides and the magnitude of intracrystalline variations in radiation damage strongly affect the mechanics of zircon dissolution (McKanna et al., 2023). Radionuclide zoning explains the inconsistent dissolution behavior evidenced in Fig. 5. For example, the percent zircon dissolved in each leaching step decreases from L1 to L3 for AS3 zircon, remains constant or decreases for SAM-47 zircon, and remains constant or increases for KR18-04 zircon. This non-pattern occurs because the percent zircon dissolved is not only a function of alpha dose, but also 1) the volumetric proportion of zircon with a given alpha dose, and 2) which portions of a crystal are in contact with HF at any given time during the leaching process. Building a comprehensive model for chemical abrasion will ultimately require both geochemical and textural inputs.
5. Conclusions

Single-crystal stepwise dissolution experiments performed at 180 °C and 210 °C provide new insights into the geochronological and geochemical effects of chemical abrasion on zircon datasets. Because of the insulating properties of the PTFE-lined pressure dissolution vessel, stepwise dissolution in three 4-h leaching steps is not equivalent to a 12-h single-step chemical abrasion, the method most commonly used by the zircon ID-TIMS U-Pb community. We estimate that our stepwise dissolution approach is roughly equivalent to 8-h single-step chemical abrasion. Stepwise dissolution at 180 °C produced over-dispersed U-Pb datasets affected by both residual Pb-loss and leaching-induced or leaching-exposed artefacts which present as reverse discordance. Without the context of the 210 °C results, reverse discordance in the 180 °C datasets could easily be mistaken for prolonged crystallization or inheritance and lead to spurious geological interpretations. Longer leaching durations are likely needed to produce robust geochronological datasets at 180 °C.

Stepwise dissolution at 210 °C outperformed the 180 °C experiments by all measures for the three zircon samples analyzed producing more reproducible, concordant results. Ultimately, how a zircon sample responds to any chemical abrasion protocol will be sample-dependent. However, our results suggest that 8-h single-step chemical abrasion at 210 °C may be effective at mitigating Pb loss and reverse discordance for a wide range of zircon samples. Further study of different zircon samples is needed. Our results, however, clearly demonstrate that leaching durations longer than an 8-h single step are required for chemical abrasion at 180 °C to be effective.

U concentration, Pb*/Pb, and LREE enrichment are useful tools for tracking the dissolution of inclusions and radiation-damaged or altered material during stepwise dissolution. These geochemical indicators, however, are not effective at identifying residual Pb loss in the zircon residues analyzed.

We attempted to constrain the relationship between Pb loss and radiation damage by calculating an alpha dose for each leachate based on its measured radionuclide concentration and an estimated damage accumulation interval informed by the sample’s geologic history. “Pb loss” alpha dose estimates suggest that Pb may mobilize within the zircon structure at alpha doses as low as $6 \times 10^{17} \alpha$/g. “Present day” alpha dose estimates indicate that many residues treated by stepwise dissolution at 180 °C have alpha doses above the $6 \times 10^{17} \alpha$/g threshold, and consequently, many 180 °C residues are affected by residual Pb loss. The majority of residues treated at 210 °C – and many L2 and L3 leachates – have “present day” alpha doses below this threshold. Grains expected to have accumulated alpha doses $< 6 \times 10^{17} \alpha$/g based on expected radionuclide concentrations and damage accumulation intervals are unlikely to be affected by Pb loss and may not require chemical abrasion. However, chemical abrasion may help improve the precision of U-Pb analyses even in low-damage grains by dissolving Pb-bearing inclusions. The effectiveness of any chemical abrasion protocol will ultimately be sample-dependent, since zircon dissolution depends not only on a grain’s bulk chemistry, but also the spatial distribution and magnitude of intracrystalline variations in radiation damage.
Data availability. All data presented are included in this paper or the Supplement.

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

Author contributions. AJM carried out the experiments and wrote the manuscript. All authors – AJM, DS, and BS – contributed to the experiment design and data reduction, interpretation, and presentation.

Competing interests. The contact author has declared that none of the authors has any competing interests.

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Review statement.

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