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1 **Metasomatic alteration of zircon at lower crustal P-T conditions utilizing alkali-**
2 **and F-bearing fluids: trace element incorporation, depletion, and resetting the**
3 **zircon geochronometer**

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19 **ABSTRACT**

20 Natural alteration of zircon takes place in melts or fluids either via dissolution coupled with

21 overgrowth or via a coupled dissolution-reprecipitation process. The latter results in the zircon

22 being partially or totally replaced by new, compositionally re-equilibrated zircon or a new mineral

23 phase or both. In this study, fragments (50 – 300 µm) from a large, inclusion-free, clear, 520 to 530

24 Ma euhedral zircon with light radiation damage from a nepheline syenite pegmatite, Seiland

25 Igneous Province, northern Norway, were experimentally reacted in 20 mg batches with 5 mg of

26 $\text{ThO}_2 + \text{ThSiO}_2 + \text{SiO}_2$ and a series of alkali-bearing fluids in sealed Pt capsules at 900 °C and 1000
27 MPa for 6 to 11 days in the piston cylinder press using a CaF_2 setup with a cylindrical graphite
28 oven. $\text{ThO}_2 + \text{ThSiO}_2 + \text{SiO}_2$ was present at the end of the experiment. In experiments involving
29 H_2O , $\text{H}_2\text{O} + \text{NaCl}$, $\text{H}_2\text{O} + \text{KCl}$, and 2N KOH, no reaction textures formed other than a slight
30 dissolution of the zircon grain fragments. Experiments involving 2N NaOH, $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$, and
31 $\text{NaF} + \text{H}_2\text{O}$ resulted in zircon reaction textures with varying degrees of intensity, which took the
32 form of partial replacement by compositionally modified zircon via a coupled dissolution-
33 reprecipitation process. In the $\text{NaF} + \text{H}_2\text{O}$ experiment some overgrowth also occurred. Altered
34 zircon is separated by sharp compositional boundaries from unaltered zircon. Secondary ion mass
35 spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-
36 MS) analysis indicates that, relative to the unaltered zircon, the altered zircon is strongly enriched in
37 Th, and heavily to moderately depleted in U and (Y+REE). In all the experiments, ^{206}Pb (3 to 5
38 ppm in unaltered zircon) is depleted in the altered zircon to below the SIMS detection limit and to at
39 or below the LA-ICP-MS detection limit. Hafnium and Ti concentrations in the altered zircon
40 retained the same approximate value (within error) as the original zircon. The results from these
41 experiments demonstrate that zircon can be compositionally modified by alkali-bearing and alkali-
42 F-bearing fluids via a coupled dissolution-reprecipitation process. Near to total loss of radiogenic
43 Pb via such processes under high-grade conditions resets the internal zircon geochronometer.
44 Although the end result is the same as with zircon overgrowth, i.e. the production of new generation
45 zircon at the time of a metasomatic/metasomatic event, such replacement processes can explain
46 incomplete isotopic ‘resetting’; inclusion production through unmixing of solid solutions in
47 metastable zircon compositions; and ‘ghost’ textures that preserve initial growth features but with
48 isotopic disturbance. Diagnostic replacement features produced in experiments, such as interface
49 geometries between altered and unaltered zircon, provide markers of the mechanism and aid in
50 zircon interpretation. A major implication from this study is that if zircon with low radiation
51 damage can be metasomatically altered under high-grade conditions this would have important

52 consequences with respect to zircons presumed role as an impregnable container for mineral
53 inclusions. Namely the mineral inclusions contained within zircon could also be altered, reset as a
54 geochronometer, or even replaced by another mineral.

55

56 **Keywords:** zircon, Th, U, Pb, REE, petrochronology, coupled dissolution-reprecipitation, alkali-
57 bearing fluids, experimental petrology

58

59 **1. Introduction**

60 In nature zircon is one of the principal accessory minerals used for the dating of geologic processes.
61 Its chemically and mineralogically robust nature allows it to survive its igneous origins and be re-
62 incorporated into either successive igneous protoliths, through melting of zircon-bearing source
63 rocks, or into sedimentary protoliths, as detritus. Zircon can also survive metamorphism,
64 metasomatism, and/or partial melting of the host rock. However, such survival is typically partial.
65 The cores of the zircon grain tend to preserve its origins whereas the rims and replacement textures
66 can record changes wrought during diagenesis, metasomatism, metamorphism, and re-incorporation
67 into a magma (e.g. [Harlov et al., 2022](#)).

68 Zircon is a principal host for U, Th, Hf, Y, and HREEs in various sedimentary,
69 metamorphic, and igneous rocks, and as such can contain a significant fraction of the whole rock
70 abundance of these elements depending on the presence or lack of other minerals such as monazite,
71 xenotime, allanite, apatite, and garnet. Despite its reputation as a refractory mineral, zircon can
72 interact with diverse fluids and/or melts under a range of crustal P-T conditions. For example, the
73 chemical stability of metamict zircon, radiation-damaged zircon, and synthetic (pristine) zircon with
74 respect to various fluids has been explored experimentally as well as speculated upon in a series of
75 studies of natural examples utilizing a variety of analytical techniques, as summarized in [Geisler et al. \(2007\)](#);
76 see also [Pidgeon et al. \(1966\)](#), [Rizvanova et al. \(2000\)](#), [Geisler et al. \(2002, 2003\)](#),
77 [Tomaschek \(2004, 2010\)](#), [Lenting et al. \(2010\)](#), and [Lewerentz et al. \(2019\)](#). Both experimentally

78 and in nature, compared to pristine zircon or zircon with a low degree of radiation damage,
79 metamict zircon and zircon with a high degree of radiation damage is highly susceptible to fluid-
80 assisted alteration down to relatively low P-T conditions (e.g., 175 °C and 250 bars) (Geisler et al.,
81 2007).

82 In addition to metamict and radiation damaged zircon, reaction textures, presumed to be
83 produced by fluids or melts, can also be seen in zircons with a low degree of radiation damage from
84 both igneous and high-grade metamorphic rocks under cathodoluminescence (CL) imaging.
85 Examples include zircons from a ca. 983 Ma anorthosite, Eastern Ghats Mobile Belt, India
86 (Chatterjee et al., 2008); orthopyroxene-bearing granulite-facies granitoids (charnockites) from the
87 Shevaroy Massif, southern India (Harlov et al., 2022); polymetamorphic migmatites, Valle
88 d'Arbedo, Switzerland (Vonlanthen et al., 2012); granulite-facies meta-granitoids, Queensland,
89 Australia (Hoskin and Black, 2000); and granitic gneisses in a contact aureole associated with the
90 Rogaland anorthite-norite intrusive complex, southern Norway (Möller et al., 2002). Here CL-
91 bright or CL-dark areas of apparent alteration overprint the original magmatic zoning (Fig. 1). The
92 irregular and/or lobate shapes of these altered areas, which extend inward into the zircon from the
93 grain rim, are difficult to ascribe to overgrowth of either the original zircon grain or partially
94 dissolved zircon grain, but rather resemble the partial replacement textures in monazite that have
95 been shown to be the result of fluid-induced coupled dissolution-reprecipitation processes as
96 opposed to overgrowth (Harlov et al., 2011).

97 In this study, fragments of an inclusion-free, faintly banded zircon (CL imaging) with light
98 radiation damage from the Seiland Igneous Province, northern Norway (Fig. 2) are used in a series
99 of piston cylinder metasomatism experiments involving both pure H₂O and a variety of alkali-
100 bearing solutions at 900 °C and 1000 MPa. A ThSiO₄ + ThO₂ + SiO₂ mix was added to all of the
101 experiments with the goal of seeing whether or not Th could be metasomatically incorporated into
102 the zircon crystal lattice replacing Zr utilizing reactive fluids. After quench and extraction, the
103 reacted zircon grain fragments are then mounted, polished to cross section, and evaluated using

104 high-contrast backscattered electron (BSE) imaging, CL imaging, transmission electron
105 microscopic (TEM) imaging, electron microprobe (EMP) analysis, sensitive high-resolution ion
106 microprobe (SHRIMP) analysis, and laser ablation inductively coupled plasma mass spectrometry
107 (LA-ICP-MS) analysis. The results from the experimentally reacted zircons are then compared with
108 metasomatically altered zircons from nature and the reaction textures are interpreted chemically,
109 physically, and from a petrochronological perspective.

110

111 **2. Experimental and Analytical Procedures**

112 *2.1 Experimental protocol*

113 Experiments were run at 900 °C and 1000 MPa using the two piston cylinder apparatus as described
114 by Johannes et al. (1971) and Johannes (1973) and are summarized in Table 1. The zircon chosen
115 for the experiments was obtained from the Natural History Museum at the University of Oslo, Oslo,
116 Norway. It consists of a large (2 cm), transparent, inclusion-free, light brownish, euhedral crystal
117 fragment from a nepheline syenite pegmatite located in the Seiland Magmatic Province, northern
118 Norway (523 ± 2 to 531 ± 2 Ma; Pedersen et al., 1989). A fragment of this crystal was broken up
119 into 50 to 300 μm size irregular grains. The transparent, inclusion-free, lightly brown-pink grain
120 fragments were washed in ethanol in an ultrasonic bath. Size sorting was not done. High contrast
121 BSE and CL imaging reveal that the grains are totally texture-free except for a very faint magmatic
122 zoning (Fig. 2).

123 Solids in the experimental charge consisted of 20 mg of zircon, 5 mg of a $\text{ThSiO}_4 + \text{ThO}_2 +$
124 SiO_2 mix, and 5 mg of fluid (Table 1). Reactants in the experimental charge included doubled
125 distilled nanopore H_2O , $\text{NaCl} + \text{H}_2\text{O}$, $\text{KCl} + \text{H}_2\text{O}$, 2N NaOH , 2N KOH , $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$, and NaF
126 $+ \text{H}_2\text{O}$. All chemicals used were spec pure to 99.99% or better. The experimental charge was placed
127 in a 3 mm wide, 1 cm long, tempered (1000 °C) Pt capsule, which was arc-welded shut and placed
128 vertically, four at a time, in a CaF_2 setup with a cylindrical graphite oven (Fig. 3). The capsules
129 were separated from each other by thin sheets of biotite. The presence of a graphite oven under the

130 airtight conditions of the experiment implies that the system/experiments, at least in theory, should
131 have been buffered to graphite-CO-CO₂ once the oven was heated to 900 °C. The thermocouple tip
132 was placed such that it reached halfway up alongside the Pt capsules (Fig. 3). The temperature
133 differential along the capsules was approximately 40 °C with either capsule end at 860 °C compared
134 to the sweet spot at the center of the capsules at the measured 900 °C. The pressure measured
135 during the experiment was corrected for friction due to the CaF₂ pressure medium. Non-isobaric
136 quench was achieved within 20 to 30 seconds by turning off the current.

137 After each experiment, the Pt capsule was cleaned, weighed, and punctured. The Pt capsules
138 were then dried at 105 °C for several hours, and weighed again to determine fluid loss. Due to the
139 very small amounts of fluid used in the experiments (5 mg), accurate trace element analysis of the
140 fluid was not possible. The reacted charge was then carefully removed from the Pt capsule with as
141 little mechanical disturbance as possible. The charge was then mounted and polished down to cross
142 section in an epoxy grain mount.

143

144 *2.2 Scanning electron microscope (SEM)*

145 Experimental charges were first evaluated using high contrast BSE and CL imaging on a JEOL
146 JSM-5900LV Scanning Electron Microscope (SEM) equipped with a Gatan MiniCL detector and
147 JEOL SmileStation stage automation and image-capture software at the National Institute for Polar
148 Research (NIPR), Tachikawa-shi, Tokyo-to, Japan.

149

150 *2.3 Electron probe microanalysis (EPMA)*

151 Electron probe microanalysis (EPMA) of zircon was carried out using the JEOL electron
152 hyperprobe with field emission gun at the GeoForschungsZentrum (GFZ) Potsdam using an
153 accelerating voltage of 15 kV and beam current of 15 nA. Individual spot analyses were made
154 using a focused electron beam with a diameter of 1 micron. Elements analyzed for in zircon
155 included P, Si, Ti, Zr, Hf, Th, U, Y, Gd, Tb, Dy, Ho, Er, Yb, Lu, Ca, Pb, and Na, with counting

156 times of 20 to 120 seconds depending on the relative amount of the element. Standards for the REE
157 were taken from synthetic REE phosphates prepared by [Jarosewich and Boatner \(1991\)](#). The
158 remaining standards were taken from both the CAMECA and Smithsonian standard sets
159 ([Jarosewich et al., 1980](#)). The full EMP analysis data set is contained in [Table S1](#).

160

161 *2.4 Sensitive high-resolution ion microprobe (SHRIMP)*

162 *2.4.1 Zircon U-Th-Pb measurement*

163 Mounted zircon grains were cleaned to eliminate surface contamination by common Pb, and coated
164 with 100 Angstroms of high-purity gold. Mounts were imaged at high resolution by CL and BSE
165 with a JEOL JSM-5900LV Scanning Electron Microscope (SEM) equipped with a Gatan MiniCL
166 detector and JEOL SmileStation stage automation and image-capture software, at NIPR,
167 Tachikawa-shi, Tokyo-to, Japan.

168 Spots were carefully chosen from SEM imaging for Th, U, and Pb analysis during multiple
169 sessions by a SHRIMP-II at NIPR, using a primary O₂-ion beam with a typical sample surface
170 current of 4 to 7 nA to produce 25 to 30 μm long, flat-floored oval pits. Secondary ionization was
171 measured on a single electron multiplier on mass stations 196 (Zr₂O) through to 254 (UO), with a
172 mass resolution of > 5000 for ²³⁸U¹⁶O and a sensitivity on ²⁰⁶Pb of 17 to 20 cps per ppm per nA of
173 primary current. Mass stations were measured through 5 to 6 cycles, with typical count times of 10
174 s per cycle for ²⁰⁴Pb, background (at 204.04 amu) and ²⁰⁶Pb, and 20s for ²⁰⁷Pb. Reduction of raw
175 data for standards and samples was performed using the SQUID v.1.12a ([Ludwig, 2001](#)), and
176 Isoplot v.3.71 ([Ludwig, 2003](#)) add-ins for Microsoft Excel 2003. Abundance of U was calibrated
177 against in-house reference zircon YBr157 (580 ppm U, as estimated by TIMS; provided by Allen
178 Kennedy of the John de Laeter Centre, Curtin University of Technology, Western Australia,
179 Australia). Corrections for common Pb on U/Pb values and ages were done with the common Pb
180 estimated from ²⁰⁴Pb counts and the [Stacey and Kramers \(1975\)](#) common Pb model for the
181 approximate U-Pb age for each analysis. (Pb/U)/(UO/U)² values were calibrated against

182 measurements on reference zircon TEMORA-2 (417 Ma; [Black et al., 2004](#)). Zircon SHRIMP
183 mean U-Th-Pb data for the reacted zircons listed in [Table 1](#) is contained in [Table 2](#). The full
184 SHRIMP analytical U-Th-Pb zircon data set is contained in [Table S2](#).

185

186 *2.4.2 Zircon Y+REE analysis*

187 Yttrium, REEs, and Hf contents were estimated for a subset of U-Th-Pb isotopic analyses by re-
188 analyzing the same spots ([Table 2](#)). Considering the small penetration depth (< 3 micron) of the
189 SHRIMP analytical spots, and the lack of strong chemical zoning in the starting material these
190 contents are considered to be equivalent to those in zircon analyzed for U-Th-Pb. Spot sizes and
191 mass resolutions were the same as for age analyses, with each station measured for 10 s through 6
192 cycles. To minimize the interference of LREE-MREE oxide peaks on MREE-HREE and Hf
193 measurements, energy filtering was applied to reduce ^{180}Hf to 10% of the unfiltered signal. This
194 reduces potential REEO⁺ interference to less than 1% of the unfiltered signals. Counts were
195 normalized against ^{92}Zr from the NIST610 standard glass, and compared periodically against
196 published values for zircon reference material 91500 ([Wiedenbeck et al., 2004](#); [Iizuka and Hirata,](#)
197 [2004](#)). All estimates were within 10% of published values. Zircon SHRIMP mean REE data for
198 the reacted zircons listed in [Table 1](#) is contained in [Table 2](#). The full SHRIMP analytical zircon
199 REE data set is contained in [Table S3](#). Chondrite-normalized REE plots of the SHRIMP REE data
200 are contained in [Figure S1](#).

201

202 *2.5 Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)*

203 Trace element abundances in zircon were measured at the Institute of Geological Sciences, Polish
204 Academy of Sciences, Kraków Research Centre, Krakow, Poland using an ArF excimer laser-
205 ablation system RESolution M50 by Resonetics coupled with a quadrupole ICP-MS XSeriesII by
206 FisherScientific. Ablation took place in a double volume Laurine technology cell in pure He (flow
207 rate of 0.9 L/min), for which the Ar nebuliser gas (flow rate of 0.5 – 0.55 L/min) was mixed

208 downstream from the sample cell. After passing through a signal-smoothing manifold, the analyte
209 was delivered to the ICP source. A small addition of nitrogen (0.005 – 0.008 L/min) was used to
210 enhance the sensitivity of the ICP-MS. The oxide to metal ratio $^{248}\text{ThO}/^{232}\text{Th}$ was kept below 0.5 %.
211 Analyses were performed using a rotating rectangular slit with a length of 50 μm and a width of 8
212 and 16 μm . An energy density of 4 to 5 J/cm^2 at a repetition rate of 5 Hz was applied. Twenty
213 seconds of gas blank was measured prior to each 30 s ablation, which was followed by 30 s washout
214 time. Sample runs were bracketed by measurements of the NIST 612 glass (Jochum et al., 2011).
215 The zircon reference material 91500 (Wiedenbeck et al., 2004; Iizuka and Hirata, 2004) was
216 frequently measured as a secondary standard along with the unknowns. The ZrO_2 content from
217 previously acquired electron microprobe analyses of the Seiland zircon ($\text{ZrO}_2 = 66.65$; $\text{SiO}_2 =$
218 32.20 ; $\text{HfO}_2 = 0.70$) was used as an internal standard (Table S1). Data processing was performed
219 using the Glitter 4.0 software from Macquarie University, Australia (Griffin et al., 2008). Zircon
220 LA-ICP-MS mean U-Th-Pb and REE analyses for the reacted zircons listed in Table 1 is contained
221 in Table 3. The full LA-ICP-MS analytical U-Th-Pb and REE zircon data set is contained in Table
222 S4.

223

224 2.6 Transmission electron microscopy (TEM)

225 Reacted zircon grains, suitable for TEM investigation, were first selected using BSE and SEM
226 images. Sampling was accomplished by using focused ion beam (FIB) milling (Wirth, 2004, 2009).
227 FIB preparation was conducted under ultra-high vacuum conditions in an oil-free vacuum system
228 using a FEI FIB200 instrument at the GeoForschungsZentrum Potsdam. TEM-ready foils of
229 approximately $15 \times 8 \times 0.15 \mu\text{m}$ representing cross sections perpendicular to and across the reaction
230 front (separating the altered and unaltered zircon) were sputtered directly from the zircon grain in
231 the epoxy grain mount using a 30 kV Ga-ion beam. The TEM foil was protected from sputtering by
232 the Ga-ion beam by a 1 μm thick, Pt layer deposited using a high-purity organic Pt gas ($\text{C}_9\text{H}_{16}\text{Pt}$,
233 99.9 %), which decomposes under the Ga-ion beam. Once cut, the TEM foils were placed on a

234 perforated carbon film, which was placed on a copper grid. Carbon coating to prevent charging in
235 the TEM was not applied.

236 TEM on the zircon foils was carried out in a TECNAI F20 XTwin instrument operated at
237 200 kV and equipped with a FEG electron source. The TEM is equipped with a Gatan imaging filter
238 (GIF Tridiem), a Fishione high-angle annular dark field detector (HAADF), and an EDAX X-ray
239 analyzer with an ultrathin window. TEM bright field images (HREM) were acquired as energy-
240 filtered images applying a 10 eV window to the zero-loss peak.

241

242 3. Results

243 All experiments were run at 900 °C and 1000 MPa over periods of 144 to 192 hours (6 – 8 days).
244 Whereas, the zircon grain fragments were a light pinkish brown before the experiment, at quench
245 the reacted zircon grain fragments were colorless and transparent, which suggests that any radiation
246 damage in the zircon had been healed. This is supported by a variety of annealing experiments at
247 comparable or lower temperatures and/or pressures (cf. [Nasdala et al., 2001, 2002](#); [Montario et al.,](#)
248 [2008](#); [Ginster et al., 2019](#); [Herrmann et al., 2021](#); [Ende et al., 2021](#); [Härtel et al., 2022](#)). Of the
249 eight experimental runs reported here and listed in [Table 1](#), in those experiments involving pure
250 H₂O, NaCl + H₂O, KCl + H₂O, and 2N KOH, the zircon did not react with the fluid, other than
251 showing a little dissolution along the grain fragment edge. In contrast, zircon in experiments
252 involving Na₂Si₂O₅ + H₂O ([Fig. 4](#)), 2N NaOH ([Fig. 5](#)), and NaF + H₂O (2 experiments; [Table 1](#),
253 [Fig. 6](#)) developed reaction textures under CL imaging to varying degrees. In each of these
254 experiments, due to the relatively large amount of the ThSiO₄ + ThO₂ + SiO₂ mix added ([Table 1](#)),
255 all three phases persisted to the end of the experiment and were visible in the reacted charge.

256 While not obvious in high contrast BSE images, under CL imaging the altered areas in these
257 four experimental runs appear lighter (CL-light) than the unaltered areas (CL-dark). CL-light areas
258 are separated from CL-dark areas by sharp boundaries. In the experiments involving Na₂Si₂O₅ +
259 H₂O (ZF-5; [Fig. 4](#)) and 2N NaOH (ZF-9; [Fig. 5](#)), the reaction textures are considerably less

260 extensive than in runs involving NaF + H₂O (ZF-16, ZF-40; Fig. 6). In the case of run ZF-9, only
261 two zircon fragments with a reaction texture were found amongst 30 grain fragments exposed in the
262 polished mount, which makes up about half of the total experimental product. In the case of ZF-5,
263 about half of the grains in the grain mount had reaction textures. In contrast, in the NaF + H₂O
264 experiment (ZF-16, ZF-40), all the zircon grains developed reaction textures ranging from slight to
265 extensive. In runs ZF-5 and ZF-9, a lack of crystal face formation and the preservation of irregular
266 grain fragment boundaries would suggest that the reaction textures are due to the replacement of the
267 original zircon by altered zircon. In runs ZF-16 and ZF-40, the development of new crystal faces as
268 a product of overgrowth is evident on some of the grains (e.g. Fig. 6a). However, reaction textures
269 have also developed that are lobate and convex inwards, away from edges of zircon grain regardless
270 of whether they have overgrowths or not (e.g. Figs. 6a,c,d). A second type of reaction texture occurs
271 along cracks and possible cleavage planes inside of the zircon grains, which extends outwards from
272 the crack into the zircon (Figs. 6e,f). There is a general lack of crystal face formation despite the
273 fact that, due to the high ratio of fluid to zircon grain fragments by mass (Table 1), each individual
274 grain was totally surrounded by fluid during the experiment and, hence, not in direct contact with
275 any of the other grains unless it was overgrown by a neighboring grain (e.g. Fig. 6a).

276 TEM bright field images of foils sampled across the reaction front, as defined by CL
277 imagery, in zircon grains from runs ZF-5 (Figs. 4a,b), ZF-9 (Figs. 5a,b), and ZF-16 (Figs. 6a,b),
278 show no differences in texture on the sub-micron scale between the altered and unaltered areas in
279 the zircon, no mineral inclusions, nor any evidence of a boundary or reaction front between the
280 unaltered and altered zircon.

281 In general, both SHRIMP and LA-ICP-MS spot analyses indicate that the CL-light altered
282 areas are moderately to heavily depleted in U and Y + HREE and enriched in Th relative to the CL-
283 dark unaltered areas of the zircon grains, which retain the trace element abundances of the original
284 zircon grain (Tables 2 and 3; Fig. 7; Fig. S1; Tables S2, S3, and S4). The low Th and U contents in
285 the original Seiland zircon would imply that the amount of radiation damage to the crystallographic

286 lattice should be relatively minor after some 520 to 530 Ma (Table 3; Tables S2 and S4). One
287 exception was ZF-5 ($\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$). Here Gd showed no depletion within the altered areas (Fig.
288 7a, Fig. S1; Tables 3 and 4). In contrast, altered areas in all the experiments are heavily depleted in
289 Pb to or below the detection limit in both the SHRIMP and LA-ICP-MS analytical data, whereas
290 Hf and Ti show little difference in their abundances (within analytical error) between the altered
291 and unaltered areas in the zircon (Tables 2 and 3; Tables S3 and S4).

292

293 4. Discussion

294 4.1 Formation of reaction textures in zircon

295 A series of previous studies have focused on the experimental alteration of zircon, though most of
296 these have involved metamict or zircon with a high degree of radiation damage under temperatures
297 and pressures lower than the ones considered in this study (Pidgeon et al., 1966; Geisler et al.,
298 2001a,b, 2002, 2003, 2004, 2007; Rizvanova et al., 2000, 2007; Lenting et al., 2010; Lewerentz et
299 al., 2019). In general, these experiments have involved a variety of fluids (H_2O , HCl , $\text{Ca}(\text{OH})_2 +$
300 H_2O , $\text{CaCl}_2 + \text{H}_2\text{O}$, and $\text{AlCl}_3 + \text{H}_2\text{O}$) over a broad range of temperatures (200 – 700 °C) and
301 pressures (100 – 500 MPa). The zircon in these experiments generally shows a high degree of
302 reactivity during the experiment due to the large amount of chemical potential energy stored in the
303 disordered, amorphous areas in the zircon or in the radiation-damaged zircon crystallographic
304 lattice (see discussion in Geisler et al., 2007). Other experiments at high P-T have focused on
305 annealing of zircon in restricted chemical systems (Morales et al., 2022), the relationship between
306 zircon and baddeleyite as a function of the Ca and Si activity in fluids (Lewerentz et al., 2019), or
307 on the dissolution of zircon in a variety of silicate melts (Borisov and Aranovich, 2019; Baker et al.,
308 2002; Schmidt et al., 2013) and in a series of fluids (Schmidt et al., 2006; Newton et al., 2010;
309 Ayers et al., 2012; Wilke et al., 2012; Bernini et al., 2013; Ayers and Peters, 2018).

310 In this study, utilizing pressures and temperatures that are normally characteristic of the
311 lower crust/lithospheric mantle, the goal was to partially alter a natural zircon with a low degree of

312 radiation damage metasomatically while at the same time incorporating Th in the altered areas. The
313 reaction textures produced in the experimentally metasomatized zircon show a sharp contrast, both
314 texturally and compositionally (trace elements), between the altered (CL-bright) and unaltered (CL-
315 dark) zircon (Figs. 4, 5, and 6). The lobate intergrowths of altered zircon into the unaltered zircon as
316 seen in Figures 6a, 6c, and 6d can be argued as not being a product of overgrowth, but rather a
317 product of mineral replacement (see comments above). Similar textures, both lobate and otherwise,
318 have been recognized in metasomatically altered monazite (cf. Harlov et al., 2011), xenotime
319 (Harlov and Wirth, 2012), and apatite (Harlov et al., 2002, 2003, 2005) both experimentally and
320 from nature, and have been interpreted as partial replacement textures due to a coupled dissolution-
321 reprecipitation process (Putnis, 2002, 2009; Putnis et al., 2005; Putnis and Putnis, 2007; Putnis and
322 Austrheim, 2010, 2013; Aftree-Williams et al., 2015). This is especially obvious in Figures 4c, 6e,
323 and 6f where alteration occurs along cracks and possible cleavage planes within the zircon grains as
324 partial replacement textures extending into the zircon, similar to that seen in partial replacement
325 textures involving experimental replacement of monazite by huttonite (ThSiO_4) (cf. Harlov et al.,
326 2007, their figure 2h). During coupled dissolution-reprecipitation, the original zircon is dissolved in
327 the presence of these alkali-bearing fluids while simultaneously being replaced by new zircon that
328 compositionally is in thermodynamic equilibration with the fluid chemistry under the particular P-T
329 conditions of the system. During this process, the new zircon uses the original zircon as a
330 crystallographic template for purposes of nucleation and subsequent growth/replacement. In
331 essence coupled dissolution-reprecipitation is the basis for mineral pseudomorphism, and is a
332 commonly observed process in nature for many minerals. It is also the principal process by which
333 fossilization of organic material, such as bone and wood, occurs.

334 In minerals, the process of coupled dissolution-reprecipitation has been shown to occur
335 along a very thin (10 nm wide or less) fluid-filled reaction front between the original dissolving
336 mineral and the newly growing mineral (Putnis, 2002, 2009; Aftree-Williams et al., 2015). This
337 reaction front is physically connected to the fluid surrounding the mineral grain via an actively

338 evolving, non-static, interconnected porosity prevalent throughout the newly grown mineral phase.
339 This allows for active fluid-aided mass transfer between the fluid along the reaction front and the
340 fluid surrounding the grain during the replacement process. Porosity formation can result from a
341 variety of causes such as differences in the molar volume between the original and replacement
342 phase or differences in solubility between the two phases (Putnis, 2009). Once this replacement
343 process stops due to changing P-T-X conditions in an open fluid-mineral system or, in the case of a
344 closed system, due to limited amounts of the reactive fluid (e.g. the experiments in this study), the
345 reaction front will cease to advance and the altered areas of the mineral will begin to recrystallize
346 such that the original interconnected porosity will evolve into isolated nano- and micron-size fluid
347 inclusions often along with mineral inclusions, both those genetically derived from the host mineral
348 and those originating from minerals outside of the host mineral (Putnis, 2002, 2009; Harlov et al.,
349 2005, 2011; Harlov and Wirth, 2012; Harlov et al., 2016).

350 As can be seen in Figures 4b, 5c, and 6b, for each of the alkali-bearing fluid-zircon
351 metasomatism experiments, neither a remnant porosity nor mineral inclusions remain in the altered
352 areas of the zircon under CL imaging nor in TEM foils taken perpendicular to the reaction front,
353 which includes both altered zircon and unaltered zircon. Here the reaction front, so clearly visible
354 under CL imaging, is not visible in the TEM foils, i.e. the altered zircon appears texturally
355 indistinguishable from the unaltered zircon (cf. Figs. 4b, 5b, and 6b). This is not what is seen in the
356 reaction textures and accompanying TEM foils taken across reaction fronts in experimentally
357 metasomatized fluorapatite (Harlov et al., 2005), monazite (Harlov et al., 2011), and xenotime
358 (Harlov et al., 2012) from experiments done under the same approximate P-T conditions. It is also
359 not seen in experimentally metasomatized metamict or radiation-damaged zircon (Geisler et al.,
360 2007), nor in metamict or radiation-damaged zircon from nature (Geisler et al., 2002, 2003, 2007).
361 In all of these cases the metasomatically altered areas are characterized by numerous fluid
362 inclusions and mineral inclusions, such as ThSiO_4 , USiO_4 , ThO_2 , UO_2 , ZrO_2 , xenotime, feldspar,
363 quartz, etc..

364 One explanation for this striking difference in zircon textures is that the alteration textures
365 seen in [Figures 4, 5, and 6](#) appear to be specific to zircon with low amounts of radiation damage,
366 characteristic of the 520 to 530 Ma Seiland zircon, the high P-T conditions of the experiments, and
367 the reactivity of the alkali-bearing and F-bearing fluid chemistry of the system. Total elimination of
368 the porosity during the course of the experiment, after growth of the altered area had stopped, could
369 be due to a rapid coarsening effect, which would be consistent with attaining textural equilibration
370 driven by reduction in the surface area as defined by the interior surface area of the pores. Hence,
371 the original porosity, which was transient to begin with, would have totally disappeared as textural
372 equilibration was achieved, and in this particular case achieved rather quickly during the course of
373 the experiment. Similar phenomena have been observed in the KBr-KCl-H₂O replacement
374 experiments of [Putnis et al. \(2005\)](#). Rapid disappearance of the porosity would have also
375 discouraged mineral inclusion formation since the pores normally act as nucleation sites for
376 inclusions in the altered/reacted areas (see discussion in [Harlov et al., 2005](#)). What overgrowth that
377 did occur was also totally recrystallized as per the above mechanism eliminating any porosity that
378 might have formed during crystal growth outwards. The sharp compositional boundary seen
379 between the altered zircon and unaltered zircon under CL imaging would indicate that element
380 diffusion across the boundary was negligible at 900 °C and 1000 MPa over the course of the
381 experiment. This observation agrees with the U, Th, and Hf diffusion experiments of [Cherniak et al.](#)
382 [\(1997a\)](#) and REE diffusion experiments of [Cherniak et al. \(1997b\)](#), both of which indicate very
383 slow diffusion rates at high temperatures for these elements in zircon.

384 Comparison of the reaction textures resulting from the experiments ([Figs. 4 – 6](#)) with similar
385 textures in natural zircons in [Figure 1](#) support the proposition that high-grade, high pH, alkali-
386 bearing/F-bearing fluids could have been responsible for them. The examples provided in [Figure 1](#)
387 are found in both metamorphic and igneous rocks in a fluid-rich environment with broadly granitoid
388 and hence alkali-rich compositions or else are associated with such rocks. These observations are
389 supported by [Aranovich et al. \(2017\)](#) who make a strong case for alkali-bearing fluids causing

390 partial to total alteration of zircon grains in gabbroids and plagiogranites from the Mid-Atlantic
 391 Ridge. In another example, zircons from a leucocratic granite of the Weondong region of South
 392 Korea show four types of partial metasomatic alteration, which the authors attribute to the action of
 393 F-rich fluids during post-magmatic alteration (Park et al., 2016; their figures 3 and 5). The textures
 394 of these metasomatised zircon grains broadly mimic some of the reaction textures obtained in the
 395 NaF-fluid experiments (Fig. 6).

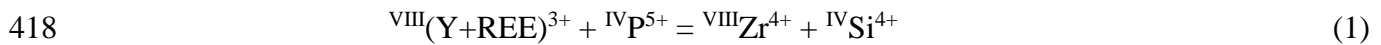
396

397 *4.2 Alteration of the zircon trace element chemistry*

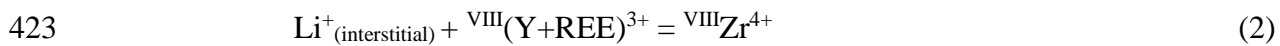
398 Relative to the original unaltered Seiland zircon, the altered areas in the zircon are significantly
 399 enriched in Th, significantly depleted in U, moderately to strongly depleted in Y + HREE, and
 400 nearly to totally depleted in Pb to within the detection limit of both SIMS and LA-ICP-MS. In
 401 contrast, there is little or no change in the Hf or Ti content within the measurement precision
 402 (Tables 2 and 3; Fig. 7). These abundances contrast with the fluids used in the experiments, which
 403 were saturated in Th + Si, and totally devoid of U, Pb, Y+REE, Ti, and Hf (Table 1).

404 In the zircon crystallographic lattice, U^{4+} , Th^{4+} , and Hf^{4+} are conventionally considered to
 405 substitute for Zr^{4+} on the 8-fold Zr site (Finch and Hanchar, 2003; Hoskin and Schaltegger, 2003).
 406 While, Th and U have a limited solid solution with zircon as tetragonal thorite ($ThSiO_4$), and
 407 tetragonal coffinite ($USiO_4$), respectively (Ushakov et al., 1999), Hf has a complete solid solution
 408 with zircon as tetragonal hafnon ($HfSiO_4$) (Speer and Cooper, 1982). This is due to the fact that on
 409 the 8-fold Zr site Hf^{4+} (0.83 Å) can completely substitute for Zr^{4+} (0.84 Å) (effective ionic radii;
 410 Shannon, 1976; Harley and Kelly, 2007). In contrast, the relatively larger 8-fold ionic radii of U^{4+}
 411 (0.86 Å) and Th^{4+} (1.05 Å) (Shannon, 1976; Harley and Kelly, 2007), compared to 8-fold Zr^{4+} (0.84
 412 Å), would explain their relatively limited solid solution in zircon. It would also explain as to why
 413 U^{4+} was so easily removed and Th^{4+} only incorporated in limited amounts during each of the
 414 metasomatism experiments despite the fluid being supersaturated with Th (Table 3; Tables S2 and
 415 S4).

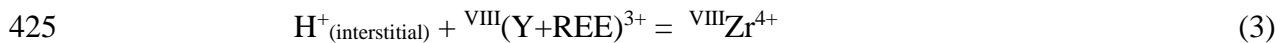
416 Yttrium and the REE are generally thought to be incorporated into zircon via a xenotime-
417 type coupled substitution or:



419 (Finch and Hanchar, 2003; Hoskin and Schaltegger, 2003) with (Y+REE)³⁺ going on the 8-fold Zr
420 site and P⁵⁺ (0.17 Å) on the 4-fold Si⁴⁺ (0.26 Å) site (effective ionic radii; Shannon, 1976). Other
421 possible coupled substitutions for (Y+REE) in zircon which have been described in the literature
422 include:



424 (Finch et al., 2001; Wang and Trail, 2022), and:



426 (Trail et al., 2016) where Li and H substitute on interstitial sites in the zircon structure (Finch and
427 Hanchar, 2003). In all of these cases, 8-fold (Y + HREE)³⁺ (1.019, 1.079 – 0.977 Å) are strongly
428 preferred over the 8-fold LREE³⁺ (1.160 – 1.109 Å) due to their better fit on the 8-fold Zr (0.84 Å)
429 site (Hoskin and Schaltegger, 2003; Shannon, 1976).

430 From the LA-ICP-MS data in Table S4, (Y+HREE)³⁺ plus the approximate value for P⁵⁺
431 when plotted vs. Zr⁴⁺ + Si⁴⁺ for both unaltered and altered zircon in each of the experiments show
432 an approximate linear relationship with a positive shallow slope. This indicates that an additional
433 coupled substitution mechanism must have been responsible for Y+HREE incorporation in both the
434 altered and unaltered zircon. These additional mechanisms could have included coupled
435 substitutions (2) and/or (3), each to varying degrees, though this must be treated as speculation
436 since neither Li nor H⁺ were measured.

437 The observation that Ti was not depleted in the altered areas (Table 3) is more curious
438 considering that the alkali-bearing solutions in each of the experiments were not buffered by rutile,
439 i.e. TiO₂, or some other Ti-rich mineral such as ilmenite or titanite; though each of the solutions was
440 buffered to an SiO₂ activity of 1 due to the presence of free SiO₂ in the capsule at the end of the
441 experiment. In zircon, relatively limited amounts of Ti, as ^{IV}Ti⁴⁺ (0.42 Å) are believed to substitute

442 for ${}^{\text{IV}}\text{Si}^{4+}$ (0.26 Å) (effective ionic radii; [Shannon, 1976](#)) on the tetrahedral site with the amount of
 443 Ti present increasing as a function of increasing temperature for a system nominally buffered at a
 444 constant TiO_2 activity ([Watson and Harrison, 2005](#); [Watson et al., 2006](#); [Ferry and Watson, 2007](#);
 445 [Harley and Kelly, 2007](#); [Tailby et al., 2011](#)). The fact that Ti remained in the altered areas of the
 446 zircon at 900 °C and 1000 MPa in a Ti-free system ([Table 1](#)), as opposed to selectively partitioning
 447 into the solution, would suggest that for minor amounts of Ti, the partitioning coefficients for NaF-,
 448 NaOH-, and $\text{Na}_2\text{Si}_2\text{O}_5$ -bearing solutions apparently favor Ti remaining on the tetrahedral site in
 449 zircon at the P-T of the experiments. Such an observation could have implications for the Ti-in-
 450 zircon geothermometer in alkali fluid-bearing systems whether they are buffered with respect to
 451 TiO_2 or not (cf. [Ferry and Watson, 2007](#)).

452 Lead appears to be broadly incompatible in the zircon structure with respect to substitution
 453 on either the tetrahedral Si site or the octahedral Zr site due to its much larger size, i.e. ${}^{\text{IV}}\text{Pb}^{4+}$ (0.65
 454 Å) vs. ${}^{\text{IV}}\text{Si}^{4+}$ (0.26 Å) and ${}^{\text{VIII}}\text{Pb}^{4+}$ (0.94 Å) vs. ${}^{\text{VIII}}\text{Zr}^{4+}$ (0.84 Å) (effective ionic radii; [Shannon,](#)
 455 [1976](#); [Watson et al., 1997](#); [Mezger and Krogstad, 1997](#); [Geisler et al., 2003](#); [Utsunomiya et al.,](#)
 456 [2004](#); [Kogawa et al., 2012](#)). This assumes that Pb would occur as Pb^{4+} in the zircon structure,
 457 which would seem highly unlikely assuming that the experiments were presumably buffered to
 458 graphite- CO_2 (see above). If Pb in the original, unaltered zircon existed only as Pb^{2+} , in addition to
 459 there being a question of charge balance, the misfit of Pb on both the Si and Zr sites becomes even
 460 greater, i.e. 0.98 vs. 0.26 Å and 1.29 vs. 0.84 Å, respectively. This would imply that the only Pb
 461 present in the original zircon should be from the radioactive decay of U, Th, and their short-lived
 462 daughter isotopes in the form of small accumulations in amorphous radiation-damaged domains
 463 and/or along cleavage planes, or as nano-inclusions in annealed zircon ([Geisler et al., 2003](#); [Nasdala](#)
 464 [et al., 2005](#); [Kogawa et al., 2012](#); [Seydoux-Guillaume et al., 2015](#); [Valley et al., 2014, 2015](#); [Lyon](#)
 465 [et al., 2019](#)). A similar case has been made for Pb accumulation in monazite ([Fougerouse et al.,](#)
 466 [2018](#)). The fact that Pb is so readily removed from the altered areas of the zircon to the extent of
 467 being at or below the detection limits of both LA-ICP-MS and SIMS implies that Pb, at least in

468 trace amounts, is apparently highly soluble in NaF-, NaOH-, and Na₂Si₂O₅-bearing fluids at 900 °C
469 and 1000 MPa most likely due to complexing with either OH⁻ or F⁻ in solution (Bottari and
470 Ciavatta, 1965; Perera et al., 2001).

471 The addition of Th, loss of U, and near to total loss of Pb in the altered areas of the zircon
472 would imply that the U-Th-Pb geochronometer has been near to totally reset compared to the
473 unaltered areas. This obviously has major implications with regard to zircon geochronology.
474 Namely that the zircon U-Th-Pb geochronometer can be metasomatically reset, which is an idea
475 that has long been speculated upon in the literature (Hoskin and Schaltegger, 2003; Hoskin, 2005;
476 Geisler et al., 2007; Soman et al., 2010; Van Lankvelt et al., 2016; Peterman et al., 2016; Aranovich
477 et al., 2017; Chen and Zhou, 2017; Wang et al., 2018; Zi et al., 2022). Natural resetting of this
478 geochronometer via Pb diffusion in zircon under fluid-absent conditions has been demonstrated to
479 be a very slow, almost negligible process even if the zircon experiences relatively high temperatures
480 (> 900 °C) for at least 1 Myr (Möller et al., 2002; see also Cherniak and Watson, 2000). In the
481 experiments from this study, the geochronometer was reset due to alkali-bearing high pH or alkali-
482 fluoride fluids at 900 °C and 1000 MPa over a period of days. Such fluids might explain the zircon
483 alteration textures seen in Figure 1 since each of these examples occur in granitoid rocks rich in
484 alkali-bearing feldspars, which have experienced metasomatism/metamorphism under high-grade
485 conditions. In each of these cases, the CL-bright metasomatized areas tend to be younger by some
486 millions to 10's of millions of years than the CL-dark zircon cores, which the authors generally tend
487 to attribute to metamorphic/metasomatic processes. Similar conclusions were reached by
488 Lewerentz et al. (2019) in experiments (600 – 900 °C; 600 – 1000 MPa) involving the partial
489 alteration of a natural zircon in CaCl₂- and Ca(OH)₂-bearing fluids to baddeleyite. While the newly
490 formed baddeleyite and altered areas in the zircon contained U, Th, and Y + REE derived from the
491 zircon, Pb in both the baddeleyite and the altered areas of the zircon was below the detection limit
492 of the SIMS.

493 The depletion of the Y + HREE in the altered areas of the zircon (Fig. 7) is due in part to
494 the fact that the alkali-bearing fluids used in these experiments contained negligible amounts of
495 REE. This apparently allowed for a fraction of the Y+HREE to be partitioned into the fluid where
496 they presumably complexed with OH⁻ (ZF-5 and ZF-9) (Haas et al., 1995; Wood et al., 2002;
497 Poutier et al., 2010; Perry and Gysi, 2018) and/or with F⁻ (ZF-16 and ZF-40) (Haas et al., 1995;
498 Tropper et al., 2011, 2013; Mair et al., 2017). Depletion or enrichment of REE in zircon is a
499 commonly observed phenomena in granitoid rocks and generally presumed due to metasomatically
500 induced alteration via fluids and/or melts. Examples include zircons with metasomatically altered
501 areas depleted in REE from fluid-induced charnockite patches in granitoid rocks from Kottavattom,
502 Trivandrum Block, southern India (Taylor et al., 2014); metasomatically altered areas depleted in
503 REE in metamorphosed zircons from the leucocratic portion of a migmatite, Ticino, Switzerland
504 (Vonlanthen et al., 2012); and zircons from high grade metagranitoids, Queensland, Australia where
505 the metasomatically altered areas are depleted in REE (Hoskin and Black, 2000).

506

507 **5. Summary and implications**

508 In this study it has been demonstrated in a series of experiments that natural zircon with relatively
509 small amounts of radiation damage can be metasomatically altered using alkali- and F-bearing
510 solutions under the high grade P-T conditions commonly found in the lower crust. This involved the
511 incorporation of Th and the removal of U and REE, and the near to total removal of Pb to below
512 LA-ICP-MS and SIMS detection limits in the altered areas, which implies a basic resetting of the
513 U-Th-Pb geochronometer. If this is also the case for zircons in nature, then this would imply that
514 similar textures, as illustrated in Figure 1, could be metasomatically induced and thus could
515 potentially be used to date metasomatic events.

516 A second major implication from these experiments is that if zircon with low radiation
517 damage can be metasomatically altered this would have important consequences with respect to
518 zircons presumed role as an impregnable container for mineral inclusions. Namely the mineral

519 inclusions contained within the zircon could also be altered, reset as a geochronometer, or even
520 replaced by another mineral. This has important consequences especially with respect to how the
521 mineral inclusions within the Hadean detrital zircons from Jack Hills, Australia have been utilized
522 in an attempt to discern the geochemical and physical conditions on the very early Earth during the
523 Hadean period (4.0 – 4.54 Ga) ([Mojzsis et al., 2001](#); [Wilde et al., 2001](#); [Valley et al., 2002, 2014](#)).
524 The fact that these inclusions have apparently experienced varying degrees of alteration has been
525 amply demonstrated by [Rasmussen et al. \(2011\)](#) who, in a study of monazite and xenotime
526 inclusions in the 4.35 to 3.35 Ga Jack Hills detrital zircons, concluded that these inclusions formed
527 as the result of a metamorphic event at either 2.68 or 0.8 Ga and at monazite-xenotime temperatures
528 ([Gratz and Heinrich, 1997](#)) of around 420 to 475 °C. The Ti content of the quartz inclusions in these
529 same zircons gave temperatures of 350 to 490 °C using the geothermometer of [Thomas et al.](#)
530 [\(2010\)](#). They also noted that most of the mineral inclusions have the same composition and
531 abundances as the minerals in the original metamorphic matrix in which the zircons were found.
532 This is consistent with the idea that these inclusions, which include K-feldspar, albite, muscovite,
533 and biotite, formed during metamorphism due perhaps to the replacement of what could have been
534 originally apatite inclusions, which are one of the more common types of mineral inclusions in
535 zircon and generally not observed in Jack Hills zircons. If this replacement of mineral inclusions
536 did occur, it would probably have occurred via a coupled dissolution-precipitation process as
537 outlined by the experiments in this study. These observations are backed by a CO₂ fluid inclusion
538 study of the Jack Hills zircons by [Menneken et al. \(2017\)](#). Here the formation of these CO₂
539 inclusions appears to be related to a later metamorphic event as opposed to the primary igneous
540 event presumed responsible for the genesis of the zircons.

541 Mineral inclusion formation in zircon grain interiors via a fluid-aided coupled dissolution-
542 reprecipitation process are not limited to the Jack Hills zircons. For example, [Troch et al. \(2018\)](#)
543 documented the fluid-aided formation, via coupled dissolution-precipitation, of U-Th-REE phases
544 as mineral inclusions in trace element-rich zircons from the Island Park-Mount Jackson rhyolite,

545 Yellowstone volcanic field, Wyoming, USA. Similar conclusions have also been reached for ultra-
546 high pressure mineral inclusions, such as coesite and jadeite, in zircon from a jadeite quartzite,
547 Dabie orogen, central China ([Gao et al., 2015](#)). While the zircons here are presumed to have a
548 detrital, igneous mid-crustal origin, the inclusions could only have formed during a fluid-rich event,
549 perhaps as a result of coupled dissolution-reprecipitation, under the ultra-high pressure
550 metamorphic conditions present during the continental subduction conditions experienced by the
551 jadeite quartzite during the Dabie orogeny.

552 Similar conclusions have been reached for entirely different mineral systems. For example,
553 [Krause et al. \(2013\)](#) documented metasomatically altered apatite inclusions in clinopyroxene from a
554 nepheline-bearing clinopyroxenite located in the Uralian-Alaskan-type complexes of Kytlym and
555 Nizhny Tagil, Ural Mountains, Russian Federation. Here the clinopyroxene experienced partial
556 metasomatic alteration via coupled dissolution-reprecipitation by a CaCl_2 -enriched saline fluid,
557 which also altered the apatite inclusions in these areas from fluor-chlorapatite to chlor-fluorapatite
558 giving them a composition similar to the apatites in the surrounding mineral matrix. In those areas
559 of the clinopyroxene not metasomatically altered, the apatites retained their original fluor-
560 chlorapatite composition. In another example, where apatite is the host mineral, the formation of
561 magnetite and quartz inclusions in metasomatically altered areas of fluorapatite from the Pea Ridge
562 iron oxide-apatite ore body is attributed to fluid-aided mass transfer of Fe and Si into the
563 fluorapatite from magnetite and quartz in the surrounding mineral matrix, again during a process of
564 coupled dissolution-reprecipitation ([Harlov et al., 2016](#)).

565 In all of these cases, the key point here is that the chemistry of a fluid encountered by
566 zircon, or any other mineral, will dictate whether or not the mineral will experience alteration, and
567 whether this alteration occurs by simple partial dissolution, overgrowth, or metasomatic alteration,
568 either partial or total, via a coupled dissolution-reprecipitation process. This last process can also
569 result in the total replacement of one mineral phase by another mineral phase as proposed for the
570 inclusions in the zircon, clinopyroxene, or fluorapatite as discussed above. The pressure and

571 temperature under which such a process will or could occur is of less importance since nature has
572 time on its side as opposed to the very finite lifetime of laboratory experiments (see discussion in
573 [Harlov et al., 2002, 2003, 2005](#)).

574 The basic conclusion here is that if the typical sort of zircon commonly found in crustal
575 rocks, with radiation damage ranging from light to metamict, encounters a chemically reactive fluid,
576 such as the alkali-bearing and F-bearing fluids used in these experiments, it could be partially to
577 totally altered chemically with respect to its trace elements including U, Th, Pb, and the Y+REE.
578 This could result in the U-Th-Pb geochronometer in the altered areas being reset if all the Pb is
579 removed thus allowing for the metasomatic event responsible to be dated. Just as importantly any
580 inclusions in the altered areas of the zircon could also experience potential chemical alteration,
581 depending on their reactivity to the fluid, with respect to both major and trace element composition,
582 or be replaced by other minerals more in equilibrium with both the infiltrating fluid and the mineral
583 assemblage surrounding the zircon.

584

585 **Declaration of Competing Interest**

586 The authors declare that they have no known competing financial interests or personal relationships
587 that could have appeared to influence the work reported in this paper.

588

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601

602 **Appendix A. Supplementary Material**

603 The supplementary materials for this manuscript include four supplementary tables (**Tables S1, S2,**
604 **S3, and S4**) and one supplementary figure (**Figure S1**). **Table S1** contains all EPMA data acquired
605 from these zircon metasomatism experiments. **Tables S2, S3, and S4** contain all the raw LA-ICP-
606 MS and SHRIMP data utilized to assemble **Tables 2 and 3** and the REE chondrite-normalized plots
607 in **Figure 7** and **Figure S1**. In **Figure S1**, the chondrite normalized REE data from the SHRIMP
608 analyses (**Table S3**) and the LA-ICP-MS analyses (**Table S4**) are plotted for comparison.

609 Supplementary materials attached to this article can be found online at

610

611

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946 **Figures**
947

948 **Figure 1:** CL images of zircon from (a,b) the Shevaroy Massif (granulite-facies charnockite),
949 Tamil Nadu, southern India (Harlov et al., 2022); (c) an anorthosite, Eastern Ghats Belt, India
950 (Chatterjee et al., 2008; their Figure 2B); (d) polymetamorphic migmatites, Valle d'Arbedo, Ticino,
951 Switzerland (Vonlanthen et al., 2012); (e) high-grade granulite-facies metagranitoids, Queensland,
952 Australia (Hoskin and Black, 2000); and (f) a granitic gneiss in the contact aureole of the Rogaland
953 anorthosite-norite intrusive complex, southwest Norway (Möller et al., 2002). Terms sz, oz, and og
954 in Figure 1c stand for sector zoned, oscillatory zoned, and over growth, respectively. In Figure 1d,
955 the circles 5a, 5b, 5c, and 5d indicate areas where TEM foils were cut. In Figure 1e, P stands for
956 protolith zircon; C₁ and C₂ stands for inherited core; OZP stands for oscillatory zircon; and the scale
957 bars are all 50 µm. Under CL imaging for all images, the light areas in the zircon are depleted in Th
958 and U relative to dark areas in the zircon.

959

960 **Figure 2:** (a) BSE and (b) CL images of a grain fragment of the starting zircon from a nepheline
961 syenite pegmatite, Seiland igneous province, northern Norway.

962

963 **Figure 3:** Sketch of the CaF₂ assembly used in the experiments with the piston cylinder apparatus
964 showing the location of the four Pt capsules separated by biotite sheets.

965

966 **Figure 4:** (a,c,d) CL images of a zircon grain fragment reacted in a Na₂Si₂O₅ + H₂O solution +
967 ThO₂ + ThSiO₄ + SiO₂ at 900 °C and 1000 MPa. Altered areas (light areas in CL) are enriched in
968 Th and depleted in U, Pb, and (Y+REE) (see Tables 2 and 3). Figure 4b is a TEM foil taken from
969 the elongated area located across the reaction front shown in Figure 4a. Note the lack of any
970 reaction texture in the TEM foil nor the indication of a reaction front (the sharp boundary between

971 light and dark areas in [Figure 4b](#)). Dark ovals in the background are from the carbon foil upon
972 which the TEM foil rests.

973

974 **Figure 5:** BSE (a) and CL (b) images of a zircon grain fragment reacted in a 2N NaOH solution +
975 $\text{ThO}_2 + \text{ThSiO}_4 + \text{SiO}_2$ at 900 °C and 1000 MPa. Altered areas (light areas in CL) are enriched in
976 Th and depleted in U, Pb, and (Y+REE) (see [Tables 2 and 3](#)). [Figure 5b](#) is a TEM foil taken from
977 the elongated area across the reaction front shown in [Figure 5a](#). Note the lack of any reaction
978 texture in the TEM foil nor the indication of a reaction front (the sharp boundary between light and
979 dark areas in [Figure 5b](#)). Dark ovals in the background are from the carbon foil upon which the
980 TEM foil rests.

981

982 **Figure 6:** (a,c,d,e,f) CL images of zircon reacted in a NaF + H₂O solution + $\text{ThO}_2 + \text{ThSiO}_4 +$
983 SiO_2 at 900 °C and 1000 MPa. Altered areas (light areas in CL) are enriched in Th and depleted in
984 U, Pb, and (Y+REE) (see [Tables 2 and 3](#)). [Figure 6b](#) is a TEM foil taken from the elongated area
985 across the reaction front shown in [Figure 6a](#). Note the lack of any reaction texture in the TEM foil
986 nor the indication of a reaction front (the sharp boundary between light and dark areas in [Figure 6b](#)).
987 Dark ovals in the background are from the carbon foil upon which the TEM foil rests. Note also the
988 overgrowth of zircon near the top of [Figure 6a](#) (sharp crystallographic faces) and compare this to
989 the lack of crystallographic faces along the bottom of the grain where intergrowth occurs into the
990 zircon body via fluid-aided coupled dissolution-reprecipitation. In [Figures 6e and 6f](#) alteration is
991 seen along cracks and possible cleavage planes in the zircon.

992

993 **Figure 7:** Chondrite normalized ([McDonough and Sun, 1995](#)) plots of Y + HREE from altered and
994 unaltered areas of zircon in experiments (a) ZF-5 ($\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$), (b) ZF-9 (2N NaOH), (c) ZF-
995 16 (NaF + H₂O), and (d) ZF-40 (NaF + H₂O) (see [Tables 2 and 3](#); [Table S4](#)).

1 **Metasomatic alteration of zircon at lower crustal P-T conditions utilizing alkali-**
2 **and F-bearing fluids: trace element incorporation, depletion, and resetting the**
3 **zircon geochronometer**

4

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19 **ABSTRACT**

20 Natural alteration of zircon takes place in melts or fluids either via dissolution coupled with
21 overgrowth or via a coupled dissolution-reprecipitation process. The latter results in the zircon
22 being partially or totally replaced by new, compositionally re-equilibrated zircon or a new mineral
23 phase or both. In this study, fragments (50 – 300 μm) from a large, inclusion-free, clear, 520 to 530
24 Ma euhedral zircon with light radiation damage from a nepheline syenite pegmatite, Seiland
25 Igneous Province, northern Norway, were experimentally reacted in 20 mg batches with 5 mg of

26 $\text{ThO}_2 + \text{ThSiO}_2 + \text{SiO}_2$ and a series of alkali-bearing fluids in sealed Pt capsules at 900 °C and 1000
27 MPa for 6 to 11 days in the piston cylinder press using a CaF_2 setup with a cylindrical graphite
28 oven. $\text{ThO}_2 + \text{ThSiO}_2 + \text{SiO}_2$ was present at the end of the experiment. In experiments involving
29 H_2O , $\text{H}_2\text{O} + \text{NaCl}$, $\text{H}_2\text{O} + \text{KCl}$, and 2N KOH, no reaction textures formed other than a slight
30 dissolution of the zircon grain fragments. Experiments involving 2N NaOH, $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$, and
31 $\text{NaF} + \text{H}_2\text{O}$ resulted in zircon reaction textures with varying degrees of intensity, which took the
32 form of partial replacement by compositionally modified zircon via a coupled dissolution-
33 reprecipitation process. In the $\text{NaF} + \text{H}_2\text{O}$ experiment some overgrowth also occurred. Altered
34 zircon is separated by sharp compositional boundaries from unaltered zircon. Secondary ion mass
35 spectrometry (SIMS) and laser ablation inductively coupled plasma mass spectrometry (LA-ICP-
36 MS) analysis indicates that, relative to the unaltered zircon, the altered zircon is strongly enriched in
37 Th, and heavily to moderately depleted in U and (Y+REE). In all the experiments, ^{206}Pb (3 to 5
38 ppm in unaltered zircon) is depleted in the altered zircon to below the SIMS detection limit and to at
39 or below the LA-ICP-MS detection limit. Hafnium and Ti concentrations in the altered zircon
40 retained the same approximate value (within error) as the original zircon. The results from these
41 experiments demonstrate that zircon can be compositionally modified by alkali-bearing and alkali-
42 F-bearing fluids via a coupled dissolution-reprecipitation process. Near to total loss of radiogenic
43 Pb via such processes under high-grade conditions resets the internal zircon geochronometer.
44 Although the end result is the same as with zircon overgrowth, i.e. the production of new generation
45 zircon at the time of a metasomatic/metasomatic event, such replacement processes can explain
46 incomplete isotopic 'resetting'; inclusion production through unmixing of solid solutions in
47 metastable zircon compositions; and 'ghost' textures that preserve initial growth features but with
48 isotopic disturbance. Diagnostic replacement features produced in experiments, such as interface
49 geometries between altered and unaltered zircon, provide markers of the mechanism and aid in
50 zircon interpretation. A major implication from this study is that if zircon with low radiation
51 damage can be metasomatically altered under high-grade conditions this would have important

52 consequences with respect to zircons presumed role as an impregnable container for mineral
53 inclusions. Namely the mineral inclusions contained within zircon could also be altered, reset as a
54 geochronometer, or even replaced by another mineral.

55

56 **Keywords:** zircon, Th, U, Pb, REE, petrochronology, coupled dissolution-reprecipitation, alkali-
57 bearing fluids, experimental petrology

58

59 **1. Introduction**

60 In nature zircon is one of the principal accessory minerals used for the dating of geologic processes.
61 Its chemically and mineralogically robust nature allows it to survive its igneous origins and be re-
62 incorporated into either successive igneous protoliths, through melting of zircon-bearing source
63 rocks, or into sedimentary protoliths, as detritus. Zircon can also survive metamorphism,
64 metasomatism, and/or partial melting of the host rock. However, such survival is typically partial.
65 The cores of the zircon grain tend to preserve its origins whereas the rims and replacement textures
66 can record changes wrought during diagenesis, metasomatism, metamorphism, and re-incorporation
67 into a magma (e.g. [Harlov et al., 2022](#)).

68 Zircon is a principal host for U, Th, Hf, Y, and HREEs in various sedimentary,
69 metamorphic, and igneous rocks, and as such can contain a significant fraction of the whole rock
70 abundance of these elements depending on the presence or lack of other minerals such as monazite,
71 xenotime, allanite, apatite, and garnet. Despite its reputation as a refractory mineral, zircon can
72 interact with diverse fluids and/or melts under a range of crustal P-T conditions. For example, the
73 chemical stability of metamict zircon, radiation-damaged zircon, and synthetic (pristine) zircon with
74 respect to various fluids has been explored experimentally as well as speculated upon in a series of
75 studies of natural examples utilizing a variety of analytical techniques, as summarized in [Geisler et
76 al. \(2007\)](#); see also [Pidgeon et al. \(1966\)](#), [Rizvanova et al. \(2000\)](#), [Geisler et al. \(2002, 2003\)](#),
77 [Tomaschek \(2004, 2010\)](#), [Lenting et al. \(2010\)](#), and [Lewerentz et al. \(2019\)](#). Both experimentally

78 and in nature, compared to pristine zircon or zircon with a low degree of radiation damage,
79 metamict zircon and zircon with a high degree of radiation damage is highly susceptible to fluid-
80 assisted alteration down to relatively low P-T conditions (e.g., 175 °C and 250 bars) (Geisler et al.,
81 2007).

82 In addition to metamict and radiation damaged zircon, reaction textures, presumed to be
83 produced by fluids or melts, can also be seen in zircons with a low degree of radiation damage from
84 both igneous and high-grade metamorphic rocks under cathodoluminescence (CL) imaging.
85 Examples include zircons from a ca. 983 Ma anorthosite, Eastern Ghats Mobile Belt, India
86 (Chatterjee et al., 2008); orthopyroxene-bearing granulite-facies granitoids (charnockites) from the
87 Shevaroy Massif, southern India (Harlov et al., 2022); polymetamorphic migmatites, Valle
88 d'Arbedo, Switzerland (Vonlanthen et al., 2012); granulite-facies meta-granitoids, Queensland,
89 Australia (Hoskin and Black, 2000); and granitic gneisses in a contact aureole associated with the
90 Rogaland anorthite-norite intrusive complex, southern Norway (Möller et al., 2002). Here CL-
91 bright or CL-dark areas of apparent alteration overprint the original magmatic zoning (Fig. 1). The
92 irregular and/or lobate shapes of these altered areas, which extend inward into the zircon from the
93 grain rim, are difficult to ascribe to overgrowth of either the original zircon grain or partially
94 dissolved zircon grain, but rather resemble the partial replacement textures in monazite that have
95 been shown to be the result of fluid-induced coupled dissolution-reprecipitation processes as
96 opposed to overgrowth (Harlov et al., 2011).

97 In this study, fragments of an inclusion-free, faintly banded zircon (CL imaging) with light
98 radiation damage from the Seiland Igneous Province, northern Norway (Fig. 2) are used in a series
99 of piston cylinder metasomatism experiments involving both pure H₂O and a variety of alkali-
100 bearing solutions at 900 °C and 1000 MPa. A ThSiO₄ + ThO₂ + SiO₂ mix was added to all of the
101 experiments with the goal of seeing whether or not Th could be metasomatically incorporated into
102 the zircon crystal lattice replacing Zr utilizing reactive fluids. After quench and extraction, the
103 reacted zircon grain fragments are then mounted, polished to cross section, and evaluated using

104 high-contrast backscattered electron (BSE) imaging, CL imaging, transmission electron
105 microscopic (TEM) imaging, electron microprobe (EMP) analysis, sensitive high-resolution ion
106 microprobe (SHRIMP) analysis, and laser ablation inductively coupled plasma mass spectrometry
107 (LA-ICP-MS) analysis. The results from the experimentally reacted zircons are then compared with
108 metasomatically altered zircons from nature and the reaction textures are interpreted chemically,
109 physically, and from a petrochronological perspective.

110

111 **2. Experimental and Analytical Procedures**

112 *2.1 Experimental protocol*

113 Experiments were run at 900 °C and 1000 MPa using the two piston cylinder apparatus as described
114 by Johannes et al. (1971) and Johannes (1973) and are summarized in Table 1. The zircon chosen
115 for the experiments was obtained from the Natural History Museum at the University of Oslo, Oslo,
116 Norway. It consists of a large (2 cm), transparent, inclusion-free, light brownish, euhedral crystal
117 fragment from a nepheline syenite pegmatite located in the Seiland Magmatic Province, northern
118 Norway (523 ± 2 to 531 ± 2 Ma; Pedersen et al., 1989). A fragment of this crystal was broken up
119 into 50 to 300 μm size irregular grains. The transparent, inclusion-free, lightly brown-pink grain
120 fragments were washed in ethanol in an ultrasonic bath. Size sorting was not done. High contrast
121 BSE and CL imaging reveal that the grains are totally texture-free except for a very faint magmatic
122 zoning (Fig. 2).

123 Solids in the experimental charge consisted of 20 mg of zircon, 5 mg of a $\text{ThSiO}_4 + \text{ThO}_2 +$
124 SiO_2 mix, and 5 mg of fluid (Table 1). Reactants in the experimental charge included doubled
125 distilled nanopore H_2O , $\text{NaCl} + \text{H}_2\text{O}$, $\text{KCl} + \text{H}_2\text{O}$, 2N NaOH, 2N KOH, $\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$, and NaF
126 + H_2O . All chemicals used were spec pure to 99.99% or better. The experimental charge was placed
127 in a 3 mm wide, 1 cm long, tempered (1000 °C) Pt capsule, which was arc-welded shut and placed
128 vertically, four at a time, in a CaF_2 setup with a cylindrical graphite oven (Fig. 3). The capsules
129 were separated from each other by thin sheets of biotite. The presence of a graphite oven under the

130 airtight conditions of the experiment implies that the system/experiments, at least in theory, should
131 have been buffered to graphite-CO-CO₂ once the oven was heated to 900 °C. The thermocouple tip
132 was placed such that it reached halfway up alongside the Pt capsules (Fig. 3). The temperature
133 differential along the capsules was approximately 40 °C with either capsule end at 860 °C compared
134 to the sweet spot at the center of the capsules at the measured 900 °C. The pressure measured
135 during the experiment was corrected for friction due to the CaF₂ pressure medium. Non-isobaric
136 quench was achieved within 20 to 30 seconds by turning off the current.

137 After each experiment, the Pt capsule was cleaned, weighed, and punctured. The Pt capsules
138 were then dried at 105 °C for several hours, and weighed again to determine fluid loss. Due to the
139 very small amounts of fluid used in the experiments (5 mg), accurate trace element analysis of the
140 fluid was not possible. The reacted charge was then carefully removed from the Pt capsule with as
141 little mechanical disturbance as possible. The charge was then mounted and polished down to cross
142 section in an epoxy grain mount.

143

144 *2.2 Scanning electron microscope (SEM)*

145 Experimental charges were first evaluated using high contrast BSE and CL imaging on a JEOL
146 JSM-5900LV Scanning Electron Microscope (SEM) equipped with a Gatan MiniCL detector and
147 JEOL SmileStation stage automation and image-capture software at the National Institute for Polar
148 Research (NIPR), Tachikawa-shi, Tokyo-to, Japan.

149

150 *2.3 Electron probe microanalysis (EPMA)*

151 Electron probe microanalysis (EPMA) of zircon was carried out using the JEOL electron
152 hyperprobe with field emission gun at the GeoForschungsZentrum (GFZ) Potsdam using an
153 accelerating voltage of 15 kV and beam current of 15 nA. Individual spot analyses were made
154 using a focused electron beam with a diameter of 1 micron. Elements analyzed for in zircon
155 included P, Si, Ti, Zr, Hf, Th, U, Y, Gd, Tb, Dy, Ho, Er, Yb, Lu, Ca, Pb, and Na, with counting

156 times of 20 to 120 seconds depending on the relative amount of the element. Standards for the REE
157 were taken from synthetic REE phosphates prepared by [Jarosewich and Boatner \(1991\)](#). The
158 remaining standards were taken from both the CAMECA and Smithsonian standard sets
159 ([Jarosewich et al., 1980](#)). The full EMP analysis data set is contained in [Supplementary Material](#)
160 [Table S1](#).

161

162 *2.4 Sensitive high-resolution ion microprobe (SHRIMP)*

163 *2.4.1 Zircon U-Th-Pb measurement*

164 Mounted zircon grains were cleaned to eliminate surface contamination by common Pb, and coated
165 with 100 Angstroms of high-purity gold. Mounts were imaged at high resolution by CL and BSE
166 with a JEOL JSM-5900LV Scanning Electron Microscope (SEM) equipped with a Gatan MiniCL
167 detector and JEOL SmileStation stage automation and image-capture software, at NIPR,
168 Tachikawa-shi, Tokyo-to, Japan.

169 Spots were carefully chosen from SEM imaging for Th, U, and Pb analysis during multiple
170 sessions by a SHRIMP-II at NIPR, using a primary O₂-ion beam with a typical sample surface
171 current of 4 to 7 nA to produce 25 to 30 µm long, flat-floored oval pits. Secondary ionization was
172 measured on a single electron multiplier on mass stations 196 (Zr₂O) through to 254 (UO), with a
173 mass resolution of > 5000 for ²³⁸U¹⁶O and a sensitivity on ²⁰⁶Pb of 17 to 20 cps per ppm per nA of
174 primary current. Mass stations were measured through 5 to 6 cycles, with typical count times of 10
175 s per cycle for ²⁰⁴Pb, background (at 204.04 amu) and ²⁰⁶Pb, and 20s for ²⁰⁷Pb. Reduction of raw
176 data for standards and samples was performed using the SQUID v.1.12a ([Ludwig, 2001](#)), and
177 Isoplot v.3.71 ([Ludwig, 2003](#)) add-ins for Microsoft Excel 2003. Abundance of U was calibrated
178 against in-house reference zircon YBr157 (580 ppm U, as estimated by TIMS; provided by Allen
179 Kennedy of the John de Laeter Centre, Curtin University of Technology, Western Australia,
180 Australia). Corrections for common Pb on U/Pb values and ages were done with the common Pb
181 estimated from ²⁰⁴Pb counts and the [Stacey and Kramers \(1975\)](#) common Pb model for the

182 approximate U-Pb age for each analysis. $(\text{Pb}/\text{U})/(\text{UO}/\text{U})^2$ values were calibrated against
183 measurements on reference zircon TEMORA-2 (417 Ma; [Black et al., 2004](#)). Zircon SHRIMP
184 mean U-Th-Pb data for the reacted zircons listed in [Table 1](#) is contained in [Table 2](#). The full
185 SHRIMP analytical U-Th-Pb zircon data set is contained in ~~Supplementary Material Table S2~~.

186

187 *2.4.2 Zircon Y+REE analysis*

188 Yttrium, REEs, and Hf contents were estimated for a subset of U-Th-Pb isotopic analyses by re-
189 analyzing the same spots ([Table 2](#)). Considering the small penetration depth (< 3 micron) of the
190 SHRIMP analytical spots, and the lack of strong chemical zoning in the starting material these
191 contents are considered to be equivalent to those in zircon analyzed for U-Th-Pb. Spot sizes and
192 mass resolutions were the same as for age analyses, with each station measured for 10 s through 6
193 cycles. To minimize the interference of LREE-MREE oxide peaks on MREE-HREE and Hf
194 measurements, energy filtering was applied to reduce ^{180}Hf to 10% of the unfiltered signal. This
195 reduces potential REEO⁺ interference to less than 1% of the unfiltered signals. Counts were
196 normalized against ^{92}Zr from the NIST610 standard glass, and compared periodically against
197 published values for zircon reference material 91500 ([Wiedenbeck et al., 2004](#); [Iizuka and Hirata,](#)
198 [2004](#)). All estimates were within 10% of published values. Zircon SHRIMP mean REE data for
199 the reacted zircons listed in [Table 1](#) is contained in [Table 2](#). The full SHRIMP analytical zircon
200 REE data set is contained in ~~Supplementary Material Table S3~~. Chondrite-normalized REE plots of
201 the SHRIMP REE data are contained in ~~Supplementary Material Figure S1~~.

202

203 *2.5 Laser ablation inductively coupled plasma mass spectrometry (LA-ICP-MS)*

204 Trace element abundances in zircon were measured at the Institute of Geological Sciences, Polish
205 Academy of Sciences, Kraków Research Centre, Krakow, Poland using an ArF excimer laser-
206 ablation system RESOLUTION M50 by Resonetics coupled with a quadrupole ICP-MS XSeriesII by
207 FisherScientific. Ablation took place in a double volume Laurine technology cell in pure He (flow

208 rate of 0.9 L/min), for which the Ar nebuliser gas (flow rate of 0.5 – 0.55 L/min) was mixed
209 downstream from the sample cell. After passing through a signal-smoothing manifold, the analyte
210 was delivered to the ICP source. A small addition of nitrogen (0.005 – 0.008 L/min) was used to
211 enhance the sensitivity of the ICP-MS. The oxide to metal ratio $^{248}\text{ThO}/^{232}\text{Th}$ was kept below 0.5 %.
212 Analyses were performed using a rotating rectangular slit with a length of 50 μm and a width of 8
213 and 16 μm . An energy density of 4 to 5 J/cm^2 at a repetition rate of 5 Hz was applied. Twenty
214 seconds of gas blank was measured prior to each 30 s ablation, which was followed by 30 s washout
215 time. Sample runs were bracketed by measurements of the NIST 612 glass (Jochum et al., 2011).
216 The zircon reference material 91500 (Wiedenbeck et al., 2004; Iizuka and Hirata, 2004) was
217 frequently measured as a secondary standard along with the unknowns. The ZrO_2 content from
218 previously acquired electron microprobe analyses of the Seiland zircon ($\text{ZrO}_2 = 66.65$; $\text{SiO}_2 =$
219 32.20 ; $\text{HfO}_2 = 0.70$) was used as an internal standard (Supplementary Material Table S1). Data
220 processing was performed using the Glitter 4.0 software from Macquarie University, Australia
221 (Griffin et al., 2008). Zircon LA-ICP-MS mean U-Th-Pb and REE analyses for the reacted zircons
222 listed in Table 1 is contained in Table 3. The full LA-ICP-MS analytical U-Th-Pb and REE zircon
223 data set is contained in Supplementary Material Table S4.

224

225 2.6 Transmission electron microscopy (TEM)

226 Reacted zircon grains, suitable for TEM investigation, were first selected using BSE and SEM
227 images. Sampling was accomplished by using focused ion beam (FIB) milling (Wirth, 2004, 2009).
228 FIB preparation was conducted under ultra-high vacuum conditions in an oil-free vacuum system
229 using a FEI FIB200 instrument at the GeoForschungsZentrum Potsdam. TEM-ready foils of
230 approximately $15 \times 8 \times 0.15 \mu\text{m}$ representing cross sections perpendicular to and across the reaction
231 front (separating the altered and unaltered zircon) were sputtered directly from the zircon grain in
232 the epoxy grain mount using a 30 kV Ga-ion beam. The TEM foil was protected from sputtering by
233 the Ga-ion beam by a 1 μm thick, Pt layer deposited using a high-purity organic Pt gas ($\text{C}_9\text{H}_{16}\text{Pt}$,

234 99.9 %), which decomposes under the Ga-ion beam. Once cut, the TEM foils were placed on a
235 perforated carbon film, which was placed on a copper grid. Carbon coating to prevent charging in
236 the TEM was not applied.

237 TEM on the zircon foils was carried out in a TECNAI F20 XTwin instrument operated at
238 200 kV and equipped with a FEG electron source. The TEM is equipped with a Gatan imaging filter
239 (GIF Tridiem), a Fishione high-angle annular dark field detector (HAADF), and an EDAX X-ray
240 analyzer with an ultrathin window. TEM bright field images (HREM) were acquired as energy-
241 filtered images applying a 10 eV window to the zero-loss peak.

242

243 3. Results

244 All experiments were run at 900 °C and 1000 MPa over periods of 144 to 192 hours (6 – 8 days).
245 Whereas, the zircon grain fragments were a light pinkish brown before the experiment, at quench
246 the reacted zircon grain fragments were colorless and transparent, which suggests that any radiation
247 damage in the zircon had been healed. This is supported by a variety of annealing experiments at
248 comparable or lower temperatures and/or pressures (cf. [Nasdala et al., 2001, 2002](#); [Montario et al.,
249 2008](#); [Ginster et al., 2019](#); [Herrmann et al., 2021](#); [Ende et al., 2021](#); [Härtel et al., 2022](#)). Of the
250 eight experimental runs reported here and listed in [Table 1](#), in those experiments involving pure
251 H₂O, NaCl + H₂O, KCl + H₂O, and 2N KOH, the zircon did not react with the fluid, other than
252 showing a little dissolution along the grain fragment edge. In contrast, zircon in experiments
253 involving Na₂Si₂O₅ + H₂O ([Fig. 4](#)), 2N NaOH ([Fig. 5](#)), and NaF + H₂O (2 experiments; [Table 1](#),
254 [Fig. 6](#)) developed reaction textures under CL imaging to varying degrees. In each of these
255 experiments, due to the relatively large amount of the ThSiO₄ + ThO₂ + SiO₂ mix added ([Table 1](#)),
256 all three phases persisted to the end of the experiment and were visible in the reacted charge.

257 While not obvious in high contrast BSE images, under CL imaging the altered areas in these
258 four experimental runs appear lighter (CL-light) than the unaltered areas (CL-dark). CL-light areas
259 are separated from CL-dark areas by sharp boundaries. In the experiments involving Na₂Si₂O₅ +

260 H₂O (ZF-5; Fig. 4) and 2N NaOH (ZF-9; Fig. 5), the reaction textures are considerably less
261 extensive than in runs involving NaF + H₂O (ZF-16, ZF-40; Fig. 6). In the case of run ZF-9, only
262 two zircon fragments with a reaction texture were found amongst 30 grain fragments exposed in the
263 polished mount, which makes up about half of the total experimental product. In the case of ZF-5,
264 about half of the grains in the grain mount had reaction textures. In contrast, in the NaF + H₂O
265 experiment (ZF-16, ZF-40), all the zircon grains developed reaction textures ranging from slight to
266 extensive. In runs ZF-5 and ZF-9, a lack of crystal face formation and the preservation of irregular
267 grain fragment boundaries would suggest that the reaction textures are due to the replacement of the
268 original zircon by altered zircon. In runs ZF-16 and ZF-40, the development of new crystal faces as
269 a product of overgrowth is evident on some of the grains (e.g. Fig. 6a). However, reaction textures
270 have also developed that are lobate and convex inwards, away from edges of zircon grain regardless
271 of whether they have overgrowths or not (e.g. Figs. 6a,c,d). A second type of reaction texture occurs
272 along cracks and possible cleavage planes inside of the zircon grains, which extends outwards from
273 the crack into the zircon (Figs. 6e,f). There is a general lack of crystal face formation despite the
274 fact that, due to the high ratio of fluid to zircon grain fragments by mass (Table 1), each individual
275 grain was totally surrounded by fluid during the experiment and, hence, not in direct contact with
276 any of the other grains unless it was overgrown by a neighboring grain (e.g. Fig. 6a).

277 TEM bright field images of foils sampled across the reaction front, as defined by CL
278 imagery, in zircon grains from runs ZF-5 (Figs. 4a,b), ZF-9 (Figs. 5a,b), and ZF-16 (Figs. 6a,b),
279 show no differences in texture on the sub-micron scale between the altered and unaltered areas in
280 the zircon, no mineral inclusions, nor any evidence of a boundary or reaction front between the
281 unaltered and altered zircon.

282 In general, both SHRIMP and LA-ICP-MS spot analyses indicate that the CL-light altered
283 areas are moderately to heavily depleted in U and Y + HREE and enriched in Th relative to the CL-
284 dark unaltered areas of the zircon grains, which retain the trace element abundances of the original
285 zircon grain (Tables 2 and 3; Fig. 7; Supplementary Material Fig. S1; and Tables S2, S3, and S—4).

286 The low Th and U contents in the original Seiland zircon would imply that the amount of radiation
287 damage to the crystallographic lattice should be relatively minor after some 520 to 530 Ma (Table
288 3; ~~Supplementary Material Tables S2 and S4~~). One exception was ZF-5 ($\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$). Here
289 Gd showed no depletion within the altered areas (Fig. 7a, ~~Supplementary Material Figure S1~~;
290 Tables 3 and 4). In contrast, altered areas in all the experiments are heavily depleted in Pb to or
291 below the detection limit in both the SHRIMP and LA-ICP-MS analytical data, whereas Hf and Ti
292 show little difference in their abundances (within analytical error) between the altered and unaltered
293 areas in the zircon (Tables 2 and 3; ~~Supplementary Material Tables S3 and S4~~).
294

295 4. Discussion

296 4.1 Formation of reaction textures in zircon

297 A series of previous studies have focused on the experimental alteration of zircon, though most of
298 these have involved metamict or zircon with a high degree of radiation damage under temperatures
299 and pressures lower than the ones considered in this study (Pidgeon et al., 1966; Geisler et al.,
300 2001a,b, 2002, 2003, 2004, 2007; Rizvanova et al., 2000, 2007; Lenting et al., 2010; Lewerentz et
301 al., 2019). In general, these experiments have involved a variety of fluids (H_2O , HCl , $\text{Ca}(\text{OH})_2 +$
302 H_2O , $\text{CaCl}_2 + \text{H}_2\text{O}$, and $\text{AlCl}_3 + \text{H}_2\text{O}$) over a broad range of temperatures (200 – 700 °C) and
303 pressures (100 – 500 MPa). The zircon in these experiments generally shows a high degree of
304 reactivity during the experiment due to the large amount of chemical potential energy stored in the
305 disordered, amorphous areas in the zircon or in the radiation-damaged zircon crystallographic
306 lattice (see discussion in Geisler et al., 2007). Other experiments at high P-T have focused on
307 annealing of zircon in restricted chemical systems (Morales et al., 2022), the relationship between
308 zircon and baddeleyite as a function of the Ca and Si activity in fluids (Lewerentz et al., 2019), or
309 on the dissolution of zircon in a variety of silicate melts (Borisov and Aranovich, 2019; Baker et al.,
310 2002; Schmidt et al., 2013) and in a series of fluids (Schmidt et al., 2006; Newton et al., 2010;
311 Ayers et al., 2012; Wilke et al., 2012; Bernini et al., 2013; Ayers and Peters, 2018).

312 In this study, utilizing pressures and temperatures that are normally characteristic of the
313 lower crust/lithospheric mantle, the goal was to partially alter a natural zircon with a low degree of
314 radiation damage metasomatically while at the same time incorporating Th in the altered areas. The
315 reaction textures produced in the experimentally metasomatized zircon show a sharp contrast, both
316 texturally and compositionally (trace elements), between the altered (CL-bright) and unaltered (CL-
317 dark) zircon (Figs. 4, 5, and 6). The lobate intergrowths of altered zircon into the unaltered zircon as
318 seen in Figures 6a, 6c, and 6d can be argued as not being a product of overgrowth, but rather a
319 product of mineral replacement (see comments above). Similar textures, both lobate and otherwise,
320 have been recognized in metasomatically altered monazite (cf. Harlov et al., 2011), xenotime
321 (Harlov and Wirth, 2012), and apatite (Harlov et al., 2002, 2003, 2005) both experimentally and
322 from nature, and have been interpreted as partial replacement textures due to a coupled dissolution-
323 reprecipitation process (Putnis, 2002, 2009; Putnis et al., 2005; Putnis and Putnis, 2007; Putnis and
324 Austrheim, 2010, 2013; Altree-Williams et al., 2015). This is especially obvious in Figures 4c, 6e,
325 and 6f where alteration occurs along cracks and possible cleavage planes within the zircon grains as
326 partial replacement textures extending into the zircon, similar to that seen in partial replacement
327 textures involving experimental replacement of monazite by huttonite (ThSiO_4) (cf. Harlov et al.,
328 2007, their figure 2h). During coupled dissolution-reprecipitation, the original zircon is dissolved in
329 the presence of these alkali-bearing fluids while simultaneously being replaced by new zircon that
330 compositionally is in thermodynamic equilibration with the fluid chemistry under the particular P-T
331 conditions of the system. During this process, the new zircon uses the original zircon as a
332 crystallographic template for purposes of nucleation and subsequent growth/replacement. In
333 essence coupled dissolution-reprecipitation is the basis for mineral pseudomorphism, and is a
334 commonly observed process in nature for many minerals. It is also the principal process by which
335 fossilization of organic material, such as bone and wood, occurs.

336 In minerals, the process of coupled dissolution-reprecipitation has been shown to occur
337 along a very thin (10 nm wide or less) fluid-filled reaction front between the original dissolving

338 mineral and the newly growing mineral (Putnis, 2002, 2009; Aftree-Williams et al., 2015). This
339 reaction front is physically connected to the fluid surrounding the mineral grain via an actively
340 evolving, non-static, interconnected porosity prevalent throughout the newly grown mineral phase.
341 This allows for active fluid-aided mass transfer between the fluid along the reaction front and the
342 fluid surrounding the grain during the replacement process. Porosity formation can result from a
343 variety of causes such as differences in the molar volume between the original and replacement
344 phase or differences in solubility between the two phases (Putnis, 2009). Once this replacement
345 process stops due to changing P-T-X conditions in an open fluid-mineral system or, in the case of a
346 closed system, due to limited amounts of the reactive fluid (e.g. the experiments in this study), the
347 reaction front will cease to advance and the altered areas of the mineral will begin to recrystallize
348 such that the original interconnected porosity will evolve into isolated nano- and micron-size fluid
349 inclusions often along with mineral inclusions, both those genetically derived from the host mineral
350 and those originating from minerals outside of the host mineral (Putnis, 2002, 2009; Harlov et al.,
351 2005, 2011; Harlov and Wirth, 2012; Harlov et al., 2016).

352 As can be seen in Figures 4b, 5c, and 6b, for each of the alkali-bearing fluid-zircon
353 metasomatism experiments, neither a remnant porosity nor mineral inclusions remain in the altered
354 areas of the zircon under CL imaging nor in TEM foils taken perpendicular to the reaction front,
355 which includes both altered zircon and unaltered zircon. Here the reaction front, so clearly visible
356 under CL imaging, is not visible in the TEM foils, i.e. the altered zircon appears texturally
357 indistinguishable from the unaltered zircon (cf. Figs. 4b, 5b, and 6b). This is not what is seen in the
358 reaction textures and accompanying TEM foils taken across reaction fronts in experimentally
359 metasomatized fluorapatite (Harlov et al., 2005), monazite (Harlov et al., 2011), and xenotime
360 (Harlov et al., 2012) from experiments done under the same approximate P-T conditions. It is also
361 not seen in experimentally metasomatized metamict or radiation-damaged zircon (Geisler et al.,
362 2007), nor in metamict or radiation-damaged zircon from nature (Geisler et al., 2002, 2003, 2007).
363 In all of these cases the metasomatically altered areas are characterized by numerous fluid

364 inclusions and mineral inclusions, such as ThSiO₄, USiO₄, ThO₂, UO₂, ZrO₂, xenotime, feldspar,
365 quartz, etc..

366 One explanation for this striking difference in zircon textures is that the alteration textures
367 seen in [Figures 4, 5, and 6](#) appear to be specific to zircon with low amounts of radiation damage,
368 characteristic of the 520 to 530 Ma Seiland zircon, the high P-T conditions of the experiments, and
369 the reactivity of the alkali-bearing and F-bearing fluid chemistry of the system. Total elimination of
370 the porosity during the course of the experiment, after growth of the altered area had stopped, could
371 be due to a rapid coarsening effect, which would be consistent with attaining textural equilibration
372 driven by reduction in the surface area as defined by the interior surface area of the pores. Hence,
373 the original porosity, which was transient to begin with, would have totally disappeared as textural
374 equilibration was achieved, and in this particular case achieved rather quickly during the course of
375 the experiment. Similar phenomena have been observed in the KBr-KCl-H₂O replacement
376 experiments of [Putnis et al. \(2005\)](#). Rapid disappearance of the porosity would have also
377 discouraged mineral inclusion formation since the pores normally act as nucleation sites for
378 inclusions in the altered/reacted areas (see discussion in [Harlov et al., 2005](#)). What overgrowth that
379 did occur was also totally recrystallized as per the above mechanism eliminating any porosity that
380 might have formed during crystal growth outwards. The sharp compositional boundary seen
381 between the altered zircon and unaltered zircon under CL imaging would indicate that element
382 diffusion across the boundary was negligible at 900 °C and 1000 MPa over the course of the
383 experiment. This observation agrees with the U, Th, and Hf diffusion experiments of [Cherniak et al.](#)
384 [\(1997a\)](#) and REE diffusion experiments of [Cherniak et al. \(1997b\)](#), both of which indicate very
385 slow diffusion rates at high temperatures for these elements in zircon.

386 Comparison of the reaction textures resulting from the experiments ([Figs. 4 – 6](#)) with similar
387 textures in natural zircons in [Figure 1](#) support the proposition that high-grade, high pH, alkali-
388 bearing/F-bearing fluids could have been responsible for them. The examples provided in [Figure 1](#)
389 are found in both metamorphic and igneous rocks in a fluid-rich environment with broadly granitoid

390 and hence alkali-rich compositions or else are associated with such rocks. These observations are
391 supported by [Aranovich et al. \(2017\)](#) who make a strong case for alkali-bearing fluids causing
392 partial to total alteration of zircon grains in gabbroids and plagiogranites from the Mid-Atlantic
393 Ridge. In another example, zircons from a leucocratic granite of the Weondong region of South
394 Korea show four types of partial metasomatic alteration, which the authors attribute to the action of
395 F-rich fluids during post-magmatic alteration ([Park et al., 2016](#); their figures 3 and 5). The textures
396 of these metasomatised zircon grains broadly mimic some of the reaction textures obtained in the
397 NaF-fluid experiments ([Fig. 6](#)).

398

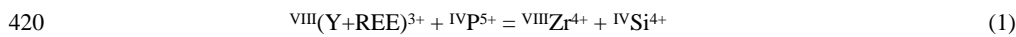
399 *4.2 Alteration of the zircon trace element chemistry*

400 Relative to the original unaltered Seiland zircon, the altered areas in the zircon are significantly
401 enriched in Th, significantly depleted in U, moderately to strongly depleted in Y + HREE, and
402 nearly to totally depleted in Pb to within the detection limit of both SIMS and LA-ICP-MS. In
403 contrast, there is little or no change in the Hf or Ti content within the measurement precision
404 ([Tables 2 and 3](#); [Fig. 7](#)). These abundances contrast with the fluids used in the experiments, which
405 were saturated in Th + Si, and totally devoid of U, Pb, Y+REE, Ti, and Hf ([Table 1](#)).

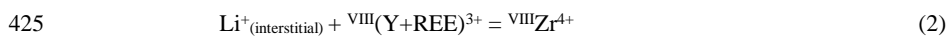
406 In the zircon crystallographic lattice, U^{4+} , Th^{4+} , and Hf^{4+} are conventionally considered to
407 substitute for Zr^{4+} on the 8-fold Zr site ([Finch and Hanchar, 2003](#); [Hoskin and Schaltegger, 2003](#)).
408 While, Th and U have a limited solid solution with zircon as tetragonal thorite ($ThSiO_4$), and
409 tetragonal coffinite ($USiO_4$), respectively ([Ushakov et al., 1999](#)), Hf has a complete solid solution
410 with zircon as tetragonal hafnon ($HfSiO_4$) ([Speer and Cooper, 1982](#)). This is due to the fact that on
411 the 8-fold Zr site Hf^{4+} (0.83 Å) can completely substitute for Zr^{4+} (0.84 Å) (effective ionic radii;
412 [Shannon, 1976](#); [Harley and Kelly, 2007](#)). In contrast, the relatively larger 8-fold ionic radii of U^{4+}
413 (0.86 Å) and Th^{4+} (1.05 Å) ([Shannon, 1976](#); [Harley and Kelly, 2007](#)), compared to 8-fold Zr^{4+} (0.84
414 Å), would explain their relatively limited solid solution in zircon. It would also explain as to why
415 U^{4+} was so easily removed and Th^{4+} only incorporated in limited amounts during each of the

416 metasomatism experiments despite the fluid being supersaturated with Th (Table 3; Supplementary
 417 Material-Tables S2 and S4).

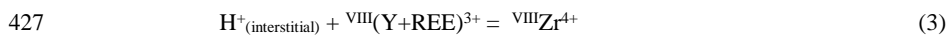
418 Yttrium and the REE are generally thought to be incorporated into zircon via a xenotime-
 419 type coupled substitution or:



421 (Finch and Hanchar, 2003; Hoskin and Schaltegger, 2003) with (Y+REE)³⁺ going on the 8-fold Zr
 422 site and P⁵⁺ (0.17 Å) on the 4-fold Si⁴⁺ (0.26 Å) site (effective ionic radii; Shannon, 1976). Other
 423 possible coupled substitutions for (Y+REE) in zircon which have been described in the literature
 424 include:



426 (Finch et al., 2001; Wang and Trail, 2022), and:



428 (Trail et al., 2016) where Li and H substitute on interstitial sites in the zircon structure (Finch and
 429 Hanchar, 2003). In all of these cases, 8-fold (Y + HREE)³⁺ (1.019, 1.079 – 0.977 Å) are strongly
 430 preferred over the 8-fold LREE³⁺ (1.160 – 1.109 Å) due to their better fit on the 8-fold Zr (0.84 Å)
 431 site (Hoskin and Schaltegger, 2003; Shannon, 1976).

432 From the LA-ICP-MS data in ~~Supplementary Material-Table S4~~, (Y+HREE)³⁺ plus the
 433 approximate value for P⁵⁺ when plotted vs. Zr⁴⁺ + Si⁴⁺ for both unaltered and altered zircon in each
 434 of the experiments show an approximate linear relationship with a positive shallow slope. This
 435 indicates that an additional coupled substitution mechanism must have been responsible for
 436 Y+HREE incorporation in both the altered and unaltered zircon. These additional mechanisms
 437 could have included coupled substitutions (2) and/or (3), each to varying degrees, though this must
 438 be treated as speculation since neither Li nor H⁺ were measured.

439 The observation that Ti was not depleted in the altered areas (Table 3) is more curious
 440 considering that the alkali-bearing solutions in each of the experiments were not buffered by rutile,
 441 i.e. TiO₂, or some other Ti-rich mineral such as ilmenite or titanite; though each of the solutions was

442 buffered to an SiO₂ activity of 1 due to the presence of free SiO₂ in the capsule at the end of the
443 experiment. In zircon, relatively limited amounts of Ti, as ^{IV}Ti⁴⁺ (0.42 Å) are believed to substitute
444 for ^{IV}Si⁴⁺ (0.26 Å) (effective ionic radii; [Shannon, 1976](#)) on the tetrahedral site with the amount of
445 Ti present increasing as a function of increasing temperature for a system nominally buffered at a
446 constant TiO₂ activity ([Watson and Harrison, 2005](#); [Watson et al., 2006](#); [Ferry and Watson, 2007](#);
447 [Harley and Kelly, 2007](#); [Tailby et al., 2011](#)). The fact that Ti remained in the altered areas of the
448 zircon at 900 °C and 1000 MPa in a Ti-free system ([Table 1](#)), as opposed to selectively partitioning
449 into the solution, would suggest that for minor amounts of Ti, the partitioning coefficients for NaF-,
450 NaOH-, and Na₂Si₂O₅-bearing solutions apparently favor Ti remaining on the tetrahedral site in
451 zircon at the P-T of the experiments. Such an observation could have implications for the Ti-in-
452 zircon geothermometer in alkali fluid-bearing systems whether they are buffered with respect to
453 TiO₂ or not (cf. [Ferry and Watson, 2007](#)).

454 Lead appears to be broadly incompatible in the zircon structure with respect to substitution
455 on either the tetrahedral Si site or the octahedral Zr site due to its much larger size, i.e. ^{IV}Pb⁴⁺ (0.65
456 Å) vs. ^{IV}Si⁴⁺ (0.26 Å) and ^{VIII}Pb⁴⁺ (0.94 Å) vs. ^{VIII}Zr⁴⁺ (0.84 Å) (effective ionic radii; [Shannon,](#)
457 [1976](#); [Watson et al., 1997](#); [Mezger and Krogstad, 1997](#); [Geisler et al., 2003](#); [Utsunomiya et al.,](#)
458 [2004](#); [Kogawa et al., 2012](#)). This assumes that Pb would occur as Pb⁴⁺ in the zircon structure,
459 which would seem highly unlikely assuming that the experiments were presumably buffered to
460 graphite-CO₂ (see above). If Pb in the original, unaltered zircon existed only as Pb²⁺, in addition to
461 there being a question of charge balance, the misfit of Pb on both the Si and Zr sites becomes even
462 greater, i.e. 0.98 vs. 0.26 Å and 1.29 vs. 0.84 Å, respectively. This would imply that the only Pb
463 present in the original zircon should be from the radioactive decay of U, Th, and their short-lived
464 daughter isotopes in the form of small accumulations in amorphous radiation-damaged domains
465 and/or along cleavage planes, or as nano-inclusions in annealed zircon ([Geisler et al., 2003](#); [Nasdala](#)
466 [et al., 2005](#); [Kogawa et al., 2012](#); [Seydoux-Guillaume et al., 2015](#); [Valley et al., 2014, 2015](#); [Lyon](#)
467 [et al., 2019](#)). A similar case has been made for Pb accumulation in monazite ([Fougerouse et al.,](#)

468 [2018](#)). The fact that Pb is so readily removed from the altered areas of the zircon to the extent of
469 being at or below the detection limits of both LA-ICP-MS and SIMS implies that Pb, at least in
470 trace amounts, is apparently highly soluble in NaF-, NaOH-, and Na₂Si₂O₅-bearing fluids at 900 °C
471 and 1000 MPa most likely due to complexing with either OH⁻ or F⁻ in solution ([Bottari and](#)
472 [Ciavatta, 1965](#); [Perera et al., 2001](#)).

473 The addition of Th, loss of U, and near to total loss of Pb in the altered areas of the zircon
474 would imply that the U-Th-Pb geochronometer has been near to totally reset compared to the
475 unaltered areas. This obviously has major implications with regard to zircon geochronology.
476 Namely that the zircon U-Th-Pb geochronometer can be metasomatically reset, which is an idea
477 that has long been speculated upon in the literature ([Hoskin and Schaltegger, 2003](#); [Hoskin, 2005](#);
478 [Geisler et al., 2007](#); [Soman et al., 2010](#); [Van Lankvelt et al., 2016](#); [Peterman et al., 2016](#); [Aranovich](#)
479 [et al., 2017](#); [Chen and Zhou, 2017](#); [Wang et al., 2018](#); [Zi et al., 2022](#)). Natural resetting of this
480 geochronometer via Pb diffusion in zircon under fluid-absent conditions has been demonstrated to
481 be a very slow, almost negligible process even if the zircon experiences relatively high temperatures
482 (> 900 °C) for at least 1 Myr ([Möller et al., 2002](#); see also [Cherniak and Watson, 2000](#)). In the
483 experiments from this study, the geochronometer was reset due to alkali-bearing high pH or alkali-
484 fluoride fluids at 900 °C and 1000 MPa over a period of days. Such fluids might explain the zircon
485 alteration textures seen in [Figure 1](#) since each of these examples occur in granitoid rocks rich in
486 alkali-bearing feldspars, which have experienced metasomatism/metamorphism under high-grade
487 conditions. In each of these cases, the CL-bright metasomatized areas tend to be younger by some
488 millions to 10's of millions of years than the CL-dark zircon cores, which the authors generally tend
489 to attribute to metamorphic/metasomatic processes. Similar conclusions were reached by
490 [Lewerentz et al. \(2019\)](#) in experiments (600 – 900 °C; 600 – 1000 MPa) involving the partial
491 alteration of a natural zircon in CaCl₂- and Ca(OH)₂-bearing fluids to baddeleyite. While the newly
492 formed baddeleyite and altered areas in the zircon contained U, Th, and Y + REE derived from the

493 zircon, Pb in both the baddeleyite and the altered areas of the zircon was below the detection limit
494 of the SIMS.

495 The depletion of the Y + HREE in the altered areas of the zircon (Fig. 7) is due in part to
496 the fact that the alkali-bearing fluids used in these experiments contained negligible amounts of
497 REE. This apparently allowed for a fraction of the Y+HREE to be partitioned into the fluid where
498 they presumably complexed with OH⁻ (ZF-5 and ZF-9) (Haas et al., 1995; Wood et al., 2002;
499 [Pourtier et al., 2010](#); [Perry and Gysi, 2018](#)) and/or with F⁻ (ZF-16 and ZF-40) (Haas et al., 1995;
500 [Tropper et al., 2011, 2013](#); [Mair et al., 2017](#)). Depletion or enrichment of REE in zircon is a
501 commonly observed phenomena in granitoid rocks and generally presumed due to metasomatically
502 induced alteration via fluids and/or melts. Examples include zircons with metasomatically altered
503 areas depleted in REE from fluid-induced charnockite patches in granitoid rocks from Kottavattom,
504 Trivandrum Block, southern India ([Taylor et al., 2014](#)); metasomatically altered areas depleted in
505 REE in metamorphosed zircons from the leucocratic portion of a migmatite, Ticino, Switzerland
506 ([Vonlanthen et al., 2012](#)); and zircons from high grade metagranitoids, Queensland, Australia where
507 the metasomatically altered areas are depleted in REE ([Hoskin and Black, 2000](#)).

508

509 **5. Summary and implications**

510 In this study it has been demonstrated in a series of experiments that natural zircon with relatively
511 small amounts of radiation damage can be metasomatically altered using alkali- and F-bearing
512 solutions under the high grade P-T conditions commonly found in the lower crust. This involved the
513 incorporation of Th and the removal of U and REE, and the near to total removal of Pb to below
514 LA-ICP-MS and SIMS detection limits in the altered areas, which implies a basic resetting of the
515 U-Th-Pb geochronometer. If this is also the case for zircons in nature, then this would imply that
516 similar textures, as illustrated in [Figure 1](#), could be metasomatically induced and thus could
517 potentially be used to date metasomatic events.

518 A second major implication from these experiments is that if zircon with low radiation
519 damage can be metasomatically altered this would have important consequences with respect to
520 zircons presumed role as an impregnable container for mineral inclusions. Namely the mineral
521 inclusions contained within the zircon could also be altered, reset as a geochronometer, or even
522 replaced by another mineral. This has important consequences especially with respect to how the
523 mineral inclusions within the Hadean detrital zircons from Jack Hills, Australia have been utilized
524 in an attempt to discern the geochemical and physical conditions on the very early Earth during the
525 Hadean period (4.0 – 4.54 Ga) ([Mojzsis et al., 2001](#); [Wilde et al., 2001](#); [Valley et al., 2002, 2014](#)).
526 The fact that these inclusions have apparently experienced varying degrees of alteration has been
527 amply demonstrated by [Rasmussen et al. \(2011\)](#) who, in a study of monazite and xenotime
528 inclusions in the 4.35 to 3.35 Ga Jack Hills detrital zircons, concluded that these inclusions formed
529 as the result of a metamorphic event at either 2.68 or 0.8 Ga and at monazite-xenotime temperatures
530 ([Gratz and Heinrich, 1997](#)) of around 420 to 475 °C. The Ti content of the quartz inclusions in these
531 same zircons gave temperatures of 350 to 490 °C using the geothermometer of [Thomas et al.](#)
532 ([2010](#)). They also noted that most of the mineral inclusions have the same composition and
533 abundances as the minerals in the original metamorphic matrix in which the zircons were found.
534 This is consistent with the idea that these inclusions, which include K-feldspar, albite, muscovite,
535 and biotite, formed during metamorphism due perhaps to the replacement of what could have been
536 originally apatite inclusions, which are one of the more common types of mineral inclusions in
537 zircon and generally not observed in Jack Hills zircons. If this replacement of mineral inclusions
538 did occur, it would probably have occurred via a coupled dissolution-reprecipitation process as
539 outlined by the experiments in this study. These observations are backed by a CO₂ fluid inclusion
540 study of the Jack Hills zircons by [Menneken et al. \(2017\)](#). Here the formation of these CO₂
541 inclusions appears to be related to a later metamorphic event as opposed to the primary igneous
542 event presumed responsible for the genesis of the zircons.

543 Mineral inclusion formation in zircon grain interiors via a fluid-aided coupled dissolution-
544 reprecipitation process are not limited to the Jack Hills zircons. For example, [Troch et al. \(2018\)](#)
545 documented the fluid-aided formation, via coupled dissolution-reprecipitation, of U-Th-REE phases
546 as mineral inclusions in trace element-rich zircons from the Island Park-Mount Jackson rhyolite,
547 Yellowstone volcanic field, Wyoming, USA. Similar conclusions have also been reached for ultra-
548 high pressure mineral inclusions, such as coesite and jadeite, in zircon from a jadeite quartzite,
549 Dabie orogen, central China ([Gao et al., 2015](#)). While the zircons here are presumed to have a
550 detrital, igneous mid-crustal origin, the inclusions could only have formed during a fluid-rich event,
551 perhaps as a result of coupled dissolution-reprecipitation, under the ultra-high pressure
552 metamorphic conditions present during the continental subduction conditions experienced by the
553 jadeite quartzite during the Dabie orogeny.

554 Similar conclusions have been reached for entirely different mineral systems. For example,
555 [Krause et al. \(2013\)](#) documented metasomatically altered apatite inclusions in clinopyroxene from a
556 nepheline-bearing clinopyroxenite located in the Uralian-Alaskan-type complexes of Kytlym and
557 Nizhny Tagil, Ural Mountains, Russian Federation. Here the clinopyroxene experienced partial
558 metasomatic alteration via coupled dissolution-reprecipitation by a CaCl₂-enriched saline fluid,
559 which also altered the apatite inclusions in these areas from fluor-chlorapatite to chlor-fluorapatite
560 giving them a composition similar to the apatites in the surrounding mineral matrix. In those areas
561 of the clinopyroxene not metasomatically altered, the apatites retained their original fluor-
562 chlorapatite composition. In another example, where apatite is the host mineral, the formation of
563 magnetite and quartz inclusions in metasomatically altered areas of fluorapatite from the Pea Ridge
564 iron oxide-apatite ore body is attributed to fluid-aided mass transfer of Fe and Si into the
565 fluorapatite from magnetite and quartz in the surrounding mineral matrix, again during a process of
566 coupled dissolution-reprecipitation ([Harlov et al., 2016](#)).

567 In all of these cases, the key point here is that the chemistry of a fluid encountered by
568 zircon, or any other mineral, will dictate whether or not the mineral will experience alteration, and

569 whether this alteration occurs by simple partial dissolution, overgrowth, or metasomatic alteration,
570 either partial or total, via a coupled dissolution-reprecipitation process. This last process can also
571 result in the total replacement of one mineral phase by another mineral phase as proposed for the
572 inclusions in the zircon, clinopyroxene, or fluorapatite as discussed above. The pressure and
573 temperature under which such a process will or could occur is of less importance since nature has
574 time on its side as opposed to the very finite lifetime of laboratory experiments (see discussion in
575 [Harlov et al., 2002, 2003, 2005](#)).

576 The basic conclusion here is that if the typical sort of zircon commonly found in crustal
577 rocks, with radiation damage ranging from light to metamict, encounters a chemically reactive fluid,
578 such as the alkali-bearing and F-bearing fluids used in these experiments, it could be partially to
579 totally altered chemically with respect to its trace elements including U, Th, Pb, and the Y+REE.
580 This could result in the U-Th-Pb geochronometer in the altered areas being reset if all the Pb is
581 removed thus allowing for the metasomatic event responsible to be dated. Just as importantly any
582 inclusions in the altered areas of the zircon could also experience potential chemical alteration,
583 depending on their reactivity to the fluid, with respect to both major and trace element composition,
584 or be replaced by other minerals more in equilibrium with both the infiltrating fluid and the mineral
585 assemblage surrounding the zircon.

586

587 **Declaration of Competing Interest**

588 The authors declare that they have no known competing financial interests or personal relationships
589 that could have appeared to influence the work reported in this paper.

590

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Appendix A. Supplementary Material

[The supplementary materials for this manuscript include four supplementary tables \(Tables S1, S2, S3, and S4\) and one supplementary figure \(Figure S1\). Table S1 contains all EPMA data acquired from these zircon metasomatism experiments. Tables S2, S3, and S4 contain all the raw LA-ICP-MS and SHRIMP data utilized to assemble Tables 2 and 3 and the REE chondrite-normalized plots in Figure 7 and Figure S1. In Figure S1, the chondrite normalized REE data from the SHRIMP analyses \(Table S3\) and the LA-ICP-MS analyses \(Table S4\) are plotted for comparison. Supplementary materials attached to this article can be found online at](#)

[Supplementary Table 1: Electron-probe microanalytical data from experimentally metasomatised zireons](#)

[Supplementary Table 2: Zircon U-Th-Pb SHRIMP analyses](#)

[Supplementary Table 3: SHRIMP REE analyses of experimentally metasomatised zireons](#)

[Supplementary Table 4: GLITTER4.4.2: Laser Th, U, Pb, and REE Ablation Analysis Results](#)

[Supplementary Figure 1: Chondrite normalized plots of SHRIMP and LA-ICP-MS zireon data](#)

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- 954

955 **Figures**

956

957 **Figure 1:** CL images of zircon from (a,b) the Shevaroy Massif (granulite-facies charnockite),
958 Tamil Nadu, southern India (Harlov et al., 2022); (c) an anorthosite, Eastern Ghats Belt, India
959 (Chatterjee et al., 2008; their Figure 2B); (d) polymetamorphic migmatites, Valle d'Arbedo, Ticino,
960 Switzerland (Vonlanthen et al., 2012); (e) high-grade granulite-facies metagranitoids, Queensland,
961 Australia (Hoskin and Black, 2000); and (f) a granitic gneiss in the contact aureole of the Rogaland
962 anorthosite-norite intrusive complex, southwest Norway (Möller et al., 2002). Terms sz, oz, and og
963 in Figure 1c stand for sector zoned, oscillatory zoned, and over growth, respectively. In Figure 1d,
964 the circles 5a, 5b, 5c, and 5d indicate areas where TEM foils were cut. In Figure 1e, P stands for
965 protolith zircon; C₁ and C₂ stands for inherited core; OZP stands for oscillatory zircon; and the scale
966 bars are all 50 µm. Under CL imaging for all images, the light areas in the zircon are depleted in Th
967 and U relative to dark areas in the zircon.

968

969 **Figure 2:** (a) BSE and (b) CL images of a grain fragment of the starting zircon from a nepheline
970 syenite pegmatite, Seiland igneous province, northern Norway.

971

972 **Figure 3:** Sketch of the CaF₂ assembly used in the experiments with the piston cylinder apparatus
973 showing the location of the four Pt capsules separated by biotite sheets.

974

975 **Figure 4:** (a,c,d) CL images of a zircon grain fragment reacted in a Na₂Si₂O₅ + H₂O solution +
976 ThO₂ + ThSiO₄ + SiO₂ at 900 °C and 1000 MPa. Altered areas (light areas in CL) are enriched in
977 Th and depleted in U, Pb, and (Y+REE) (see Tables 2 and 3). Figure 4b is a TEM foil taken from
978 the elongated area located across the reaction front shown in Figure 4a. Note the lack of any
979 reaction texture in the TEM foil nor the indication of a reaction front (the sharp boundary between

980 light and dark areas in [Figure 4b](#)). Dark ovals in the background are from the carbon foil upon
981 which the TEM foil rests.

982

983 **Figure 5:** BSE (a) and CL (b) images of a zircon grain fragment reacted in a 2N NaOH solution +
984 $\text{ThO}_2 + \text{ThSiO}_4 + \text{SiO}_2$ at 900 °C and 1000 MPa. Altered areas (light areas in CL) are enriched in
985 Th and depleted in U, Pb, and (Y+REE) (see [Tables 2 and 3](#)). [Figure 5b](#) is a TEM foil taken from
986 the elongated area across the reaction front shown in [Figure 5a](#). Note the lack of any reaction
987 texture in the TEM foil nor the indication of a reaction front (the sharp boundary between light and
988 dark areas in [Figure 5b](#)). Dark ovals in the background are from the carbon foil upon which the
989 TEM foil rests.

990

991 **Figure 6: (a,c,d,e,f)** CL images of zircon reacted in a NaF + H₂O solution + $\text{ThO}_2 + \text{ThSiO}_4 +$
992 SiO_2 at 900 °C and 1000 MPa. Altered areas (light areas in CL) are enriched in Th and depleted in
993 U, Pb, and (Y+REE) (see [Tables 2 and 3](#)). [Figure 6b](#) is a TEM foil taken from the elongated area
994 across the reaction front shown in [Figure 6a](#). Note the lack of any reaction texture in the TEM foil
995 nor the indication of a reaction front (the sharp boundary between light and dark areas in [Figure 6b](#)).
996 Dark ovals in the background are from the carbon foil upon which the TEM foil rests. Note also the
997 overgrowth of zircon near the top of [Figure 6a](#) (sharp crystallographic faces) and compare this to
998 the lack of crystallographic faces along the bottom of the grain where intergrowth occurs into the
999 zircon body via fluid-aided coupled dissolution-reprecipitation. In [Figures 6e and 6f](#) alteration is
1000 seen along cracks and possible cleavage planes in the zircon.

1001

1002 **Figure 7:** Chondrite normalized ([McDonough and Sun, 1995](#)) plots of Y + HREE from altered and
1003 unaltered areas of zircon in experiments (a) ZF-5 ($\text{Na}_2\text{Si}_2\text{O}_5 + \text{H}_2\text{O}$), (b) ZF-9 (2N NaOH), (c) ZF-
1004 16 (NaF + H₂O), and (d) ZF-40 (NaF + H₂O) (see [Tables 2 and 3](#); [Supplementary Material Table](#)
1005 [S4](#)).

Table 1. Experimental results from metasomatic alteration of zircon.

Experiment	P (MPa)	T (°C)	Time (h)	Zrn	Th,Si Mix	NaCl	KCl	NaF	Na ₂ Si ₂ O ₅	H ₂ O	2N NaOH	2N KOH	Results
ZF-4	1000	900	144	22.54	5.2					6.4			no reaction
ZF-5	1000	900	144	21.03	5.08				10.23	5.6			reaction
ZF-6	1000	900	144	20.43	4.09							6.17	no reaction
ZF-9	1000	900	147	21.79	4.83						5.55		reaction
ZF-12	1000	900	142	19.24	4.97		3.19			2.18			no reaction
ZF-13	1000	900	144	21.85	5.02	2.63				2.18			no reaction
ZF-16	1000	900	132	20.31	4.42			1.12		4.98			strong reaction
ZF-40	1000	900	192	13.06	2.00			2.41		7.27			strong reaction

Solid and fluid in mg

Table 2. Representative SHRIMP analyses of zircon (ppm) experimentally metasomatised at 900 °C and 1000 MPa in a series of alkali-bearing fluids.

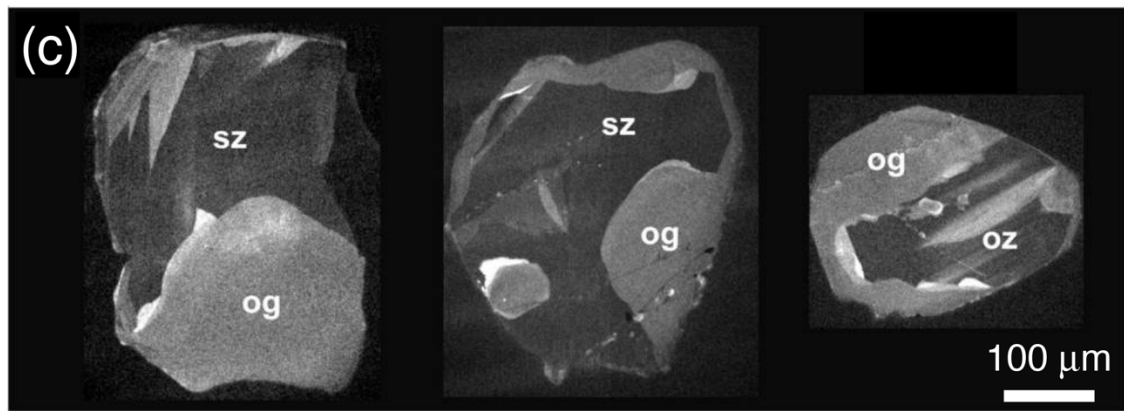
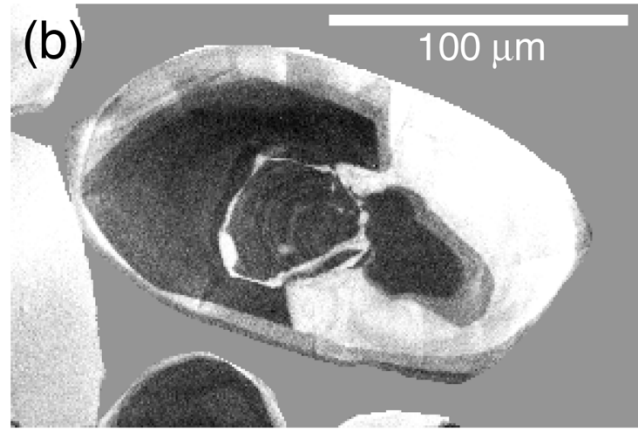
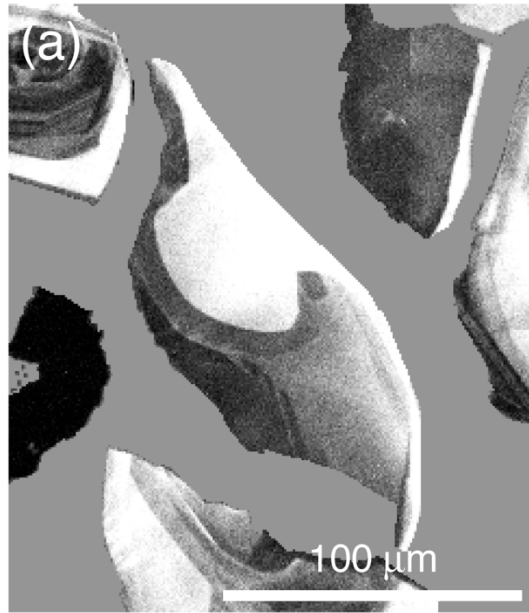
fluid zircon area Element	ZF-5				ZF-9 ^c		ZF-16			
	ThO ₂ + ThSiO ₄ + SiO ₂ + Na ₂ Si ₂ O ₅ + H ₂ O				ThO ₂ + ThSiO ₄ + SiO ₂ + 2N NaOH		ThO ₂ + ThSiO ₄ + SiO ₂ + NaF + H ₂ O			
	unaltered		altered		unaltered	altered	unaltered		altered	
	1s ^a	Mean	1s ^b			Mean	1s ^b	Mean	1s ^b	
Y89	240	1.30	123	1.63		209	2.19	24.3	10.2	
La139	0.01	0.01	0.03	0.01		0.03	0.02	0.03	0.00	
Ce140	3.23	0.08	0.06	0.03		2.67	0.18	0.05	0.01	
Pr141	0.01	0.01	0.02	0.00		0.01	0.01	0.02	0.01	
Nd146	0.15	0.13	0.06	0.09		0.17	0.15	0.10	0.08	
Sm147	0.33	0.04	0.01	0.02		0.38	0.19	0.02	0.03	
Eu153	0.57	0.04	0.06	0.02		0.40	0.05	0.02	0.02	
Gd157	2.19	0.26	3.63	2.09		2.36	0.24	0.02	0.03	
Tb159	1.21	0.03	0.16	0.04		1.18	0.09	0.08	0.03	
Dy163	16.8	0.60	2.19	1.51		15.2	0.94	1.53	0.78	
Ho165	7.09	0.15	1.64	0.72		6.69	0.12	1.18	0.52	
Er166	37.4	0.46	10.1	6.07		31.8	0.15	7.91	3.21	
Tm169	8.43	0.20	3.49	2.29		7.77	0.16	2.53	0.63	
Yb172	88.1	4.48	40.1	25.5		78.1	1.18	28.1	8.36	
Lu175	17.2	1.24	7.87	7.40		16.8	0.93	7.29	1.65	
Hf178	4731	152	4598	58.3		4360	116	4715	207	
Rad 206Pb	4.56		bd		5.06		bd	3.68	bd	
Th	51.1		1197		50.6		1070	37.4	457	
U	61.1		5.5		66.8		4.22	47.8	0.33	

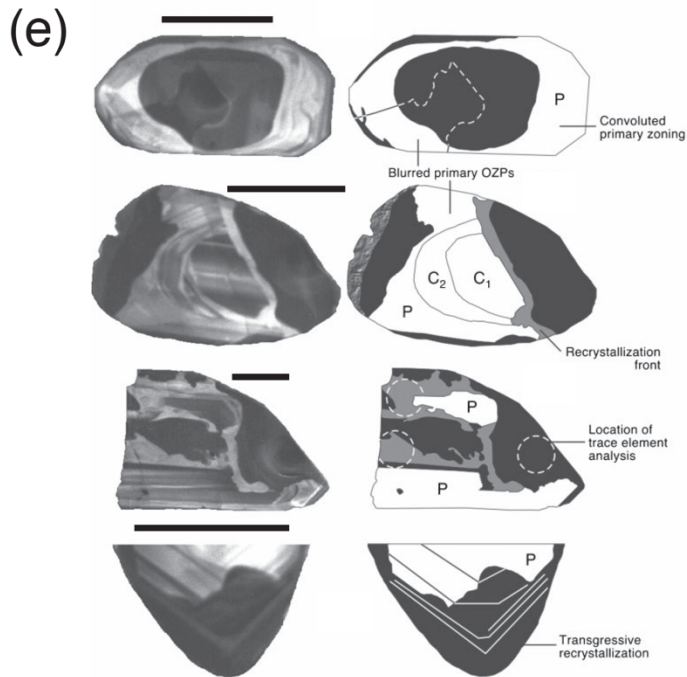
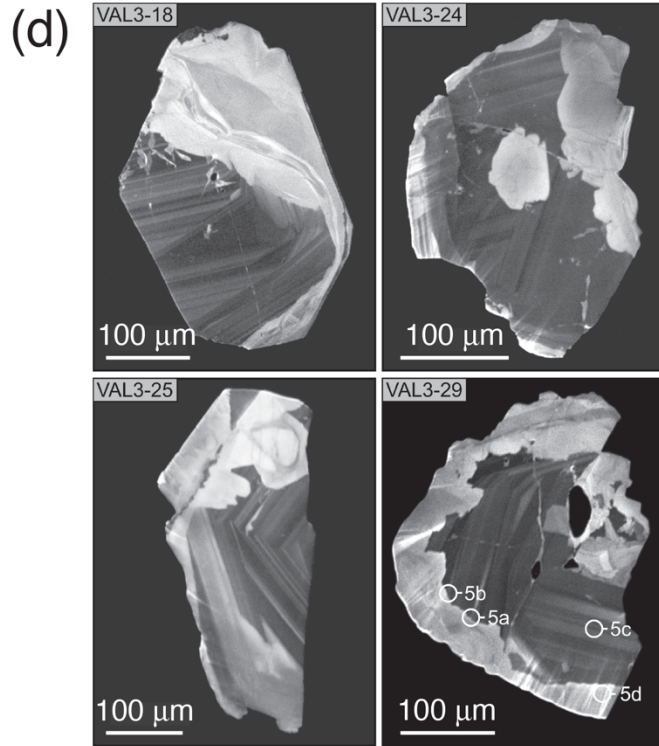
a - instrumental error; b - mean error; c - REE not measured; bd - below detection limit; Rad - radiogenic.

Table 3. LA-ICPMS analysis of zircon (ppm) experimentally metasomatised at 900 °C and 1000 MPa in a series of alkali-bearing fluids.

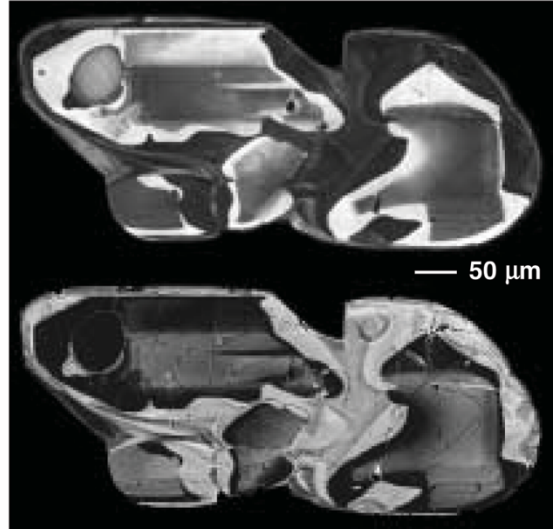
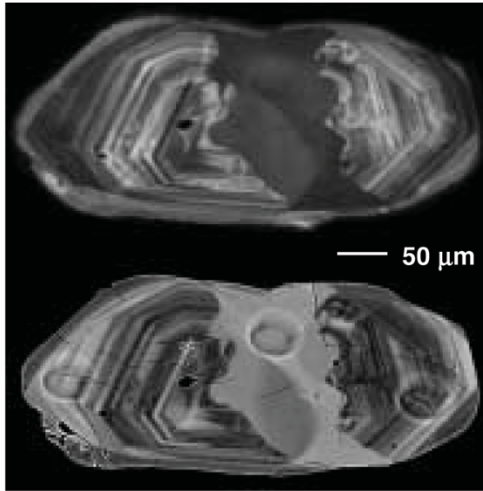
fluid	ZF-5				ZF-9			ZF-16				ZF-40			
	ThO ₂ + ThSiO ₄ + SiO ₂ + Na ₂ Si ₂ O ₅ + H ₂ O				ThO ₂ + ThSiO ₄ + SiO ₂ + 2N + NaOH			ThO ₂ + ThSiO ₄ + SiO ₂ + NaF + H ₂ O				ThO ₂ + ThSiO ₄ + SiO ₂ + NaF + H ₂ O			
	unaltered		altered		unaltered		altered	unaltered		altered		unaltered		altered	
zircon area															
#pts	2		2		7		1	4		5		16		18	
Element	Mean	1s	Mean	1s	Mean	1s		Mean	1s	Mean	1s	Mean	1s	Mean	1s
P31*	72.0	4.2	89.2	24.5	90.8	45.2	19.7	38.7	14.2	35.8	9.13	65.4	19.4	52.1	16.7
Ti47	2350	40.3	2214	96.6	2254	79.3	2152	2340	28.3	2343	60.1	2182	31.5	2188	27.3
Y89	243	0.50	116	3.40	213	22.9	90.5	209	3.64	44.8	17.9	250	27.5	67.9	17.5
La139	0.00	0.00	0.01	0.01	0.01	0.02	0.00	0.00	0.00	0.00		0.00	0.00	0.00	0.00
Ce140	3.68	0.08	0.02	0.03	3.11	0.26	0.26	3.16	0.17	0.03	0.06	3.39	0.40	6.97	1.03
Pr141	0.02	0.02	0.00	0.01	0.01	0.02	0.00	0.01	0.01	0.00	0.01	0.01	0.02	0.00	0.00
Nd146	0.11	0.16	0.06	0.09	0.16	0.12	0.00	0.15	0.04	0.01	0.02	0.24	0.18	0.02	0.02
Sm147	0.56	0.00	0.03	0.04	0.34	0.23	0.00	0.43	0.10	0.02	0.02	0.63	0.28	0.05	0.04
Eu153	0.59	0.02	0.00	0.00	0.43	0.10	0.00	0.49	0.06	0.03	0.04	0.59	0.19	0.03	0.02
Gd157	3.25	0.16	4.95	1.58	3.27	0.66	0.49	3.14	0.09	0.15	0.12	3.83	0.87	0.73	0.20
Tb159	1.58	0.16	0.24	0.05	1.29	0.18	0.39	1.32	0.04	0.19	0.06	1.60	0.33	0.55	0.14
Dy163	20.4	0.72	3.50	0.66	18.2	2.29	3.92	18.0	0.33	3.67	1.56	21.9	2.93	8.84	2.29
Ho165	8.37	0.35	2.10	0.61	7.45	1.10	3.02	7.46	0.24	2.39	1.05	8.81	1.13	4.23	1.05
Er166	46.5	1.66	16.9	2.52	38.9	4.85	18.5	38.3	1.13	17.0	7.22	45.9	5.02	25.4	6.12
Tm169	10.2	0.33	5.51	0.79	9.54	1.21	6.12	9.18	0.26	5.61	2.41	10.6	0.90	6.52	1.61
Yb172	106	1.59	65.6	4.68	93.3	11.1	54.0	93.5	3.41	62.0	24.0	108	8.79	70.6	17.1
Lu175	21.0	0.50	15.7	0.40	18.8	2.08	18.7	17.8	0.56	14.7	5.43	20.9	1.61	14.9	3.45
Hf178	6242	203	5770	169	6160	567	5483	5772	58.9	5996	495	5622	288	5752	87.7
Pb208	2.88	0.07	0.23	0.32	2.39	0.33	0.33	1.93	0.17	0.01	0.02	2.48	0.64	0.01	0.01
Th232	49.7	2.57	775	5.46	45.5	6.41	693	42.5	2.39	23124	48201	47.6	11.4	601	142
U238	62.4	1.85	3.13	0.49	53.7	5.03	6.76	52.3	2.16	5.84	1.99	56.1	9.28	0.00	0.01

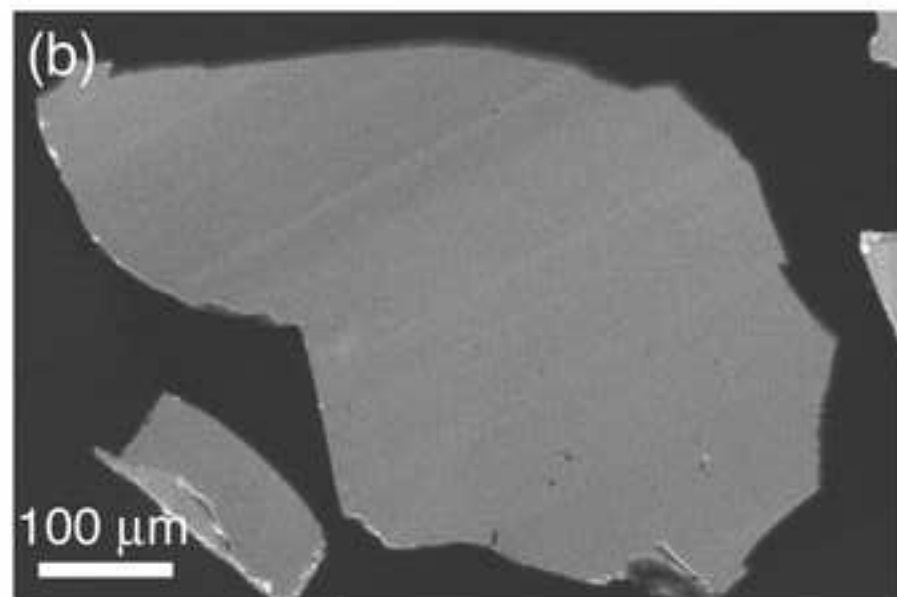
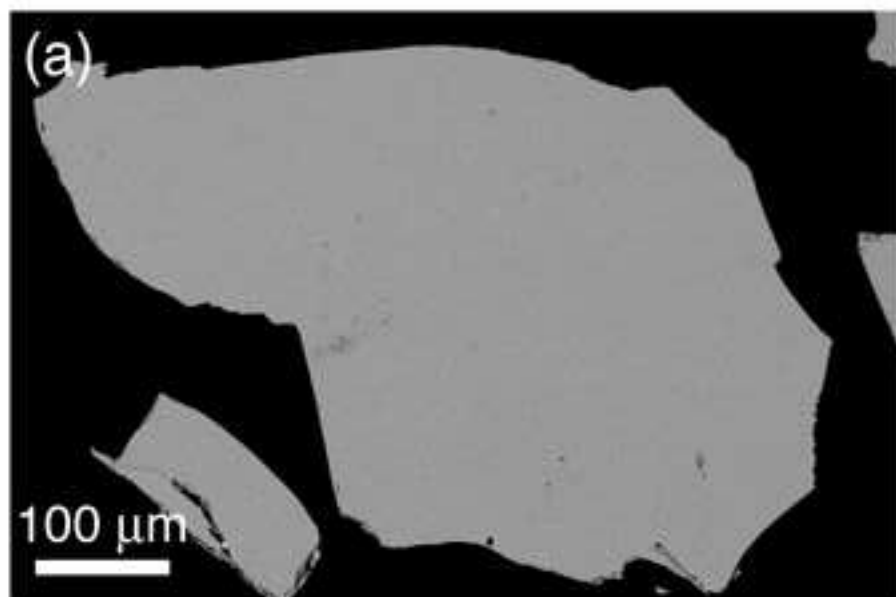
* - approximate values for P, i.e. less than the value stated.

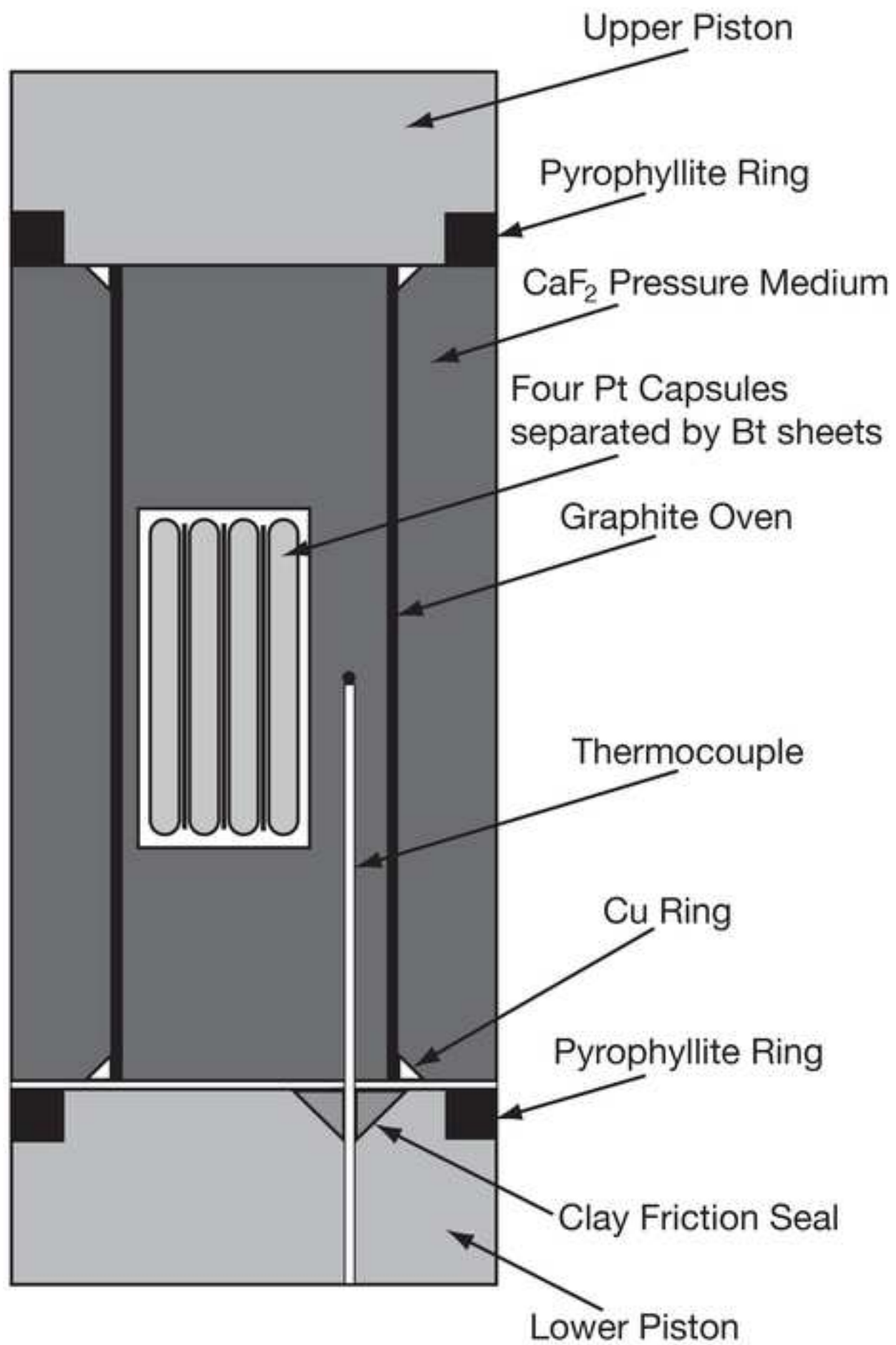


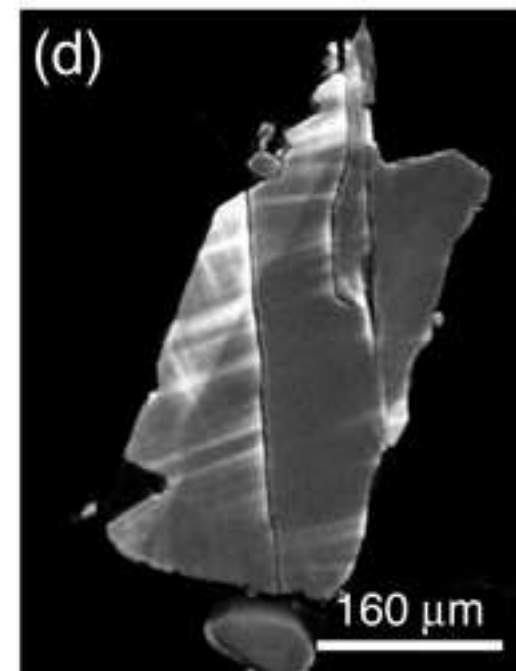
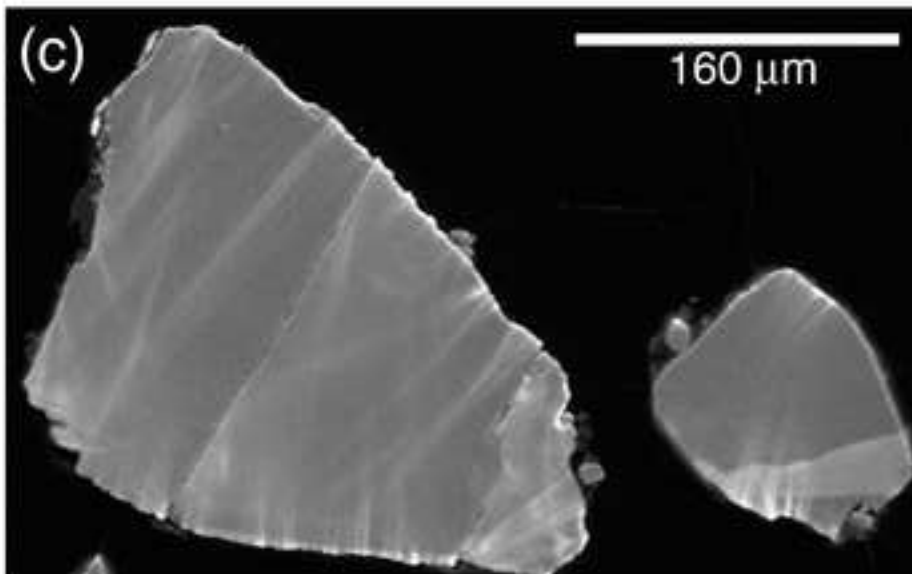
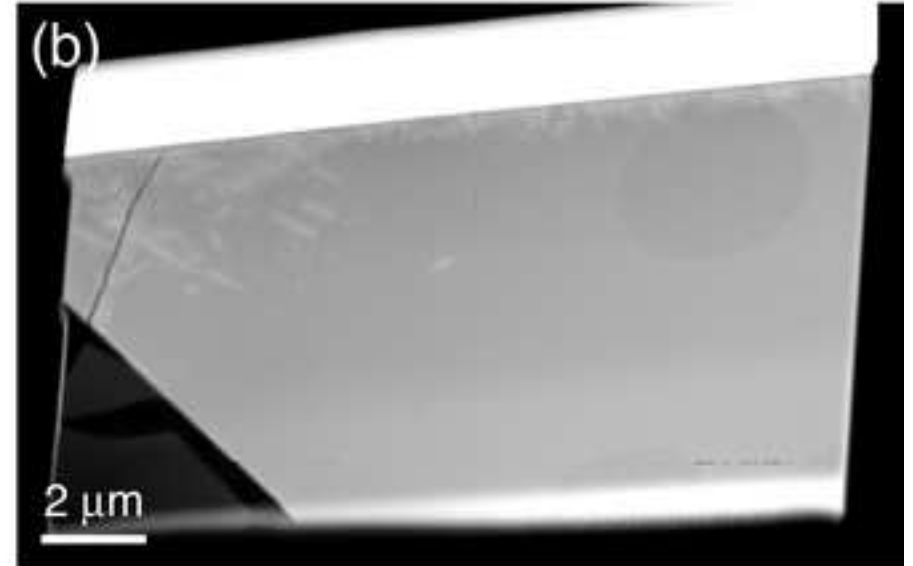
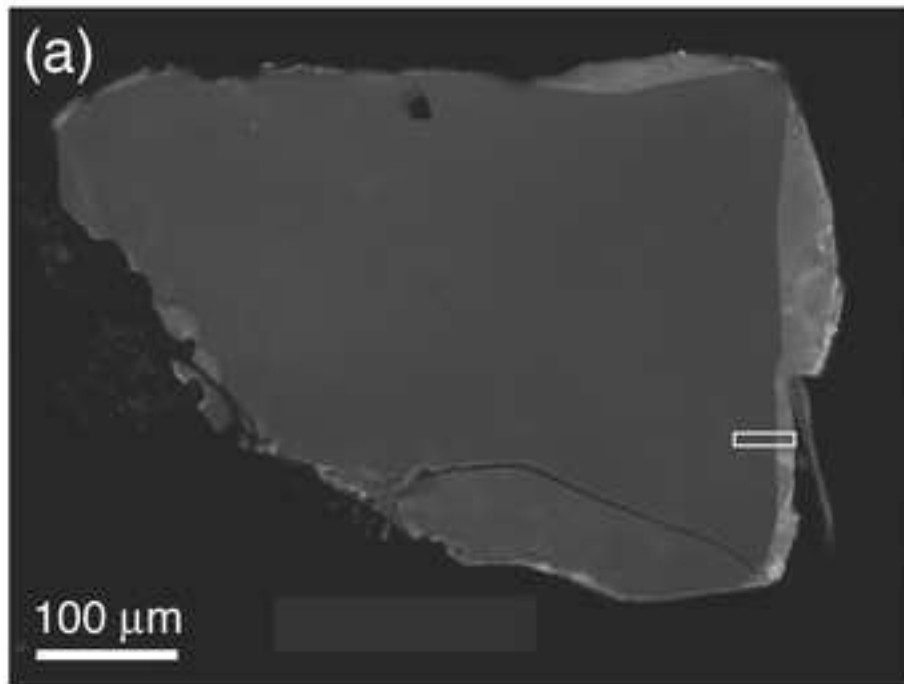


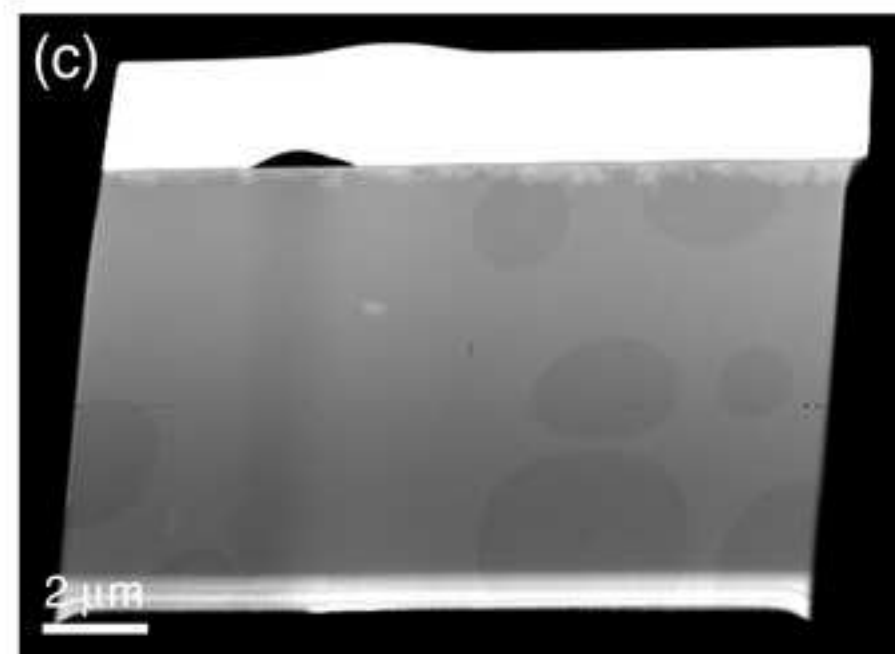
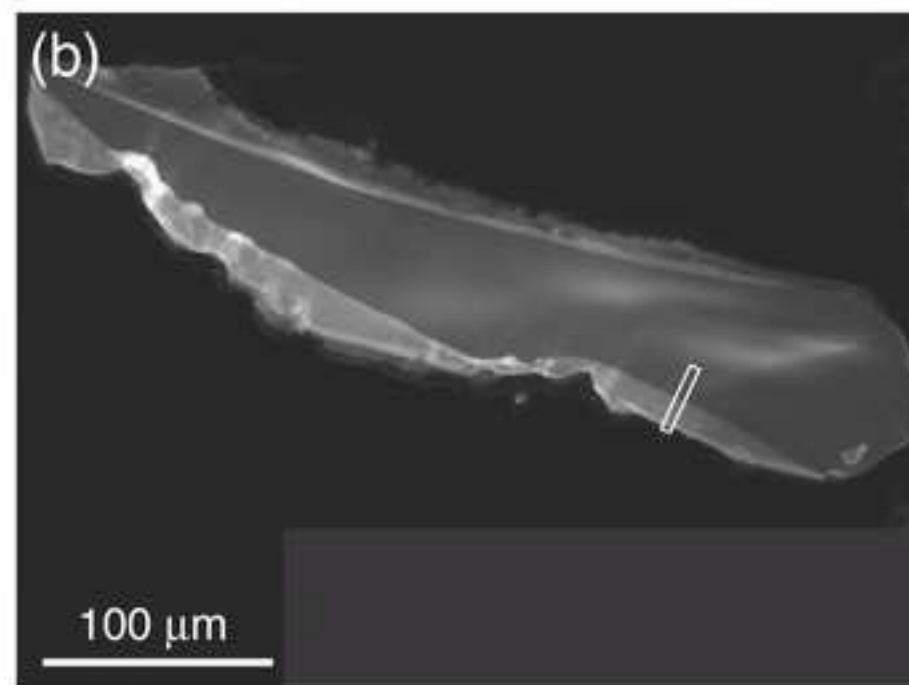
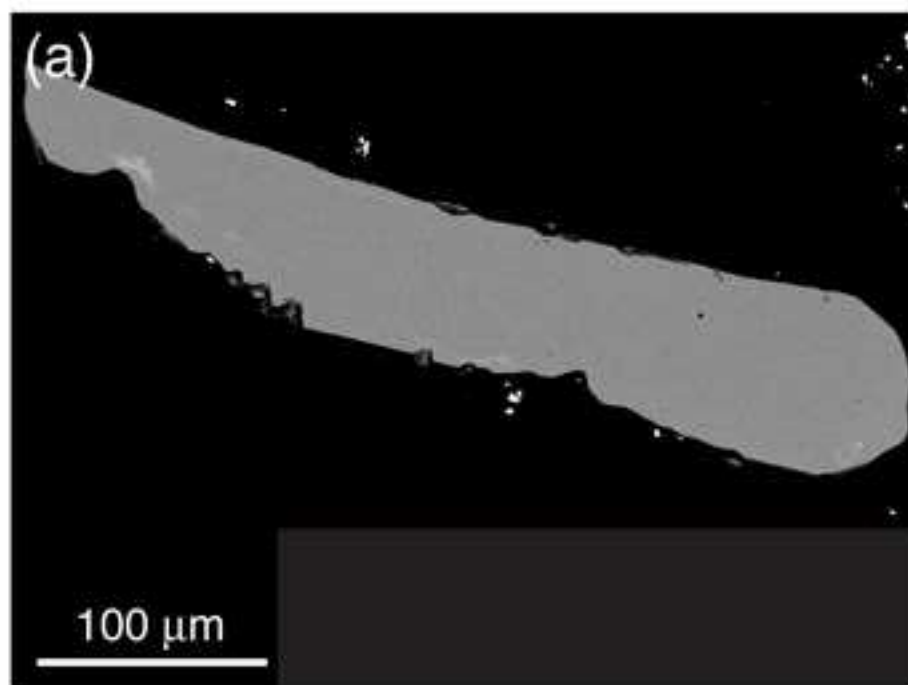
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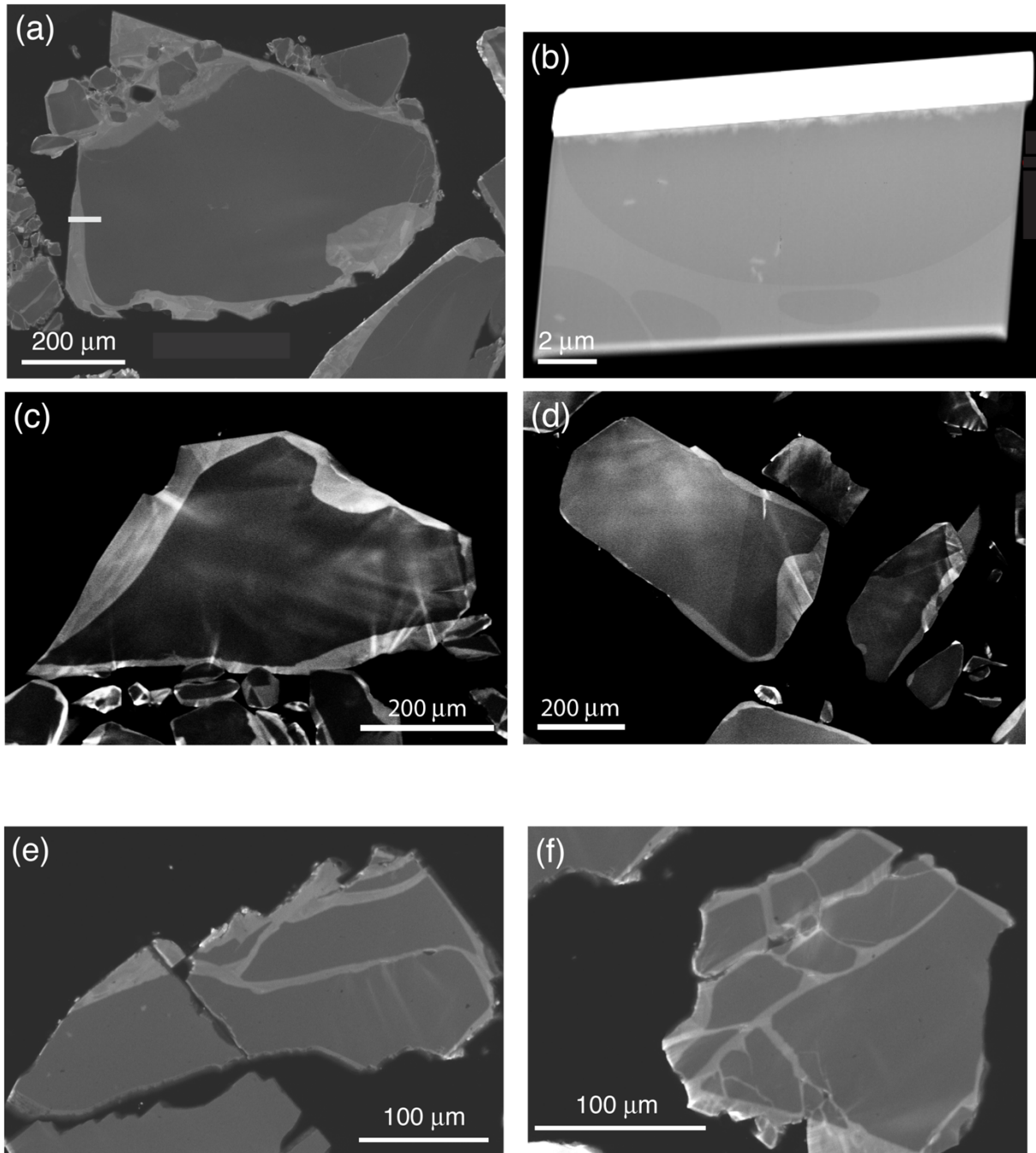


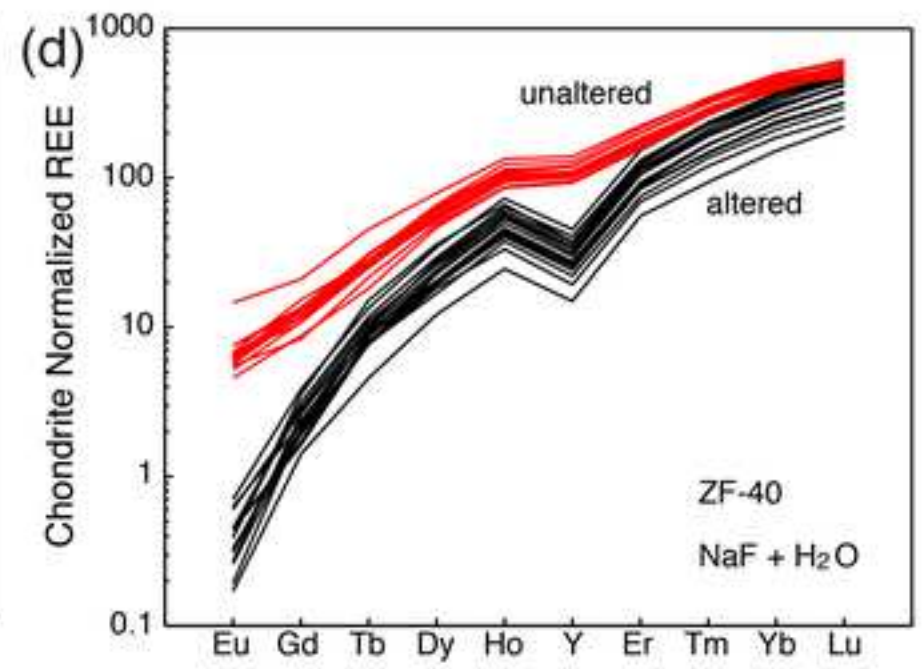
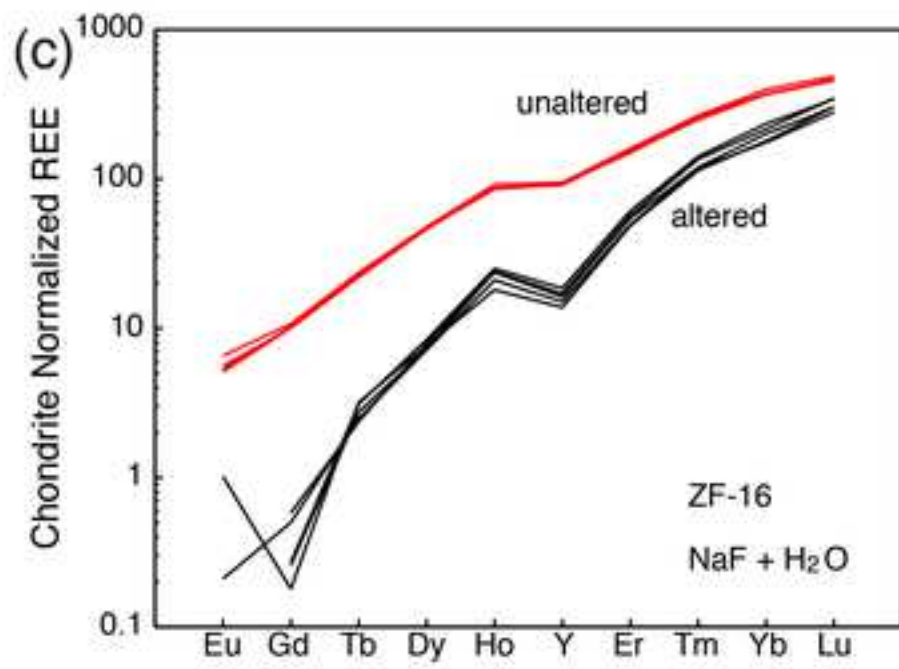
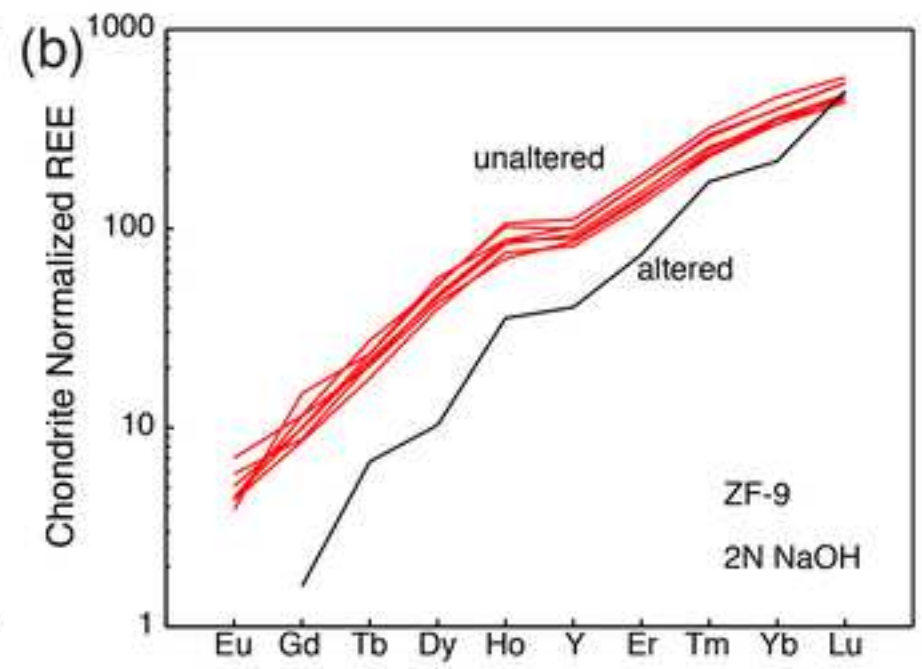
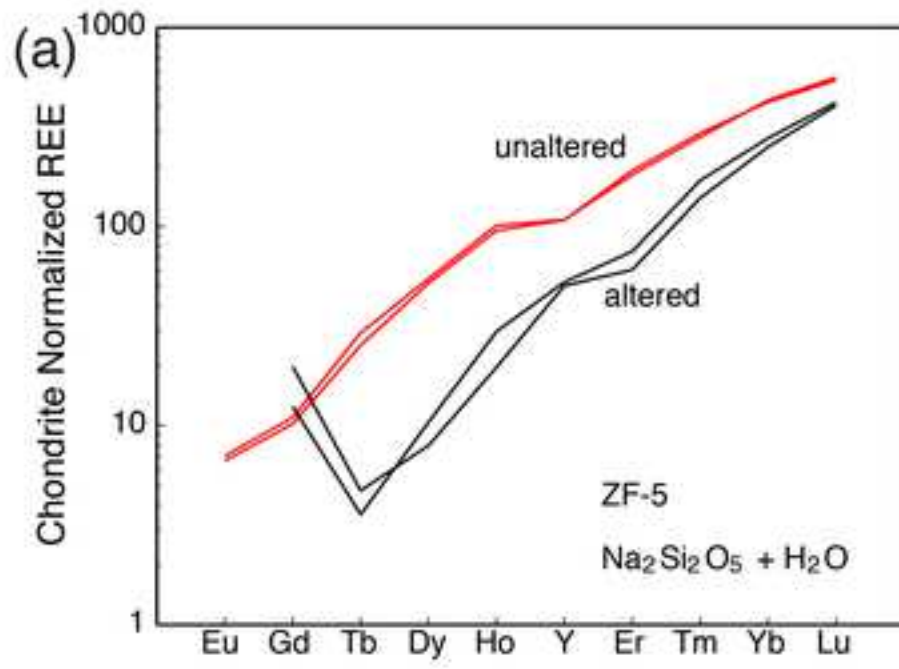






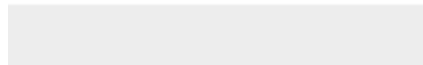






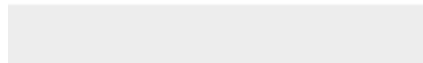


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Table S1 - EPMA Data.xls





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Table S2 - SHRIMP UThPb.xls

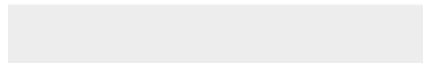




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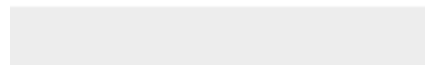
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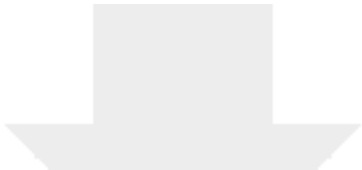
Table S3 - SHRIMP YBaREEHf.xls






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Table S4 LA-ICPMS reduced.xls





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Figure S1.pdf



Declaration of interests

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests: