

Title: Melt-mediated re-equilibration of zircon produced during meltdown of the Chernobyl reactor

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1 **Revision 2**

2 **Melt-mediated re-equilibration of zircon produced during meltdown of the Chernobyl**
3 **reactor**

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12

13 **Abstract**

14 The mineral zircon is used widely to constrain the age of rocks and the processes that
15 formed them. Although zircon is robust to a range of physical and chemical processes, it
16 may show evidence for rapid re-equilibration that is generally considered to reflect
17 interaction with hydrous fluids. Here, we show that zircon grains that crystallised from melt
18 produced during the catastrophic meltdown of the Chernobyl nuclear reactor exhibit re-
19 equilibration textures that occurred in an environment without free-water. The process of re-
20 equilibration involved a melt-mediated interface-coupled dissolution–reprecipitation that
21 took place over a few days to produce textures that are commonly observed in igneous and

22 anatectic systems. Thus, the composition of zircon can be modified even in the absence of
23 hydrous fluids in a short time-frame. Through this process, zircon crystals may track the
24 timing of the last silicate melt it interacted with.

25

26 **Introduction**

27 The catastrophic meltdown of the reactor 4 of the Chernobyl Nuclear Power Plant on April
28 26, 1986 is the worst nuclear disaster in history. The reactor experienced a suite of
29 unexpected events causing uncontrolled nuclear chain reaction (Mullner, 2019). The
30 temperature reached in excess of 2600°C causing the uranium fuel rods and their zirconium
31 alloy cladding to melt and drop at the bottom of the reactor (Burakov et al., 1996). This
32 molten material, or corium, dissolved constituents of the reactor including steel, concrete,
33 serpentine and sand, evolving to a silicate melt from which zircons [ZrSiO₄] crystallised at
34 temperature below 1250°C (Burakov et al., 1996; Pazukhin, 1994; Pöml et al., 2013; Ushakov
35 et al., 1996).

36 Zircon is a commonly used mineral to understand when and how rocks formed (Harley and
37 Kelly, 2007). Despite its chemical and physical robustness, the internal structure of zircon
38 grains can be chaotic and indicates that zircon may partially re-equilibrate in response to
39 changing pressure–temperature–composition (*P–T–X*) conditions (Martin et al., 2008;
40 Rubatto, 2017). To this day, hydrous fluids are believed to play an important role in
41 modifying particular domains within zircon, especially if they have been damaged by
42 radioactive decay (Geisler et al., 2003; Geisler et al., 2007). However, similar features are also
43 recorded in crystalline zircon grains from metamorphic environments (Rubatto et al., 2008)

44 or due to interaction with high- T magmatic fluids (Soman et al., 2010). Re-equilibration
45 textures in zircon have also been documented from a variety of settings in which hydrous
46 fluids likely played little or no role, including igneous (Bindeman and Melnik, 2016;
47 Gagnevin et al., 2010), high-grade metamorphic (Hoskin and Black, 2000; Zheng et al., 2004),
48 and experimental systems (Tomaschek, 2004). Although several mechanisms have been
49 proposed to drive reequilibration of zircon in fluid-deficient settings including solid-state
50 recrystallization (Hoskin and Black, 2000) and melt-mediated interface-coupled dissolution-
51 reprecipitation (Geisler et al., 2007), such mechanisms are poorly understood.

52 Chernobyl zircon grains, collected during an inspection of the Power Plant in 1989 are well
53 suited to study the re-equilibration of a crystalline zircon in an anhydrous melt (Shiryaev et
54 al., 2016). Although some of the Chernobyl melt interacted with water forming porous
55 ceramics in localised areas of the plant where water was pooling, the majority of the melt
56 was never in contact with water thanks to the rescue team that drained the flooded
57 basement, avoiding another, larger catastrophe. The Chernobyl melt remained at
58 atmospheric pressure during its evolution and therefore could only dissolve negligible
59 water (Carroll and Blank, 1997; Dixon et al., 1995; Silver et al., 1990). The Chernobyl zircons
60 contain high U contents, however they are virtually free of damage due to internal
61 radioactive decay. Here, we investigate the textural and chemical features of one of these
62 zircon grains using crystallographic orientation mapping, ion imaging, and nanoscale
63 analyses, with the aim of determining the mechanisms of zircon reequilibration in a dry
64 magmatic setting.

65

66 **Sample and methods**

67 At Chernobyl, several types of lava-like solidified materials have been described such as the
68 black and brown silicate glass as well as porous ceramics that formed by the interaction of
69 brown silicate melt with water (Burakov et al., 1996). The sample studied is a brown silicate
70 melt that was collected in the basement of the Chernobyl Power Plant (Borovoi, 2006).
71 Zircon grains were separated at the Khlopin Radium Institut in St. Petersburg by dissolving
72 the glass matrix in hydrofluoric acid. Secondary electron images did not reveal any signs of
73 zircon dissolution (Borovoi, 2006), and zircon grains separated without the use of
74 hydrofluoric acid have very similar textures to those reported here (Shiryaev et al., 2016).
75 Three zircon grains of a total weight of less than 0.4 mg were mounted in epoxy. The
76 radiometry measurements of the sample demonstrated relatively low activity with a dose
77 rate of about 0.25 microsieverts per hour (uSv/hr) at 5 cm from the sample. The activity of
78 the sample mount was estimated to be below 50 kBq. Radiometry measurements were
79 performed before and after the analysis to ensure that the fissile material was not lost during
80 the analysis. The sample does not contain particulate matter that could be easily lost.
81 Nevertheless, handling of the sample was carried out in controlled laminar hoods.

82 Scanning electron microscopy (SEM), focused ion beam (FIB) sample preparation,
83 transmission electron microscopy (TEM) and atom probe tomography (APT) analyses were
84 performed at the John de Laeter Centre, Curtin University. The sample was ion milled for 30
85 min at a 5° tilt using an Ar ion beam operated at a 5 kV accelerating voltage and a beam
86 current of 40 µA to remove the surface layer affected by mechanical polishing. Electron
87 backscattered imaging (BSE) and electron backscattered diffraction mapping (EBSD) were
88 performed on a Tescan Mira3 and Tescan Clara SEMs. The instruments were operated at 20
89 kV accelerating voltage and EBSD data was acquired with an Oxford Symmetry detector

90 and reduced with the Channel5 software. Samples for APT and TEM were prepared with a
91 Tescan Lyra3 Ga⁺ FIB-SEM. Pt fiducials deposited using an electron beam were used to
92 target the boundary between high- and low-U zircon (Rickard et al., 2020). The FIB was
93 operated at 30 kV during the manufacture of the APT and TEM specimens and at 2 kV to
94 remove the layer affected by high-energy Ga⁺ ion implantation. TEM analyses were
95 conducted on a FEI Talos FS200X FEG TEM operated at 200 kV in scanning mode (STEM)
96 and equipped with a Super-X EDS detector. We used the geoscience atom probe at Curtin
97 University for APT data collection (Reddy et al., 2020). The instrument (Cameca LEAP 4000X
98 HR) was used in laser pulsing mode with a UV laser ($\lambda = 355$ nm). The laser was pulsed at
99 125 kHz with a laser energy of 300 pJ and at an automated detection rate of 0.02 ion/pulse
100 and 60 K base temperature. The 3D reconstruction was performed using the Cameca IVAS
101 3.8 software using a voltage curve reconstruction and 32 V/nm evaporation field following a
102 standardised approach (Fougerouse et al., 2022; Saxey et al., 2019).

103 Scanning ion imaging was performed with a Cameca IMS 1280 equipped with Hyperion-II
104 radio-frequency oxygen ion source at the Centre for Microscopy, Characterisation and
105 Analysis, The University of Western Australia. Primary O₂⁻ ions were focused as a Gaussian
106 beam and accelerated by potential of -13 kV toward the sample under +10 kV and a beam
107 current was 70 pA. For uranium isotope analyses, ions on masses 234, 235, 236, 238 and 239
108 were detected simultaneously, and for plutonium analyses, ions on masses 238, 239, 240, 241
109 and 242 were measured. Since the IMS1280 magnet dispersion and minimal distance
110 between detectors do not allow to detect ions at such high masses simultaneously, the mass
111 dispersion was increased by using the stigmator (DSP2S1) located after the magnet. The
112 measurements were performed at a mass resolution of 2460 M/ Δ M with an entrance slit of

113 200 μm , exit slit #1 (500 μm), a field aperture of 5000 μm and a contrast aperture of 400 μm .
114 Ion images are 50x50 μm in size and were processed using CAMECA SIMS Image
115 Processing Software WinImage II.

116

117 **Results**

118 **Textural relationships and isotopic composition of zircon domains**

119 The BSE images of the zircon grain reveal complex internal textures (Fig. 1). The grain
120 contains numerous inclusions of monoclinic $(\text{Zr,U})\text{O}_2$ fuel fragments, and $(\text{U,Zr})\text{O}_2$ that
121 crystallized early at high temperature from two immiscible melts that formed when the
122 nuclear fuel interacted with the zirconium alloy cladding (Burakov et al., 1996). The
123 brightest BSE response reflects highest U content in zircon (Geisler et al., 2005; Pöml et al.,
124 2013; Shiryaev et al., 2016). The high-U domains are truncated by lower-U curvilinear,
125 finger-like domains penetrating inward from the crystal margin (Fig. 1B). Low-U domains
126 are well developed in the external part of the grain and enclose numerous inclusions of
127 $(\text{Zr,U})\text{O}_2$ and $(\text{U,Zr})\text{O}_2$ that are apparently coarser than in the high-U domain. The grain
128 preserves remnants of primary oscillatory growth zoning, as well as faint ('ghost') zoning in
129 the low-U domains that mimics the overall grain shape and is consistent with primary
130 oscillatory zoning. A typical feature is the occurrence of micrometre-sized pores near or at
131 the interface between high- and low-U zircon domains (Fig. 1D; Fig. 1P in (Geisler et al.,
132 2007)). The pores at the interface are particularly common at high-curvature boundaries,
133 such as the tips of the finger-like domains (red arrows in Fig. 1D).

134 In the EBSD data, the colour variations on the texture component analysis are spatially
135 correlated with porosity and topographical features (Fig. 1C). No significant internal
136 deformation is evident, and the crystal orientation is continuous through the interface
137 between the high and low-U domains.

138 Ion imaging confirms that the ^{238}U abundance is high in the BSE bright, low in the dark
139 domains, and that the ^{240}Pu concentration mimics that of U (Fig. 2). The $^{235}\text{U}/^{238}\text{U}$ ratio map
140 and a profile across several finger-like features indicates that the uranium isotopic
141 composition is locally constant between high- and low-U domains (Fig. 2).

142 **Nanoscale observations**

143 The nanoscale analyses focused on the boundary between the high- and low-U domains of
144 the zircon grain (Fig. 3). The atom probe mass spectra are comparable with other APT
145 studies of zircon (Peterman et al., 2016; Saxey et al., 2018) despite well-developed U^{++} , UO^{++} ,
146 UO_2^+ and UO_2^{++} peaks (Fig. DR1). The APT measurements from the selected interface (Fig.
147 1E) show that the high-U zircon contains 1.1 at.% U and the low-U domains 0.6 at.% U. The
148 increase in U is compensated by a decrease in Zr, but not by a decrease in Si, as observed in
149 a previous electron microprobe study (Geisler et al., 2005). The boundary between the two
150 domains is sharp at the nanoscale, with the U concentration changing over ~ 7 nm (Fig. 3B).
151 No enrichment of trace elements is observed at the interface. Consistent with APT data, the
152 TEM observations in both the STEM bright field (BF) image and the STEM EDS map
153 indicates that the boundary between the two domains is discrete at the nanoscale (Fig. 3).
154 Small (~ 25 nm) ZrO_2 inclusions are also present in the high-U domains. The TEM data does
155 not reveal the presence of nanoscale porosity in either the high or low-U domains.

156 Consistent with the EBSD data, the crystal orientation is continuous across the boundary,
157 with no recognizable strain fields at the interface between the two domains.

158 **Discussion**

159 **Zircon growth and modification in silicate melt**

160 The incorporation of tetravalent ions in zircon (U, Pu and Th) creates lattice strain (Ewing,
161 1999; Finch and Hanchar, 2003; Meldrum et al., 1998; Ushakov et al., 1999). Ushakov et al.
162 (1999) determined the solubility of USiO_4 at 4 ± 1 at.% in zircon at 1500 °C. By applying Ti-
163 in-zircon thermometry (Ferry and Watson, 2007), the zircon crystals in the Chernobyl brown
164 glass likely crystallised at temperatures below 1250 °C (Pöml et al., 2013). These
165 temperatures are consistent with the stability of monoclinic ZrO_2 as observed in the core of
166 many zircon crystals from Chernobyl (Pöml et al., 2013).

167 In general, zircon crystals may become metastable under changing P - T - X conditions and be
168 subjected to subsolidus modification (Rubatto, 2017). The finger-like low-U domains in the
169 zircons from the Chernobyl brown melt truncate primary oscillatory zoning, and in places
170 preserve remnants of it (Fig. 1 and 4). Similar embayment textures and 'ghost zoning'
171 whereby the primary oscillatory zoning affects the transient composition of the reaction
172 front have been attributed to re-equilibration (Black et al., 1986; Harley et al., 2007; Hoskin
173 and Black, 2000; Martin et al., 2008).

174 The composition of the Chernobyl glasses is variable and include some material that
175 interacted with water. However, the Chernobyl brown glass, from which the zircon studied
176 here has been extracted, is anhydrous within detection limits of Raman and reflectance
177 infrared spectroscopy (Shiryaev et al., 2016). As demonstrated experimentally, the water

178 solubility in silicate melts is negligible at atmospheric pressure (Carroll and Blank, 1997;
179 Dixon et al., 1995; Silver et al., 1990) and the Chernobyl silicate melt likely remained
180 anhydrous throughout its evolution. In anhydrous environment, three mechanisms have
181 been proposed to explain the observed textures: (1) dissolution of zircon in a melt followed
182 by epitaxial growth of compositionally-discrete zircon (Hibbard, 1981), (2) solid-state
183 recrystallization driven by the diffusion of REE defects (Hoskin and Black, 2000), and; (3)
184 melt-mediated interface-coupled dissolution–reprecipitation (Geisler et al., 2007).

185 The dissolution and growth model (1) is based on simple stability assumptions. In the
186 Chernobyl zircons, the U isotopic composition varies within single crystals and between
187 different zircon grains (Pöml et al., 2013). The $^{235}\text{U}/^{238}\text{U}$ composition of zircon crystals and
188 the inclusions they contains ranges from 0.0166 to 0.0088 and differs significantly from the
189 natural $^{235}\text{U}/^{238}\text{U}$ ratio of 0.007257 (Pöml et al., 2013). This can be explained by heterogeneous
190 mixing of melted uranium fuel rods that had different burnup and U isotopic composition
191 with theoretical $^{235}\text{U}/^{238}\text{U}$ value up to 0.02041 (for 2% ^{235}U enrichment) (Pöml et al., 2013). The
192 prediction from the dissolution and epitaxial growth model is that the primary and
193 secondary features should have different uranium isotope composition because of the
194 heterogeneous U isotopic composition of the brown melt. However, the $^{235}\text{U}/^{238}\text{U}$
195 composition across the different zircon domains is constant, and does not support this
196 model (Fig. 2).

197 The solid-state recrystallization model (2) is based on the slow diffusion of defects and REE
198 impurities that occur so as to reduce the lattice strain caused by impurities (Hoskin and
199 Black, 2000). Such process, is solely controlled by diffusion and is expected to produce
200 diffuse domains within zircon grains. However, the reaction front in the Chernobyl zircon is

201 sharp at the nanoscale (Fig. 3). The extremely low diffusion rate measured for U in
202 crystalline zircon ($\sim 10^{-25}$ m²/s) at 1250 °C (Cherniak et al., 1997) means that, after ten days, U
203 would diffuse over a distance of ~ 0.4 nm. As such, the operation of a process controlled by
204 diffusion is extremely unlikely and the solid-state recrystallization driven by the diffusion of
205 REE defects (Hoskin and Black, 2000) is not supported by our data.

206 The textural relationship between primary and re-equilibrated zircon is also similar to that
207 created by aqueous-fluid-mediated interface-coupled dissolution–precipitation (Geisler et
208 al., 2007). Nanoscale investigations of the reaction front in fluid-mediated replacement
209 textures in ultra-high pressure zircons have revealed a network of nanoscale planar features
210 that are enriched and/or depleted in Y, Yb, U, and high-density clusters (< 10 nm) that are
211 enriched in Y, P, Yb, U, and Al (Peterman et al., 2019). In the Chernobyl zircon, trace element
212 segregation is not observed associated with either planar features or clusters and U is the
213 only element with a detectable change in concentration at the interface between both
214 domains.

215 The sharp gradient in U concentration, which can be interpreted as a boundary, supports the
216 idea that the low-U domains were formed by a process of surface-controlled and interface-
217 coupled dissolution-precipitation. During this process, the U-rich parent zircon dissolved in
218 the surrounding melt simultaneous with precipitation of new U-poor zircon along an
219 inwardly migrating reaction interface (Fig. 4). We hypothesize that the driving force for
220 migration of the interface was undersaturation of the surrounding melt with respect to U-
221 rich zircon due to changes in the global or local physicochemical conditions (Fig. 4). The
222 composition of the brown melt evolved with the progressive incorporation of basement
223 materials, including concrete, serpentine and sand (Pöml et al., 2013). Due to rapid changes

224 in the concentration of Zr and U in the melt, we postulate that the high-U zircon became
225 unstable (Fig. 4). Dissolution of the U-rich zircon caused the local melt to become
226 oversaturated in a U-poor zircon composition that eventually precipitated topotactically on
227 the dissolving zircon surface.

228 For such a process to operate, the formation of porosity in the product phase is critical for
229 mass transport from and to the reaction interface, where dissolution–precipitation reactions
230 take place (Geisler et al., 2019; Geisler et al., 2007; Putnis, 2002). Whereas no porosity was
231 observed at the nano-scale, micrometre-sized pores occur at the reaction interface,
232 particularly at the tips of the finger-like domains (Fig. 1). These pores are related to the
233 replacement process, but they are unlikely to form a connected network that could have
234 provided continuous pathways for melt to reach the reaction interface.

235 We interpret the large pores at the tips of the secondary low-U domains to represent the
236 final products of coarsening of fine-scale porosity formed during the replacement process by
237 pore ripening processes, as suggested to explain missing interconnected porosity in fluid-
238 mediated replacement reactions (Fougerouse et al., 2016; Putnis, 2002; Vonlanthen et al.,
239 2012). Porosity must have been created during the replacement process by the molar volume
240 and solubility difference between the parent and product zircon (Geisler et al., 2007).
241 Thermodynamically, such a ripening process is driven by the reduction in surface area,
242 comparable to crack healing within a single crystal (Brantley et al., 1990).

243 Although numerous inclusions are present in the grain, these inclusions can be observed in
244 both primary and secondary domains and are unlikely to be entirely the result of the re-
245 equilibration as opposed to the process described during fluid-mediated interface-coupled
246 dissolution–precipitation (Geisler et al., 2007; Soman et al., 2010). Notably, the mineral

247 inclusions of ZrO_2 and UO_2 are coarser in the re-equilibrated domains (Fig. 1). This
248 observation suggests that these inclusions may have grown during replacement (Fig. 4). The
249 observed chemical variation between the re-equilibrated and primary zircon is significant
250 (>0.5 at.% U), but the variability is much larger in other crystals (Geisler et al., 2005; Shiryayev
251 et al., 2020). The excess U that is released from the primary zircon during its replacement
252 could be the source for coarsening of UO_2 inclusions. If true, this requires pathways for U to
253 be transported away from the reaction front.

254 **Geological implications**

255 Core–rim textures similar to those observed in the Chernobyl zircon have been described
256 from various geological systems. In magmatic systems, “patchy textures” have been
257 reported from felsic rhyolite and A-type granite (Breiter et al., 2014), monzogranite
258 (Bindeman and Simakin, 2014; Gagnevin et al., 2010) and granodiorite (Wang et al., 2002). In
259 every instance, high-U–Th–Y zircon cores were replaced by low-U–Th–Y domains that have
260 (where measured) Th/U ratios below 0.1. Magma mixing is generally accepted as the main
261 mechanism by which the melt composition is changed, which acts as the driving force for
262 replacement (Bindeman and Simakin, 2014; Gagnevin et al., 2010). Bindeman and Simakin
263 (2014) suggest that the Zr-saturation of the magma is the principal cause of reaction,
264 whereas the preferred model of Gagnevin et al. (2010) is the mixing of a metaluminous melt
265 in a peraluminous system, in which co-crystallisation of phosphate with zircon explains the
266 formation of secondary low-U–Th–Y replacement zones. A melt-mediated interface-coupled
267 dissolution-precipitation provides a mechanism that is able to explain replacement
268 textures that form under dry conditions.

269 The model commonly used to explain zircon re-equilibration textures is that they formed via
270 solid-solution recrystallization and diffusion of defects (Hoskin and Black, 2000). Such a
271 process, is expected to produce diffuse domains but is inconsistent with the sharp interface
272 between parent zircon and re-equilibrated low-U–Th–Y domains observed in high-grade
273 metamorphic rocks (Chen et al., 2013; Dong et al., 2017). Therefore, we propose that, during
274 interactions with silicate melts, melt-mediated coupled dissolution-precipitation
275 mechanism is an effective mechanism for zircon re-equilibration that produce a sharp
276 interface between the parent zircon and the re-equilibrated low-U–Th–Y domains. As Pb is
277 not incorporated in the zircon crystal lattice during crystallisation, we postulate that Pb is
278 expelled during melt-driven interface-coupled dissolution-precipitation, thereby resetting
279 the U–Th–Pb geochronometer. Thus, in case of metamorphic resetting, either the entire grain
280 or low-U–Th–Y domains (rim) of zircons may record the timing of onset of anatexis rather
281 than peak metamorphism as suggested by melt-mediated monazite experiments (Varga et
282 al., 2020). Although Chernobyl zircons have extraordinarily high-U content and could be
283 particularly reactive, this process may occur rapidly over a few days, and may record only
284 small degrees of melt–zircon interactions. Melt-driven interface-coupled dissolution-
285 reprecipitation should be considered as an age resetting mechanism when retracing P – T
286 metamorphic paths in high-grade metamorphic rocks. Such mechanism may also be
287 important during magma mixing in magmatic chambers, late-stage magmatism during
288 orogenic events and zircon recycling. It has been documented that there is a preservation
289 bias of high-U zircons in the detrital zircon record due to metamictisation and weathering
290 (Dröllner et al., 2022; Markwitz and Kirkland, 2018; Resentini et al., 2020). This study
291 suggests that melt-mediated re-equilibration is another process that can induce a
292 preservation bias of high-U zircons record, in particular if the recycling process is mediated

293 by a silicate melt. Although the Chernobyl zircon crystal are likely more reactive than
294 natural zircons, re-equilibration textures observed in a range of felsic rocks as detailed above
295 suggest that this process may be active during continental crust recycling. In addition, as Hf
296 is incorporated as a structural element in zircon (Kinny and Maas, 2003), we postulate that
297 re-equilibration of high-U zircon should preserve original Lu/Hf and Hf isotope ratios. This
298 hypothesis seems reasonable considering that metamorphic zircons preserve their
299 initial $^{176}\text{Hf}/^{177}\text{Hf}$ ratio and have comparable or lower Lu/Hf ratios compared to igneous
300 zircons (Hoskin and Black, 2000; Kinny and Maas, 2003). However, because the U–Th–Pb
301 geochronometer may be reset, it can lead to underestimate the Hf isotope composition of the
302 source. It is unclear how such bias is expressed in the detrital record for example, but
303 indicates that zircon re-equilibration texture must be considered for Lu/Hf studies.

304

305 **Conclusions**

306 This research presents microstructural, isotopic and nanoscale information of a complex
307 zircon crystal to yield unique insight into the mechanism of mineral re-equilibration in the
308 absence of water. The data show that re-equilibration likely operates through a surface-
309 controlled and interface-coupled reaction process of dissolution and reprecipitation
310 mediated by a silicate melt. The U-rich zircon dissolves and U-poor zircon simultaneously
311 precipitates following a reaction front penetrating in the zircon crystal. The reaction
312 occurred rapidly (<2 weeks) and is likely driven by the instability of high-U zircon after
313 changes in the parent melt composition and the assimilation of material from the nuclear
314 plant. The melt-mediated dissolution-reprecipitation process is likely to be common in
315 natural contexts, including but not limited to, anataxis, magma mixing, late-stage

316 magmatism during orogenic events and zircon recycling. In all cases, the geological record
317 of inherited, U-rich zircons may be lost through mineral re-equilibration.

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327

328 **Figure caption**

329 **Figure 1: Grain-scale textural analysis of a zircon grain from the Chernobyl "lava".** A) BSE
330 image; B) Contrast enhanced BSE image. The bright inclusions are a mix of UO_2 and ZrO_2 .
331 The shades of grey indicate a higher average atomic weight and correspond to the U
332 content. Low-U zircon replaces high-U zircon along inward penetrating embayments. The
333 primary oscillatory zoning is truncated but ghost zoning remains present in the low-U
334 zircon; C) Crystallographic orientation electron backscattered diffraction (EBSD) map.
335 Misorientation is colour coded from reference point "+" to maximum of 10° . No variation in
336 crystal orientation can be observed between the low- and high-U domains; D) BSE image
337 enhancement of the zircon core. The red arrows point to the finger-like embayments; B)

338 Close up of the region of interest with the atom probe tomography (APT) and transmission
339 electron microscopy (TEM) specimens location indicated.

340 **Figure 2: Ion imaging of secondary textures.** A) ^{238}U counts maps showing high and low-U
341 zircon domains and bright UO_2 inclusions; B) $^{235}\text{U}/^{238}\text{U}$ ratio map indicating that the zircon U
342 isotopic composition is locally homogeneous across all domains; C) line profile (indicated in
343 B) illustrating the ^{238}U , ^{240}Pu and $^{235}\text{U}/^{238}\text{U}$ composition of the primary and secondary
344 domains.

345 **Figure 3: Nanoscale analyses.** A) Atom probe 3D reconstruction of the APT specimen. Each
346 purple dot represents a single U atom. The U distribution is heterogeneous with a high-U
347 and a low-U domain separated by a sharp boundary; B) Chemical profile across the
348 boundary from the APT data. The location of the profile is indicated on A. The U content
349 varies by ~ 0.5 at.% over < 7 nm; C) STEM BF image across the reaction. No nanoscale
350 porosity is present in the re-equilibrated zircon; D) STEM EDS map for U confirms the sharp
351 nature of the reaction front.

352 **Figure 4: Interpretative schematic diagram of the zircon history.** Left) The zircon grows in
353 equilibrium with high-U melt with strong primary zoning and numerous inclusions;
354 Middle) the re-equilibration to low-U zircon first occurs along grain boundaries. The
355 inclusions coarsen during the dissolution-reprecipitation reaction; Right) the re-equilibration
356 becomes pervasive throughout the grain with the development of large porosity and large
357 inclusions. The primary zoning is truncated by the low-U zircon, but some primary zoning
358 is faintly preserved as ghost zoning.

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506

Figure 1

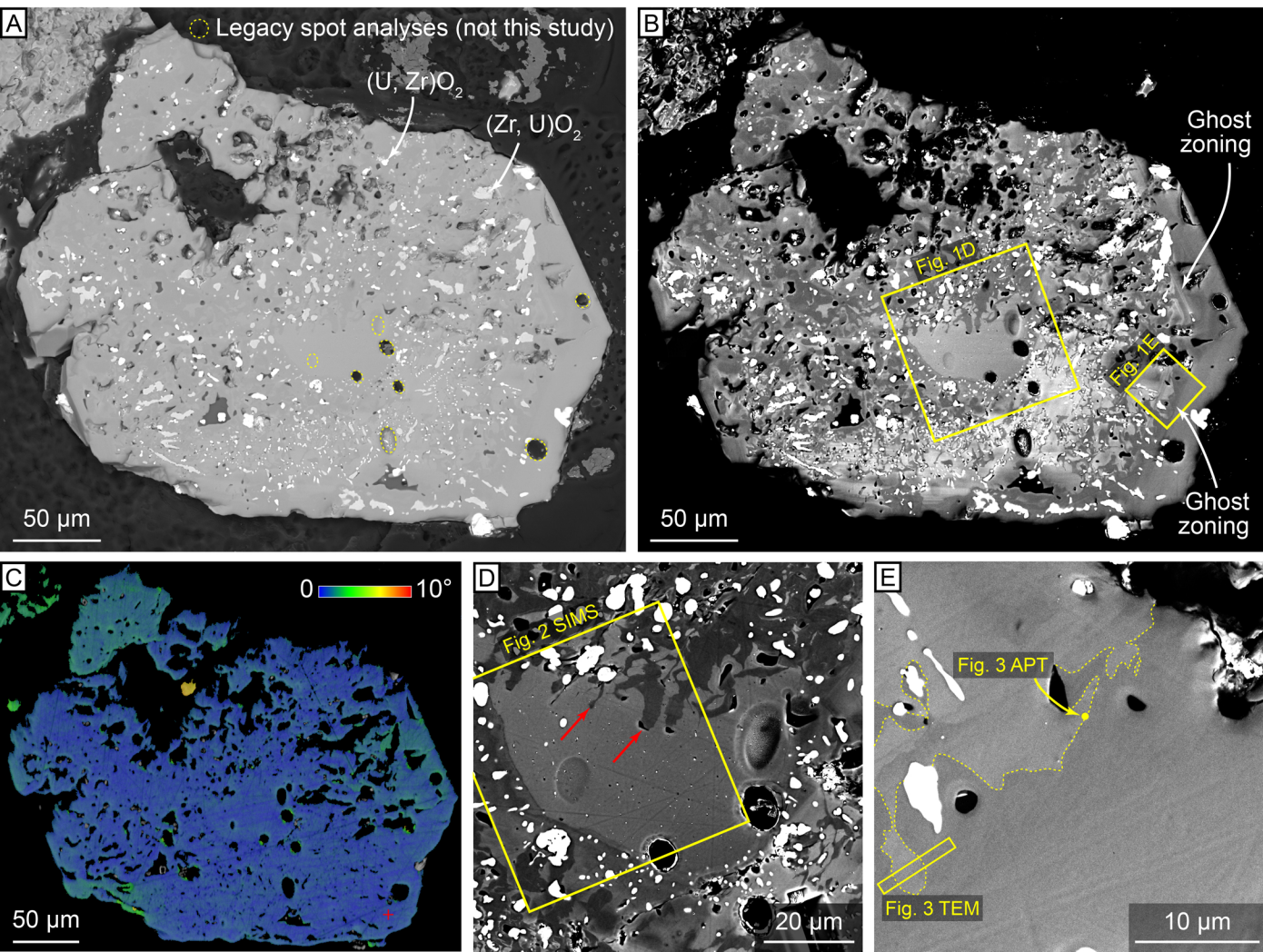


Figure 2

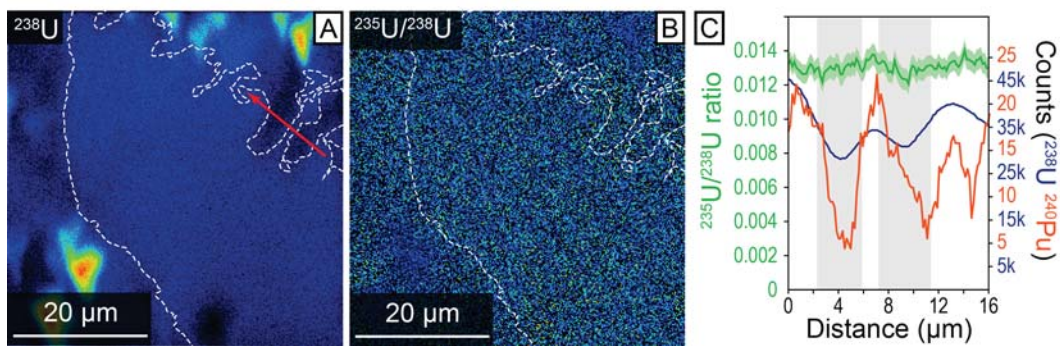


Figure 3

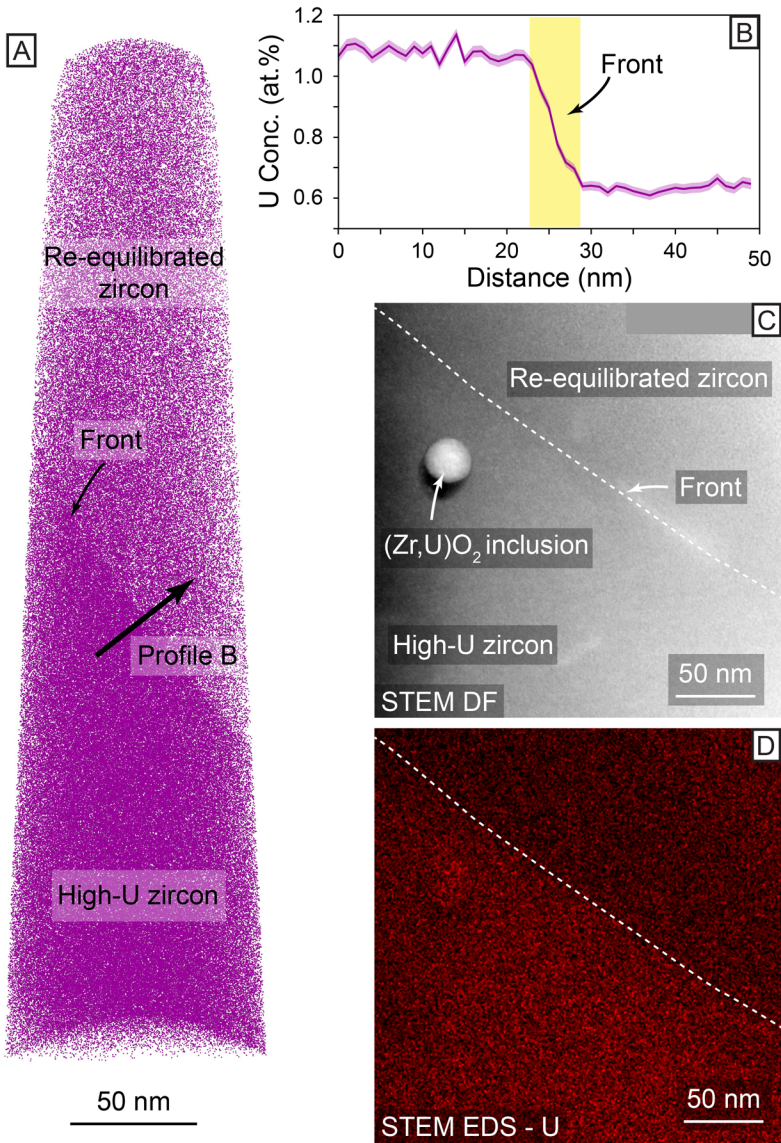


Figure 4

