

1 Revision 2

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3 **Resolving oxygen isotopic disturbance in zircon: a case study from the low $\delta^{18}\text{O}$**

4 **Scourie dykes, NW Scotland**

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15

16 **Abstract**

17 In this paper, we describe an in-situ non-destructive technique to identify areas within
18 zircon crystals that have experienced fluid exchange. We show that Raman spectroscopy
19 combined with electron microprobe trace-element analysis can be used to pinpoint areas
20 in altered, complexly zoned, and metamict zircon that record the original magmatic
21 compositions. These techniques are developed on a suite of Paleoproterozoic zircon
22 crystals from the Scourie dyke swarm in the Archean gneiss terrane of NW Scotland that
23 are known to be anomalously low in $\delta^{18}\text{O}$.

24

25 We show that zircons from the Scourie dykes record extremely low $\delta^{18}\text{O}$ isotopic
26 compositions down to ~ -3 ‰ which reflect their magmatic values. Zircon populations
27 from the dykes have a range in $\delta^{18}\text{O}$ from low values (<0 ‰) up to ~ 5 ‰ with no
28 obvious relationship between oxygen isotopic composition and cathodoluminescence.
29 Raman spectra from the zircons show evidence for fluid interaction in some areas of the
30 grains because of partial recrystallization and atypical radiation damage properties.
31 Electron microprobe analysis in the same areas documents high (>1000 ppm) U
32 concentrations and high (>1000 ppm) abundances of non-formula Ca. When the
33 combined Raman and electron microprobe data are used to filter the oxygen isotopic data,
34 the fluid altered areas of the grains show consistently higher $\delta^{18}\text{O}$ values than the areas
35 without evidence for fluid alteration. The low $\delta^{18}\text{O}$ values therefore reflect the original
36 magmatic composition of the grains and indicate that the Scourie dyke magmas were low
37 in ^{18}O . We suggest that these non-destructive techniques should be used prior to SIMS
38 analysis of complex zircons to target the least disturbed areas of the grains.

39

40

Introduction

41 In magmatic systems, oxygen isotopes are used to probe the origin of magmas, evaluate
42 inter-mineral equilibrium, and calculate the temperatures of mineral pairs (e.g. Valley et
43 al. 1986; Valley and Cole, 2001). The oxygen isotopic composition of a rock can be
44 altered through geological processes, such as metamorphism, where increased
45 temperatures and fluid-rock interaction enhance isotopic exchange between minerals via
46 grain boundary and volume diffusion (see Valley, 2001). Hydrothermal alteration may

47 also significantly alter the oxygen isotopic composition of a rock through exchange
48 between the minerals and the fluid, thereby reducing the ability to obtain meaningful
49 geological information about its origin.

50

51 Zircon is one of the most robust recorders of the oxygen isotopic composition of a
52 magmatic rock as it may retain the original isotopic signature through high-grade
53 metamorphism and even anatexis (see Valley, 2003). Both experimental and natural
54 samples suggest that oxygen isotopic diffusion in crystalline zircon is extremely slow
55 even at high temperatures (Muehlenbachs and Kushiro, 1975; Cherniak and Watson,
56 2003; Page et al. 2007; Bowman et al. 2011). However, damage to the zircon crystal
57 structure can occur through several processes, including radiation damage due to the
58 presence of elevated concentrations of radioactive elements U and Th (Booth et al. 2005).
59 Enhanced radiation damage creates amorphous domains and a porous structure that is
60 susceptible to fluid infiltration and oxygen isotopic exchange (Valley et al. 1994; Geisler
61 et al. 2003a).

62

63 Zircon that has experienced fluid exchange may be indirectly identified because the
64 exchanging fluid causes disturbance in other geochemical properties of the crystal, not
65 simply oxygen isotope systematics (e.g. Valley, 2003; Valley et al. 2005; Cavosie et al.
66 2005, 2006; Booth et al. 2005;). Zircons that have experienced fluid exchange typically
67 have disturbed U-Pb isotopic systematics, recognized by discordance in their $^{206}\text{Pb}/^{238}\text{U}$
68 and $^{207}\text{Pb}/^{235}\text{U}$ dates (e.g. Krogh, 1982; Valley et al. 1994; Geisler et al. 2003b,c;
69 Breeding et al. 2004), alteration of zoning seen in cathodoluminescence (CL) and back-

70 scattered electron images (Corfu et al. 2003; Geisler et al. 2007), elevated trace element
71 contents (Geisler et al. 2002, 2003b; Rayner et al. 2005), as well as disturbance of the
72 oxygen isotope systematics (Valley et al. 1994; Valley, 2003).

73

74 Populations of fluid-altered zircon can produce highly variable U-Pb ages and oxygen
75 isotopic compositions that are difficult to interpret, clouding the true geologic history
76 (e.g. Nemchin and Pidgeon, 1997; Pidgeon et al. 2013). In these cases, numerous
77 analyses, and often multiple techniques, are required to “see through” the effects of the
78 fluid alteration in order to determine the original age and oxygen isotopic composition of
79 the zircon and host rock (e.g. Liu and Zhang, 2013). Even so, the original magmatic
80 composition of a fluid-altered zircon may still be unclear.

81

82 Here we show that recognizing the oxygen isotopic disturbance in zircon may be better
83 evaluated through a combination of Raman spectroscopy and trace element analyses, as a
84 compliment to U-Pb dating and CL imaging. We describe a non-destructive technique
85 that can be used to determine which zircon grains or areas of grains record the original, or
86 near-original oxygen isotopic composition of a zircon population. This is especially
87 useful in scenarios where the whole rock (WR) oxygen isotopic composition has been
88 modified by secondary processes.

89

90 The technique is applied to complex zircon populations from nine mafic Paleoproterozoic
91 Scourie dykes from NW Scotland, and confirms that these zircons originated from low- δ
92 ^{18}O magmas as previously shown by Cartwright and Valley (1991). We are able to

93 identify areas in the grains that have experienced the least amount of fluid exchange and
94 therefore approach magmatic values.

95

96 **Metamictization and structural recovery**

97 Zircon (ZrSiO_4) is the most common U- and Th-bearing accessory mineral in upper
98 crustal rocks and therefore, the primary target for U-Pb geochronology (see Hanchar and
99 Hoskin, 2003). Over time, U and Th decay to different isotopes of Pb via a sequence of
100 decay reactions ejecting either an alpha particle or a combination of a beta and an
101 antineutrino particle from the nucleus. The prolonged accumulation of alpha fission track
102 and alpha recoil (radiation) damage can cause zircon to change from a crystalline to a
103 metamict state, with alpha recoil causing the majority of the radiation damage (Holland
104 and Gottfried, 1955; Weber et al. 1994; Ewing et al. 2003). During alpha recoil, the
105 heavy nucleus (daughter isotope) expends its energy in short-range elastic collisions
106 causing ~1000 atomic displacements creating a completely amorphous domain with a
107 diameter of ~5 nm (Ewing et al. 1987, 2003; Geisler et al. 2003a). These amorphous
108 domains have a unique structure with a matter-depleted core surrounded by a SiO_n
109 polymerized high-density rim (Trachenko et al. 2001, 2002, 2004; Geisler et al. 2003a).
110 Accumulation of these amorphous domains over time within zircon causes shear
111 deformation (Ríos and Salje, 1999), swelling, and volume expansion (Murakami et al.
112 1991; Weber et al. 1994), all of which result in a reduction in density (Holland and
113 Gottfried, 1955).

114

115 Once zircon has reached a state of metamictization such that the amorphous domains
116 overlap and create an interconnected network (the percolation point from Salje et al.
117 1999), its low density and porous nature result in an increase in the diffusion coefficient
118 of water by ~10 orders of magnitude from the original crystalline state (Geisler et al.
119 2003a). Interestingly, experimental and natural evidence suggests that highly metamict
120 zircon can be partially recrystallized in the presence of ~200-400 °C fluids infiltrating
121 through a diffusional process into the crystal (Geisler et al. 2003b,c). Geisler et al.
122 (2003b) suggest that the partial structural recovery (recrystallization) of zircon is
123 catalyzed by the diffusion of hydrous species into the grain, which also introduce non-
124 formula solvent cations such as Ca and Al (Geisler et al. 2002; Hoskin and Schaltegger,
125 2003; Rayner et al. 2005), and expel non compatible radiogenic Pb which builds up in
126 metamict areas resulting in Pb loss (Table 1; Pidgeon, 1992; Geisler et al. 2003c; Rayner
127 et al. 2005). This process is referred to as diffusion reaction.

128

129 Recovery from a metamict state via diffusion reaction is not favored in all studies. Putnis
130 (2002); Tomaschek et al. (2003); Putnis et al. (2005) and Hay et al. (2009) suggest that
131 metamict zircon can also be dissolved during interaction with fluids and new zircon re-
132 precipitated epitaxially in its place. This model results in crystalline but highly porous
133 new zircon growth, pseudomorphing the parent crystal. The newly grown zircon is
134 devoid of radiogenic or common Pb, has very low contents of solvent cations (U, Th, Ca
135 etc), has completely reset isotopic systematics, and often contains mineral inclusions
136 (Table 1). Both the diffusion reaction and dissolution re-precipitation models are end
137 members of the structural recovery process, and although both models require the

138 involvement of a hydrous phase, each model produces distinct features in zircon (Table 1;
139 Geisler et al. 2007).

140

141 Radiation damage and structural recovery is further complicated by the overall
142 temperature of the hydrothermal system since structural damage due to α radiation can
143 only be retained in zircon at temperatures below ~ 250 °C (Murakami et al. 1991;
144 Meldrum et al. 1999; Geisler et al. 2001; Davis and Krogh, 2000; Moser et al. 2011;
145 Pidgeon 2013).

146

147 In addition to the chemical differences described above, structural recovery through
148 diffusion or dissolution re-precipitation produces distinctive Raman spectroscopic
149 responses (Geisler et al. 2001, 2003b,c; Fig. 1). However, the connection between fluid
150 mediated recrystallization recovery, Raman spectroscopy and oxygen isotopic
151 disturbance has not previously been established

152

153 **Raman response to metamictization and structural recovery**

154 Detailed discussions of the Raman response to metamictization in zircon (Nasdala et al.
155 1995, 1998a, 2001; Zhang et al. 2000a), along with thermal annealing (Zhang et al.
156 2000b; Geisler et al. 2001a, 2002; Nasdala et al. 2002) and hydrothermal alteration of
157 zircon (Geisler et al. 2007) have been previously provided, and only the most relevant
158 aspects are reviewed here.

159

160 Raman spectrometry measures the phonon frequency of a molecular vibration in a crystal.
161 Phonon modes in crystalline solids have frequencies that relate to the short-range angle
162 and length of a particular bond, whereas the band-width (full width at half max –
163 FWHM) is related to long-range order (e.g. Dillon et al. 1984). Therefore, the Raman
164 properties of zircon are perfectly suited to studying metamictization since both short-
165 range bond damage (e.g. Frenkle defect pairs) and long-range damage (fully amorphous
166 domains) build up over time (Fig. 1).

167

168 The band-width and frequency of the Raman ν_3 (SiO_4) band at $\sim 1000 \text{ cm}^{-1}$ are one of the
169 best indicators of the degree of metamictization in zircon (Nasdala et al. 1995, 1998a,b,
170 2001; Zhang et al. 2000a). This particular Raman mode measures the degree of order, or
171 crystallinity in one particular stretching mode of the silica tetrahedra. It retains a degree
172 of order (producing a measureable peak) even in extremely metamict zircon when all of
173 the other Raman active modes have been reduced to background. During
174 metamictization, the peak of the ν_3 (SiO_4) band becomes broader, changing from a band-
175 width of $\sim 3 \text{ cm}^{-1}$ for fully crystalline zircon (position A in Fig. 1) to >30 for extremely
176 metamict grains (Fig. 1). At the same time, the band becomes less intense and reduces in
177 frequency from $\sim 1008 \text{ cm}^{-1}$ for fully crystalline zircon, to $\sim 995 \text{ cm}^{-1}$ for the most
178 metamict grains (Nasdala et al. 1995; Wopenka et al. 1996; Nasdala et al. 1998a, 2001;
179 Zheng et al. 2000, Geisler et al. 2003c). The change in parameters follows a linear trend,
180 which has been referred to as the radiation damage trend (Fig. 1; Geisler et al. 2003c).
181 When the zircon becomes highly metamict, the phonon frequency for the ν_3 (SiO_4) band

182 stops decreasing but the band-width continues to increase as the zircon moves towards a
183 completely amorphous state (Fig. 1).

184

185 Both types of fluid assisted structural recovery (described above) produce distinct Raman
186 signatures, which are described below.

187

188 **Diffusion-reaction.** A highly metamict zircon (position B in Fig. 1) will experience a
189 recovery of short range disorder (e.g. Frenkel defects) after exposure to low temperature
190 fluids (~200 °C), and this results in the recovery of the frequency of the ν_3 (SiO₄) phonon
191 mode with little recovery in the band-width (Geisler et al. 2002). The band-width of the
192 ν_3 (SiO₄) band can be completely recovered through exposure to higher temperature
193 fluids, which have higher crystallization kinetics enabling recovery of amorphous
194 domains. Once a zircon has experienced partial recovery of its radiation damage through
195 the diffusion-reaction process, the Raman band parameters should significantly deviate
196 from the radiation damage trend (see blue arrow in Fig. 1); under these conditions, it is
197 not clear how the Raman band parameters will respond to further metamictization
198 (perhaps follow the grey dashed arrow to C in Fig 1). The diffusion reaction trend for
199 structural recovery in zircon is similar to the trend produced through thermal annealing of
200 radiation damage, however, only recovery through fluid interaction is covered here.

201

202 **Dissolution-precipitation.** Zircon that newly crystallizes from metamict zircon (B in
203 Fig. 1) through dissolution-precipitation reactions should have a Raman response similar
204 to crystalline zircon (A in Fig. 1). The parent grain will have a distinct boundary between

205 the newly crystallized sections and the old metamict areas. Over time the newly
206 crystallized zircon should accumulate radiation damage along the radiation damage trend
207 (move to D in Fig. 1), although the U content of the new zircon is typically low and so it
208 is unlikely to accumulate damage quickly.

209

210 **Geological history of the samples**

211 The zircons in this study were extracted from nine dolerite and norite dykes from the
212 Scourie dyke swarm, Lewisian gneiss complex, NW Scotland (Fig. 2). All but two of the
213 dykes have been previously dated by the U-Pb TIMS technique (Davies and Heaman,
214 2014, the ages are shown in Fig. 2) with the remaining two dykes, the NAPI and JD09-2
215 dykes dated by U-Pb laser ablation inductively coupled plasma mass spectrometry (LA-
216 ICP-MS) during this study (see Sup. Table 1; Sup. Fig. 1). The zircons fall broadly into
217 three age categories; 1) ~2.5 Ga, zircons from the North Assynt and Loch a'Choin dykes,
218 which are interpreted to be xenocrysts rather than primary igneous zircons, 2) ~2.4 Ga,
219 zircons from JD09-2, Poll Eorna, Badcall Bay, Graveyard, Loch na h, and Lochan Fearna
220 dykes, and 3) ~2 Ga zircons from the NAPI dyke (Fig. 2).

221

222 All of the zircon within the dykes experienced a major Pb-loss event at ~430 Ma, thought
223 to be related to movement along the Moine thrust belt during the Caledonian orogeny
224 (Goodenough et al. 2011; Davies and Heaman, 2014). Basement rocks bounding the
225 fault zone contain metamorphic actinolite replacing hornblende and recrystallization of
226 feldspar phenocrysts, both of which suggest syntectonic temperatures of 350-400 °C
227 (upper greenschist) (Holdsworth et al. 2007). Many of the dykes also contain secondary

228 epidote group minerals and saucerization of plagioclase (Davies and Heaman, 2014),
229 which is consistent with fluid alteration of the dykes during the Caledonian.

230

231 Previous oxygen isotopic studies of the Scourie dykes have indicated that the Poll Eorna
232 and Graveyard dykes around the town of Scourie are anomalously low in $\delta^{18}\text{O}$ with WR
233 (whole rock) values of ~ 2 ‰ (Cartwright and Valley, 1991). The isotopically light
234 signature is thought to be primary and not related to contamination by the Lewisian
235 gneisses since the surrounding gneisses have $\delta^{18}\text{O}$ values of >6 ‰ (Cartwright and
236 Valley, 1991, 1992). Dykes containing more amphibole have $\delta^{18}\text{O}$ compositions of 5-6
237 ‰, which was thought to indicate interaction with crustal fluids during the Laxfordian
238 metamorphic event between 1950-1800 Ma (Cartwright and Valley, 1991). However, U-
239 Pb lower intercept ages of ~ 430 Ma from the dykes suggest that fluid alteration and Pb
240 loss likely occurred at ~ 430 Ma during the Caledonian (Davies and Heaman, 2014).

241

242

Analytical techniques

243 Secondary ion mass spectrometry (SIMS)

244 SIMS measurements were conducted using a CAMECA IMS1280 multicollector ion
245 microprobe at the Canadian Centre for Isotopic Microanalysis (CCIM), University of
246 Alberta. A 1 inch epoxy grain mount containing ~ 120 Scourie dyke zircons, along with
247 two aliquots of Mudtank and Temora reference zircons was prepared. After mechanical
248 grinding and polishing of the mount to ensure a perfectly flat surface, the mount coated
249 with 5 nm of Au prior to imaging with a scanning electron microscope (SEM). A further
250 25 nm of Au was subsequently deposited on the mounts prior to SIMS analyses.

251

252 The SIMS analytical conditions for O-isotopes used in this study broadly followed those
253 described by Ickert and Stern (2013) for garnet. Details of the specific instrument
254 conditions for the analytical session IP13048 are briefly described here. A $^{133}\text{Cs}^+$ primary
255 beam with $\sim 12\ \mu\text{m}$ diameter probe was rastered slightly during acquisition forming
256 rectangular shaped sputtered areas $\sim 15 \times 18\ \mu\text{m}$ across and $\sim 1.5\ \mu\text{m}$ deep. A normal
257 incidence electron gun was used for charge compensation. The transfer conditions for
258 negative ions from the sample included a $120\ \mu\text{m}$ entrance slit, $5 \times 5\ \text{mm}$ pre-ESA (field)
259 aperture, and 100x image magnification at the field aperture with the energy window set
260 at full transmission. Faraday cups were used to simultaneously measure the oxygen
261 isotopes. Mass resolution ($\Delta m/m$) was typically 1950 and 2250, for ^{16}O and ^{18}O
262 respectively. The stability of the Faraday cup baselines was checked at the beginning of
263 the day and the baseline was found to be sufficiently stable and low that no further
264 corrections or analysis was necessary. Secondary ion count rates for $^{16}\text{O}^-$ were $\sim 1.5 - 3 \times$
265 $10^9\ \text{c/s}$. A single analysis took 4.5 minutes and comprised rastering the probe for 30 - 60
266 s over a $20 \times 20\ \mu\text{m}$ area to clean and implant Cs^+ , followed by automated secondary ion
267 tuning, and 100 s of measurement.

268

269 Analyses of the reference materials (RM) were processed collectively for long-term drift
270 and spot-to-spot statistics for the entire analytical session (see Ickert and Stern, 2013).
271 Instrumental mass fractionation (IMF) was monitored by repeat analyses of the reference
272 materials in a 1:4 sequence (RM: unknowns) using RMs S0022 (TEM2 Temora) zircon
273 with $\delta^{18}\text{O}_{\text{VSMOW}} = +8.2\ \text{‰}$ (Black et al. 2004) or S0081 (UAMT1 Mudtank) zircon with

274 $\delta^{18}\text{O}_{\text{VSMOW}} = +4.87 \text{ ‰}$ (Stern R., unpublished data). Individual spot uncertainties for
275 $\delta^{18}\text{O}$ at 95 % confidence are typically $\pm 0.2\text{‰}$, and include within-spot (counting) and
276 between-spot (geometric) errors.

277

278 **Scanning Electron Microscopy (SEM) and Electron probe micro-analysis (EPMA)**

279 Scanning electron microscopy was carried out before EPMA analysis since the
280 microprobe at the University of Alberta is not equipped with a cathodoluminescence (CL)
281 detector. The SEM used at the University of Alberta is a Zeiss EVO MA15 instrument,
282 which operated at 15 kV and ~ 3 nA. Cathodoluminescence was detected with a high-
283 efficiency parabolic mirror coupled to a detector (ETP Semra, Pty. Ltd., Australia) using a
284 broadband, high-sensitivity photomultiplier.

285

286 EPMA analyses of the zircons were conducted using a JEOL 8900 at the University of
287 Alberta. EPMA analyses was conducted after SIMS oxygen isotopic analyses and care
288 was taken to analyze within $\sim 10 \mu\text{m}$ of the SIMS spots (and Raman spots) to ensure good
289 spatial correlation between the techniques. Three wavelength dispersive spectrometers
290 were used, with each spectrometer assigned to two elements. Counting times of 600
291 seconds on the U-M β and Th-M α peaks and 300s on the background were used along
292 with 60 seconds on the Zr-L α , Si-K α and Ca-K α peaks and 30 seconds on the
293 background. An accelerating voltage of 15 kV and a 200 nA beam current were used
294 along with a $2 \mu\text{m}$ beam diameter. Counting statistics yielded lower limits of
295 quantification of 21 ppm for Ca, 82 ppm for U and 106 ppm for Th (6σ above
296 background; calculated using the formula of Potts, 1992 with the ZAF modification by

297 John Fournelle from the University of Wisconsin, Madison). Two secondary standards
298 (the Mud Tank and Temora zircons) were analyzed 9 times throughout the analytical
299 session to check for machine drift. Averaged secondary standard values are presented in
300 Table 2. Measured U content for the Temora zircon (260 ± 70 ppm) is in good agreement
301 with the published values of 228 ± 56 ppm (Black et al. 2004). The published Th
302 abundance is ~ 100 ppm (Black et al. 2004) which is at the limit of quantification in this
303 study (6σ above background).

304

305 The U content of the Mud Tank zircon is $\sim 30 - 80$ ppm (Yuan et al. 2008) which is at the
306 lower limit of quantification for U in this study. The Th content of Mudtank is ~ 7 ppm
307 (Yuan et al. 2008), significantly below the limit of quantification obtained here. The U
308 content obtained for Mud Tank zircon during this study is 146 ± 30 ppm, which is
309 slightly higher than the U content measured during the study of Yuan et al. (2008).

310

311 **Raman spectroscopy**

312 Laser Raman spectra were collected at the MacEwan University, Edmonton, using the
313 532 nm line of an Ar⁺ laser and a Bruker Senterra Raman spectrometer. The scattered
314 Raman light was analyzed by a charge-coupled device (CCD) detector after being
315 dispersed by a grating of 1800 groves per mm. A 50x objective lens was used to focus
316 the laser beam resulting in a spot diameter of 2.5 μm , a depth resolution of 5 μm and a
317 spatial resolution of $< 10 \mu\text{m}^3$. The spectral resolution was $\sim 3 \text{ cm}^{-1}$ with a wavenumber
318 accuracy of $\pm \sim 0.5 \text{ cm}^{-1}$, which was determined by analyzing the same spot multiple
319 times throughout the analytical session. A laser power of 10 mW was used, which has

320 been shown to occasionally cause color changes in some strong light adsorbing zircons
321 (typically black and brown colored grains) at the location of the spot, and melting of the
322 surrounding epoxy due to heating of the zircons (Nasdala et al. 1998a). However, since
323 zircons in this study were all transparent, no light absorbed temperature increases were
324 observed. Also, analysis of the same spot multiple times during the analytical session
325 indicated that the 10 mW laser was causing no detectable structural changes. Detector
326 drift was also monitored by analyzing the same sample location multiple times
327 throughout the session and was determined to be negligible. Spectral data were collected
328 over a range of 50 - 1500 cm^{-1} , to ensure good counting statistics, a sequence of 10
329 second exposures were collected over a 2 minute period and summed to achieve the final
330 spectrum. A background measurement conducted prior to every analysis was subtracted
331 from the spectrum for each sample. Also each sample was inspected to document any
332 interference from the surrounding epoxy grain mount, as the small size ($<\sim 100 \mu\text{m}$) of the
333 zircons resulted in phonons from the epoxy occasionally interfering with the sample
334 phonons. The interference was monitored by the presence of the characteristic epoxy
335 peak at $\sim 821 \text{ cm}^{-1}$. SIMS analytical pits have been shown to cause no Raman detectable
336 damage to the crystal structure (Nasdala et al. 1998a). Therefore, to ensure direct
337 correlation between the Raman spectra and the oxygen isotopic composition, all of the
338 Raman analyses were conducted inside SIMS pits.

339

340 All Raman data was corrected for the effects of the finite slit width on the measured
341 band-width. The equation

342

343
$$\Gamma = \Gamma_m[1-(S/\Gamma_m)^2] \quad (1)$$

344

345 was used to correct the peak broadening associated with the finite slit width (Tanabe and
346 Hiraishi, 1980). Where Γ , Γ_m , and S are the corrected band-width, measured band-width,
347 and spectral slit width respectively.

348

349 The alpha dose is the number of atomic displacements caused by the decay of uranium
350 and thorium per gram of zircon was calculated using:

351

352
$$D\alpha = 8 \cdot \frac{cU \cdot NA \cdot 0.9928}{M_{238} \cdot 10^6} \cdot (e^{\lambda_{238t}} - 1) + 7 \cdot \frac{cU \cdot NA \cdot 0.0072}{M_{235} \cdot 10^6} \cdot (e^{\lambda_{235t}} - 1) + 6 \cdot \frac{cTh \cdot NA}{M_{232} \cdot 10^6} \cdot (e^{\lambda_{232t}} - 1) \quad (2)$$

353

354 where cU and cTh are the concentrations of U and Th in ppm, NA is Avogadro's number,
355 M_{238} , M_{235} and M_{232} are the molecular weights, λ_{238} , λ_{235} and λ_{232} are the decay constants
356 for each parent isotope (^{235}U , ^{238}U , ^{232}Th) and t is the amount of time radiation damage
357 has been accumulating.

358

359 All uncertainties reported at the 2σ confidence level unless stated otherwise. Analytical
360 techniques and results for laser ablation inductively coupled plasma mass spectrometry
361 (LA-ICP-MS) and whole rock oxygen isotope analyses are in supplementary information.

362

363

Results

364 Fluid alteration of zircon can be identified by many different techniques. First we use
365 SIMS oxygen isotopic analysis, CL imaging, U-Pb dating, and elemental composition to

366 indicate interaction between zircon and secondary fluids. We then report the new Raman
367 spectroscopy results and demonstrate how this technique provides similar and
368 complimentary information quickly and in a non-destructive manner. Elemental, isotopic
369 and Raman band parameter data are provided in Table 2.

370

371

372 **Oxygen isotopes and CL images**

373 The oxygen isotopic compositions of the zircons from the Scourie dykes are shown
374 relative to the WR oxygen isotopic compositions in Fig. 3. The high temperature
375 equilibrium oxygen isotopic fractionation between basalt and zircon is also shown and it
376 is clear that many samples contain zircon that is dis-equilibrated with the whole rock.
377 Three samples, Graveyard, NAPI and Loch a'Choin are the most homogeneous; where-as
378 the other samples have heterogeneous $\delta^{18}\text{O}_{\text{zirc}}$ values. Loch na h zircons are the most dis-
379 equilibrated with the whole rock and have $\delta^{18}\text{O}_{\text{zirc}}$ values as low as -3.7‰ with a range
380 of $\sim 3.5\text{‰}$. It is important to note that only one $\delta^{18}\text{O}$ analysis was conducted for each
381 WR sample and therefore all of the zircon analyses are compared to this one value. In
382 cases where there is a large variation in $\delta^{18}\text{O}_{\text{zirc}}$ values, the WR $\delta^{18}\text{O}$ value measured
383 from these altered rock is unlikely to record the original magmatic composition.

384

385 CL images of representative zircon samples with the $\delta^{18}\text{O}$ values and SIMS spot locations
386 are shown in Fig. 4. All grains show a weak CL response with some grains darker than
387 the epoxy, indicating that they have a high degree of metamictization (Koschek, 1992;
388 Hanchar and Miller, 1993). The zircons can be divided into three broad groups based on

389 their CL properties: 1) zircon showing some igneous oscillatory zoning – Poll Eorna,
390 Graveyard, Badcall Bay and NAPI; 2) zircon with core and rim type zoning – Loch
391 a’Choin, North Assynt and JD09-2; and 3) highly altered/metamict zircon – Loch na h,
392 and Lochan Fearnna.

393

394 Group 1 grains, with normal grain morphologies (~4:1 length-width ratio; Heaman et al.
395 1990), show divergent patterns of oxygen isotopic variation with consistent intergrain
396 values obtained for Graveyard and NAPI dyke zircons; the other samples contain inter
397 grain differences (Fig. 4). Group 1 grains typically show oscillatory CL zoning
398 suggestive of igneous growth, although there are some more complexly zoned grains
399 (highlighted with a star in Fig. 4). The complex CL zoning could be the result of
400 recrystallization of the zircon along anastomosing cracks (e.g. Ashwal et al. 1999) or
401 possibly diffusional re-crystallization associated with fluid exchange (Geisler et al. 2002;
402 2003b; 2007; Rayner et al. 2005). The recrystallization features in the Poll Eorna zircons
403 correspond to the maximum ($\delta^{18}\text{O} = 4.93 \text{ ‰}$) and minimum ($\delta^{18}\text{O} = 3.41 \text{ ‰}$) $\delta^{18}\text{O}$ values
404 in the sample, suggesting the features may be related to fluid exchange. For the Group 1
405 zircons, those from the Poll Eorna dyke are the most disequilibrated with the WR (Fig.
406 3), consistent with a complex CL response when compared with the Graveyard and NAPI
407 zircons.

408

409 Group 2 zircons have core-rim type textures that suggest they have experienced partial re-
410 crystallization (e.g. Corfu et al. 2003). Zircons from JD09-2 show convoluted zones at
411 the center of the grains, with rims of more homogeneous material, whereas Loch a’Choin

412 and North Assynt both show similar patterns of dark (metamict) cores with lighter (less
413 metamict) rims. The JD09-2 zircons are disequibrated with the WR oxygen isotopic
414 composition by up to 3 ‰ and have variable $\delta^{18}\text{O}$ values between grains (Fig. 3). It is
415 difficult to distinguish whether the different zones seen in CL in JD09-2 have distinct
416 $\delta^{18}\text{O}$ values since the zones are typically thinner than the diameter of the SIMS spots.
417 However, the darker, more metamict zones appear to have higher $\delta^{18}\text{O}$ values ~ 1 ‰,
418 whereas the lighter, more crystalline zones have lower $\delta^{18}\text{O}$ values of < 0 ‰ (Fig. 4). The
419 darker CL zones in JD09-2 also contain quartz inclusions, whereas the lighter areas do
420 not. Loch a'Choin zircons show evidence for recrystallization along cracks similar to
421 Poll Eorna (see stars, Fig. 4f), however the $\delta^{18}\text{O}$ values show no evidence of disturbance
422 (Fig. 3, Table 2). The North Assynt zircons appear very similar to the Loch a'Choin
423 zircons in CL images, however they show more oxygen isotopic variation (Fig. 3; 4).

424

425 Group 3 zircons from Loch na h and Lochan Fearna dykes, are the most metamict, and
426 have highly heterogeneous $\delta^{18}\text{O}$ values (Fig. 4). The CL images for these grains are very
427 dark, contain abundant cracks (Lochan Fearna) and only faint evidence of igneous
428 oscillatory zoning. There does not appear to be a relationship between the CL zoning and
429 $\delta^{18}\text{O}$ values, however all of the zircons are disequibrated with the WR (Fig. 3).

430

431 **Elemental composition of the zircon, constraining the alpha dose**

432 In order to better constrain the alpha dose experienced by each zircon, their chemical
433 compositions have been determined by electron microprobe analysis (Table 2). They
434 have close to stoichiometric Zr and Si ratios although the more altered grains from

435 Lochan Fearn, Loch na h and some Poll Eorna zircons are depleted in SiO_2 and ZrO_2
436 (Fig. 5a). The grains with Zr and Si depletions are also anomalously rich in U and Ca,
437 with values reaching up to 5000 ppm for Ca and 1500 ppm for U. These trace-element
438 enriched samples also display a dull CL response and more intense alpha dose, indicating
439 a high degree of radiation damage (Fig. 5b,c). Low elemental totals for all of the samples
440 (<99.5 wt%), suggests enrichment in non-formula cations or hydrous species that were
441 not analyzed (Al, Fe, HREE), and may also reflect Si mobility under the high current
442 electron beam (Morgan and London, 1996).

443

444 Alpha doses for each of the grains were calculated assuming that radiation damage has
445 been accumulating since the formation of the zircon (Fig. 5b; equation 2). The alpha
446 dose shows a positive correlation with the band-width of the ν_3 (SiO_4) band, although the
447 alpha dose amounts are very high. Nasdala et al. (2001) report band-widths of 20 cm^{-1}
448 for alpha doses of $\sim 1.5 \times 10^{18} \alpha/\text{g}$, whereas these zircons have alpha doses an order of
449 magnitude larger at $\sim 10 \times 10^{18} \alpha/\text{g}$ for the same band-width.

450

451 There is a clear relationship between alpha dose and Ca content (Fig. 5d). After the alpha
452 dose reaches a threshold dose of $\sim 7 \times 10^{18} \alpha/\text{g}$, the Ca (and U content) dramatically
453 increase, whereas below this dose the Ca and U contents are always low. There is no
454 obvious relationship between the CL patterns, trace element contents and oxygen isotope
455 compositions.

456

457 **Raman spectra**

458 Most of the Scourie dyke zircons have ν_3 (SiO_4) band parameters that follow the radiation
459 damage trend (Fig. 6). The Loch a'Choin samples have the most crystalline zircons with
460 the lowest band-width and highest frequency, which is consistent with the low alpha
461 dose, low trace-element (U, Th and Ca) contents, relatively bright CL response, and
462 equilibrium oxygen isotopic compositions (Figs. 3; 4; 5). All other zircons have band-
463 widths and frequencies that classify them as either metamict or highly metamict (see Fig.
464 1).

465

466 The Raman results were split into two groups based on the Ca contents of the zircons.
467 The dominant group from the low-Ca grains are metamict, but at relatively low degrees,
468 with band-widths of $\sim 10\text{-}15\text{ cm}^{-1}$ and frequencies around 1000 cm^{-1} . All of the grains in
469 the low-Ca group are either overlapping with the radiation damage trend, or close to
470 overlapping. Since the trend is only a guide based on published and unpublished Raman
471 measurements of various zircons (Nasdala et al. 1998b, 2001; Zheng et al. 2000a; Geisler
472 et al. 2003b,c), analyses that lie very close to the line are considered to conform to the
473 radiation damage trend.

474

475 The high-Ca grains have much greater degree of within-sample spread in Raman spectral
476 band-widths and frequencies than the low-Ca grains (Fig. 6). For example, the Poll
477 Eorna grains have band-widths and frequencies that range between $\sim 15\text{-}32\text{ cm}^{-1}$ and ~ 998
478 - 1002 cm^{-1} , respectively, that is a wider range than any other sample. The most
479 prominent feature of the high-Ca zircons is that they do not plot on the radiation damage

480 trend with highly metamict zircons showing higher frequencies for the ν_3 (SiO_4) band
481 than the band-width suggests.

482

483 **Discussion**

484 **Evidence for fluid exchange**

485 There is strong evidence for $\delta^{18}\text{O}$ disequilibrium between the WR and zircon in Poll
486 Eorna, Lochan Fearna, JD09-2, Loch na h, North Assynt and to some extent the NAPI
487 dykes (Fig. 3). The oxygen isotopic disequilibrium is coupled with U-Pb discordance
488 (Sup Fig. 2, Davies and Heaman, 2014) and high Ca contents (Fig 5), all of which point
489 towards hydrothermal alteration of the zircon. Also, the altered zircons are from dykes
490 containing abundant epidote- group minerals (Davies and Heaman, 2014), characteristic
491 of fluid alteration. However, CL imaging of the zircon do not show the distinctive
492 reaction rim patterns or copious mineral inclusions, which are typically associated with
493 hydrothermal alteration of zircon (Geisler et al. 2007; Putnis 2002; Putnis et al. 2005;
494 Tomaschek et al. 2003).

495

496 It is possible that the Scourie zircons could have obtained their seemingly altered
497 composition through magmatic processes. For example, contamination of the dyke
498 magmas by continental crust or the entrainment of xenocrystic zircon could create the
499 apparent disequilibria between the WR and zircon oxygen isotopic compositions,
500 however this is highly unlikely based on the following points.

501

502 Concentrations of the large ion lithophile (LIL) trace elements Rb, Th, U and K are up to
503 50 times higher in the dykes than in the gneisses, whereas the gneisses contain
504 enrichments in Ti and Sr relative to the dykes (Weaver and Tarney, 1981; Rollinson,
505 2012). Bulk contamination of the dykes by the gneisses would significantly reduce the
506 LIL contents of the dykes while increasing Ti and Sr, which is not observed (Tarney and
507 Weaver, 1987; Rollinson, 2012). Entrained xenocrystic zircons (presumably from the
508 surrounding gneisses) are likely to be distinctive in CL images, either as a core within
509 magmatic grains or as discrete crystals. Zircons from Loch a'Choin, North Assynt and
510 JD09-2 all have core and rim type zoning. Loch a'Choin and North Assynt zircons were
511 previously interpreted as xenocrystic by Davies and Heaman, (2014) based on U-Pb ages
512 similar to the surrounding gneisses. Zircon from tonalitic or basic gneiss surrounding the
513 dykes should have a $\delta^{18}\text{O}$ of ≥ 6 ‰ (Cartwright and Valley, 1992), which is consistent
514 with the North Assynt and Loch a'choin zircons but none of the other samples. The
515 presence of zircon xenocrysts also does not explain the elevated Ca in the zircons, and is
516 not consistent with the un-zoned zircon from Poll Eorna, Graveyard, Lochan Fearn,
517 NAPI and Badcall Bay dykes. In studies of other dyke swarms, for example the Jurassic
518 Independence dyke swarm of California, trace element and isotopic data suggest that
519 crustal contamination of mafic magmas is not significant even when enclaves of country
520 rock are present in the dykes (Glazner et al. 2008).

521

522 The high-Ca content of some of the Scourie zircons suggests that hydrothermal fluids
523 have altered the grains. Ca is not partitioned into zircon during growth (see Hoskin and
524 Schaltegger, 2003). A coupled substitution mechanism has been suggested for Ca in

525 zircon, through the hydrogrossular substitution $[\text{Ca}^{2+} + 2\text{H}^+] \leftrightarrow [\text{Zr}^{4+}]$ (Geisler et al.
526 2001), indicating that Ca may only partition into zircon in the presence of Ca rich brines.
527 We therefore reject the hypothesis that the oxygen isotopic features are related to
528 magmatic processes and concentrate on elucidating the nature of fluid alteration.

529

530 **Mechanism for fluid alteration**

531 Experimental studies, outlined below, investigating the interaction between metamict
532 zircon and hydrothermal fluids have shown that the main parameters controlling the
533 levels of exchange between the fluid and zircon are: composition of the fluid, temperature
534 of the fluid, and degree of metamictization.

535

536 Pidgeon et al. (1995) investigated the X-ray diffraction properties of amorphous zircon
537 under different hydrothermal conditions. They discovered that pure water had very little
538 effect on the structure of the zircon even after 11 hours at 500 °C, whereas experiments
539 under the same conditions using 2M NaCl and HCl solutions revealed significant
540 recovery of crystallinity, and also loss of Pb. Interestingly, during experiments
541 investigating the effect of sodium carbonate solution at 400 °C on metamict zircon,
542 Rizvanova et al. (2000) found that the structurally recovered metamict zircon did not
543 contain a reaction rim, which, at least in appearance is similar to the zircon in this study.
544 However, during the reaction with sodium carbonate solution, some of the zircon was
545 dissolved and replaced by baddeleyite and a Zr-Na phase, which is not seen in the
546 Scourie zircons. In experiments using natural brines, Hansen and Friderichsen (1989),
547 discovered that the presence of small amounts of cations like Ca^{2+} in water has a

548 significant effect on the leaching of Pb from metamict zircon as well as structural
549 recovery.

550

551 Detailed experimental studies by Geisler et al. (2001, 2002, 2003b) revealed that the
552 relationships between structural recovery, temperature and composition of the fluid are
553 complicated. They concluded that the amount of metamictization has a strong impact on
554 the structural recovery, with temperature of the fluid playing more important a role than
555 composition (as long as it is not pure H₂O). Experiments at low temperature (175 - 350
556 °C) caused small degrees of structural recovery, and did not anneal amorphous domains
557 within the crystals, however fluids leached trace elements from the zircon. They
558 attributed low temperature recovery to repairing of Frenkel defects and short-range
559 disorder in the crystal structure. As the temperature of the fluid increased, fluids diffused
560 further into the crystal and caused recrystallization of longer-range disorder and
561 amorphous domains. The increased penetration by higher temperature fluids was
562 attributed to the kinetics of fluid diffusion, and the relationship between the kinetics of
563 diffusion, and the kinetics of recrystallization. Geisler et al. (2007) also demonstrated
564 that the first percolation point (Salje, et al. 1999), where amorphous domains form
565 infinite clusters within the crystal, is the critical point where extensive fluid alteration and
566 recrystallization can occur.

567

568 The Raman signature of diffusion recrystallization is distinctive (Fig. 1), and Raman
569 results from the Scourie zircons suggest they have undergone this process (Fig. 6).
570 Geochemical data (Fig. 5) also are in agreement with the critical point model of Geisler et

571 al. (2003c, 2007), because Ca content shows a distinct increase above a critical alpha
572 dose.

573

574 There is a strong relationship between radiation damage, band-width, distance from the
575 radiation damage trend and Ca content in the zircon (Fig. 5; 6). This trend suggests that
576 the most metamict zircons experienced the greatest degree of fluid exchange, as well as
577 the most recrystallization. It is apparent that small degrees of fluid interaction, which
578 increase the Ca content to $<\sim 100$ ppm in zircon, have not caused significant
579 recrystallization. This finding is in agreement with the experimental and natural results
580 of Geisler et al. (2007).

581

582 Geological data suggest that mylonitization along the Moine thrust nappe reached
583 temperatures of 300-400 °C (Holdsworth et al. 2007), and movement along the fault has
584 likely initiated hydrothermal fluid circulation (e.g. Travé et al. 1997). However, the
585 effects of post recrystallization radiation damage on the Raman properties of zircon are
586 not well understood (it could potentially follow line C in Fig. 1). If it is assumed that
587 recrystallization occurred at the time of the Caledonian orogeny, coinciding with the
588 timing of Pb-loss, high-Ca and high U zircons have experienced ~ 400 Ma of damage
589 since recrystallization. We suggest that the levels of recrystallization shown by the
590 present-day Raman properties include radiation damage, and therefore during the fluid
591 event the degree of structural recovery experienced by the high-Ca zircons was probably
592 much higher.

593

594 **Timing of radiation damage accumulation**

595 Two main properties control the accumulation of radiation damage in zircon. First, the
596 abundance of the radioactive elements within the crystal, essentially U and Th in zircon;
597 and, second, the amount of time the zircon has spent at a temperature low enough to
598 allow radiation damage to accumulate without being thermally annealed (~150 - 250 °C;
599 Meldrum et al. 1999; Davis and Krogh, 2000; Moser et al. 2011; Pidgeon 2014).

600

601 The time that the sample has been accumulating radiation damage (t , equation 2) is not
602 necessarily known, especially with old grains that have a complex history such as the
603 Scourie zircons. However, t can be estimated by comparing the alpha dose with the
604 FWHM of the ν_3 (SiO₄) band and iteratively changing t until the samples plot along the
605 same trajectory as zircons with known thermal histories (e.g. Nasdala et al. 2001; Palenik
606 et al. 2003; Pigeon 2014, Fig. 7). The alpha doses, when calculated at emplacement age,
607 are too high compared with the expected FWHM of the ν_3 (SiO₄) band (Fig. 5b). Alpha
608 doses at these high levels ($>5 \times 10^{18} \alpha/g^{-1}$) would also result in aperiodic and amorphous
609 zircon (Ríos et al. 2000; Pidgeon, 2014).

610

611 To estimate the amount of time that the Scourie zircons have been accumulating damage,
612 we varied the t parameter in equation (2) and compared the results to zircons from the
613 Saxonian rhyolite (Nasdala et al. 1998b) and lunar zircon (Wopenka et al. 1996). The
614 Saxonian rhyolite and lunar zircon are good models for how zircon should accumulate
615 radiation damage over time, since they are thought to have stored all of their radiation
616 damage since crystallization. Since the Scourie dyke zircons have a complicated history

617 involving diffusional-reaction annealing, only the grains that haven't been annealed can
618 be used to constrain the time of damage accumulation. Linear regression lines for
619 different ages are plotted through the zircon analyses that have the lowest Ca, Th and U
620 contents and therefore are unlikely to have been recrystallized. These grains are then
621 compared to zircon from the Saxonian and lunar samples (Fig. 7). It is apparent that the
622 Scourie dyke zircons have not been accumulating radiation damage since their formation
623 in the Paleoproterozoic. The scatter in the Saxonian and lunar samples (and also the
624 Scourie zircons) makes determining a precise age of damage accumulation difficult. An
625 age of ~520 Ma fits the Saxonian and lunar zircon radiation damage profile the best,
626 although the calculations allow any age between 440 and 620 Ma. If the 520 ± 100 Ma
627 age is approximately correct, it would mean that the dykes cooled below ~250 °C at this
628 time, the zircon then began to accumulate radiation damage for ~100 Ma before coming
629 into contact with fluids causing Pb-loss and Ca-gain possibly during the emplacement of
630 the Moine thrust at 430.7 Ma (Goodenough et al. 2011).

631

632 **What can we say about the oxygen isotopic composition of the rock?**

633 The main benefit of combining trace element and Raman analyses to study the fluid
634 history of a zircon population is that together they can identify which zircons/areas of
635 zircons are not affected by fluid alteration. Separating the oxygen isotope analyses into
636 those which show evidence of fluid alteration (those with high Ca contents) and those
637 that are unaltered provides information about the original oxygen isotopic composition of
638 the zircon. Fig. 8 shows that the fluid altered zircon is generally isotopically heavier than
639 the fresh zircon. An exception is one high-Ca analysis from JD09-2, which is

640 isotopically lighter than the low-Ca analyses in this sample. One explanation for this
641 could be the temperature of the hydrothermal fluid. Using the Keiffer (1982)
642 calculations, zircon – water $\delta^{18}\text{O}$ fractionation should be $> 5.7 \text{ ‰}$ at $<100 \text{ C}$ and smaller
643 at higher temperatures. If the JD09-2 zircons exchanged with hotter hydrothermal fluids
644 than the other zircons, they would have lower $\delta^{18}\text{O}$ values.

645

646 Since the fluid alteration has caused the zircons to obtain higher $\delta^{18}\text{O}$ values, the lowest
647 $\delta^{18}\text{O}$ values recorded by the zircon are likely to be the least altered and therefore closest
648 to the magmatic value. Poll Eorna and North Assynt zircons appear to corroborate this
649 hypothesis since low-Ca zircons are closest to high temperature isotopic equilibrium with
650 the WR (Fig. 8). The low-Ca zircons from Loch na h, Lochan Fearna and to some extent,
651 NAPI dykes are all far out of equilibrium from the WR, which appears at first glance to
652 disprove the hypothesis. However, the Loch na h, and Lochan Fearna zircons crystals are
653 highly altered, therefore it is very likely that the WR $\delta^{18}\text{O}$ isotopic composition has been
654 significantly altered as well. These rocks contain epidote group minerals, and highly
655 saussuritized plagioclase, visible in thin section (See Davies and Heaman, 2014). In
656 these examples, the zircon grains are much lower in ^{18}O than the WR. Fluid-rock
657 exchange is kinetically easier than fluid-zircon exchange (Valley, 2003) therefore the
658 isotopically heavy WR values are likely to have been overprinted by the fluid (see
659 Grimes et al. 2010 where mafic zircon from oceanic gabbros record $\delta^{18}\text{O}$ values in
660 equilibrium with the mantle, whereas the WR samples which host the zircons contain
661 $\delta^{18}\text{O}$ values which range in $\delta^{18}\text{O}$ from 1.4 to 10.2 ‰). In these cases, the lowest $\delta^{18}\text{O}$ and
662 least altered zircon values may be used to estimate the original $\delta^{18}\text{O}$ composition of the

663 rock assuming equilibrium zircon-magma fractionation (using the Keiffer, 1982
664 calculations). Calculated in this way, the unaltered $\delta^{18}\text{O}$ Scourie dyke WR values are as
665 follows: NAPI ($\sim 5\text{‰}$), Lochan Fearnna ($\sim 2.3\text{‰}$), JD09-2 ($\sim 0.5\text{‰}$), and Loch na h
666 ($\sim -3.7\text{‰}$), these values are calculated from average $\delta^{18}\text{O}$ values from the lowest $\delta^{18}\text{O}$
667 zircons from each dyke (Fig. 8). The implication of this result is that all of the ~ 2.4 Ga
668 Scourie dyke magmas had $\delta^{18}\text{O}$ values much lower than the mantle value of $5.3 \pm 0.5\text{‰}$
669 (Valley, 2003). These zircons have some of the lowest oxygen isotopic compositions
670 recorded (see Spencer et al. 2014), and this study provides evidence that these low $\delta^{18}\text{O}$
671 values are reflective of low- $\delta^{18}\text{O}$ primary magmatic compositions. Cartwright and Valley
672 (1991) first identified that some Scourie dykes had low $\delta^{18}\text{O}$ compositions, although there
673 data indicated relatively consistent WR values of $\sim 2\text{‰}$. These new low- $\delta^{18}\text{O}$ zircon data
674 indicate that the low- $\delta^{18}\text{O}$ signature for Scourie magmas is variable, and is potentially as
675 low as -3.7‰ .

676

677

Implications

678 This study shows how a combination of spatially-resolved methods, including Raman
679 spectroscopy, electron microprobe analysis, and CL imaging can be used to understand
680 complex altered zircon populations and identify those that retain their original isotopic
681 composition. These techniques are recommended for all zircon populations that have
682 experienced fluid alteration, the combination of methods may be particularly useful in
683 detrital zircon studies where unidentified fluid alteration causes Pb loss and complicates
684 the interpretation of U-Pb ages (e.g. Liu and Zhang, 2013) or in studies of complex old
685 zircons e.g. the Jack hills zircons (Mojzsis et al. 2001). These non-destructive techniques

686 can be applied before SIMS analysis to target unaltered domains of complex zircon,
687 potentially significantly simplifying the results.

688

689 Zircons from the ~2.4 Ga Scourie dykes have very low $\delta^{18}\text{O}$ compositions, as low as
690 -3.78 ‰. These low values are most representative of the magmatic value and have
691 rarely been found on Earth especially in the Precambrian outside of Karelia, Russia (e.g.
692 Bindeman et al. 2010, 2014; Bindeman and Serebryakov, 2011). These data require a
693 new interpretation of the geological history of the Scourie dykes from the Lewisian high-
694 grade gneiss terrain of NW Scotland.

695

696

697

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709

References

710 Ashwal, L.D., Tucker, R.D., and Zinner, E.K. (1999) Slow cooling of deep crustal
711 granulites and Pb-loss in zircon. *Geochimica et Cosmochimica Acta*, 63, 2839–2851.

712

713 Bindeman, I.N., Schmitt, A.K., and Evans, D.A.D. (2010) Limits of hydrosphere-
714 lithosphere interaction: origin of the lowest-known ^{18}O silicate rock on Earth in the
715 Paleoproterozoic Karelian rift. *Geology*, 38, 631–34.

716

717 Bindeman, I.N., and Serebryakov, N.S. (2011) *Geology, Petrology and O and H isotope*
718 *geochemistry of remarkably ^{18}O depleted Paleoproterozoic rocks of the Belomorian Belt,*
719 *Karelia, Russia, attributed to global glaciation 2.4 Ga. Earth and Planetary Science*
720 *Letters*, 306, 163-174.

721

722 Bindeman, I.N., Serebryakov, N.S., Schmitt, A.K., Vazquez, J.A., Guan, Y., Azimov,
723 P.Ya., Astafiev, B.Yu., Palandri, J., and Dobrzhinetskaya, L. (2014) Field and
724 microanalytical isotopic investigation of ultradepleted in ^{18}O Paleoproterozoic “Slushball
725 Earth” rocks from Karelia, Russia. *Geosphere*, 10, doi:10.1130/GES00952.1

726

727 Black, L.P., Kamo, S.L., Allen, C.M., Davis, D.W., Aleinikoff, J.N., Valley, J.W.,
728 Mundil, R., Campbell, I.H., Korsch, R.J., Williams, I.S., and Fondoulis, C. (2004)
729 Improved $^{206}\text{Pb}/^{238}\text{U}$ microprobe geochronology by the monitoring of a trace-element-
730 related matrix effect; SHRIMP, ID-TIMS, ELA-ICP-MS and oxygen isotope
731 documentation for a series of zircon standards. *Chemical Geology*, 205, 115–40.

732

733 Breeding, C.M., Ague, J.J., Grove, M., and Rupke, A.L. (2004) Isotopic and chemical
734 alteration of zircon by metamorphic fluids: U-Pb age depth-profiling of zircon crystals
735 from Barrow's garnet zone, Northeast Scotland. *American Mineralogist*, 89, 1067–1077.

736

737 Booth, A.L., Kolodny, Y., Chamberlain, C.P., McWilliams, M., Schmitt, A.K., and
738 Wooden, J. (2005) Oxygen isotopic composition and U-Pb discordance in zircon.
739 *Geochimica et Cosmochimica Acta*, 69, 4895-4905.

740

741 Bowman, J.R., Moser, D.E., Valley, J.W., Wooden, J.L., Kita, N.T., and Mazdab, F.K.
742 (2011) Zircon U-Pb isotope, $\delta^{18}\text{O}$ and trace element response to 80 m.y. of high
743 temperature metamorphism in the lower crust: sluggish diffusion and new records of
744 Archean craton formation. *American Journal of Science*, 311, 719-772.

745

746 Capitani, G.C., Leroux, H., Doukhan, J.C., Ríos, S., Zhang, M., and Salje, E.K.H. (2000)
747 A TEM investigation of natural metamict zircons: structure and recovery of amorphous
748 domains. *Physics and Chemistry of Materials*, 27, 545-556.

749

750 Cartwright, I., and Valley, J.W. (1991) Low- ^{18}O Scourie dike magmas from the Lewisian
751 Complex, Northwestern Scotland. *Geology*, 19, 578-581.

752

753 Cartwright, I., and Valley, J.W. (1992) Oxygen-isotope geochemistry of the scourian
754 complex, Northwest Scotland. *Journal of the Geological Society*, 149, 115-125.

755

756 Cavosie, A.J., Valley, J.W., Wilde, S.A., and E.I.M.F. (2005) Magmatic $\delta^{18}\text{O}$ in 4400-
757 3900 Ma detrital zircons: a record of the alteration and recycling of crust in the Early
758 Archean. *Earth and Planetary Science Letters*, 235, 663-681.

759

760 Cavosie, A.J., Valley, J.W., Wilde, S.A., and E.I.M.F. (2006) Correlated microanalysis of
761 zircon: trace element, $\delta^{18}\text{O}$, and U-Th-Pb isotopic constraints on the igneous origin of
762 complex >3900 Ma detrital grains. *Geochimica et Cosmochimica Acta*, 70, 5601-5616.

763

764 Cherniak, D.J., and Watson, E.B. (2003) Diffusion in zircon. *Reviews in Mineralogy and*
765 *Geochemistry*, 53, 113-143.

766

767 Corfu, F., Hanchar, J.M., Hoskin, P.W.O., and Kinny, P. (2003) Atlas of Zircon Textures.
768 *Reviews in Mineralogy and Geochemistry*, 53, 469-500.

769

770 Davies, J.H.F.L., and Heaman, L.M. (2014) New U-Pb baddeleyite and zircon ages for
771 the Scourie dyke swarm: A long-lived large igneous province with implications for the
772 Paleoproterozoic evolution of NW Scotland. *Precambrian Research*, 249, 180-198.

773

774 Davis, D.W., and Krogh, T.E. (2001) Preferential dissolution of ^{234}U and radiogenic Pb
775 from α -recoil-damaged lattice sites in zircon: implications for thermal histories and Pb
776 isotopic fractionation in the near surface environment. *Chemical Geology*, 172, 41-58.

777

778 Dillon, R., Woollam, J., and Katkanant, V. (1984) Use of raman scattering to investigate
779 disorder and crystallite formation in as-deposited and annealed carbon films. *Physical*
780 *Review B*, 29, 3482–3489. doi:10.1103/PhysRevB.29.3482.

781

782 Ewing, R.C., Chakoumakos, B.C., and Lumpkin, G.R. (1987) The metamict state.
783 *Materials Research Society Bulletin*, 12, 58–66.

784

785 Ewing, R.C., Meldrum, A., Wang, L.M., Weber, W.J., and Corrales, L.R. (2003)
786 Radiation effects in zircon. *Reviews in Mineralogy and Geochemistry*, 53, 387-425.

787

788 Geisler, T. (2002) Isothermal annealing of partially metamict zircon: evidence for a
789 three-stage recovery process. *Physics and Chemistry of Minerals*, 29, 420–429.
790 doi:10.1007/s00269-002-0249-3.

791

792 Geisler, T., Pidgeon, R.T., van Bronswijk, W., and Pleyzier, R. (2001a) Kinetics of
793 thermal recovery and recrystallization of partially metamict zircon: a Raman
794 spectroscopic study. *European Journal of Mineralogy*, 13, 1163–1176.
795 doi:10.1127/0935-1221/2001/0013-1163.

796

797 Geisler, T., Ulonska, M., Schleicher, H., Pidgeon, R.T., and van Bronswijk, W. (2001b)
798 Leaching and differential recrystallization of metamict zircon under experimental
799 hydrothermal conditions. *Contributions to Mineralogy and Petrology*, 141 53–65.
800 doi:10.1007/s004100000202.

801

802 Geisler, T., Trachenko, K., Ríos, S., Dove, M.T., and Salje, E.K.H., (2003a) Impact of
803 self-irradiation damage on the aqueous durability of zircon (ZrSiO₄): implications for its
804 suitability as a nuclear waste form. *Journal of Physics: Condensed Matter*, 15, 597–605.
805 doi:10.1088/0953-8984/15/37/L07.

806

807 Geisler, T., Pidgeon, R.T., Kurtz, R., van Bronswijk, W., and Schleicher, H. (2003b)
808 Experimental hydrothermal alteration of partially metamict zircon. *American*
809 *Mineralogist*, 88, 1496–1513.

810

811 Geisler, T., Rashwan, A.A., Rahn, M.K.W., Poller, U., Zwingmann, H., Pidgeon, R.T.,
812 Schleicher, H., and Tomaschek, F. (2003c) Low-temperature hydrothermal alteration of
813 natural metamict zircons from the Eastern desert, Egypt. *Mineralogical Magazine*, 67,
814 485–508.

815

816 Geisler, T., Schaltegger, U., and Tomaschek, F. (2007) Re-equilibration of zircon in
817 aqueous fluids and melts. *Elements* 3, 43–50.

818

- 819 Glazner, A.F., Carl, B.S., Coleman, D.S., Miller, J.S., and Bartley, J.M. (2008) Chemical
820 variability and the composite nature of dikes from the Jurassic Independence dike swarm,
821 eastern California. Geological Society of America Special Papers, 438, 455-480.
822
- 823 Goodenough, K.M., Millar, I., Strachan, R.A., Krabbendam, M., and Evans, J.A. (2011)
824 Timing of regional deformation and development of the Moine Thrust zone in the
825 Scottish Caledonides: constraints from the U-Pb geochronology of alkaline intrusions.
826 Journal of the Geological Society, 168, 99–114.
827
- 828 Grimes, C.B., Ushikubo, T., John, B.E., and Valley, J.W. (2010) Uniformly mantle like
829 $\delta^{18}\text{O}$ in zircons from oceanic plagiogranites and gabbros. Contributions to mineralogy
830 and petrology, 161, 13-33.
831
- 832 Hansen, B.T., and Friderichsen, J.D. (1989) The influence of recent lead loss on the
833 interpretation of disturbed U-Pb systems in zircons from igneous rocks in East Greenland.
834 Lithos, 23, 209-223.
835
- 836 Hanchar, J.M., and Miller, C.F. (1993) Zircon zonation patterns as revealed by
837 cathodoluminescence and backscattered electron images: Implications for interpretation
838 of complex crustal histories. Chemical Geology, 110, 1-13.
839
- 840 Hanchar, J.M., and Hoskin P.W.O. (2003) Zircon (eds) Reviews in Mineralogy and
841 Geochemistry, Vol 53.

842

843 Hay, D.C., Dempster, T.J., Lee, M.R., and Brown, D.J. (2009) Anatomy of a low
844 temperature zircon outgrowth. *Contributions to Mineralogy and Petrology*, 159, 81–92.

845

846 Heaman, L.M., Bowins, R., and Crocket, J. (1990) The chemical composition of igneous
847 zircon suites: implications for geochemical tracer studies. *Geochimica et Cosmochimica*
848 *Acta*, 54, 1597–1607.

849

850 Holdsworth, R.E., Alsop, G.I., and Strachan, R.A. (2007) Tectonic stratigraphy and
851 structural continuity of the northernmost Moine Thrust zone and Moine nappe, Scottish
852 Caledonides. *Geological Society London Special Publications*, 272, 121–142.

853

854 Holland, H.D., and Gottfried, D. (1955) The effect of nuclear radiation on the structure of
855 zircon. *Acta Crystallographica*, 8, 291–300. doi:10.1107/S0365110X55000947

856

857 Hoskin, P.W.O., and Schaltegger, U. (2003) The composition of zircon and igneous and
858 metamorphic petrogenesis. *Reviews in Mineralogy and Geochemistry*, 53, 27-62.

859

860 Ickert, R.B., and Stern, R.A. (2013) Matrix corrections and error analysis in high-
861 precision SIMS $^{18}\text{O}/^{16}\text{O}$ measurements of Ca-Mg-Fe garnet. *Geostandards and*
862 *Geoanalytical Research*, 1-20 doi:10.1111/j.1751-908X.2013.00222.x.

863

864 Kieffer, S.W. (1982) Thermodynamics and lattice vibrations of minerals: Applications to

865 phase equilibria, isotopic fractionation and high-pressure thermodynamic properties.

866 Reviews of geophysics and space physics, 20, 827-849.

867

868 Krogh, T.E. (1982) Improved accuracy of U-Pb zircon ages by the creation of more

869 concordant systems using an air abrasion technique. *Geochimica et Cosmochimica Acta*

870 46, 637–649.

871

872 Koschek, G. (1992) Origin and Significance of the SEM cathodoluminescence from

873 zircon. *Journal of Microscopy*, 171, 233-232.

874

875 Liu, J., and Zhang, L. (2013) Neoproterozoic low to negative $\delta^{18}\text{O}$ volcanic and intrusive

876 rocks in the Qinling mountains and their geological significance. *Precambrian Research*,

877 230, 138–167. doi:10.1016/j.precamres.2013.02.006.

878

879 Meldrum, A., Boatner, L.A., Zinkle, S.J., Wang, S., Wang, L., and Ewing, R.C. (1999)

880 Effects of dose rate and temperature on the crystalline-to-metamict transformatton in the

881 ABO_4 orthosilicates. *The Canadian Mineralogist*, 37, 207–221.

882

883 Mojzsis, S.J., Harrison, M., and Pidgeon, R.T. (2001) Oxygen isotope evidence from

884 ancient zircons for liquid water at Earth's surface 4300 Myr ago. *Nature*, 409, 178-181.

885

886 Morgan, G.B., and London, D. (1996) Optimizing the electron microprobe analysis of

887 hydrous alkali aluminosilicate glasses. *American Mineralogist*, 81, 1176-1185.

888

889 Moser, D.E., Cupelli, C.L., Barker, I.R., Flowers, R.M., Bowman, J.R., Wooden, J., and
890 Hart, J.R. (2011) New zircon shock phenomena and their use for dating and
891 reconstruction of large impact structures revealed by electron nanobeam (EBSD, CL,
892 EDS) and isotopic U-Pb and (U-Th)/He analysis of the Vredefort Dome. Canadian
893 Journal of Earth Sciences, 48, 117–139.

894

895 Muehlenbachs, K., and Kushiro, I. (1975) Measurements of oxygen diffusion in silicates.
896 EOS Transaction of the American Geophysical Union, 56, 549.

897

898 Murakami, T., Chakoumakos, B.C., Ewing, R.C., Lumpkin, G.R., and Weber, W.J.
899 (1991) Alpha-decay event damage in zircon. American Mineralogist, 76, 1–23.

900

901 Nasdala, L., Irmer, G., and Wolf, D. (1995) The degree of metamictization in zircons: a
902 Raman spectroscopic study. European Journal of Mineralogy, 7, 471–478.

903

904 Nasdala, L., Pidgeon, R.T., Wolf, D., and Irmer, G. (1998a) Metamictization and U-Pb
905 isotopic discordance in single zircons: a combined Raman microprobe and SHRIMP ion
906 probe study. Mineralogy and Petrology, 62, 1–27. doi:10.1007/BF01173760.

907

908 Nasdala, L., Götze, J., Pidgeon, R.T., Kempe, U., and Seifert, T. (1998b) Constraining a
909 SHRIMP U-Pb age: micro-scale characterization of zircons from Saxonian Rotliegend
910 rhyolites. Contributions to Mineralogy and Petrology, 132, 300–306.

911

912 Nasdala, L., Wenzel, M., Vavra, G., Irmer, G., Wenzel, T., and Kober, B. (2001)
913 Metamictisation of natural zircon: accumulation versus thermal annealing of
914 radioactivity-induced damage. *Contributions to Mineralogy and Petrology*, 141, 125–
915 144. doi:10.1007/s004100000235.

916

917 Nasdala, L., Lengauer, C.L., Hanchar, J.M., Kronz, A., Wirth, R., Blanc, P., Kennedy,
918 A.K., and Seydoux-Guillaume, A-M. (2002) Annealing radiation damage and the
919 recovery of cathodoluminescence. *Chemical Geology*, 191, 121–40. doi:10.1016/S0009-
920 2541(02)00152-3.

921

922 Nemchin, A.A., and Pidgeon, R.T. (1997) Evolution of the Darling range batholith,
923 Yilgarn craton, western Australia: a SHRIMP zircon study. *Journal of Petrology*, 38,
924 625–649.

925

926 Page, F.Z., Ushikubo, T., Kita, N.T., Riciputi, L.R., and Valley, J.W. (2007) High-
927 precision oxygen isotope analysis of picogram samples reveals 2 μ m gradients and slow
928 diffusion in zircon. *American Mineralogist*, 92, 1772–1775. doi:10.2138/am.2007.2697.

929

930 Palenik, C.S., Nasdala, L., and Ewing, R.C. (2003) Radiation damage in zircon.
931 *American Mineralogist*, 88, 770-781.

932

933 Pidgeon, R.T. (1992) Recrystallisation of oscillatory zoned zircon: some

934 geochronological and petrological implications. *Contributions to Mineralogy and*
935 *Petrology*, 110, 463–472.

936

937 Pidgeon, R.T., O'Neil, J.R., and Silver, R.T. (1995) The interdependence of U-Pb
938 stability, crystallinity and external conditions in natural zircons ± an early experimental
939 study. Leon T Silver 70th Birthday Symposium and Celebration. Extended abstracts, pp
940 225-231

941

942 Pidgeon, R.T., Nemchin, A.A., and Cliff, J. (2013) Interaction of weathering solutions
943 with oxygen and U–Pb isotopic systems of radiation-damaged zircon from an Archean
944 granite, Darling Range batholith, western Australia. *Contributions to Mineralogy and*
945 *Petrology*, 166, 511–523. doi:10.1007/s00410-013-0888-z.

946

947 Pidgeon, R.T. (2014) Radiation damage ages. *Chemical Geology*, 367, 13-33.
948 doi:10.1016/j.chemgeo.2013.12.010.

949

950 Putnis, A. (2002) Mineral replacement reactions: from macroscopic observations to
951 microscopic mechanisms. *Mineralogical Magazine*, 66, 689–708.
952 doi:10.1180/0026461026650056.

953

954 Putnis, C.V., Tsukamoto, K., and Nishimura, Y. (2005) Direct observations of
955 pseudomorphism: compositional and textural evolution at a fluid-solid interface.
956 *American Mineralogist*, 90, 1909–1912. doi:10.2138/am.2005.1990.

957

958 Rayner, N., Stern, R.A., and Carr, S.D. (2005) Grain-scale variations in trace element
959 composition of fluid-altered zircon, Acasta gneiss complex, northwestern Canada.
960 Contributions to Mineralogy and Petrology, 148, 721–734. doi:10.1007/s00410-004-
961 0633-8.

962

963 Ríos, S., Salje, E.K.H., Zhang, M., and Ewing, R.C. (2000) Amorphization in zircon:
964 evidence for direct impact damage. Journal of Physics: Condensed Matter, 12, 2401–
965 2412. doi:10.1088/0953-8984/12/11/306.

966

967 Rizvanova, N.G., Levchenkov, O.A., and Belous, A.E. (2000) Zircon reaction and
968 stability of the U-Pb isotope system during interaction with carbonate fluid: experimental
969 hydrothermal study. Contributions To Mineralogy and Petrology, 139, 101-114.

970

971 Rollinson, H. (2012) Geochemical constraints on the composition of Archaean lower
972 continental crust partial melting in the Lewisian granulites. Earth and Planetary Science
973 Letters, 351-352, 1–12. doi:10.1016/j.epsl.2012.07.018.

974

975 Salje, E.K.H., Chrosch, J., and Ewing, R.C. (1999) Is ‘metamictization’ of zircon a phase
976 transition? American Mineralogist, 84, 1107–1116.

977

978 Spencer, C.J., Cawood, P.A., Hawkesworth, C.J., Raub, T.D., Prave, A.R., and Roberts,

- 979 N.M.W. (2014) Proterozoic onset of crustal reworking and collisional tectonics:
980 reappraisal of the zircon oxygen isotope record. *Geology*, 42 (5), 451-454.
981
- 982 Tanabe, K., and Hiraishi, J. (1980) Correction of finite slit width effects on Raman line
983 widths. *Spectrochimica Acta Part a: Molecular Spectroscopy*, 36, 341–344.
984
- 985 Tarney, J., and Weaver, B.L. (1987) Mineralogy, petrology and geochemistry of the
986 Scourie dykes: petrogenesis and crystallization processes in dykes intruded at depth.
987 *Geological Society London Special Publications*, 27, 217-233.
988
- 989 Tomaschek, F., Kennedy, A.K., Villa, I.M., Lagos, M., and Ballhaus, C. (2003) Zircons
990 from Syros, Cyclades, Greece—recrystallization and mobilization of zircon during high-
991 pressure metamorphism. *Journal of Petrology*, 44, 1977–2002.
992 doi:10.1093/petrology/egg067.
993
- 994 Trachenko, K.O. (2004) Understanding resistance to amorphization by radiation damage
995 *Journal of Physics: Condensed Matter*, 16, 1491-1515.
996
- 997 Trachenko, K.O., Dove, M.T., and Salje, E.K.H. (2001) Atomistic modelling of radiation
998 damage in zircon. *Journal of Physics: Condensed Matter*, 13, 1947–1959.
999 doi:10.1088/0953-8984/13/9/317.
1000
- 1001 Trachenko, K.O., Dove, M.T., and Salje, E.K.H. (2002) Structural changes in zircon

1002 under α -decay irradiation. Physical Review B, 65, 180102R.

1003 doi:10.1103/PhysRevB.65.180102.

1004

1005 Valley, J.W., Taylor, H.P.Jr., and O'Neil, J.R. (1986) Stable isotopes in high temperature
1006 geological processes. (eds), Reviews in Mineralogy, Vol 16.

1007

1008 Valley, J.W., Chiarenzelli, J.R., and McLelland, J.M. (1994) Oxygen isotope
1009 geochemistry of zircon. Earth and Planetary Science Letters, 126, 187–206.

1010

1011 Valley, J.W. (2001) Stable isotope thermometry at high temperatures. Reviews in
1012 Mineralogy and Geochemistry, 43, 365-413

1013

1014 Valley, J.W., and Cole, D.R. (2001) Stable isotope geochemistry (eds), Reviews in
1015 Mineralogy and geochemistry, Vol 43.

1016

1017 Valley, J.W. (2003) Oxygen isotopes in zircon. Reviews in Mineralogy and
1018 Geochemistry, 53, 343-385.

1019

1020 Valley, J.W., Lackey, J.S., Cavosie, A.J., Clechenko, C.C., Spicuzza, M.J., Basei,
1021 M.A.S., Bindeman, I.N., Ferreira, V.P., Sial, A.N., King, E.M., Peck, W.H., Sinha, A.K.,
1022 and Wei, C.S. (2005) 4.4 billion years of crustal maturation: oxygen isotope ratios of
1023 magmatic zircon. Contributions to Mineralogy and Petrology, 150, 561–580.

1024

1025 Weaver, B.L., and Tarney, J. (1981) The Scourie dyke suite: petrogenesis and
1026 geochemical nature of the Proterozoic sub-continental mantle. Contributions to
1027 Mineralogy and Petrology, 78, 175–188.

1028

1029 Weber, W.J., Ewing, R.C., and Wang, L M. (1994) The radiation-induced crystalline-to-
1030 amorphous transition in zircon. Journal of Materials Research, 9, 688–698.

1031

1032 Wopenka, B, Jolliff, B.L., Zinner, E., and Kremser, D.T. (1996) Trace element zoning
1033 and incipient metamictization in a lunar zircon: application of three microprobe
1034 techniques. American Mineralogist, 81, 902–912.

1035

1036 Yuan, H.L., Gao, S., Dai, M.N., Zong, C.L., and Günther, D. (2008) Simultaneous
1037 determinations of U–Pb age, Hf isotopes and trace element compositions of zircon by
1038 Excimer laser-ablation quadrupole and multiple-collector ICP-MS. Chemical Geology,
1039 247, 100-118.

1040

1041 Zhang, M., Salje, E.K.H., Farnan, I., Graeme-Barber, A., Daniel, P., Ewing, R.C., Clark,
1042 A.M., and Leroux, H. (2000a) Metamictization of zircon: Raman spectroscopic study.
1043 Journal of Physics: Condensed Matter, 12, 1915-1925.

1044

1045 Zhang, M., Salje, E.K.H., Capitani, G.C., Leroux, H., Clark, A.M., Schlüter, J., and
1046 Ewing, R.C. (2000b) Annealing of alpha-decay damage in zircon: a Raman spectroscopic

1047 study. Journal of Physics: Condensed Matter, 12, 3131-3148. doi:10.1088/0953-
1048 8984/12/8/333.

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Figure captions

1053 Figure 1

1054 Zircon Raman model showing how the band-width and frequency of the ν_3 (SiO₄) band
1055 respond to the accumulation of radiation damage, and how annealing of radiation damage
1056 either thermally, or catalyzed by fluids influences these parameters. For an explanation
1057 of the numbers and arrows see the text. The radiation damage trend is mainly based on
1058 data from Sri Lankan zircons and zircons from a Saxonian rhyolite which encompassed
1059 data from Nasdala et al. (1998b; 2001); Zheng et al. (2000a); Geisler et al. (2003b,c);
1060 Geisler unpublished. The Thermal annealing trend shown by the red arrow is from
1061 Geisler et al. 2001a, and the diffusional recovery trend is based on experimental and
1062 natural data from Geisler et al. (2003b,c).

1063

1064 Figure 2

1065 Simplified high-resolution geological map of the Loch Assynt area on the Scottish
1066 mainland. The map is modified from a 1:25,000 scale geological map from the BGS and
1067 figure 2b from Goodenough et al. (2010). The dyke samples are located along with their
1068 emplacement age and 2σ error (Davies and Heaman, 2014).

1069

1070

1071 Figure 3

1072 $\delta^{18}\text{O}$ Zircon vs $\delta^{18}\text{O}$ whole rock (WR) for the Scourie dykes. The lines represent
1073 equilibrium fractionation between zircon and WR with a fractionation factor (α) of 0.88.
1074 The darkest line, represents equilibrium fractionation at 1200 °C, each lighter colored line
1075 represent the larger fractionations associated with lower temperatures, each lighter line
1076 represents a 100 °C drop in temperature down to the lightest grey line which represents
1077 equilibrium fractionation at 600°C. The symbols are bigger than the 2σ errors for each
1078 analysis.

1079

1080 Figure 4

1081 CL images of zircons from the Scourie dykes with SIMS analysis spots and the oxygen
1082 isotope values located. Oxygen isotopes are all $\delta^{18}\text{O}$ values with 2σ uncertainties of 0.2
1083 ‰ or less. The WR oxygen isotopic composition of each sample is also given, these are
1084 also $\delta^{18}\text{O}$ values with 2σ uncertainties. The white bar in the bottom left of each image is
1085 a 20 μm scale bar. The white stars indicate grains with a complicated CL structure within
1086 a zircon population of typical igneous oscillatory zoning.

1087

1088 Figure 5

1089 Geochemistry of the Scourie zircons. A) SiO_2 vs ZrO_2 all values are in percentage B)
1090 Alpha dose accumulation since zircon formation age vs the band-width of the v3 (SiO4)
1091 band, note the black squares close to the y-axis, these represent the expected relationship
1092 between band-width and alpha dose, and are from the Saxonian rhyolites and lunar zircons

1093 (Nasdala 1998b; Wopenka et al. 1996). C) Ca and U elemental compositions of the
1094 Scourie zircons in ppm. D) The relationship between Ca content and the alpha dose, note
1095 the abrupt change in Ca content once a threshold alpha dose has been reached, this
1096 threshold is interpreted as the first percolation point in the crystalline-amorphous
1097 transition, see discussion for details. All 2σ errors are smaller than the symbol sizes.

1098

1099 Figure 6

1100 Band-width for the ν_3 (SiO_4) band vs frequency. The upper graph contains raman results
1101 from zircon spots with less than 100 ppm Ca. The lower graph contains raman results for
1102 the zircons spots with higher than 100 ppm Ca. The Grey shaded field is the Radiation
1103 Damage trend from Geisler et al. 2003c which encompassed data from Nasdala et al.
1104 1998b; 2001; Zheng et al. 2000b; Geisler et al. 2003c; Geisler unpublished)

1105

1106 Figure 7

1107 Different models for the radiation damage accumulation age of the low Ca zircons. The
1108 models are compared to the expected relationship between band-width and frequency of
1109 the ν_3 (SiO_4) band and age. The black squares are from the Saxonian rhyolites and lunar
1110 zircons (Nasdala et al. 1998b; Wopenka et al. 1996) and the black line represents a robust
1111 linear regression through these data.

1112

1113 Figure 8

1114 $\delta^{18}\text{O}$ Zircon vs $\delta^{18}\text{O}$ whole rock (WR) for the Scourie dykes separated by Ca abundance
1115 in the zircon. Ca is used to separate the zircons; it is a non-formula element that

1116 accumulates in zircon during fluid alteration. The large diagonal lines through both of
1117 the graphs represent high temperature (1200 °C) equilibrium between zircon and mafic
1118 melt. The small lines attached to individual analyses in the High Ca graph represent Ca
1119 analyses >1000 ppm.

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	Diffusion reaction	dissolution re-precipitation
CL/BSE features	Irregular inward propagating reaction zones along metamict domains in the crystal, features may be obscured by radiation damage post fluid interaction.	
Mineral Inclusions	typically no mineral inclusions in the newly crystallized domains	mineral inclusions are common and the species are controlled to the composition of the fluid
Elemental features	increase in non-formula elements, Ca, Al, Fe, Ba. Loss of Pb	Newly grown zircon is often devoid of non-formula elements.
Isotopic features	Mixture between the original isotopic composition and the composition of the newly crystallized zircon	isotopic information is completely reset in the newly crystallized zircon
Raman features	The v3 band moves away from the radiation damage trend	newly crystallized zircon behaves like pristine zircon.

isotopic and textural properties of the two end member reactions between fluids and metamict zircon
 Modified from Geisler et al. 2007)

Dyke name	Spot ID	U-Pb age	Oxygen isotopes (‰)	Chemistry	Ca ²⁺	Th ¹	Frequency	v, SiO ₂ parameters (cm ⁻¹)	Alpha dose 10 ¹⁶ g ⁻²		
			δ ¹⁸ O whole rock, 2σ ^a , δ ¹⁸ O zircon	ZrO ₂ ^b	SiO ₂ ^b	Zr	Line width	χ ² /ν (reduced)	Calculated using Dyke age		
Badcall Bay	3-1	2395.6 ± 4.8 Ma ^c	4.18	0.20	32.1	66.3	555	1000	3	5.9	
	4-1		4.96	0.19	32.1	65.6	538	998	31	5.5	
	5-1		4.96	0.19	32.1	65.3	539	1001	17	4.1	
	3-2		4.36	0.19	31.5	64.8	1003	1002	28	10.5	
Graveyard	10-1	2391.7 ± 1.6 Ma ^c	0.43	0.12	31.8	65.6	450	998	12	4.9	
	10-2		0.42	0.23	31.7	65.9	432	998	15	4.8	
	3-1		0.35	0.17	31.6	66.6	309	1000	10	3.2	
	3-2		0.38	0.18	32.0	66.4	317	1000	12	1	
	5-1		0.38	0.21	32.0	66.9	485	999	11	5	
	6-1		0.51	0.21	32.0	66.4	326	1000	10	1	
	7-1		0.37	0.18	31.8	66.5	443	1000	10	3	
	7-2		0.27	0.18	32.0	66.3	414	1000	9	4.7	
	8-1		0.37	0.18	32.0	66.3	626	1001	10	1	
	9-1		0.33	0.19	32.0	66.2	405	1001	11	4	
9-2		0.17	0.2	31.9	65.7	335	1000	9	1		
1-1		0.4	0.22	31.4	65.9	397	1002	7	2		
5-2		0.48	0.22	32.1	66.7	123	1000	11	3		
10-1	2344 ± 80 Ma ^c	3.10	0.12	0.76	30.8	63.7	544	1000	13	7.0	
11-1		0.76	0.19	31.4	64.6	306	1000	10	2		
11-2		-0.11	0.19	31.3	64.5	300	1005	8	3		
2-1		1.01	0.18	31.3	63.5	473	364	1772	30	29	
3-1		1.56	0.16	31.1	62.4	176	132	136	16	3	
5-1		-1.34	0.17	31.6	64.1	-	132	1451	17	12	
6-1		1.13	0.18	31.8	63.6	829	211	943	103	12	
8-1		1.84	0.16	31.7	64.5	617	855	765	1000	11	
9-1		-0.18	0.20	31.7	62.5	176	-	200	1002	9	
1-1	2480 ± 17 Ma ^c	6.80	0.12	6.18	31.1	63.3	167	-	1006	3	
1-2		6.13	0.16	32.2	65.4	97	-	21	1006	3	
2-1		6.15	0.16	31.3	66.3	141	-	64	1005	4	
3-1		6.06	0.16	32.1	66.3	159	-	21	1005	4	
4-1		6.02	0.17	31.1	64.7	141	-	57	1007	2	
5-1		6.1	0.18	31.2	62.7	167	-	21	1006	4	
6-2		6.16	0.16	32.3	66.4	132	-	64	1005	5	
6-1		6.16	0.16	31.8	66.2	167	-	59	1005	5	
7-1		5.96	0.16	32.1	66.2	176	-	36	1005	4	
7-2		6.03	0.17	31.9	66.2	256	-	93	1006	4	
2-1	2395 ± 7.6 Ma ^c	5.43	0.12	-0.74	31.3	65.1	670	475	1687	997	21
3-1		-3.73	0.17	31.3	65.1	203	-	1002	9	4	
3-1		-3.83	0.16	31.9	66.5	167	-	57	1002	8	
6-1		-3.05	0.16	31.7	65.9	705	562	457	997	15	
9-2		-2.19	0.16	31.1	63.5	1410	1643	4939	997	17	
9-1		-1.14	0.17	30.6	62.8	934	1257	2709	997	18	
1-1		0.06	0.16	31.1	64.8	820	747	1615	998	16	
2-2		-1.79	0.17	31.6	64.0	978	817	2659	996	22	
1-1	2367.7 ± 8.6 Ma ^c	4.83	0.12	1.61	0.19	32.1	66.3	370	998	19	
10-1		3.37	0.18	31.2	63.1	705	932	786	999	17	
11-1		2.08	0.18	32.0	65.7	441	193	50	1001	10	
12-1		3.6	0.18	30.7	63.6	835	1037	2451	99	20	
13-1		2.82	0.18	31.8	66.2	791	822	1526	999	16	
3-1		2.84	0.17	31.1	62.9	1489	791	4481	998	16	
5-1		2.33	0.17	31.2	64.3	987	808	1665	998	19	
6-1		1.91	0.18	32.0	66.0	361	149	21	1001	9	
7-1		5.3	0.18	31.3	63.8	1164	1107	3481	996	31	
8-1		2.32	0.18	31.8	65.8	547	448	114	999	16	
9-1		3.6	0.17	30.5	63.1	1014	1591	2058	998	25	
2-1	2540 ± 10 Ma ^c	6.00	0.12	6.62	32.1	66.9	264	114	999	14	
2-2		6.12	0.16	31.6	66.5	306	100	10	1000	13	
3-2		7.35	0.17	32.2	66.5	439	29	99	1000	13	
4-1		6.13	0.16	32.1	66.9	405	132	36	999	10	
4-2		5.74	0.16	32.2	66.8	591	167	-	999	13	
5-1		6.78	0.18	31.7	66.0	723	343	465	998	15	
5-2		7.24	0.18	32.1	65.3	247	-	364	1000	16	
6-1		7.13	0.17	32.2	66.8	476	281	-	1001	9	
6-2		7.19	0.17	31.1	66.5	411	102	-	1000	7	
7-1		6.44	0.16	31.9	66.0	829	560	214	999	13	















