1 # Interpreting U-Pb data from primary and secondary

2 # features in lunar zircon

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ABSTRACT

In this paper, we describe primary and secondary microstructures and textural characteristics found in lunar zircon and discuss the relationships between these features and the zircon U-Pb isotopic systems and the significance of these features for understanding lunar processes. Lunar zircons can be classified according to: (i) textural relationships between zircon and surrounding minerals in the host breccias, (ii) the internal microstructures of the zircon grains as identified by optical microscopy, cathodoluminescence (CL) imaging and electron backscattered diffraction (EBSD) mapping and (iii) results of in-situ ion microprobe analyses of the Th-U-Pb isotopic systems. Primary zircon can occur as part of a cogenetic mineral assemblage (lithic clast) or as an individual mineral clast and is unzoned, or has sector and/or oscillatory zoning. The age of primary zircon is obtained when multiple ion microprobe analyses across the polished surface of the grain give reproducible and essentially concordant data. A secondary set of microstructures, superimposed on primary zircon, include localised recrystallised domains, localised amorphous domains, crystal-plastic deformation, planar deformation features and fractures, and are associated with impact processes. The first two secondary microstructures often yield internally consistent and close to concordant U-Pb ages that we interpret as dating impact events. Others secondary microstructures such as planar deformation features, crystal-plastic deformation and micro-fractures can provide channels for Pb diffusion and result in partial resetting of the U-Pb isotopic systems.

Key Words: lunar zircon − shock features − deformation − U-Pb ages − EBSD − impact metamorphism

1. INTRODUCTION

The first high precision U-Pb measurements on lunar zircon were determined using the newly developed SHRIMP I (Sensitive High Resolution Ion Micro Probe) at the Australian National University (Compston et al., 1984). Early results (Meyer et al., 1985; 1989; 1996) demonstrated that lunar zircons retained their primary U-Pb ages and that magmatic activity on the Moon lasted from ~4.37 to ~3.90 Ga. However, complexities in the U-Pb ages and internal structures were found in lunar zircons by Pidgeon et al. (2007), Nemchin et al. (2009), Grange et al. (2009; 2011) and Timms et al. (2012), and attributed to disturbance of the U-Pb systems during impact. The presence of variably isotopically disturbed zircon presents problems in interpreting U-Pb ages which require distinguishing between primary and secondary microstructures. In this contribution we describe primary and secondary features in lunar zircons and link these with the behaviour of the U-Pb system.

2. ANALYTICAL TECHNIQUES

Analytical methods applied to determine the origin of zircon grains in lunar samples include investigation of (i) spatial relationships between zircon grains and surrounding minerals using optical microscopy and scanning electron microscopy (SEM) with secondary and backscattered electron detectors (SE and BSE, respectively), and energy-dispersive X-ray spectroscopy (EDS); (ii) internal compositional domains / zoning of zircon grains using BSE and cathodoluminescence (CL) imaging; (iii) fractures using SE imaging; (iv) quantitative data on crystallographic orientation using electron backscatter diffraction (EBSD) mapping that can reveal domains affected by crystal-plastic deformation, containing planar deformation features, microtwins, and/or fracture-related misorientation; (v) qualitative and quantitative data on the degree of metamictisation of zircon using SE/BSE/CL imaging and Raman spectroscopy, respectively; and (vi) in situ U-Pb age determination using SIMS (Secondary Ion Mass Spectrometry). The analytical protocols for these techniques are given elsewhere (Williams, 1998; Pidgeon et al., 2007; Reddy et al., 2007; Timms and Reddy, 2009; Nemchin et al., 2009; Grange et

al., 2009). The combination of BSE and EDS has also been used to identify minerals surrounding zircon grains.

Twelve large zircon grains from Apollo 14 and two from Apollo 17 landing sites showing characteristic internal structures (Table 1) and U-Pb age patterns (Table 2) are described in this study. These grains have been studied using the analytical protocol described above. All errors for the U-Pb data obtained on individual ion microprobe spots (Table 2) are shown as 1-sigma, while errors of average, concordia and intercept ages are given at the 95% confidence level. In addition a set of previously studied grains is utilised in this discussion for completeness. The full description of these zircons can be found in Pidgeon et al. (2007), Nemchin et al. (2009), Grange et al. (2009, 2011) and Timms et al. (2012).

3. CHARACTERISTICS OF LUNAR ZIRCONS AND THEIR U-Pb SYSTEMS

Nemchin et al. (2008) proposed a classification of lunar zircons according to their morphology and recognised a range of morphological types such as euhedral to rounded zircon grains in breccia matrices and related these features to a relative history of mechanical abrasion. This classification is useful for answering questions on the late history of a matrix zircon grain but is not sufficient for addressing more fundamental questions such as the meaning of zircon U-Pb ages. To provide a basis for interpreting SIMS U-Pb ages on lunar zircons we have extended the earlier classification by describing primary and secondary features observed in lunar zircon grains. We also consider the implications of these features for the interpretation of U-Pb ages and for deciphering lunar magmatic and impact processes. We use new analyses of selected grains (Tables 1 and 2) and previous analytical results to illustrate U-Pb behaviour associated with selected primary or secondary features.

To avoid terminological ambiguity, we refer to (i) texture when describing relationships of the zircon grains with the surrounding minerals (e.g., within a lithic clast or enclosed in the breccia matrix) and (ii) structure and microstructure of the zircons when describing internal features of the zircon grains (e.g., zoning, fractures, etc).

3.1. Zircon-rock textural relationships

3.1.1. Cogenetic zircon in lithic clasts.

Zircon grains occur as cogenetic mineral phases in lithic clasts and attached to other mineral(s) representing original rock. In these occurrences, zircon grains can be relatively large (e.g., 100-800 μm for the 'pomegranate' zircon from thin section 73235,82; Pidgeon et al., 2007). In cases where the lithic clast is large or where a zircon grain is attached to more than one mineral, the composition of the plutonic rock can be determined from the mineral assemblage. For example, the 'pomegranate' zircon (sample 73235,82; Pidgeon et al., 2007) is completely enclosed within an anorthosite clast and interpreted to have crystallised at the same time as the anorthosite (Figure 1a-b). The composition of plagioclase (An_{80-85}) indicates that the clast belongs to the Mg-suite of rocks (Warren and Wasson, 1979), rather than the ferroan anorthosites. Compston et al. (1984) described a large zircon grain with truncated zoning and attached to an ilmenite grain. These authors deduced that the zircon belonged to the population of gabbronorite clasts and crystallised within a gabbronorite pluton. Another example of zircon grain that is completely enclosed in a rock fragment is the 'cracker' zircon (sample 73235,60#5; Grange et al., 2011; Figure 1c) which is located within a rock fragment described by Meyer et al. (1996) as a "small granophyric clast of silica and ternary feldspar", and is interpreted to have crystallized from a felsic melt. Zircon grains included in lithic clasts usually preserve their original (often euhedral) shape and also exhibit various degrees of fracturing (e.g., the 'cracker' zircon described above preserves its original prismatic habit).

3.1.2. Zircon growth in impact melt

There have been several reports of lunar zircons that have crystallised directly from impact melt (Gnos et al., 2004; Grange et al., 2009; Liu et al., 2009, 2010, 2012). These grains are relatively small compared to those previously described (<20 μm) and show distinctive morphological features supporting contemporaneous growth of zircon in the melt. Poikilitic zircons (i.e., zircon grains enclosing other minerals) described within the Sayh al Uhaymir 169 (SaU 169) lunar meteorite, have been interpreted to have formed by crystallisation from small pockets of interstitial impact

melt (Gnos et al., 2004; Liu et al., 2009; Figure 2a). Zircons with similar textures were described in impact melt breccias collected at the Apollo 12 landing site (samples 12032 and 12033), and provide further evidence of zircon crystallization from an impact melt (Liu et al., 2010, 2012). An acicular zircon grain in lunar sample 73217,52 surrounded by felsic glass was also interpreted to have formed during quenching of an impact melt (Figure 2b) (Huber and Warren, 2008; Grange et al., 2009). The unusual shape of this grain, together with the similar shape of surrounding phases such as ilmenite and K-feldspar (Figure 2b), indicate that they have formed as a result of rapid crystallisation in the melt.

3.1.3. Zircon clasts

Most zircons in lunar breccias occur as individual broken and rounded grains that have been subjected to a history of impact events prior to incorporation in the breccia (Figure 3). Zircon #3 of the aphanitic impact melt breccia 73235,59 ('tiger' zircon, Figure 3a) and the 'arrowhead' zircon (sample 76295,91; Figure 3b), as well zircon #2 from 14306,60 (Figure 4h) and the 'teardrop' zircon (zircon #1 from 14083,35, Figure 4a-b) are large compared to grain size of other rock-forming minerals that constitute the breccia matrix. The first two zircons have subrounded grain boundaries, and are anhedral, whereas zircon #2 from 14306,60 (Figure 4h) and the 'teardrop' zircon (zircon #1 from 14083,35, Figure 4a-b) are subhedral. In addition, many of the studied zircon clasts (with the exception of the 'tiger' zircon) show oscillatory and/or sector zoning that indicate crystallisation within a magma chamber or a thick melt sheet (Figure 4). However, many zircon clasts are small (Figure 3c-d) and have irregular and angular or rounded shapes that resulted from mechanical abrasion and fragmentation during transport in the ejecta. The loss of physical connection of individual zircon clasts with their igneous source rock, and modification of their external morphology as a result of abrasion and/or fragmentation during transport are analogous to detrital zircon grains found in sedimentary rocks on Earth. Consequently, intragrain microstructures, grain chemistry and the U-Th-Pb system are the only features of these grains that can be used to interpret their history prior to fragmentation and incorporation into their host breccia sample

3.2. Zircon microstructures

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Most of the studied lunar zircon grains have primary features indicative of a magmatic origin and a simple post-crystallisation history. However, several grains have secondary internal microstructures, geochemical variability and a disturbed U-Pb system.

3.2.1. Primary zircon microstructures

3.2.1.1 Zircon grains with primary zoning. Oscillatory and sector zoning in terrestrial zircons are commonly used as an indicator of magmatic crystallisation and the same applies to zoned lunar zircon grains. Examples of oscillatory zoning in lunar zircons characterised by multiple, thin, concentric euhedral layers with different birefringence, BSE and CL properties are shown in Figure 4a-e. Lunar zircons with sector zoning, where grains comprising several, sometimes irregular, sectors with sharp boundaries and significant differences in birefringence, BSE and CL properties are shown in Figure 4f-h. The difference in CL signal intensity, from one thin zone (or sector) to another commonly correlates with different concentrations of REE, U and Th. For example, the darkest zone of zircon grain 14306,60#2 (Figure 4h) has U and Th concentration of 51 and 32 ppm respectively (analysis 306-60-203, Table 2), whereas the bright zone has U and Th content of 13 and 4 ppm (analyses 306-60-201 and -202, Table 2). Variations in U and Th concentration between sectors contrast with their narrow range within individual sectors. U-Pb systems of zircons with internal structures interpreted to have a magmatic origin with no superimposed secondary microstructures usually show internally reproducible ages from multiple analyses, suggesting that zircons exhibiting these structures have not experienced any significant Pb-loss. Consequently, these analyses define the crystallisation age of the grains in their plutonic setting. This is the case for the 'teardrop' zircon (zircon#1 of 14083,35; Figure 4a-b) that shows both oscillatory (see insert in Figure 1b) and sector (white arrow in Figure 1b) zoning indicative of a magmatic origin: the ^{207}Pb/^{206}Pb weighted average of the six analyses (Table 2) yield an age of 4040 ± 3 Ma (95% conf., MSWD = 0.47) that is consistent with the intercept age (4039 ± 6 Ma; Figure 5a-b). The U and Th contents of the grain range from 52 to 113 ppm and 35 to 84 ppm respectively, with Th/U between 0.68 and 0.97. These values demonstrate the uniformity in age across the grain and a limited variation in U and Th contents (Table

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210 2). This is a typical primary zircon and the consistent age is interpreted as dating the
211 original crystallisation of the zircon.

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213 *3.2.1.2. Unzoned grains.* Grains that are completely homogenous and featureless, as
214 indicated by all available imaging techniques are also interpreted as primary
215 magmatic zircon (e.g., the 'hexagon' zircon, sample 73235,60#4, Figure 4i-j). These
216 grains generally have low yet uniform CL intensity, a very limited range of U and Th
217 concentrations and consistent U-Pb ages. Interpretations of the origin and age from
218 this type can be ambiguous as there is still a possibility that such grains could have
219 been completely reset by impact. Nevertheless, in the absence of evidence to the
220 contrary, zircons showing homogenous internal structures, chemistry and age are
221 interpreted as dating primary magmatic growth. The 'hexagon' grain shows a
222 homogenous internal structure (Figure 4i-j) and yields a weighted average $^{207}Pb/^{206}Pb$
223 age obtained from 6 analyses at 4364 ± 5 Ma (95% conf., MSWD = 1.10, Grange et
224 al., 2011), which is also similar to the intercept age (4364 ± 5Ma; Figure 5c-d). The U
225 (100-128 ppm) and Th (57-73 ppm) contents across the grain show very good
226 consistency and little variation corresponding to Th/U from 0.58 to 0.60 (Grange et
227 al., 2011).

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229 3.2.2. Secondary zircon microstructures

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231 *3.2.2.1. Solid state recrystallisation microstructures.* Microstructures that indicate
232 solid state recrystallisation in terrestrial zircon are characterised by the formation of
233 intrusive domains of homogeneous bright CL zircon with sharp, irregular boundaries
234 that truncate primary zoning. The external morphology of a grain is not changed
235 (Pidgeon 1992; Geisler et al., 2007). Similar relationships are also found in some
236 lunar zircons. Multiple ion microprobe analyses of low U and secondary patches in
237 lunar zircon grains are commonly internally consistent and suggest complete resetting
238 of U-Pb during the event that formed these structures. The 'tiger' grain (impact melt
239 breccia 73235,59; Grange et al., 2011; Timms et al., 2012) contains two small zones
240 along its border visible in BSE and CL images (Figures 3a and 6a) that are brighter in
241 CL and have better quality EBSD patterns. The U-Pb age of these highly crystalline
242 secondary parts along the edges of the grain are much younger than the bulk part of
243 the grain (about 250 m.y. younger; Figure 7a; Grange et al., 2011). They also show

244   significantly lower U and Th contents, 19 and 7 ppm respectively, as well as lower

245   Th/U (0.37) while the rest of the grain has U and Th concentrations above 48 and 24

246   ppm and Th/U ratios above 0.51 (Grange et al., 2011). This bright CL patch might be

247   interpreted as a truncated overgrowth but as it actually transgresses the main body of

248   the grain we interpret it as an area of solid state recrystallisation (secondary zircon).

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250   *3.2.2.2. Zircon as a product of reaction structures.* In addition to solid state

251   modification of magmatic zircon, new zircon can form by reaction of other Zr-rich

252   minerals. An example has been observed in the sample 73217,52 (Figure 6b, Grange

253   et al., 2009) and shows a corona of microcrystalline zircon around a single

254   baddeleyite grain. It is interpreted to represent a reaction of baddeleyite with

255   surrounding silica-rich melt to create new granular zircon. The formation of zircon by

256   reaction of baddeleyite with melt is summarised by ZrO_2 (baddeleyite) + SiO_2 (silica)

257   = $ZrSiO_4$ (zircon). The new zircon has U ranging from 65 to 74 ppm and Th from 46

258   to 50 ppm, Th/U between 0.64 and 0.79 and a consistent U-Pb age of 3929 ± 10 Ma

259   which is much younger than the parent baddeleyite age of >4275 Ma (Grange et al.,

260   2009). The difference in ages indicates that the granular zircon has grown during a

261   secondary event.

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263   *3.2.2.3. Structures showing amorphous domains.* The 'pomegranate' zircon, first

264   described by Smith et al. (1986) and studied in detail by Pidgeon et al. (2007) is an

265   example of localised amorphous domains. The original (primary) zircon preserves

266   sector zoning in CL (Figure 4f and Figure 8a), characteristic of a magmatic growth,

267   and has been broken into numerous angular fragments that are bound by a modified

268   (secondary) zircon that is dark in CL and has low surface relief in SE, high U and Th

269   contents and no EBSD patterns (Figure 8a-c). Detailed U-Pb analyses of this grain

270   (Pidgeon et al., 2007) showed that the secondary zircon yields a weighted mean

271      $^{207}Pb/^{206}Pb$ age of 4187 ± 11 Ma (95% conf.), interpreted to be the age of an impact

272   event. The crystalline fragments give ages approximately 130 m.y. older (Figure 7b)

273   and have higher Th/U and lower U content than the secondary zircon (Figure 9). The

274   'propeller' grain (zircon #6 from sample 73215) also has narrow dark CL domains

275   with similar characteristics as the 'pomegranate' zircon (Figure 8d-e). The unmodified

276   parts of these two grains show high relief in SE images, low U and Th concentrations,

277   and EBSD patterns with high band contrast indicating that they have retained their

278   crystal integrity. However, the propeller grain is more complex and has also domains
279   that have undergone crystal-plastic deformation.

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281   *3.2.2.4. Crystal-plastic deformation.* Many of the studied lunar zircon grains preserve
282   crystallographic distortions in the form of deformation bands and subgrain
283   microstructures that are formed by the formation and migration of dislocations, and
284   can be seen by EBSD mapping. Recent research on terrestrial zircon has shown that
285   distortion of the lattice by crystal-plasticity facilitate U, Th, REE, Ti and Pb to
286   migrate through the zircon (Reddy et al., 2006; Timms et al., 2006; Moser et al., 2009,
287   2011; Timms and Reddy, 2009; Timms et al., 2011). In lunar zircon, this type of
288   deformation is accompanied by a spread of U-Pb ages along the concordia curve (i.e.,
289   form a discordia close to the concordia curve) that is taken as evidence of partial
290   resetting of the U-Pb system. The 'tiger' (73235,59#3; Figure 10a), the 'oldest'
291   (72215,195; Figure 10b), the 'arrowhead' (76291,195; Figure 10c) and the 'propeller'
292   (73215,122#6; Figure 8d) zircon grains preserve crystal-plastic deformation
293   microstructures leading to various degrees of cumulative misorientation (respectively,
294   4º, 12º, 15º and 22º; Timms et al., 2012). U-Pb data for these grains show a
295   continuous spread of ages rather than a single age (Figure 7a and 11; see also
296   Nemchin et al., 2009, for the oldest zircon). The 'arrowhead' grain (sample 76295,91)
297   has ages between 4276 ± 9 and 4110 ± 9 Ma (Table 2) and shows a complex
298   relationship between U-Pb systems and deformations microstructures. The main part
299   of the 'propeller' grain (73215,122#6) also shows a significant range of U-Pb ages,
300   most likely resulting from different degrees of resetting via fast pathway diffusion
301   during crystal-plastic deformation (Figures 6b and 11). If the low-crystalline domains
302   of the 'propeller' zircon (see above; Figures 8 and 9) formed during a secondary
303   event, then the two U-Pb ages obtained for the tips of the grain could tentatively be
304   used to define this event at 4308 ± 11 Ma (Figure 11). However, there is a possibility
305   that the youngest age only represents an oldest limit for the age of the secondary
306   event. Conversely, the oldest analyses may only represent a youngest limit for the age
307   of igneous crystallisation.

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309   *3.2.2.5. Discrete planar deformation features (PDFs).* Although lunar zircons have
310   been subjected to a history of impact events, they only rarely show impact generated
311   parallel deformation features such as those observed in zircons from terrestrial impact

312   environments (Pidgeon et al., 2011). However, a recent study (Timms et al., 2012)

313   reported two lunar zircon grains with thin planar features, visible under the optical

314   microscope, in EBSD mapping and some in CL images. These microstructures

315   comprise thin (<200 nm) lamellae that occur along a limited number of rational, low

316   index crystallographic planes, containing either zircon with a high defect density, or

317   diaplectic glass (Timms et al., 2012). Some PDFs contain microtwin lamellae with a

318   $65°⁄\{110\}$ symmetry relationship (Timms et al., 2012). The 'tiger' (73235,59#3), the

319   'arrowhead' (76295,91) and the zircon #62 from the sample 14306,60 have two very

320   similar sets of planar features visible in cross-polarised light (Figure 12a-c), and to a

321   lesser extent in plain-polarised light, and also as low EBSD pattern quality features in

322   EBSD maps (Figures 10c and 12d). Up to five PDFs with different crystallographic

323   orientations have been recognised in single lunar zircon grain (i.e., 'tiger' and

324   'arrowhead' grains; Timms et al., 2012). However, they are not visible in BSE or CL

325   images, and do not index as another phase (such as reidite) during the EBSD

326   acquisition. They cut through both the bright CL domains of the 'tiger' grain (formed

327   by solid state recrystallisation) and the weak plastically deformed main part of the

328   grain, indicating that they postdate these structures. Zircon grain (14303,49#3) shows

329   a well-developed set of planar features that are visible in plain- and cross-polarised

330   light and CL images (Figure 12e). One primary fragment in the 'pomegranate' zircon

331   (73235,82) also shows planar features visible in cross-polarised light (Figures 7 and

332   8b of Pidgeon et al., 2007). Grains such as the 'tiger', the 'pomegranate' and the

333   'arrowhead', are also deformed by dislocation creep and so, PDFs could represent fast

334   diffusion pathways and channel Pb diffusion through the grain and contribute to the

335   observed scatter of U-Pb analyses. However, the widths of these microstructures (<5

336   μm) are much less than the diameter of typical in situ SIMS pits (~20 μm), which

337   precludes dating them directly.

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339   *3.2.2.6. Fractures.* Unlike PDFs, fractures in lunar zircons are irregular, do not follow

340   specific crystallographic orientations and seem to be randomly distributed throughout

341   the grains (see discussion in Pidgeon et al., 2011). Fragmentation by fracturing can

342   result in significant relative rotation of individual zircon parts (Figure 13). EBSD

343   mapping shows that fragments of the 'cracker' zircon (73235,60#5) are misoriented

344   relative to each other (up to 40°), but none of the fragments are deformed internally.

345   The individual fragments give similar ages, showing that this structure results only in

346   mechanical damage with no visible chemical or isotopic effect, unless analyses cross

347   one of the fractures, where contamination is likely. For example, the 'cracker' and

348   zircon #1 from sample 14303,49 show a scatter of U-Pb data along a discordia close

349   to the concordia curve of 45 m.y. and 90 m.y. respectively (Figure 14a-b). However,

350   when the analyses representing spots that overlap fractures are removed based on the

351   after run investigation of spot locations within the grains (Figure 14b-c), remaining

352   analyses produce internally consistent weighted mean ages of 4208 ± 8 Ma and 4317

353   ± 11 Ma, respectively.

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355   *3.2.2.7. Radiation damage.* Damage to the crystal lattice is caused by nuclide recoil

356   and alpha emission during radioactive decay of U and Th. The degree of radiation

357   damage depends on the total α-dose received by the zircon, which is a function of the

358   Th and U content and time. Lunar zircons formed between 4.3 and 3.9 Ga with low

359   concentrations of radioactive elements (i.e., U and Th contents rarely exceeding 100

360   ppm; Table 2) will, to the present day, have accumulated an α-dose between about

361   2.5×10^{18} and 3.5×10^{18} α-decays/g. This is slightly higher than the first percolation

362   point defined at $\sim 3.0 \times 10^{18}$ α-decays/g (Murakami et al., 1991; Salje et al., 1999),

363   indicating that the radiation damage of these grains have reached the point where

364   metamict domains are interconnected (i.e., forming opened pathways for diffusion)

365   only in the last billion year. A 4.3 Ga zircon with average low concentrations of U and

366   Th will have less than 0.5×10^{18} α-decays/g by 3.9 Ga, suggesting that such zircon has

367   remained crystalline through the early history of the Moon and that radiation damage

368   is not a significant factor in the re-setting or disturbance of U-Pb systems of lunar

369   zircons that have experienced impact events between 4.4 and 3.9 Ga. Only zircons

370   with an age of ~4.3 Ga and concentrations of U in excess of 400-500 ppm and Th

371   above 200-300 ppm will have accumulated sufficient α-dose to reach the first

372   percolation point by 3.9 Ga, and become susceptible to diffusional Pb-loss during

373   impact metamorphism. The only zircon grains that may have suffered radiation

374   damage within a relatively short time frame (i.e., a few hundreds of million years) are

375   zircons from 14321,1613. They have U and Th concentrations (Table 2) that would

376   have created an alpha dose 10 to 100 times higher than the other zircon grains,

377   making them more susceptible to Pb loss. These zircons have younger, ages

378   comprised between 3.97 and 4.00 Ga (Table 2), yet concordant to slightly discordant,

379   indicating that even those grains may not have suffered huge amount of Pb loss before

380   3.9 Ga.

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383   **4. INTERPRETING U-Pb DATA IN LUNAR ZIRCONS**

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385   **4.1. Origin of U-Pb system disturbance in lunar zircon**

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387   Lunar breccias contain a record of multiple impact events which have

388   repeatedly shocked, pulverised, metamorphosed and mixed materials such that the

389   largest surviving fragments of igneous rock rarely exceed 1 cm in size and adjacent

390   apparently identical rock fragments and mineral grains can have different origins and

391   ages. This introduces serious problems of sample selection for geochronological

392   methods that analyse composite mineral samples. In addition, the vulnerability of

393   systems such as Rb-Sr and Ar-Ar to resetting during thermal events associated with

394   impact metamorphism constrains the ability of these techniques to date events that

395   occurred before the last major impact. On the other hand our results and earlier studies

396   (e.g., Meyer et al., 1996) show that the U-Pb system of zircon remains closed under

397   all but the most extreme lunar impact events giving this system a unique importance

398   in investigating the early history of the Moon. Another great advantage of zircon

399   geochronology is that robust U-Pb ages can be determined from a single zircon grain,

400   and the consistency of the age can be tested by making a number of in situ ion

401   microprobe U-Pb analyses on different parts of the grain. However, the meaning of

402   the age is a major question and understanding of the significance of the internal

403   structures of lunar zircon grains is vital to clarify whether the ages date a primary

404   igneous event or represent a secondary U-Pb disturbance (complete or partial).

405   Several of these lunar processes are similar to those known to form specific

406   zircon microstructures and textures on Earth. Consequently, understanding the

407   formation of these microstructures and textures in lunar zircons can build from the

408   extensive experience of studying terrestrial rocks. However, evidence for a number of

409   processes very common on Earth, such as hydrothermal alteration and metamorphism,

410   especially metamorphism accompanied by the migration of large volumes of fluid has

411   never been recorded on the Moon. Although water has been detected in some apatite

412   grains from mare basalts and picritic glass beads (e.g. Saal et al., 2008; Boyce et al.,

2010; Hauri et al., 2011) suggesting that the Moon is not completely dry, a total absence of hydrous minerals such as amphiboles and micas in lunar rocks argues strongly for very subdued, if not absent, influence of water-rich fluid on the formation of lunar rocks. As a result several features present in lunar zircon that resemble those observed in terrestrial zircons are interpreted to form by different processes. In particular hydrothermal processes and metamorphism have to be excluded from consideration when explaining textures and microstructures of lunar zircons. Magmatism and impacts appear to be the only major processes that can be invoked to interpret these textures and microstructures.

4.2. U-Pb in zircon with primary microstructures

One of the microstructures common in magmatic zircon on Earth is sector zoning. It is also common in lunar zircons (Figure 4f-h) and is interpreted as primary igneous feature. The consistency and concordance of SIMS U-Pb ages on different sectors in such grains is strong evidence that the age represents primary crystallisation (Figure 15a). On the other hand, oscillatory zoning is rare in zircons from lunar breccias. The poor representation of oscillatory zoning in lunar zircon is a striking feature and could be taken as an additional indication of absence of water in lunar magmas, resulting in significantly higher solidus temperature, lower degree of polymerisation and lower viscosity of these melts, which makes diffusion of trace elements (such as REE) within the magma more efficient. Formation of oscillatory zoning is possibly determined by the relative rates of supply of trace elements to the growing zircon interface (Mattinson et al., 1996). Faster diffusion will, therefore, be expected to reduce the probability of development of inhomogeneities such as oscillatory zoning in the zircon grains and favour the development of homogeneous grains. Vavra (1990) interpreted the different patterns of zoning as reflecting different conditions of zircon saturation (high for oscillatory zoning and low for sector zoning) of the melt and linked growth zoning with growth kinematics. It is therefore likely that the zoning of the lunar zircon is associated with the chemical composition of the melt and its liquidus temperature. Notwithstanding the reasons for scarcity of oscillatory zoned zircons in lunar rocks, when this microstructure is present, the grains can be viewed as formed by crystallisation from magma and their ages representing magmatic crystallisation.

447   One group of zircon grains which is usually difficult to interpret in both
448 terrestrial and lunar rocks are those without any internal structures as revealed by
449 cathodoluminescence (e.g., Figure 4i). In rocks on Earth these grains can be formed
450 by both magmatic and metamorphic processes. Lunar grains found as fragments in the
451 breccia matrixes can be interpreted as crystallising from a magma or representing a
452 complete recrystallization and resetting of U-Pb system during impacts. However,
453 where ion microprobe U-Pb ages over the polished surface of such unzoned grains are
454 consistent and concordant we tentatively interpret the ages as dating igneous
455 crystallisation.

456

457 **4.3. U-Pb in zircon grown from the impact melt**

458

459   The presence of zircon grains in quenched and poikilitic impact melts (Figure
460 2) offers a useful opportunity to unequivocally date an impact event (Figure 15b). In
461 addition, the habits of these grains also provide information on viscosity and melt
462 polymerisation. The small zircon grains from the SaU 169 meteorite and from Apollo
463 12 breccia samples are intergrown with other minerals in poikilitic melts, whereas the
464 zircon growing in the melt from 73217,52 sample is acicular, almost dendritic. These
465 habits indicate rapid crystallisation in an impact melt and consistent ion microprobe
466 ages on such grains are reliably interpreted as dating the impact. Differences in the
467 texture of these impact melt zircons are likely to be the result of contrasting chemical
468 composition of the impact melts, mafic in the SaU 169 and Apollo 12 samples and
469 silica-rich, high-K in the sample 73217,52. It is also likely that these differences in
470 chemistry are linked to the saturation and temperature of crystallisation of the zircon.
471 It is worth noting that the impact origin of the melt in 73217,52 has been subject of
472 controversy (for full discussion and references see Grange et al., 2009). Nevertheless,
473 the acicular shape of zircon leaves little doubt that it could only form in this melt and
474 therefore dates the time of its quenching, interpreted to be caused by an impact (Huber
475 and Warren, 2008).

476

477 **4.4. U-Pb data in zircon with secondary microstructures**

478

479   Whereas undisturbed primary structures in lunar zircons described above have
480 petrological significance, the consistency of ion microprobe U-Pb ages throughout the

481 grain is an essential criterion for interpreting the age as a primary age. As
482 demonstrated in this contribution and previous studies (e.g. Pidgeon et al., 2007), U-
483 Pb ages within primary lunar zircons can be severely disturbed by secondary
484 processes. Generally such disturbances are accompanied by the development of
485 secondary structures. Some of these structures are well known in zircons from
486 terrestrial impacts making their interpretation in lunar zircons relatively
487 straightforward. However, some microstructures observed in impactites on Earth are
488 rare in zircons from the Moon. For example, the high pressure zircon polymorph
489 (reidite) has never been found in lunar impact samples. Other impact deformation
490 structures such as planar deformations features, micro-twins and crystal-plastic
491 deformation have only been recently found in lunar zircon (Grange et al., 2011;
492 Timms et al., 2012; Figures 10 and 12). Many of these microstructures, such as PDFs
493 cannot be targeted for in-situ U-Pb analyses due to their small size and therefore
494 cannot be used to determine the age of an impact. However, they could provide fast
495 diffusion pathways for Pb which can lead to scatter in the U-Pb ages. Therefore, it is
496 important to recognise such features and be aware of their potential effects on the U-
497 Pb system (Figure 15c). In addition, the occurrence of planar microstuctures is related
498 to the shock pressure and temperature experienced by the sample at the time of impact
499 and can give some insight into conditions attained by the sample during shock
500 metamorphism and enable recognition of multiple impact events (Timms et al., 2012).
501
502 4.4.1. Reaction products
503
504 As mentioned before, several microstructures identified in lunar zircons
505 resemble those formed in terrestrial rocks by processes that do not exist on the Moon.
506 One of these is the growth of zircon around a baddeleyite core which has been
507 described in terrestrial mafic rocks by Davidson and van Breeman (1988) and
508 Heaman and LeCheminant (1993) who reported formation of zircon coronas around
509 baddeleyite as a result of increased silica activity during metamorphism. As
510 conditions for regional metamorphism do not exist on the Moon, formation of zircon
511 coronas around baddeleyite in lunar samples can only be explained by (i) reaction of
512 silica-rich melt with baddeleyite or (ii) solid state reaction between silica-rich glass
513 and baddeleyite. The single published example of this reaction (Grange et al., 2009;
514 Figure 6b) is complicated as the silica melt reacting with the baddeleyite, is

515 significantly older (~ 4.3 Ga, as dated by the acicular zircon growing in the melt) than

516 the granular zircon in the corona (~3.9 Ga). Solid state reaction is unlikely as

517 baddeleyite will probably react as soon as it gets in contact with the silica saturated

518 melt. Thus, the age difference can be explained by either remelting of the silica glass

519 or complete Pb loss from the granular zircon during a later (~3.9 Ga) event. Both

520 mechanisms require a secondary thermal pulse at about 3.9 Ga, likely to be associated

521 with an impact event.

522

523 4.4.2. Recrystallisation and amorphisation

524

525   An important observation described in this report is the recognition of two

526 contrasting types of secondary microstructures in a number of grains, namely solid

527 state recrystallisation and amorphisation. These microstructures are particularly

528 important because they involved resetting of U-Pb system and can form domains and

529 patches large enough to be dated, and therefore, provide information about the timing

530 of secondary events (Figure 15d). Recrystallised domains in terrestrial zircons are

531 often formed as a result of metamorphic reaction involving fluid and possibly melt.

532 Also, inherited zircon grains can react with a melt nearly saturated in Zr, be partially

533 dissolved and re-crystallise as new zircon forming distinct rims around inherited

534 cores. However, mafic nature of lunar melts would require significant degrees

535 (Dickinson and Hess, 1982) of crystallisation before Zr saturation is reached even if

536 the starting melt is enriched in incompatible elements, which will probably result in a

537 complete dissolution of any potential inherited zircon. Consequently, common

538 processes occurring on Earth cannot explain lunar zircon recrystallised domains

539 (Figure 6a) that are likely to be formed as a result of impacts, their U-Pb ages

540 reflecting the timing of these impacts. Amorphous domains in terrestrial grains reflect

541 initial variability of radioactive elements in the grains and therefore follow specific

542 pattern consistent with the zircon zoning. Two main features make non-planar

543 amorphous domains in lunar zircon different from their terrestrial counterparts. First,

544 their irregular distribution is inconsistent with the primary trace elements variations in

545 zircon. Second there is a relatively short time between primary and secondary events,

546 which mean that the lunar zircon is crystalline at the time of disturbance.

547 Consequently, process other than radiation damage appears to be responsible for the

548 formation of amorphous zircon domains. The process is likely to be propagation of

shock during impact, which can explain the formation of irregular diaplectic glass domains, especially on the interfaces between different mineral phases, accompanied by chemical modification and re-setting of the U-Pb system.

Although the formation of both re-crystallised and amorphous zircon is accompanied by complete resetting of the U-Pb system, the modifications of the zircon lattice and chemistry associated with these microstructures are very different and provide evidence of two basically different sets of impact conditions. They may represent formation during different stages of an impact event (Timms et al., 2012). The 'tiger' grain (73235,59#3; Figure 6a) shows a recrystallised zone, characterised by a sharp difference in age (Figure 7a), a sharp decrease in U content and Th/U ratio compared to the rest of the grain. This can be explained by recrystallisation of the lattice with concurrent removal of impurities during an impact. In contrast, the 'propeller' (73215,122#6) and the 'pomegranate' (73235,82) zircons contain areas that experienced a significant loss of crystallinity, by shock induced amorphisation, accompanied by an increase of U concentration and decreasing Th/U (Figures 8 and 9). The two contrasting processes of amorphisation and recrystallisation represent a 3D modification of zircon grains and reflect different stages of compression during an impact. The initial compression shock wave is believed to be accompanied, in a 3D poly-mineralic rock, by inhomogeneous shock pressures at the grain scale, resulting in a heterogeneous distribution of shock microstructures, especially localised at the grains interfaces and near the cracks and pores (e.g., Sharp and DeCarli, 2006). However, this inhomogeneity exists only for the first fractions of millisecond and the destructive shock wave quickly decays into seismic (elastic) waves (e.g., Sharp and DeCarli, 2006). The effect on the crystalline zircon lattice of severe shock is not well understood, however, experimental results of Gucsik et al. (2002, 2004) suggest that severe shock can result in damage to the zircon lattice similar to that caused by radiation. It is therefore possible that shock created a randomly distributed network of amorphous domains (diaplectic glass) surrounding fragments of highly crystalline zircon in the 'pomegranate' grain. These amorphous domains completely lack any other overprinting microstructures. The recovery properties of shock induced amorphisation are not known, however, by analogy with radiation damage, it is suspected that annealing could occur during a subsequent thermal pulse. Pidgeon et al. (2007) envisaged the secondary zircon of the 'pomegranate' grain to be localised in the areas of pressure release after the combined shock fracturing and friction heating

583   induced by an impact. This was accompanied by complete Pb-loss during the transient

584   high temperature conditions during the impact event, locally resetting the U-Pb

585   system, and therefore the age given by the secondary zircon defines the age of the

586   impact.

587

588   4.4.3. Fractures

589

590   The formation of any type of fracture in zircon (Figures 13 and 14) introduces

591   fast pathways for trace element and isotope exchange between the grain and external

592   environment. For purely brittle fractures, geochemical modification occurs via volume

593   diffusion from the fracture interface only, over length scales that would depend on the

594   temperature-time history and diffusivity of the trace element (Figure 15e). The

595   process of brittle fracture could potentially be coupled with crystal-plastic strain at

596   some conditions, especially at crack tips. Given that crystal-plasticity of terrestrial

597   zircon is accompanied by enhanced, heterogeneous diffusion of trace elements,

598   including U and Th (Timms et al., 2006; Reddy et al., 2007; Timms et al., 2011,

599   2012), it is important to fully characterise the nature of fractures in lunar zircon. The

600   studied grains neither show evidence of coupled brittle-ductile process for the

601   formation of fractures, nor any measurable variations in the U-Pb ages adjacent to the

602   fractures.

603

604   4.4.4 PDFs and micro-twins

605

606   PDFs and micro-twins are potential pathways for fast diffusion that facilitate

607   alteration, trace element mobility and Pb-loss during impact or subsequent processes.

608   For example, PDFs in shocked terrestrial quartz can be decorated by fluid inclusions

609   that have exsolved during the alteration of diaplectic glass (e.g., Leroux and Doukhan

610   1996, Grieve et al. 1996). Even if complete resetting occurs along PDFs and micro-

611   twins, these features are too narrow (typically <1 μm; Figure 12) to be analysed in situ

612   with ion microprobe. In some terrestrial cases, entire populations of shocked zircon

613   containing PDF and micro-twin shock features preserve the host rock ages with no

614   impact-related Pb-loss (Deutsch and Schärer, 1990; Cavosie et al., 2010; Moser et al.,

615   2011). In other terrestrial examples, zircon with PDFs and granular textures can be

616   highly discordant, and intercept ages from discordant, incompletely reset grains have

been used to infer impact ages (Krogh et al., 1993a,b; Deloule et al., 2001). However, the precise role of PDFs and micro-twins on the U-Pb system in lunar zircon is difficult to evaluate with the currently available techniques.

4.4.4. Dislocation creep

Crystal-plasticity by dislocation creep introduces fast diffusion pathways that can permit partial or complete resetting of the U-Pb system in zircon at modest pressure-temperature conditions in terrestrial rocks (Reddy et al., 2006, 2007; Timms et al., 2006, 2011, 2012; Moser et al., 2009; Figure 15f). Available data suggests that U, Th and Pb are mobilised during deformation along dislocations and low-angle boundaries, with little post-deformation modification (Timms et al., 2006, 2011). Therefore, the timing of crystal-plastic deformation is likely to be preserved where complete resetting of the U-Pb system is achieved. Nemchin et al. (2009) showed that U-Pb resetting can be heterogeneous at the scale of a single zircon grain, and demonstrated a correlation between the extent of U-Pb resetting and local lattice misorientation ('oldest' grain 72215,195; Figure 10b). The resulting mean age of 4333 ± 7 Ma for the most deformed and reset domains is interpreted to represent the age of a lunar impact event. Other studied crystal-plastically deformed lunar zircon grains also record a spread of ages, indicating variable degrees of resetting of the U-Pb system within each grain (Figures 10 and 11). However, the precision of individual analysis and the sub-parallel distribution close to concordia precludes using lower intercept ages to determine an impact age for these grains with confidence. Nevertheless, in situ U-Pb analysis of crystal-plastically deformed zircon could be a useful approach to resolve lunar impact ages in scenarios where the impact occurred significantly later than the initial zircon crystallisation age, as demonstrated for terrestrial impacts (Moser et al., 2009; 2011), and/or if the precision of in situ analytical techniques could be improved.

5. SUMMARY AND CONCLUSIONS

In this report we demonstrate the importance of microstructures in lunar zircons for the interpretation of U-Pb ages and for providing information on the nature

20

of lunar processes. Where zircons have secondary microstructures like amorphisation or recrystallisation overprinting primary structures, it is possible to obtain the age of both primary zircon and secondary impact event within the same grain. Where zircons are individual clasts in the breccia matrix, identification of internal microstructures is vital in targeting areas for ion microprobe analyses and is necessary for interpreting the significance of the U-Pb data. The recognition of zircon internal microstructures has a growing role in providing basic information on lunar processes such as conditions during magmatic crystallisation and impact. Specific conclusions are:

1) Consistent U-Pb ion microprobe ages obtained on isotopically homogenous lunar zircon grains with igneous internal microstructures (e.g., sector and/or oscillatory zoning) can be interpreted as magmatic crystallisation ages (primary ages);

2) Impact ages can be obtained with a high degree of confidence (i) where there is evidence zircon has grown within the impact melt (acicular habits or poikilitic textures) or (ii) where lunar zircons show either recrystallised zones or domains that have lost their crystallinity. In these last cases, multiple analyses of different textural domains in the zircons help to better constrain the precise timing of both magmatic and impact events;

3) Some microstructures, including fractures, planar deformation features and crystal-plastic deformation can facilitate diffusion of Pb, and therefore their identification should prompt a careful examination of the U-Pb ages and their significance;

4) Secondary zircon formed by (i) recrystallisation has a lower U and lower Th/U and (ii) amorphisation has a higher U associated with lower Th/U, than the primary zircon. Mechanisms responsible for these observations are yet to be determined.

21

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852

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FIGURE CAPTIONS

862

863 **Figure 1 – Zircon enclosed into lithic clast**

864 **(a)** 'Pomegranate' zircon (sample 73235,82; Pidgeon et al., 2007) in cross-polarised

865 light and **(b)** in reflected light, the square indicates the location of the detailed images

866 of the grains in Figure 8; **(c)** BSE image of zircon #5 from sample 73235,60 (a.k.a.

867 'cracker' grain). The dashed lines underline the limit of the anorthite clast. zrc =

868 zircon; fsp = feldspar.

869

870 **Figure 2 – Zircon grown in the melt**

871 **Poikilitic zircon: (a)** BSE image of a zircon grain within meteorite sample SaU 169

872 (courtesy of E. Gnos). **Acicular shape: (b)** BSE image of zircon #2 from sample

873 73217,52 (Grange et al., 2009), the zircon is outlined by a dashed line, the other bright

874 needle-like minerals are ilmenite; K-feldspar, shown with an arrow, are the small

875 acicular features within the glass. Same abbreviations as in Figure 1. plg =

876 plagioclase; px = pyroxene; ilm = ilmenite.

877

878

879 **Figure 3 – Zircon clasts in breccia matrix**

880 **(a)** BSE image of the zircon #3 from sample 73235,59 (a.k.a. 'tiger' zircon); the black

881 arrows indicate recrystallised zones (see text for details); **(b)** CL image of the zircon

882 from sample 76295,91 (a.k.a. 'arrowhead' zircon); the bright lines are gold coating

883 filling the fractures of the grain; **(c)** BSE image of the zircon #3 from sample

884 73235,60; **(d)** BSE image of the zircon #1 from sample 14305,93.

885

886 **Figure 4 – Internal structures of magmatic grains**

887 **Oscillatory zoning:** Images of zircon #1 from sample 14083,35 (a.k.a. 'teardrop'

888 zircon) in **(a)** cross-polarised light and **(b)** CL, the insert shows details of the

889 oscillatory zoning, the white arrow shows the sector zoning; images of zircon #1 from

890 sample 14303,49 in **(c)** cross-polarised light and **(d)** CL; **(e)** CL image of a zircon

891 grain extracted from A14 soil. **Sector zoning: (f)** detail of the zircon from 73235,82

892 (a.k.a. 'pomegranate' zircon; Pidgeon et al., 2007) in CL; **(g)** CL image of the zircon

893 #1 from 14306,60; **(h)** CL image of the zircon #2 from 14306,60. **No zoning**

894 **(homogenous grain): (i)** BSE image of the zircon #4 from sample 73235,60 (a.k.a.

895   'hexagon' zircon); **(j)** cumulative misorientation map obtained by EBSD on the

896   73235,60#4. Same abbreviations as in Figure 1 and qtz = quartz; K-fs = K-feldspar;

897   cpx = clinopyroxene; opx = orthopyroxene.

898

899   **Figure 5** – **Ages of magmatic grains**

900   Age of a zircon with oscillatory and sector zoning: the 'teardrop' (sample

901   14083,35#1; Table 2), **(a)** weighted average; **(b)** normal concordia diagram. Age of an

902   homogenous grain: the 'hexagon' (sample 73235,60#4; Grange et al., 2011), **(c)**

903   weighted average; **(d)** normal concordia diagram. Errors are given at the 95% conf.

904   level; boxes and ellipses are drawn at 2σ with Isoplot (Ludwig, 2008).

905

906   **Figure 6 – Zircon with recrystallised zones**

907   **(a)** CL image of the 'tiger' grain (sample 73235,59#3) showing two brightly

908   luminescent recrystallised zones of secondary zircon; **(b)** BSE image of the zircon-

909   baddeleyite aggregate from sample 73217,52 (zircon type-3, Grange et al., 2009), the

910   zircon formed from a reaction between baddeleyite and surrounding Si-rich melt.

911

912   **Figure 7** – **Ages of zircons with primary and secondary parts**

913   **(a)** Concordia diagram of the 'tiger' grain; **(b)** Concordia diagram of the pomegranate

914   grain with matrix vs fragments (after Pidgeon et al., 2007). The ages reported for the

915   primary magmatic (Zrc I) and secondary impact (Zrc II) zircon are weighted average

916    $^{207}Pb/^{206}Pb$ ages with errors at the 95% conf. level; the white ellipses are those not

917   used in the age calculation; ellipses have been drawn at 2σ with Isoplot (Ludwig,

918   2008). Data after Grange et al. (2011).

919

920   **Figure 8 – Loss of crystallinity**

921   Primary fragments **(a)** CL image of a part of the 'pomegranate' zircon (as shown in

922   Figure 1b) showing sector zoning (see scale and legend in (c)), the dashed line

923   indicates the limit between the zircon and the surrounding plagioclase (plg) of the

924   anorthite clast, zrc I correspond to primary zircon "fragments" (see text) and zrc II

925   corresponds to secondary zircon "matrix"; **(b)** SE image of a piece of the

926   'pomegranate' zircon, illustrating the difference in relief between zircon I and II,

927   plagioclase appears in black, the square corresponds to the field of view of (e); **(c)**

928   EBSD map of the same part of the 'pomegranate' grain as shown in (a) and (c), the

similar colour correspond to similar crystalline orientation (the Euler colors are defines by 3 colors channels assigned to 3 Euler angles to describe orientation; Prior et al., 1999); **(d)** cumulative misorientation (in degrees from the red cross) derived from EBSD measurements of the 'propeller' grain, the arrows show parts of the secondary zircon (zrc II) that are not indexed in EBSD and appear in black, the dashed line delimits the zircon; **(e)** SE image of the 'propeller' grain, the top of the image corresponding to the edge of the thin section has been hidden with a black cover to reduce the brightness resulting of the high relief of the edge, the arrows point toward the most obvious differences in relief between zrc I and II.

Figure 9 – **U and Th content vs ages for both pomegranate and 'propeller' grains**
(a) Th/U vs ages for the two parts of the 'pomegranate' zircon; **(b)** Th/U vs U content of the 'pomegranate' grain, the ellipse includes the data with U<40 ppm (see text); **(c)** Th/U vs ages for the 'propeller' grain, the two zrc II analyses have been obtained on the least crystalline parts of the grain; **(d)** Th/U vs U content of the 'propeller' zircon. (data after Table 2 and Pidgeon et al., 2007; Grange et al., 2011).

Figure 10 – **Ductile (crystal-plastic) deformation**
Cumulative misorientation derived from EBSD mapping for **(a)** the 'tiger' zircon (sample 73235,59); **(b)** the 'oldest' zircon (sample 72215,195, Nemchin et al., 2009); **(c)** the 'arrowhead' zircon (sample 76295,195); the insert shows a set of planar features (underlined by the dashed line) that is not seen under an optical microscope (see text for details). For every image, the colours reflect the cumulative crystallographic misorientation in degrees from a reference orientation indicated by the cross.

Figure 11 – **Concordia of the 'propeller' zircon**
The white ellipses represent analyses obtained on the primary zircon (zrc I) while the analyses made on the secondary zircon (zrc II) are shown in grey ellipses. The weighted average of the two analyses of zrc II is 4308 ± 11 Ma (95 % conf. level) and probably represents a maximum age for the impact event. The ages of zrc I overlap this mean and range from 4305 to 4378 Ma (Table 2).

Figure 12 – **Planar features**

Planar features as seen with optical microscope in cross-polarised light: **(a)** image of the 'tiger' zircon (sample 73235,59); **(b)** image of the 'arrowhead' zircon (sample 76295,91); **(c)** image of zircon #62 from sample 14306,60 (U-Pb not analysed). **(d)** Planar features of the 'tiger' zircon (73235,59) evidenced by EBSD pattern quality (band contrast) map. Grain is shaded from poor (black) to good (white) EBSD pattern quality. **(e)** Planar features of zircon #3 from sample 14303,49 imaged by CL.

Figure 13 – Fractures

Cumulative misorientation map derived from EBSD mapping of the 'cracker' zircon (zircon #5 from sample 73235,60); the black lines delimit the domains of similar lattice orientation and correspond to the fractures affecting the grain as seen in Figure 1c. The grain is coloured for cumulative crystallographic misorientation in degrees from a reference orientation indicated by the cross.

Figure 14 – Concordia of fractured zircons

(a) Concordia diagram of the 'cracker' zircon (sample 73235,60 zircon #5) showing the scatter of ages along the concordia curve (Grange et al., 2011); **(b)** Concordia diagram of the zircon #1 from sample 14303,49; analyses #5 and #9 are the most discordant, while analyse #3 is both concordant and the oldest and therefore probably represents the best estimate of the zircon crystallisation age (Table 2); **(c)** BSE image of the zircon #1 from sample 14303,49 showing the location of the three spots evidenced in the concordia diagram shown in (b); the inserts are SE images of the 3 spots, with spots #5 and #9 clearly located across small fractures whereas spot #3 is located in a non-fractured zone of the zircon.

Figure 15 – Zircon U-Pb phenomena cartoon

Schematic representation of the behaviour of U-Pb systems in lunar zircon in relation with observed microstructure. The small ellipses drawn on the grains represent the ion microprobe analyses and refer to the age ellipses reported on the concordia diagrams below. See text for details.

Table(s)

Table 1: description of new zircon grains

Sample Name	Size	Habit	TEXTURE	STRUCTURE					
				Internal Zoning	Recrystal-lisation	Loss of Crystallinity	Ductile deformation	Discrete planar features	Fractures
	(µm)			*as seen in CL*			*in degrees of misorientation*		
APOLLO 17									
73215,122 #6 (propeller)	200x25	anhedral with 3 "arms"	enclosed in plagioclase grains	no	no	at the tips of the arms	22°	no	no
76295,91 #2 (arrowhead)	300x100	anhedral	matrix	sector zoning	no	no	15°	5 sets	no
APOLLO 14									
14083,35 #1 (teardrop)	350x200	subhedral	matrix	sector and oscillatory zoning	no	no	N/A	no	no
14163 #10 (soil sample)	100x50	subhedral (broken)	in the soil	oscillatory zoning	no	no	N/A	no	no
14303,49 #1	1200x350	anhedral	granite clast	oscillatory zoning	no	no	N/A	no	yes
14303,49 #3 (*)	70x70	anhedral	matrix	no	no	no	N/A	1 set	no
14305,93 #1	80x70	anhedral	matrix	sector zoning	no	no	N/A	no	no
14306,60 #1 (simcard)	200x160	subhedral	clast	sector and oscillatory zoning	no	no	N/A	no	no
14306,60 #2	330x150	subhedral	matrix	sector zoning	no	no	N/A	no	no
14306,60 #62 (*)	120x80	anhedral	matrix	no	no	no	N/A	2 sets	no
14321,1613 #1	170x130	anhedral	N/A	faint sector zoning	no	partly metamict	N/A	no	no
14321,1613 #2	100x70	anhedral	N/A	faint sector zoning	no	partly metamict	N/A	no	no

(*) no U-Pb data for this grain

Table 2: U-Pb results for zircon

Samples / Zircon-spots	U (ppm)	Th (ppm)	Th/U	Pb* (ppm)	$\frac{^{206}Pb}{^{204}Pb}$ (b)	$\frac{^{207}Pb}{^{206}Pb}$ total	err % 1σ	$\frac{^{238}U}{^{206}Pb}$ total	err % 1σ	$\frac{^{207}Pb^*}{^{235}U}$	err % 1σ	$\frac{^{206}Pb^*}{^{238}U}$	err % 1σ	ρ (c)	$\frac{^{207}Pb^*}{^{206}Pb^*}$	err % 1σ	$\frac{^{207}Pb^*}{^{206}Pb^*}$ (age Ma)
APOLLO 17																	
73215,122																	
zircon #6 - propeller																	
122-6-1	94	29	0.31	75	29020	0.5178	1.41	1.078	1.75	66.15	2.25	0.927	1.75	0.78	0.5176	1.41	4292 ± 21
122-6-2	64	28	0.43	51	1940	0.5288	0.48	1.074	1.79	66.84	1.87	0.922	1.80	0.96	0.5256	0.50	4315 ± 7
122-6-3	58	26	0.44	48	5920	0.5371	0.47	1.043	1.82	70.66	1.89	0.956	1.82	0.97	0.5360	0.47	4344 ± 7
122-6-4	46	18	0.39	37	1940	0.5325	1.24	1.060	1.86	68.24	2.25	0.935	1.87	0.83	0.5293	1.26	4325 ± 18
122-6-5	52	21	0.41	43	9120	0.5483	1.21	1.025	1.86	73.53	2.22	0.974	1.86	0.84	0.5476	1.21	4375 ± 18
122-6-6	46	18	0.39	38	3840	0.5430	2.93	1.050	1.87	70.75	3.50	0.948	1.87	0.54	0.5415	2.96	4358 ± 43
122-6-7	59	23	0.39	49	7430	0.5495	1.41	1.031	1.83	73.19	2.32	0.967	1.83	0.79	0.5488	1.42	4378 ± 21
122-6-8	72	26	0.37	60	18930	0.5225	0.45	1.021	1.83	70.47	1.89	0.979	1.83	0.97	0.5222	0.45	4305 ± 7
122-6-9	58	22	0.39	47	5750	0.5319	0.46	1.053	1.83	69.31	1.89	0.947	1.83	0.97	0.5308	0.47	4329 ± 7
122-6-10	100	34	0.34	81	5880	0.5247	0.41	1.064	2.07	67.63	2.11	0.937	2.07	0.98	0.5236	0.42	4309 ± 6
122-6-11 (1-1) (a)	65	27	0.42	107	9520	0.5387	0.48	0.995	1.11	74.39	1.30	1.003	1.20	0.93	0.5381	0.48	4349 ± 7
122-6-12 (1-2) (a)	68	28	0.42	110	34320	0.5292	0.34	1.012	1.19	72.04	1.30	0.988	1.20	0.97	0.5290	0.34	4324 ± 5
122-6-13 (1-3) (a)	71	27	0.38	117	6170	0.5315	0.57	0.986	1.12	73.98	1.30	1.011	1.20	0.91	0.5305	0.57	4328 ± 8
76295,91																	
zircon #2 - arrowhead (**)																	
91-1	59	39	0.67	48	13353	0.4715	0.28	1.073	1.70	60.46	1.73	0.931	1.70	0.99	0.4709	0.29	4153 ± 4
91-2	61	38	0.64	48	12092	0.4699	0.28	1.105	1.70	58.49	1.72	0.904	1.70	0.99	0.4693	0.28	4148 ± 4
91-3	55	31	0.57	43	17350	0.4702	0.53	1.094	1.70	59.15	1.78	0.913	1.70	0.95	0.4698	0.53	4149 ± 8
91-4	53	36	0.71	42	109431	0.4710	0.28	1.069	1.71	60.73	1.73	0.935	1.71	0.99	0.4709	0.29	4153 ± 4
91-5	55	32	0.60	43	201943	0.4762	0.29	1.101	1.71	59.63	1.73	0.908	1.71	0.99	0.4762	0.29	4169 ± 4
91-6	43	25	0.60	32	11946	0.4732	0.35	1.144	1.72	56.88	1.76	0.873	1.73	0.98	0.4726	0.35	4158 ± 5
91-7	40	23	0.61	31	29570	0.4614	0.59	1.108	1.73	57.35	1.83	0.902	1.73	0.95	0.4612	0.59	4122 ± 9
91-8	73	43	0.60	51	-	0.4900	0.37	1.219	1.71	55.48	1.75	0.821	1.71	0.98	0.4902	0.37	4212 ± 5
91-9	72	46	0.67	54	16561	0.4859	0.34	1.141	1.73	58.60	1.77	0.875	1.73	0.98	0.4855	0.34	4198 ± 5
91-10	58	33	0.59	41	13184	0.4770	0.41	1.209	1.73	54.28	1.79	0.826	1.74	0.97	0.4765	0.43	4170 ± 6
91-11 (m91.1)	55	33	0.63	42	16401	0.4579	0.59	1.122	2.43	56.14	2.50	0.890	2.43	0.97	0.4575	0.60	4110 ± 9
91-12 (m91.2)	54	30	0.58	44	6527	0.5129	0.58	1.043	2.45	67.50	2.52	0.956	2.45	0.97	0.5120	0.58	4276 ± 9
91-13 (m91.3)	40	23	0.59	31	-	0.5002	0.81	1.100	2.54	62.91	2.67	0.911	2.54	0.95	0.5008	0.81	4243 ± 12
91-14 (m91.4)	52	34	0.68	40	10381	0.4695	0.68	1.130	2.42	57.10	2.52	0.883	2.43	0.96	0.4688	0.68	4146 ± 10
91-15 (m91.5)	60	39	0.66	47	17261	0.4975	0.62	1.091	2.40	62.76	2.48	0.916	2.40	0.97	0.4971	0.62	4233 ± 9
91-16 (m91.6)	40	23	0.59	31	15763	0.4945	1.26	1.094	2.59	62.17	2.88	0.913	2.59	0.90	0.4941	1.27	4224 ± 19
91-17 (m91.7)	55	35	0.65	41	8768	0.4956	1.73	1.152	2.39	59.11	2.95	0.866	2.39	0.81	0.4948	1.74	4226 ± 26
APOLLO 14																	
14083,35																	
zircon #1 - teardrop																	
083-35-101	113	84	0.77	82	161112	0.4358	0.20	1.193	0.69	50.36	0.72	0.838	0.69	0.96	0.4357	0.21	4037 ± 3
083-35-102	63	46	0.76	46	36613	0.4371	0.45	1.163	0.76	51.78	0.91	0.860	0.78	0.86	0.4368	0.47	4041 ± 7
083-35-103	80	69	0.89	58	14408	0.4381	0.25	1.184	0.75	50.91	0.79	0.844	0.75	0.95	0.4375	0.25	4043 ± 4

Table 2: U-Pb results for zircon

Samples / Zircon-spots	U (ppm)	Th (ppm)	Th/U	Pb* (ppm)	$\frac{^{206}Pb}{^{204}Pb}$ (b)	$\frac{^{207}Pb}{^{206}Pb}$ total	err % 1σ	$\frac{^{238}U}{^{206}Pb}$ total	err % 1σ	$\frac{^{207}Pb^*}{^{235}U}$	err % 1σ	$\frac{^{206}Pb^*}{^{238}U}$	err % 1σ	ρ (c)	$\frac{^{207}Pb^*}{^{206}Pb^*}$	err % 1σ	$\frac{^{207}Pb^*}{^{206}Pb^*}$ (age Ma)
083-35-104	52	35	0.70	39	18859	0.4358	0.31	1.154	1.14	51.97	1.18	0.866	1.14	0.97	0.4354	0.31	4036 ± 5
083-35-105	48	37	0.80	36	-	0.4363	0.31	1.140	0.87	52.83	0.93	0.878	0.88	0.94	0.4365	0.32	4040 ± 5
083-35-106	73	68	0.97	53	28230	0.4371	0.27	1.174	1.52	51.27	1.55	0.851	1.52	0.98	0.4368	0.28	4041 ± 4
14163 (soil)																	
163-10	103	73	0.61	162	34070	0.5357	0.47	1.083	1.20	68.19	1.29	0.923	1.20	0.93	0.5357	0.47	4343 ± 7
14303,49																	
zircon #1																	
303-49-101	88	31	0.37	72	6889	0.5157	0.24	1.047	0.96	67.61	0.99	0.953	0.96	0.97	0.5148	0.25	4284 ± 4
303-49-102	112	48	0.44	89	946	0.5286	0.20	1.060	0.91	66.65	0.94	0.926	0.92	0.97	0.5220	0.22	4304 ± 3
303-49-103	128	58	0.47	104	25198	0.5346	0.19	1.053	0.91	69.92	0.93	0.949	0.91	0.98	0.5343	0.19	4339 ± 3
303-49-104	70	25	0.37	57	1710	0.5303	0.25	1.049	0.98	68.53	1.03	0.944	0.99	0.97	0.5267	0.27	4318 ± 4
303-49-105	70	25	0.37	53	851	0.5033	0.38	1.112	0.98	60.16	1.08	0.881	1.00	0.92	0.4954	0.41	4228 ± 6
303-49-106	61	21	0.35	51	3126	0.5312	0.27	1.018	1.00	71.25	1.04	0.976	1.01	0.96	0.5292	0.28	4325 ± 4
303-49-107	81	30	0.39	66	6734	0.5289	0.23	1.051	0.96	69.10	0.99	0.949	0.96	0.97	0.5279	0.24	4321 ± 4
303-49-108	65	24	0.38	53	8079	0.5298	0.27	1.062	0.99	68.52	1.03	0.939	0.99	0.97	0.5291	0.27	4324 ± 4
303-49-109	82	33	0.42	63	42628	0.5063	0.24	1.111	1.01	62.80	1.05	0.900	1.02	0.97	0.5062	0.26	4259 ± 4
14305,93																	
zircon #1																	
305-93-101	77	23	0.31	60	21498	0.4862	1.44	1.103	0.80	60.67	1.65	0.906	0.80	0.48	0.4858	1.44	4199 ± 21
305-93-102	68	27	0.41	52	4504	0.4747	0.97	1.120	1.14	58.02	1.51	0.889	1.14	0.76	0.4731	0.98	4159 ± 15
305-93-103	166	52	0.32	129	387621	0.4916	1.23	1.105	0.68	61.34	1.41	0.905	0.68	0.48	0.4916	1.23	4216 ± 18
14306,60																	
zircon #1 - simcard																	
306-60-101	51	33	0.67	40	10187	0.4939	0.31	1.099	0.91	61.76	0.97	0.908	0.91	0.94	0.4932	0.32	4221 ± 5
306-60-102	30	16	0.57	23	-	0.4880	0.40	1.081	1.61	62.28	1.66	0.926	1.61	0.97	0.4881	0.40	4206 ± 6
306-60-103	19	6	0.35	16	62337	0.4887	0.51	1.058	1.32	63.64	1.41	0.945	1.32	0.93	0.4886	0.51	4207 ± 8
306-60-104	23	9	0.42	19	233	0.5221	0.82	0.972	1.18	64.55	1.65	0.950	1.29	0.78	0.4929	1.03	4220 ± 15
306-60-105	20	7	0.34	17	-	0.4920	0.50	1.056	1.32	64.23	1.44	0.947	1.34	0.93	0.4920	0.54	4217 ± 8
306-60-106	37	17	0.49	30	-	0.4855	0.38	1.042	1.01	64.27	1.10	0.960	1.02	0.93	0.4855	0.40	4198 ± 6
zircon #2																	
306-60-201	13	4	0.35	10	4979	0.4893	1.16	1.096	2.59	61.18	2.86	0.909	2.60	0.91	0.4880	1.18	4205 ± 17
306-60-202	13	4	0.35	10	814	0.4973	0.66	1.110	1.69	59.40	1.93	0.881	1.76	0.91	0.4889	0.79	4208 ± 12
306-60-203	51	32	0.66	41	13581	0.4894	0.31	1.063	0.92	63.36	0.99	0.940	0.94	0.94	0.4889	0.34	4208 ± 5
14321,1613																	
zircon #1																	
321-zrc1-1	352	192	0.55	473	32874	0.4171	0.26	1.160	1.38	49.59	1.40	0.862	1.38	0.98	0.4171	0.26	3972 ± 4
321-zrc1-2	724	261	0.37	959	92183	0.4255	0.18	1.148	1.36	51.11	1.38	0.871	1.36	0.99	0.4255	0.18	4002 ± 3
321-zrc1-3	569	196	0.35	751	323137	0.4227	0.23	1.145	1.39	50.89	1.41	0.873	1.39	0.99	0.4227	0.23	3992 ± 3

Table 2: U-Pb results for zircon

Samples Zircon-spots	U (ppm)	Th (ppm)	Th/U	Pb* (ppm)	$\frac{^{206}Pb}{^{204}Pb}$ (b)	$\frac{^{207}Pb}{^{206}Pb}$ total	err % 1σ	$\frac{^{238}U}{^{206}Pb}$ total	err % 1σ	$\frac{^{207}Pb^*}{^{235}U}$	err % 1σ	$\frac{^{206}Pb^*}{^{238}U}$	err % 1σ	ρ (c)	$\frac{^{207}Pb^*}{^{206}Pb^*}$	err % 1σ	$\frac{^{207}Pb^*}{^{206}Pb^*}$ (age Ma)
321-zrc1-4	919	354	0.38	1202	101799	0.4226	0.23	1.161	1.36	50.17	1.38	0.861	1.36	0.99	0.4226	0.23	3992 ± 3
321-zrc1-5	625	217	0.35	827	76289	0.4242	0.29	1.141	1.35	51.27	1.38	0.877	1.35	0.98	0.4242	0.29	3997 ± 4
321-zrc1-6	518	167	0.33	703	43826	0.4261	0.29	1.111	1.37	52.91	1.40	0.900	1.37	0.98	0.4261	0.29	4004 ± 4
zircon #2																	
321-zrc2-1	333	183	0.51	415	25252	0.4151	0.27	1.246	1.30	45.92	1.32	0.802	1.30	0.98	0.4151	0.27	3965 ± 4
321-zrc2-2	326	178	0.51	407	63867	0.4135	0.34	1.241	1.30	45.93	1.34	0.806	1.30	0.97	0.4135	0.34	3959 ± 5
321-zrc2-3	365	205	0.50	457	70770	0.4221	0.32	1.243	1.30	46.84	1.34	0.805	1.30	0.97	0.4221	0.32	3990 ± 5
321-zrc2-4	986	542	0.48	1230	85604	0.4238	0.16	1.248	1.32	46.83	1.33	0.802	1.32	0.99	0.4238	0.16	3996 ± 2

* indicates radiogenic Pb, i.e. corrected from common Pb (after Stacey and Kramers, 1975)

** Data on arrowhead zircon have been obtained in 2003 (spot name starting with m) and 2009

(a) data published in Nemchin et al. (2008) as the name shown in bracket

(b) (-) indicate that the amount of ^{204}Pb is too small to give a significant ratio

(c) error correlation bewteen ($^{235}U/^{207}Pb^*$) and ($^{238}U/^{206}Pb^*$)

Errors on individual age are given at 1σ

(a) Anorthite clast
zrc
73235,82
pomegranate'
200 μm

(b)
200 μm

(c)
matrix
Felsic clast
SiO₂
zrc
zrc
fsp
73235,60 zircon #5 ('cracker')
100 μm

Figure 1

(a) SaU169

zrc

20 µm

(b) K-fs

px

zrc

ilm

glass

73217,52

plg

100 µm

Figure 2

Big grains

(a) matrix, zrc, zrc II, 100 μm, 73235,59 zircon #3 ('tiger')

(b) zrc, matrix, 100 μm, 76295,91 ('arrow's head')

Small grains

(c) matrix, 73235,60 zircon #3, 50 μm

(d) matrix, 14305,93 zircon #1, 50 μm
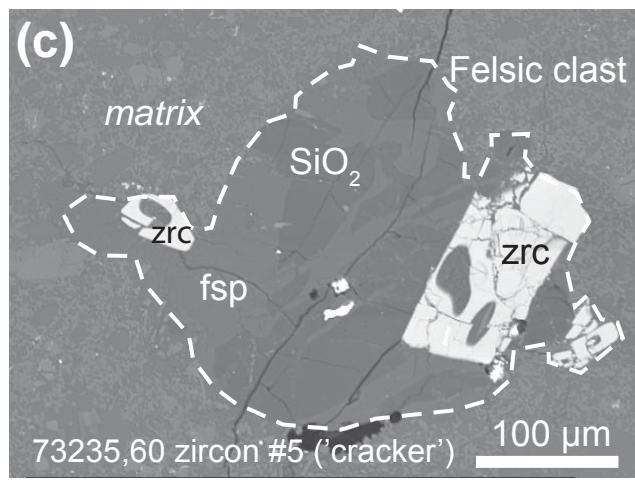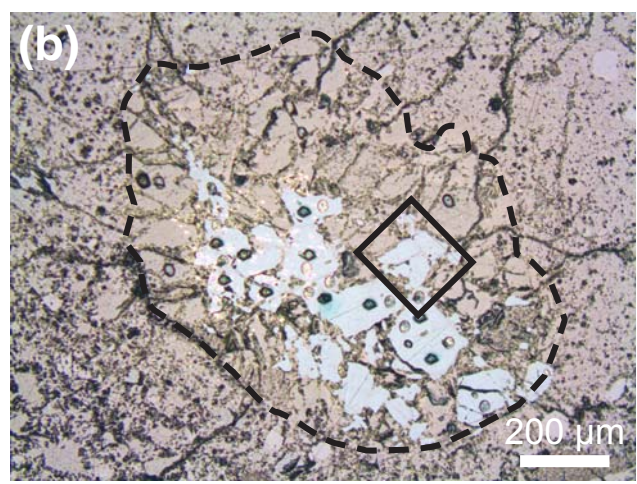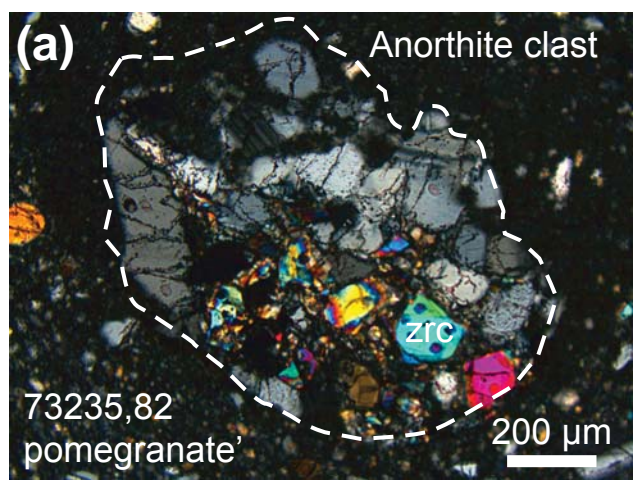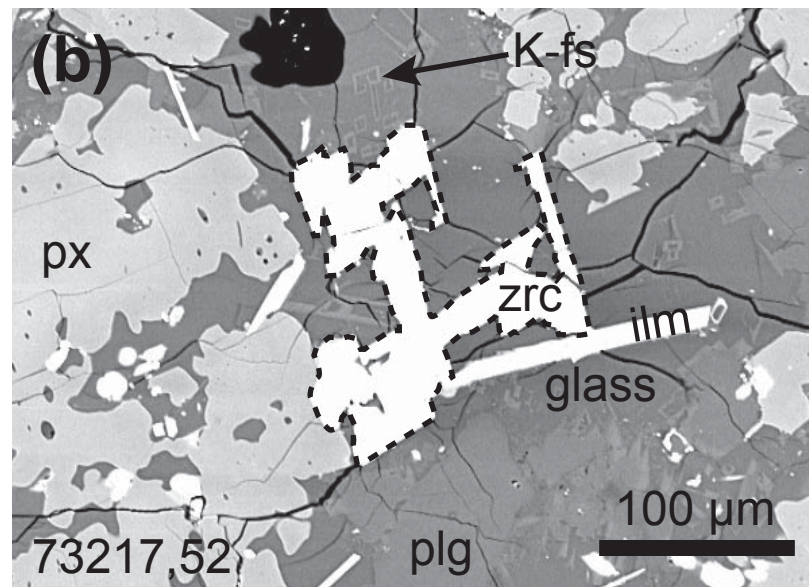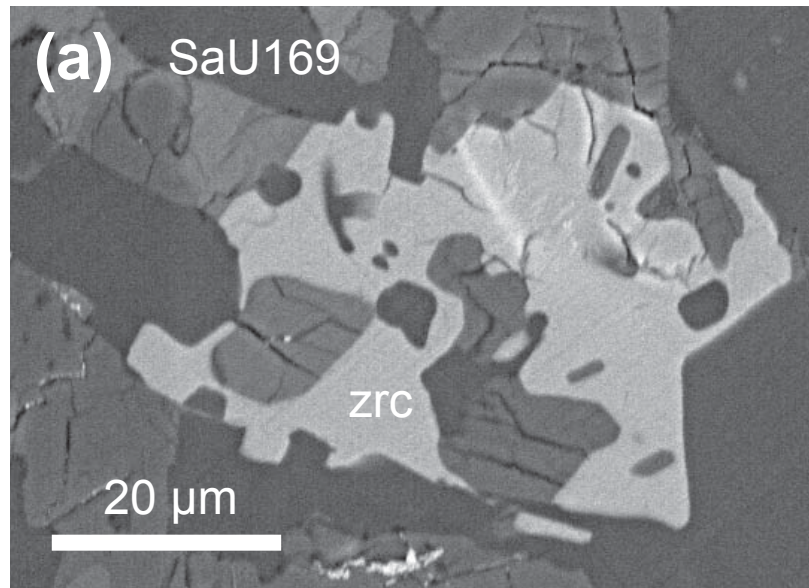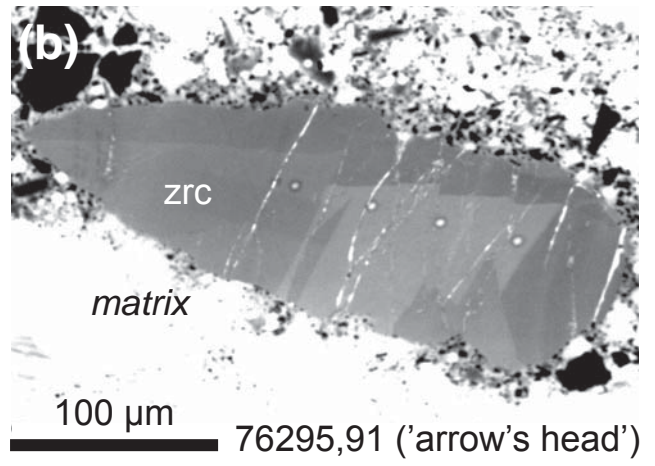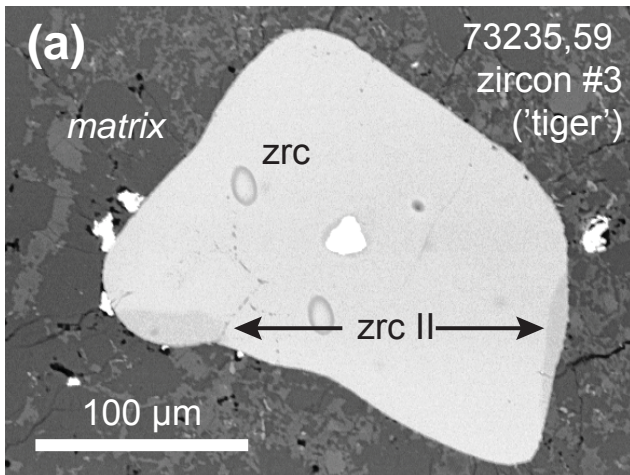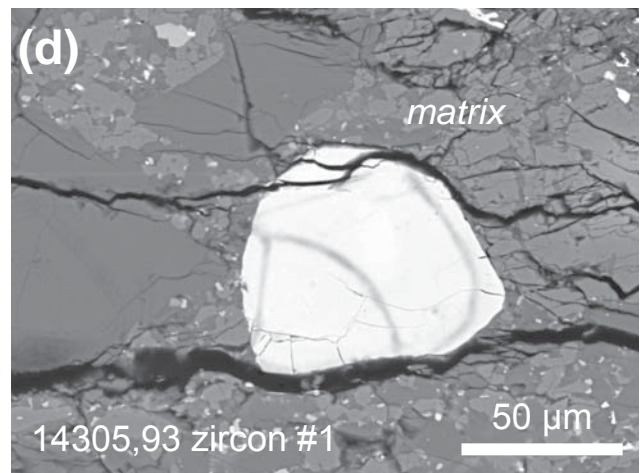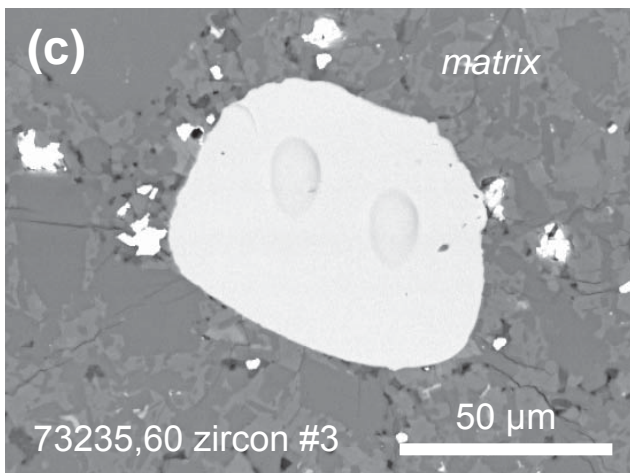
Figure 3

Oscillatory Zoning

(a) 14083,35 zircon #1 (teardrop)

(b) 100 μm

(c) 14303,49 zircon #1

(d) 200 μm

(e) 14163 (soil)   20 μm

Sector Zoning

(f) 73235,82 (pomegranate)   100 μm

(g) 14306,60 zircon #1
plg. cpx matrix plg qtz K-fs cpx +opx   100 μm

(h) 14306,60 zircon #2   matrix   100 μm
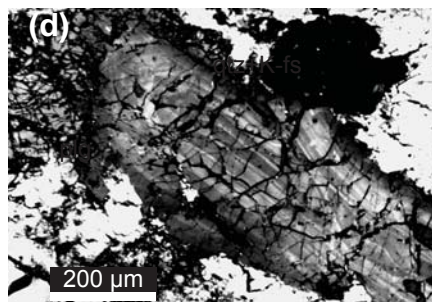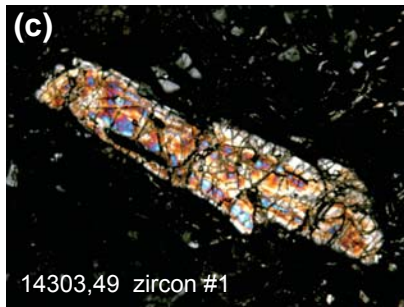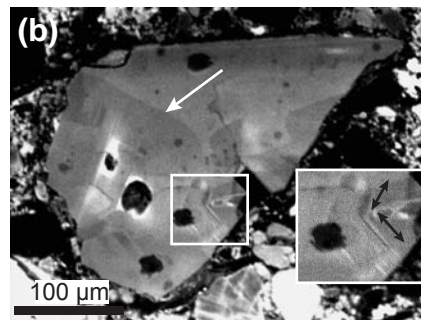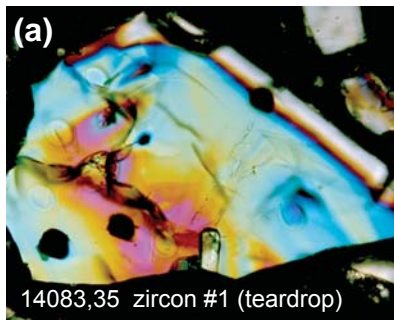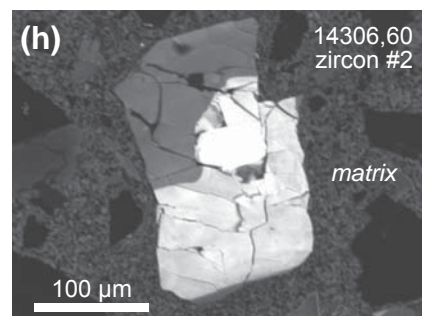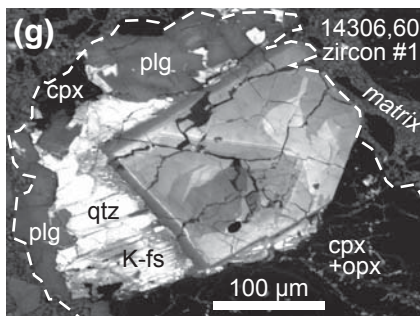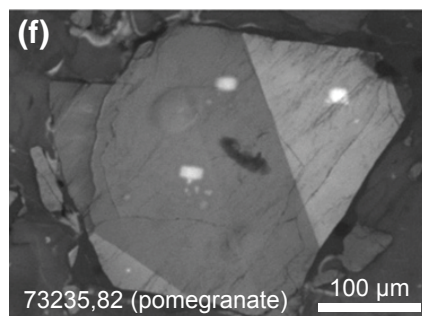
No zoning (homogenous grain)

(i) 73235,60 zircon #4   50 μm

(j) 10°   0   40 μm

Figure 4
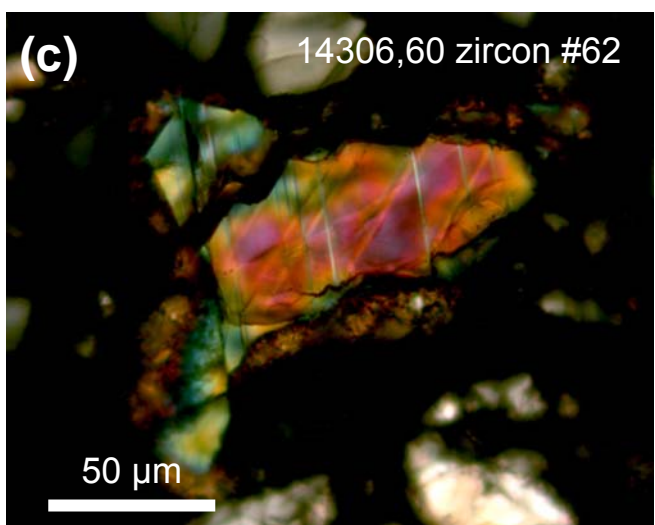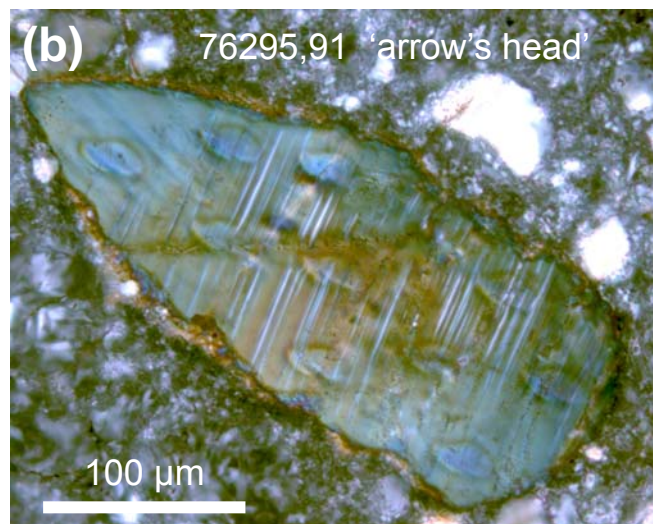
Figure 05

(a) 73235,59 'tiger'
matrix
zrc I
zrc II
100 μm

(b) 73217,52 zircon #3
glass
zrc
bdl
50 μm
matrix

Figure 6

Figure 7

(a) zrc II · zrc I · plg

(b) 73235,82 'pomegranate' · zrc II · zrc I · plg · 50 μm

(c) zrc II · zrc I · zrc I · plg

Zircon orientation
0 *Euler 1* 180
0 *Euler 2* 180
0 *Euler 3* 180

(d) 73215,122 zircon #6 'propeller' · edge of thin section · plg · zrc II · 50 μm
0 — 24°

(e) 73215,122 zircon #6 'propeller' · zrc I · plg · matrix · zrc II · 50 μm

Figure 8

Figure 9

(a) 73235,59 'tiger'

10°

0

100 µm

(b)

12°

0

'oldest'
72215,195

200 µm

(c) 76295,91 'arrowhead'

0   15°

100 µm

Figure 10

Figure 11

(a) 73235,59 'tiger'

100 µm

(b) 76295,91 'arrow's head'

100 µm

(c) 14306,60 zircon #62

50 µm

(d) 73235,59 'tiger'

high

low

100 µm

(e)

14303,49 zircon #3

50 µm

Figure 12

Figure 13

Figure 14

Figure 15