

1 **Crystallization and impact history of a meteoritic sample of early lunar crust (NWA**  
2 **3163) refined by atom probe geochronology**

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14  
15 **Granulitic lunar meteorites offer rare insights into the timing and nature of igneous,**  
16 **metamorphic and impact processes in the lunar crust. Accurately dating the different**  
17 **events recorded by these materials is very challenging, however, due to low trace**  
18 **element abundances (e.g. Sm, Nd, Lu, Hf), micrometer-scale U-Th-bearing accessory**  
19 **minerals, and disturbed Ar-Ar systematics following a multi-stage history of shock and**  
20 **thermal metamorphism. Here we report on micro-baddeleyite grains in granulitic mafic**  
21 **breccia NWA 3163 for the first time and show that targeted microstructural analysis**  
22 **(electron backscatter diffraction) and nanoscale geochronology (atom probe**  
23 **tomography) can overcome these barriers to lunar chronology. A twinned (~90°/<401>)**  
24 **baddeleyite domain yields a <sup>232</sup>Th/<sup>208</sup>Pb age of 4328 ± 309 Ma, which overlaps with a**  
25 **robust secondary ion mass spectrometry (SIMS) <sup>207</sup>Pb/<sup>206</sup>Pb age of 4308 ± 18.6 Ma and**  
26 **is interpreted here as the crystallization age for an NWA 3163 protolith. A second**  
27 **microstructural domain, < 2µm in width, contains patchy overprinting baddeleyite and**  
28 **yields a Th-Pb age of 2175 ± 143 Ma, interpreted as dating the last substantial impact**  
29 **event to affect the sample. This finding demonstrates the potential of combining**  
30 **microstructural characterization with nanoscale geochronology when resolving complex**  
31 ***P-T-t* histories in planetary materials, here yielding the oldest measured crystallization**  
32 **age for components of lunar granulite NWA 3163 and placing further constraints on the**  
33 **formation and evolution of lunar crust.**

## 35 1. Introduction

36 Northwest Africa (NWA) 3163, along with paired stones NWA 4881 and NWA 4483,  
37 potentially represents the largest sample of granulitic lunar crust available for study (i.e.  
38 Hudgins et al., 2011). These stones appear to represent a region of the Moon that has not  
39 been directly sampled by either the Apollo or Luna missions, facilitating a more global  
40 appraisal of lunar crustal processes (Hudgins et al., 2011; McLeod et al. 2016). Generating  
41 accurate, precise and robust ages for specific events recorded within these samples is  
42 paramount to testing contrasting models for the formation, differentiation and bombardment  
43 history of the Moon, such as whether there was a global lunar magma ocean (Borg et al.,  
44 2011) and, later, a period of intense impact bombardment known as the lunar cataclysm at  
45 ~3.9 Ga (Cohen et al., 2000). Such efforts are further complicated in meteoritic samples by  
46 additional deformation induced during shock loading and ejection from the lunar surface (i.e.  
47 Joy and Arai, 2013), which can overprint mineralogical evidence of both crystallization and  
48 earlier, more severe impact events that cumulatively result in bombardment. More recently,  
49 dating of microstructurally characterised accessory phases, such as titanite (Papapavlou et al.,  
50 2018) and monazite (Erickson et al., 2017), have proven to be useful impact chronometers,  
51 though these phases are less widespread in planetary (lunar, martian, asteroidal) lithologies.  
52 Robust Zr-bearing phases, such as zircon ( $\text{ZrSiO}_4$ ) and baddeleyite ( $\text{ZrO}_2$ ), have proven to be  
53 ideal U-Th-Pb chronometers in such materials, often preserving a spread of ages between  
54 crystallization and bombardment despite extensive overprinting by younger deformation  
55 (Moser et al., 2013; Cavosie et al., 2015; Darling et al., 2016). Baddeleyite is particularly  
56 promising as a planetary chronometer given the wide-spread occurrence of the phase within  
57 the mafic rocks that dominate the Solar System (Herd et al., 2018) and the exclusion of  
58 common Pb during crystallization (Heaman and LeCheminant, 1993). However, discrete  
59 domains with varying U-Th-Pb ages may often be preserved on the micrometre to sub  
60 nanometre scale in highly shocked zircon and baddeleyite (Moser et al., 2011; Cavosie et al.,  
61 2015; White et al., 2017a). These can be unravelled by coupling techniques such as electron  
62 backscatter diffraction (EBSD; Cavosie et al. 2015; Darling et al. 2016; White et al. 2018),  
63 secondary ionisation mass spectrometry (SIMS; Moser et al., 2013) and atom probe  
64 tomography (APT; White et al., 2017a; White et al., 2017b) to generate structurally  
65 characterised ages. Here we analyse baddeleyite grains in a unique piece of the deep lunar  
66 crust (NWA 3163; Irving et al., 2006) to yield an accurate age for both crystallization and  
67 shock loading of the sample. Despite major efforts with the Sr and Ar isotopic systems  
68 (McLeod et al., 2016; Hudgins et al., 2011; Fernandes et al., 2009), very broad chronological

69 brackets have so far been interpreted for the evolution of NWA 3163. Our goal is to further  
70 refine this chronology with attention to the mineral crystallization (as opposed to mantle  
71 separation) age and timing of granularization in such challenging samples using minimally  
72 destructive techniques as a contribution to lunar and meteorite chronology.

73

## 74 **2. Material and Methods**

75 Lunar meteorite NWA 3163 is a breccia composed of centimeter-sized gabbroic and  
76 gabbro-anorthositic clasts within a finer grained matrix exhibiting a granulitic texture cross-  
77 cut by later shock veining (**Figure 1**). Chemically, the breccia plots as part of the ferroan  
78 anorthosite suite (FAS), suggesting its lithic components can be traced to an early lunar crust  
79 which formed directly from remelting and recrystallization of differentiated lunar magma  
80 ocean products (McLeod et al., 2016). The sample contains pervasive maskelynite (diaplectic  
81 glass of plagioclase composition) which, given the composition of the feldspar ( $An_{94}$ ), is  
82 suggestive of shock pressures in excess of 20 – 24 GPa (Fritz et al., 2011). Mantle separation  
83 of parental magma for the breccia components is placed at  $4340 \pm 57$  Ma based on a source  
84 model Sr  $T_{RD}$  age (McLeod et al. 2016). Uniformity of Sr and trace element composition  
85 among components suggests derivation from a single source of early (~4300 Ma) lunar crust  
86 of the FAS (McLeod et al. 2016). Ar-Ar geochronology yields ages of ~3350 Ma (McLeod et  
87 al. 2016) and ~1980 Ma (Hudgins et al. 2011), which are attributed to granularization of the  
88 sample and a younger shock event, respectively.

89

90 Target baddeleyite grains were located and imaged in three thin sections of NWA  
91 3163 using a combination of automated backscatter electron (BSE) and energy-dispersive X-  
92 ray spectroscopy (EDS) techniques using the Oxford Instruments INCA 'Feature' modules  
93 and Oxford X-Max 80 detector installed on electron microscopes at the Zircon and Accessory  
94 Phase Laboratory (ZAPLab) at the University of Western Ontario, Canada. Target grains were  
95 imaged using BSE and secondary electron (SE) techniques, and micro- to nano-scale  
96 structural analysis was conducted by electron backscatter diffraction (EBSD) using an Oxford  
97 Instruments Nordlys EBSD detector mounted on a Hitachi SU6600 field emission gun SEM  
98 (FEG-SEM; ZAPLab) following previously reported analytical conditions (i.e. Darling et al.,  
99 2016). Generated baddeleyite diffraction patterns were matched to inorganic crystal structure  
100 database (ICSD) card 15,983 using crystal lattice parameters of  $a = 5.21$ ,  $b = 5.26$ ,  $c = 5.37$ ,  
101 and  $\alpha = 90^\circ$ ,  $\beta = 80.5^\circ$ ,  $\gamma = 90^\circ$  (Smith & Newkirk 1965). Wild spike reduction was

102 completed on all EBSD datasets, although no other form of raw data correction was  
103 conducted.

104

105 Within a separate mount, secondary ion mass spectrometry (SIMS) analysis of U-Th-Pb  
106 systematics was conducted on three grains following previously reported procedure (Schmitt  
107 et al., 2010; Moser et al., 2013; Darling et al., 2016). Correlative EBSD work was not  
108 conducted on these grains prior to analysis.

109

110 Grain #12,112 was selected for detailed atom probe tomography (APT) analysis  
111 following EBSD characterisation. The grain was extracted using a Zeiss NVision 40 SEM  
112 hosted by the Canadian Centre for Electron Microscopy (CCEM) at McMaster University,  
113 Canada, using a focused Ga ion beam (FIB) operating at 30 kV and 13 nA. A 10 kV 80 pA  
114 beam was used for final sharpening to minimize any potential damage or Ga ion  
115 implantation. The lift out of the grain was subsampled to yield five microtip specimens for  
116 APT analysis. Microtips were analysed using a CAMECA local electrode atom probe  
117 (LEAP) 4000X HR instrument housed at CCEM, following analytical procedures outlined by  
118 previous baddeleyite APT studies (White et al., 2017a; White et al., 2017b), operating the  
119 355nm wavelength laser at 100 pJ and 125 kHz, with a targeted detection rate of 3%. Mass-  
120 to-charge peaks were background corrected using the IVAS software package using a local  
121 range assisted estimate of the background. Isotopic uncertainties are calculated by  
122 propagating counting statistics errors of the individual background corrected peaks through to  
123 the final isotopic ratio. Full details regarding APT instrument settings, data reduction and  
124 reconstruction can be found in the supplementary materials, reported following the  
125 recommendations of Blum et al. 2018.

126

### 127 **3. Results**

#### 128 **3.1 Correlative imaging, microscopy and chronology of baddeleyite**

129 SEM scans of three thin sections of NWA 3163 reveal a total of nine baddeleyite  
130 grains. These grains are generally  $< 10\mu\text{m}$  in the longest dimension, occurring primarily in  
131 association with ilmenite (~90%) and rarely with flow-textured feldspathic melt veins. Most  
132 grains appear homogenous in backscatter electron imaging, with no visible fractures or  
133 surface defects of note, though one of the examined baddeleyite contains cross-cutting, open  
134 fractures which we ascribe to the ejection event (**Figure 2**). EBSD analysis of four grains

135 reveals a range of complex microstructures, including polysynthetic twinning, patchy  
136 baddeleyite domains with small (sub-micrometre) granules, and domains of poorly diffracting  
137 ZrO<sub>2</sub> (**Figure 3**). Two grains completely enclosed in highly fractured ilmenite contain larger  
138 subdomains of crystal plastically deformed (< 10°) baddeleyite of a single orientation  
139 (**Figure 3b,d**), though this deformation is largely controlled by fracturing and associated  
140 deformation within the crystals. Within directional pole figures for baddeleyite, clusters of  
141 orthogonally related (90°) crystallographic orientations can be observed, though these do not  
142 demonstrate the localised ~18° crosses associated with reversion from high pressure and  
143 temperature ZrO<sub>2</sub> phases (Timms et al., 2017; White et al., 2018).

144

145 SIMS analysis was attempted on three grains in a separate mount, though only a  
146 single analysis yielded a high amount of radiogenic Pb (98%). The two analyses with low  
147 percentages of radiogenic Pb (40 and 19% respectively) are ascribed to difficulty in targeting  
148 these single micron scale grains during SIMS analysis. The successfully targeted baddeleyite  
149 crystal yields a <sup>207</sup>Pb/<sup>206</sup>Pb age of 4308 ± 37 Ma (2σ) and has U-Pb systematics that are  
150 concordant, albeit with relatively large uncertainties on U-Pb ratios. All SIMS data are  
151 reported in the supplementary materials.

152

153 During extraction of the atom probe microtips, the target baddeleyite grain (#12,112)  
154 was imaged prior to lift out. This reveals that large fractures in the surrounding ilmenite  
155 phase form a complex structural network surrounding the baddeleyite, though these features  
156 terminate at the baddeleyite grain boundary (**Figure 4a,b**). In addition, the baddeleyite itself  
157 contains minor nanoscale fractures, though appears relatively undeformed compared to the  
158 surrounding mineral assemblage. EBSD analysis of the grain reveals similar microstructural  
159 features to those observed in all other grains, principally subdomains of degraded crystallinity  
160 (**Figure 4c**) and complex crystalline subdomains. The surrounding ilmenite (**Figure 4d**) is  
161 highly crystalline, preserving undeformed lamellae twins which record 180°/<  $\bar{2}110$   
162 relationships. The baddeleyite grain contains two distinct subdomains, with polysynthetic  
163 twins yielding ~90°/<401> orientation relationships, and a patchy baddeleyite domain which  
164 is consistently misorientated ~120°/< relative to the primary orientations (**Figure 4e**).  
165 In isolation, only the twinned domain hosts orthogonal relationships, while the patchy  
166 domains (purple data points in **Figure 4f**) contain no obvious microstructural complexity.

167

### 168 **3.2 Nanostructural geochronology by atom probe tomography (APT)**

169 Of the five prepared microtip specimens, two produced reliable (< 20 ppm/ns  
170 background) APT datasets in excess of 38.6 (#01665) and 112 (#01667) million collected  
171 ions. These tips were extracted from microstructurally distinct domains of the target  
172 baddeleyite grain (grey and white stars in **Figure 4e**), with microtip #01665 representing the  
173 patchy domain and microtip #01667 sampling the polysynthetically twinned central domain.  
174 The tips are chemically similar, yielding ~99 atomic percent (at%) Zr and O cations and  
175 molecular species, predominately evaporated as ZrO and ZrO<sub>2</sub>. Trace element impurities are  
176 quantified in both microtips, with the most prominent contaminants (Hf, Ti, Nb, P) being  
177 measured to within  $\pm \sim 1\%$   $2\sigma$  certainty due to the large amount of ionic counts. Other species  
178 (Mg, Al, La, Ce, Mn) yield minimal counts and fall below the detection threshold of APT,  
179 particularly in the smaller dataset (**Supplementary Materials**). Fe/Si ratios are comparable  
180 in both tips (~8). All atoms and compounds are homogeneously distributed throughout both  
181 tips, suggesting that no nanoscale structures (beyond those revealed by EBSD) have been  
182 subsampled by the APT lift out.

183

184 Th and Pb can be identified in the mass-to-charge spectrum for each dataset, with  
185 <sup>232</sup>Th<sup>++</sup> forming a discrete peak at 116 Da and <sup>208</sup>Pb<sup>++</sup> a peak at 104 Da (**Figure 5**). Peaks  
186 from singly charged or compound ions (e.g. ThO or ThO<sub>2</sub>) could not be observed in either  
187 mass-to-charge spectrum. Th and Pb are distributed homogeneously within both microtips,  
188 further supporting the lack of internal structure inferred from trace element distribution.  
189 Calculating the <sup>208</sup>Pb/<sup>232</sup>Th ratio for microtip #01665 (subsamped from the patchy domain)  
190 yields a Pb-Th age of  $2175 \pm 143$  (1 $\sigma$ ) Ma, whereas microtip #01667 (sampled from the  
191 polysynthetically twinned domain) yields a Pb-Th age of  $4328 \pm 309$  (1 $\sigma$ ) Ma. Although  
192 <sup>206</sup>Pb and <sup>207</sup>Pb could not be confidently measured above background in younger microtip  
193 #01665, a calculated <sup>207</sup>Pb/<sup>206</sup>Pb age of  $4559 \pm 396$  (1 $\sigma$ ) Ma in older microtip #01667 falls  
194 within uncertainty of the measured Pb-Th age. <sup>238</sup>U could not be confidently identified or  
195 quantified from the spectra in either dataset.

196

## 197 **4. Discussion**

### 198 **4.1 Nanostructural characteristics of lunar baddeleyite**

199 Baddeleyite in lunar meteorite NWA3163 exhibit a subset of the nano-scale features  
200 observed through EBSD analyses of baddeleyite from other shock metamorphic settings

201 (White et al., 2018) whereas the APT results differ (White, et al., 2017a). EBSD analysis  
202 reveals orthogonally-related crystallographic domains that result in an apparent overprinting  
203 of a polysynthetically twinned domain. Orthogonally related crosses defined by orientation  
204 data have been used to indicate partial to complete reversion from a high symmetry ZrO<sub>2</sub>  
205 polymorph (Cayron et al., 2010; Timms et al., 2017; White et al., 2018), though these  
206 relationships are incomplete in two of the grains (e.g. **Figure 3**) and absent in the grain  
207 chosen for APT analysis (**Figure 4**). Regarding APT results, phase transitions within  
208 baddeleyite grains at the Sudbury impact site (White et al., 2018) have previously been  
209 associated with the genesis of ~15 nm Fe clusters (White et al., 2017a; White et al., 2017b),  
210 whereby the introduction of nanoscale defects during phase transition (to either a high  
211 pressure or temperature polymorph) allowed cation mobility across nanometre-scale  
212 distances. The absence of clusters within NWA3163 baddeleyite suggests that either; (1) such  
213 nanoscale defects were not generated during phase transition, (2) that incompatible elements  
214 were forced from the lattice entirely during the shock and annealing process, preventing the  
215 formation of clusters, or (3) that the grain did not undergo transition to and reversion from a  
216 high symmetry polymorph. The decoration of subgrain boundaries by incompatible trace  
217 elements seen at the Sudbury site (White et al. 2017a) are also absent in our lunar sample.  
218 Given the absence of distinctive orthogonally related crosses in EBSD pole figures, we  
219 suggest that the core, polysynthetically twinned domain of grain #12,112 has not undergone  
220 any transition to the high symmetry tetragonal, orthorhombic or cubic ZrO<sub>2</sub> structures, and  
221 given the distinct orientation and texture of the partial rim around the core domain (Figure 4)  
222 we suggest that this microstructural domain represents recrystallization during a thermal  
223 event. Combined with the absence of phase transition related features in APT analysis, we  
224 suggest that the grain has not undergone transformation to a high symmetry ZrO<sub>2</sub> polymorph.

225

## 226 **4.2 Accurate age resolution of lunar evolution**

### 227 ***4.2.1 Targeting nanometre scale reset Th-Pb reservoirs to date impact events***

228 The youngest Th-Pb APT age reported here ( $2175 \pm 143$  Ma) derives from the rim  
229 domain of grain #12,112, and overlaps with Ar-Ar estimates of late metamorphism between  
230 2.0 and 2.5 Ga (Hudgins et al., 2011). The measured age also correlates with a purported high  
231 flux in lunar impacts between 1.8 and 2.2 Ga (Fernandes et al., 2013). This overlap allows the  
232 interpretation that the patchy baddeleyite domain overprints a primary, polysynthetically  
233 twinned core, accurately recording the timing of a major shock metamorphism event at ~2.1

234 Ga. It is expected that this younger age could not be spatially isolated using SIMS analysis as  
235 a result of the sub-micrometre size of the age reservoirs, yielding homogenized data variably  
236 influenced by lead loss and a common Pb component inherited from surrounding phases. A  
237 similar correlation between the deformational state of the grain and the extent of impact  
238 induced Pb loss has also been observed within SIMS analysis of martian shergottite NWA  
239 5298 (Moser et al., 2013; Darling et al., 2016), suggesting that baddeleyite may record  
240 accurate impact ages within nanoscale domains in a wide variety of planetary materials.  
241 However, nanoscale targeting of shock reset domains, such as the overprinting baddeleyite  
242 rim revealed here by EBSD, using APT is required to confidently generate the youngest  
243 possible impact age. This approach could be critical for accurately verifying an intense period  
244 of lunar bombardment at ~3.9 Ga (Kring and Cohen, 2002; Cohen et al., 2000), evidence of  
245 which is notably absent in the baddeleyite record of NWA 3163.

246

#### 247 ***4.2.2 Extraction of ancient U-Th-Pb crystallization ages from complex lunar materials***

248 Given the occurrence of baddeleyite as a late-stage accessory phase in a large suite of  
249 mafic achondritic meteorites (Herd et al. 2017), it is likely that the analysed baddeleyite  
250 population crystallized directly from the final Zr-enriched magma associated with an early  
251 mafic melt such as a global lunar magma ocean (i.e. Elrado et al. 2011) or a re-working of it  
252 due to remelting and crystallization (McLeod et al. 2016). This provides a new approach to  
253 dating the more primitive forms of lunar magmatism recorded by NWA 3163 despite  
254 extensive granularization of the sample. Although acquired from an uncharacterised  
255 baddeleyite grain, the most robust Pb-Pb SIMS age ( $4308 \pm 19$  Ma; 98% radiogenic Pb)  
256 overlaps with the Th-Pb APT age generated from the polysynthetically twinned primary  
257 domain of grain #12,112 ( $4328 \pm 309$  Ma). Given the correlation of these ages with the  
258 calculated Rb-Sr model age for the source of NWA 3163 ( $4340 \pm 57$  Ma; McLeod et al.,  
259 2016) we suggest that the U-Th-Pb systematics of certain nanometre-scale domains (or  
260 rarely, whole grains) of baddeleyite record a robust crystallization age for the primary mafic  
261 protolith (**Figure 6**). While age analysis of these domains using individual microtip specimen  
262 produces accurate ages, these dates are largely imprecise ( $\pm 13.1$  to  $14.3\%$   $2\sigma$ ) due to the  
263 inherent counting statistical uncertainties associated with small ( $< 1,000$  ions) peaks in the  
264 APT mass-to-charge spectra. As such, generating a reliable age from these domains will  
265 require either supplementary, higher precision chronology (i.e. SIMS) or weighted average  
266 measurements of multiple microtip specimens (e.g. White et al., 2017b) until such a time as



267 there are improvements to the sensitivity of APT (Saxey et al., 2018). Assuming an initial  
268 formation age for the Moon of 4.51 Ga (Barboni et al., 2017), our new U-Th-Pb baddeleyite  
269 age (correlated by both APT and SIMS analysis) suggests primary mafic magmatism was still  
270 actively ongoing ~210 million years after lunar formation. Given that the ages of ferroan  
271 anorthosite suite rocks have previously been incorporated into studies which evidence the  
272 presence of a global lunar magma ocean until ~4290 Ma (Borg et al., 1999), it appears that  
273 the crystallization age attained here through both APT and SIMS analysis of NWA 3163  
274 baddeleyite provides further support for either a prolonged lunar magma ocean or, more  
275 likely based on previous studies (e.g. McLeod et al., 2016), a major remixing event at c. 4.3  
276 Ga. This chronological evidence is otherwise opaque in such highly metamorphosed samples.  
277 Such efforts will augment ongoing work to date these earliest lunar processes using zircon  
278 geochronology (Nemchin et al., 2009; Crow et al., 2017), and aid in refining the timeline for  
279 the formation and evolution of the Moon.

280

## 281 **5. Conclusions**

282 Coupled EBSD, SIMS and APT analysis of micro-baddeleyite grains has allowed for  
283 targeted U-Th-Pb dating of nanoscale crystallization (~4.33 Ga) and impact (~2.18 Ga) age  
284 domains in granulitic lunar breccia NWA 3163. Nanostructural analysis of the baddeleyite  
285 population reveals an abundance of complex, sub-micrometre features which are  
286 unresolvable at the length scales of SIMS analysis alone. Targeted extraction of these  
287 domains using FIB-SEM techniques allows for atom probe analysis of isolated subdomains,  
288 allowing high accuracy, low precision resolution of chronological end members. This  
289 facilitates the improved interpretation of more precise U-Pb SIMS data even for structurally  
290 uncharacterised baddeleyite. For NWA 3163, this includes placing an empirical  
291 crystallization age on the mafic protolith of the sample which, until now, has not been  
292 directly measured by radiogenic isotope systematics. This approach to nanogeochronology  
293 holds great promise in extracting accurate ages for the formation of many lunar, asteroidal  
294 and martian lithologies otherwise overprinted by metamorphic and bombardment events.  
295 Notably, these younger events can also be accurately (but imprecisely) dated using current  
296 APT technology.

297

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310

### 311 **References**

- 312 Barboni, M., Boehnke, P., Keller, B., Kohl, I.E., Schoene, B., Young, E.D., and McKeegan,  
313 K.D., 2017, Early formation of the Moon 4.51 billion years ago: *Science Advances*, v. 3,  
314 p. e1602365.
- 315 Blum, T.B., Darling, J.R., Kelly, T.F., Larson, D.J., Moser, D.E., Perez-Huerta, A., Prosa,  
316 T.J., Reddy, S.M., Reinhard, D.A., Saxey, D.W., Ulfig, R.M., and Valley, J.W., 2018,  
317 Best Practises for Reporting Atom Probe Analysis of Geological Materials, *in* Moser,  
318 D.E., Corfu, F., Darling, J.R., Reddy, S.M., and Tait, K. eds., *Microstructural*  
319 *Geochronology: Planetary Records Down to Atom Scale*, Wiley & Sons, p. 369–373.
- 320 Borg, L.E., Connelly, J.N., Boyet, M., and Carlson, R.W., 2011, Chronological evidence that  
321 the Moon is either young or did not have a global magma ocean.: *Nature*, v. 477, p. 70–  
322 72, doi: 10.1038/nature10328.
- 323 Borg, L., Norman, M., Nyquist, L., Bogard, D., Snyder, G., Taylor, L., and Lindstrom, M.,  
324 1999, Isotopic studies of ferroan anorthosite 62236: A young lunar crustal rock from a  
325 light rare-earth-element-depleted source: *Geochimica et Cosmochimica Acta*, v. 63, p.  
326 2679–2691.
- 327 Cavosie, A.J., Erickson, T.M., Timms, N.E., Reddy, S.M., Talavera, C., Montalvo, S.D.,  
328 Pincus, M.R., Gibbon, R.J., and Moser, D., 2015, A terrestrial perspective on using ex  
329 situ shocked zircons to date lunar impacts: *Geology*, v. 43, p. 999–1002, doi:  
330 10.1130/G37059.1.
- 331 Cayron, C., Douillard, T., Sibil, A., Fantozzi, G., and Sao-Jao, S., 2010, Reconstruction of  
332 the cubic and tetragonal oarent grains from electron backscatter diffraction maps of  
333 monoclinic zirconia: *Journal of the American Ceramic Society*, v. 93, p. 2541–2544,  
334 doi: 10.1111/j.1551-2916.2010.03894.x.

335 Cohen, B.A., Swindle, T.D., and Kring, D.A., 2000, Support for the lunar cataclysm  
336 hypothesis from lunar meteorite impact melt ages: *Science*, v. 290, p. 1754–1756, doi:  
337 10.1126/science.290.5497.1754.

338 Crow, C.A., McKeegan, K.D., and Moser, D.E., 2017, Coordinated U-Pb geochronology,  
339 trace element, Ti-in-zircon thermometry and microstructural analysis of Apollo zircons:  
340 *Geochimica et Cosmochimica Acta*, v. 202, p. 264–284.

341 Darling, J.R., Moser, D.E., Barker, I.R., Tait, K.T., Chamberlain, K.R., Schmitt, A.K., and  
342 Hyde, B.C., 2016, Variable microstructural response of baddeleyite to shock  
343 metamorphism in young basaltic shergottite NWA 5298 and improved U–Pb dating of  
344 Solar System events: *Earth and Planetary Science Letters*, v. 444, p. 1–12, doi:  
345 10.1016/j.epsl.2016.03.032.

346 Elrado, S.M., Draper, D.S., and Shearer Jr, C.K., 2011, Lunar Magma Ocean crystallization  
347 revisited: Bulk composition, early cumulate mineralogy, and the source regions of the  
348 highlands Mg-suite: *Geochimica et Cosmochimica Acta*, v. 75, p. 3024–3045.

349 Erickson, T.M., Timms, N.E., Kirkland, C.L., Tohver, E., Cavosie, A.J., Pearce, M.A., and  
350 Reddy, S.M., 2017, Shocked monazite chronometry: integrating microstructural and in  
351 situ isotopic age data for determining precise impact ages: *Contributions to Mineralogy  
352 and Petrology*, v. 172, p. 1–19, doi: 10.1007/s00410-017-1328-2.

353 Fernandes, V.A.S.M., Fritz, J., Weiss, B.P., Garrick-Bethell, I., and Shuster, D.L., 2013, The  
354 bombardment history of the Moon as recorded by  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  chronology: *Meteoritics &  
355 Planetary Science*, v. 48, p. 241–269.

356 Fernandes, V.A., Irving, A.J., Kuehner, S.M., Gellissen, M., Korotev, R.L., and Bandfield,  
357 J.L., 2009, Petrology, Bulk Composition, Ar-Ar Age and IR Emission Spectrum of  
358 Lunar Granulite Northwest Africa 4881, *in* 40th Lunar and Planetary Science  
359 Conference, The Woodlands, Texas,.

360 Fritz, J., Wunnemann, K., Greshake, A., Fernandes, V.A.S.M., Boettger, U., and  
361 Hornemann, U., 2011, Shock pressure calibration for lunar plagioclase, *in* 42nd Lunar  
362 and Planetary Science Conference, p. 1196.

363 Heaman, L.M., and LeCheminant, A.N., 1993, Paragenesis and U-Pb systematics of  
364 baddeleyite (  $\text{ZrO}_2$  ): *Chemical Geology*, v. 110, p. 95–126.

365 Herd, C.D.K., Moser, D.E., Tait, K., Darling, J.R., Shaulis, B.J., and McCoy, T.J., 2018,  
366 Crystallization of Baddeleyite in Basaltic Rocks from Mars, and Comparisons with the  
367 Earth, Moon and Vesta, *in* Moser, D.E., Corfu, F., Darling, J.R., Reddy, S.M., and Tait,  
368 K. eds., *Microstructural Geochronology: Planetary Records Down to Atom Scale*,

369 American Geophysical Union, p. 137–165.

370 Hudgins, J., Kelley, S.P., Korotev, R.L., and Spray, J.G., 2011, Mineralogy, geochemistry,  
371 and  $^{40}\text{Ar}$ - $^{39}\text{Ar}$  geochronology of lunar granulitic breccia Northwest Africa 3163 and  
372 paired stones: Comparisons with Apollo samples: *Geochimica et Cosmochimica Acta*, v.  
373 75, p. 2865–2881.

374 Irving, A.J., Kuehner, S.M., Korotev, R.L., Rumble III, D., and Hupe, G.M., 2006, Mafic  
375 granulitic impactites NWA 3163: A unique meteorite from the deep lunar crust, *in* 37th  
376 Lunar and Planetary Science Conference, Houston, Texas,.

377 Joy, K.H., and Arai, T., 2013, Lunar meteorites: new insights into the geological history of  
378 the Moon: *Astronomy and Geophysics*, v. 54, p. 4.28-4.32.

379 Kring, D.A., and Cohen, B., 2002, Cataclysmic bombardment throughout the inner solar  
380 system 3.9–4.0 Ga: *Journal of Geophysical Research*, v. 107, p. 5009, doi:  
381 10.1029/2001JE001529.

382 McLeod, C.L., Brandon, A.D., Fernandes, V.A., Peslier, A.H., Fritz, J., Lapen, T., Shafer,  
383 J.T., Butcher, A.R., and Irving, A.J., 2016, Constraints on formation and evolution of the  
384 lunar crust from feldspathic granulitic breccias NWA 3163 and 4881: *Geochimica et*  
385 *Cosmochimica Acta*, v. 187, p. 350–374.

386 Moser, D.E., Chamberlain, K.R., Tait, K.T., Schmitt, A. K., Darling, J.R., Barker, I.R., and  
387 Hyde, B.C., 2013, Solving the Martian meteorite age conundrum using micro-  
388 baddeleyite and launch-generated zircon.: *Nature*, v. 499, p. 454–7, doi:  
389 10.1038/nature12341.

390 Moser, D.E., Cupelli, C.L., Barker, I.R., Flowers, R.M., Bowman, J.R., Wooden, J., and Hart,  
391 J.R., 2011, New zircon shock phenomena and their use for dating and reconstruction of  
392 large impact structures revealed by electron nanobeam (EBSD, CL, EDS) and isotopic  
393 U–Pb and (U–Th)/He analysis of the Vredefort dome: *Canadian Journal of Earth*  
394 *Sciences*, v. 48, p. 117–139, doi: 10.1139/E11-011.

395 Nemchin, A., Timms, N., Pidgeon, R., Geisler, T., Reddy, S., and Meyer, C., 2009, Timing of  
396 crystallization of the lunar magma ocean constrained by the oldest zircon: *Nature*  
397 *Geoscience*, v. 2, p. 133–136.

398 Papapavlou, K., Darling, J.R., Moser, D.E., Barker, I.R., White, L.F., Lightfoot, P.C., Storey,  
399 C.D., and Dunlop, J., 2018, U–Pb isotopic dating of titanite microstructures: potential  
400 implications for the chronology and identification of large impact structures:  
401 *Contributions to Mineralogy and Petrology*, v. 173, p. 82, doi: 10.1007/s00410-018-  
402 1511-0.

403 Saxey, D.W., Moser, D.E., Piazzolo, S., Reddy, S.M., and Valley, J.W., 2018, Atomic worlds:  
404 Current state and future of atom probe tomography in geoscience: *Scripta Materialia*, v.  
405 148, p. 115–121.

406 Schmitt, A.K., Chamberlain, K.R., Swapp, S.M., and Harrison, T.M., 2010, In situ U-Pb  
407 dating of micro-baddeleyite by secondary ion mass spectrometry: *Chemical Geology*, v.  
408 269, p. 386–395, doi: 10.1016/j.chemgeo.2009.10.013.

409 Smith, D.K., and Newkirk, W., 1965, The crystal structure of baddeleyite (monoclinic ZrO<sub>2</sub>)  
410 and its relation to the polymorphism of ZrO<sub>2</sub>: *Acta Crystallographica*, v. 18, p. 983–991,  
411 doi: 10.1107/S0365110X65002402.

412 Timms, N.E., Erickson, T.M., Zanetti, M.R., Pearce, M.A., Cayron, C., Cavosie, A.J., Reddy,  
413 S.M., Wittmann, A., and Carpenter, P.K., 2017, Cubic zirconia in >2370 °C impact melt  
414 records Earth's hottest crust: *Earth and Planetary Science Letters*, v. 477, p. 52–58, doi:  
415 10.1016/j.epsl.2017.08.012.

416 White, L.F., Darling, J.R., Moser, D.E., Cayron, C., Barker, I., Dunlop, J., and Tait, K.T.,  
417 2018, Baddeleyite as a widespread and sensitive indicator of meteorite bombardment in  
418 planetary crusts: *Geology*, v. 46, p. 719–722, doi: 10.1130/G45008.1.

419 White, L.F., Darling, J.R., Moser, D.E., Reinhard, D.A., Dunlop, J., Larson, D.J., Lawrence,  
420 D., and Martin, I., 2017, Complex nanostructures in shocked, annealed and  
421 metamorphosed baddeleyite defined by atom probe tomography, *in* Moser, D., Corfu, F.,  
422 Reddy, S., Darling, J., and Tait, K. eds., *Microstructural Geochronology: Planetary*  
423 *Records Down to Atom Scale*, Hoboken, NJ, John Wiley & Sons, Inc.

424 White, L.F., Darling, J.R., Moser, D.E., Reinhard, D.A., Prosa, T.J., Bullen, D., Olson, D.,  
425 Larson, D.J., Lawrence, D., and Martin, I., 2017, Atomic scale age resolution of  
426 planetary events: *Nature Communications*, doi: 10.1038/ncomms15597.

427

## 428 **Figure Captions**

429 **Figure 1:** Hand sample photograph of NWA 3163. The highly brecciated nature of the  
430 sample is apparent at this scale (~15cm long), with large fractured anorthositic clasts  
431 occurring in a fine-grained matrix. The complex nature of this meteorite makes the  
432 generation and interpretation of robust age data a challenge (Photo credit: Brian Boyle,  
433 ROM).

434

435 **Figure 2:** Backscatter electron (BSE) imaging of baddeleyite (Bdl) grains in NWA 3163.  
436 Grains are commonly in association with ilmenite (Ilm), though a single baddeleyite occurs

437 in flow textured plagioclase (#2294). The sample is highly brecciated, consisting of  
438 maskelynite (diaplectic glass of plagioclase composition) and pyroxene clasts within a fine-  
439 grained matrix.

440

441 **Figure 3:** Backscatter electron (BSE) and electron backscatter diffraction (EBSD) data for  
442 baddeleyite grains #5135 (**A, B**), #10350 (**C, D**) and #2294 (**E, F**). For all grains, inverse pole  
443 figure (IPF) colouring relative to the z-axis correlates with coloured pixels in presented  
444  $\langle 001 \rangle$  pole figure diagrams. All datasets contain tight groups of orthogonally related  
445 orientations, while a small amount of crystal plastic deformation ( $< 10^\circ$ ) can be seen in larger  
446 baddeleyite domains (i.e. red data in grain #5135, pink data in grain #10350).

447

448 **Figure 4:** Backscatter electron (BSE) images show the mineralogical setting of target  
449 baddeleyite (bdl) grain #12,112, which is comparable to all analysed grains, the euhedral  
450 morphology of the grain, and the relationship with the associated ilmenite (Ilm) grain (**A**).  
451 During FIB extraction of the grain for atom probe analysis (following cross sectional line C-  
452 C'), a perpendicular BSE image of the grain was captured, allowing better visualisation of the  
453 baddeleyite – ilmenite grain boundary in 3D (**B**). Band contrast imaging (**C**) reveals the  
454 highly variable crystallinity of the grain, with regions of poorly diffracting  $ZrO_2$  occurring as  
455 discrete bands and domains throughout the grain, parallel to twin and grain boundaries. Phase  
456 mapping of both ilmenite and baddeleyite confirms the association of the two phases (**D**).  
457 Two discrete microstructural domains in inverse pole figure (IPF, z-axis) colouring of the  
458 baddeleyite dataset (**E**), comprised of a preserved core region with polysynthetic twinning,  
459 and an overprinting rim. The grey star represents the location of microtip specimen #01665  
460 within the rim, while the white star highlights tip #01667 within the twinned core. Ilmenite  
461 retains undeformed polysynthetic twins. Indexed baddeleyite yields clusters of orthogonally  
462 related crystallographic orientations in all pole figures (i.e.  $\langle 001 \rangle$ , **F**). EBSD data was  
463 collected at 75nm step size.

464

465 **Figure 5:** Full mass-to-charge spectra and mass-to-charge peaks for  $^{232}Th^{++}$  (116 Da) and  
466  $^{208}Pb^{++}$  (104 Da) as isolated by atom probe tomography in microtip specimen #01665. All  
467 cation species, including Th and Pb, are predominately homogenously distributed throughout  
468 both analysed microtips; #01665 (baddeleyite rim, grey star) and #01667 (baddeleyite core,  
469 white star). Of note, the decoupling of Th and Pb observed in tip #1665 (grey star) does not

470 appear to affect the measured Th/Pb age, with the exclusion of the domain yielding an age  
471 within uncertainty of the whole tip age (2350 Ma).

472

473 **Figure 6:** SIMS  $^{207}\text{Pb}/^{206}\text{Pb}$  and APT  $^{208}\text{Pb}/^{232}\text{Th}$  ages for NWA 3163. Error bars represent  
474  $1\sigma$  uncertainties. These results reveal two discrete U-Th-Pb age reservoirs in baddeleyite,  
475 which can be correlated with the crystallization age of the rock ( $\sim 4.3$  Ga, as defined by  
476 published Rb-Sr age models (McLeod et al., 2016)) and the last known impact event to affect  
477 the sample ( $\sim 1.95$  Ga, defined by Ar-Ar dating (McLeod et al., 2016)). SIMS analysis further  
478 supports a  $4308 \pm 38$  Ma crystallization age, yielding a concordant U-Pb age (2 s.e.  
479 uncertainty) from an uncharacterised grain. No evidence of a  $\sim 3.4$  Ga granularization event,  
480 as determined by published Ar-Ar data (Hudgins et al., 2011; McLeod et al., 2016) was found  
481 in the chronological record of baddeleyite. By correlating with EBSD analysis of the grain  
482 (Figure 4) we show that the crystallographic domain preserving igneous polysynthetic  
483 twinning retains a  $\sim 4.3$  Ga Th-Pb age, while the metamorphic rim records a younger  $\sim 2.1$  Ga  
484 age. Isolated dating of these nanometre scale domains can only be achieved using APT.

Figure 1





Figure 2

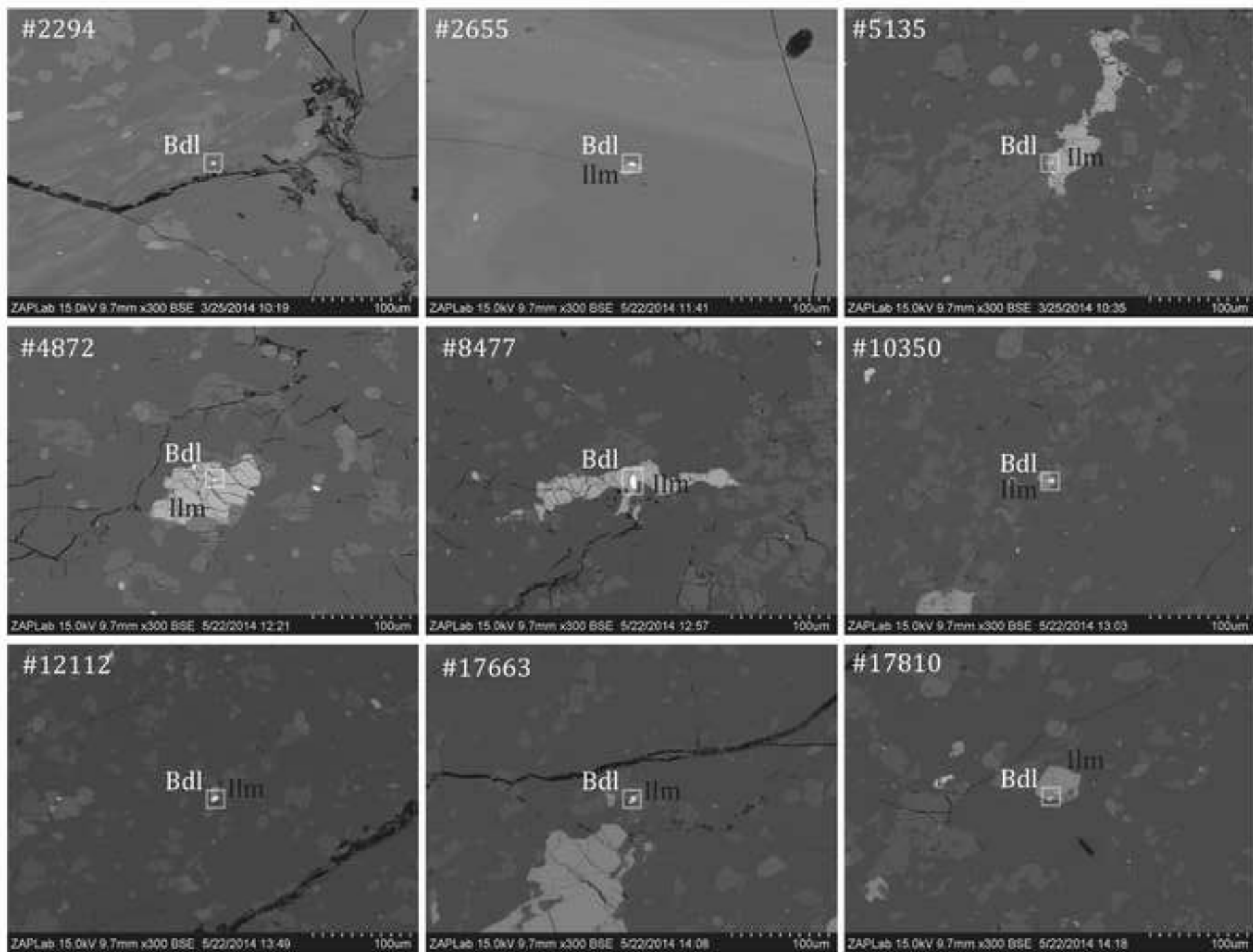


Figure 3

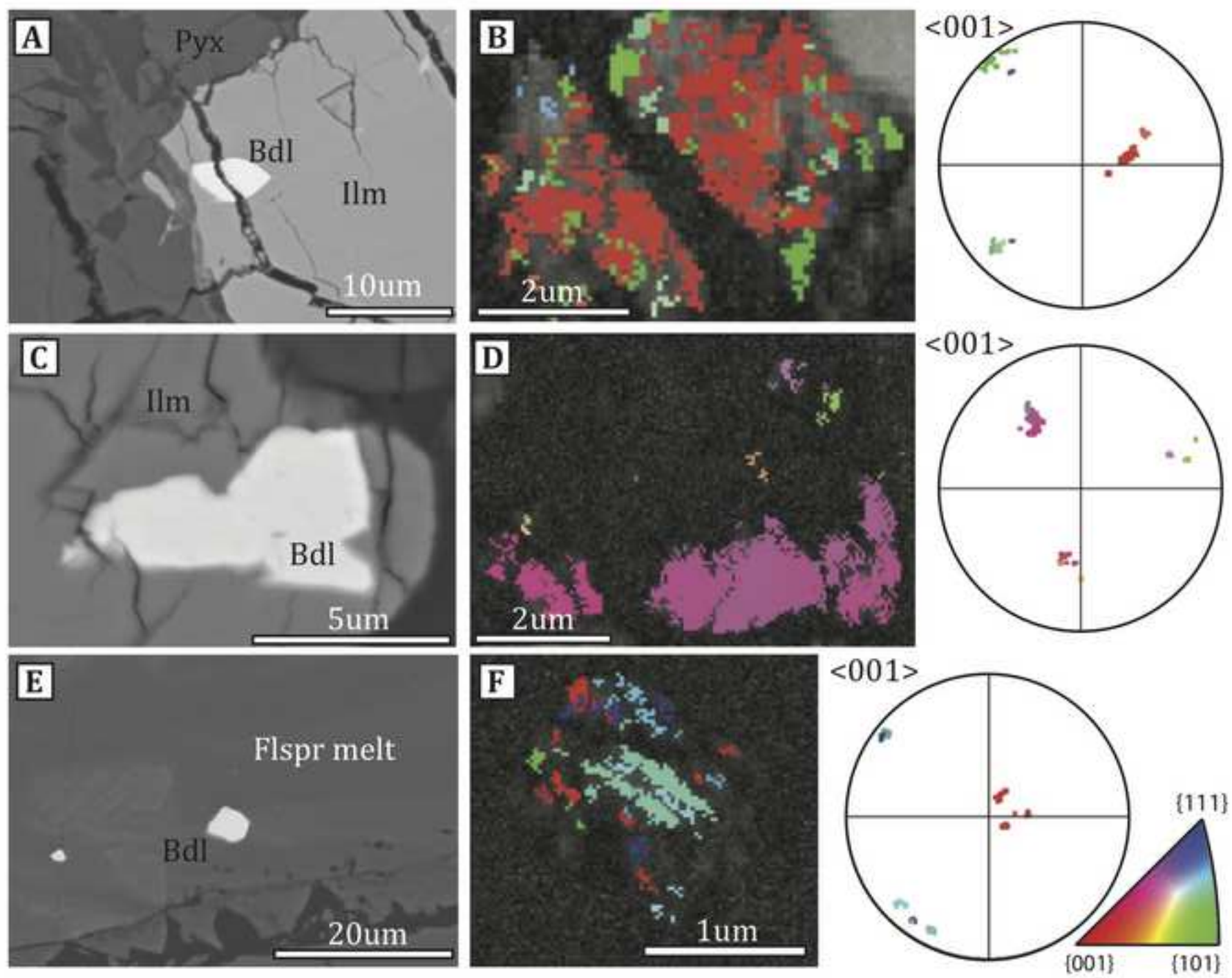


Figure 4

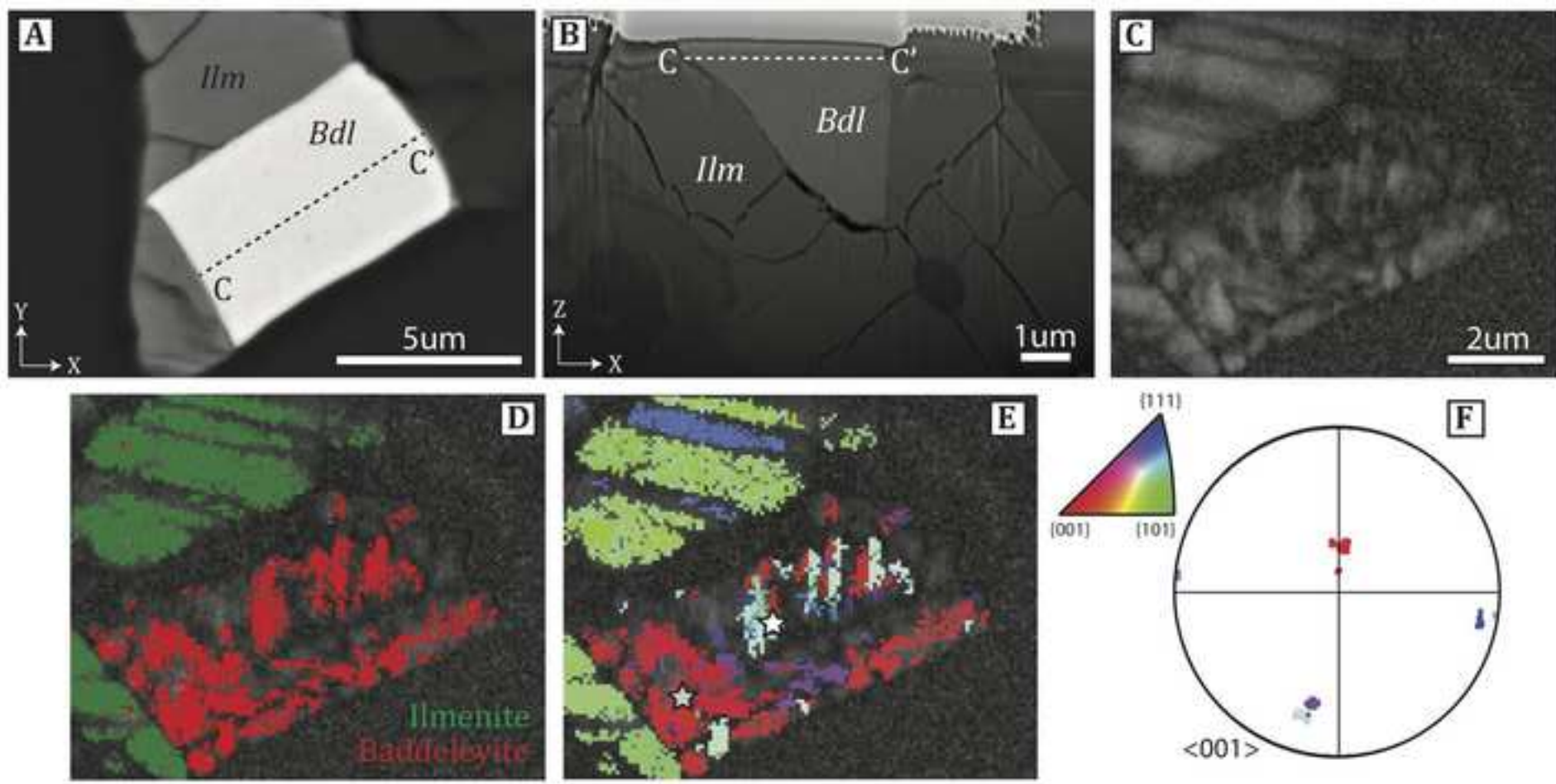


Figure 5

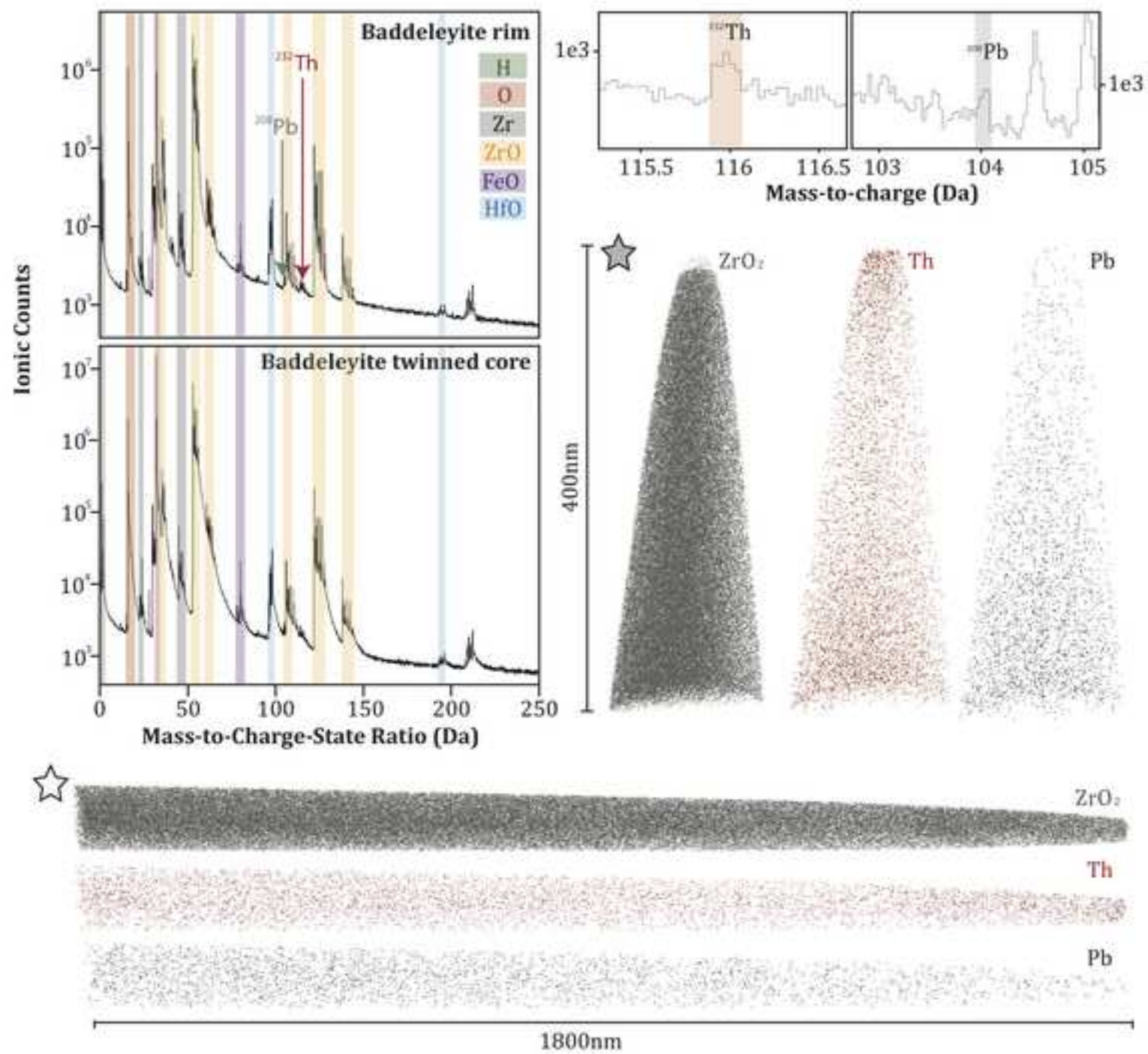


Figure 6

