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1 **Bridging the shocked monazite gap- Deformation microstructures in natural**
2 **and laser shock-loaded samples.**

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14

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16 Microscope – Vredefort impact

17

18 **ABSTRACT**

19 Impact-related damage in minerals and rocks provides key evidence to identify impact structures, and
20 deformation of U-Th-minerals in target rocks, such as monazite, makes possible precise dating and
21 determination of pressure-temperature conditions for impact events. Here a laser-driven shock
22 experiment using a high-energy laser pulse of ns-order duration was carried out on a natural monazite
23 crystal to compare experimentally produced shock-deformation microstructures with those observed
24 in naturally shocked monazite. Deformation microstructures from regions that may have experienced
25 up to ~50 GPa and 1000°C were characterized using Raman spectroscopy and transmission electron

26 microscopy. Experimental results were compared with nanoscale observations of deformation
27 microstructures found in naturally shocked monazite from the Vredefort impact structure (South
28 Africa). Raman-band broadening observed between unshocked and shocked monazite, responsible
29 for a variation of $\sim 3 \text{ cm}^{-1}$ in the FWHM, is interpreted to result from the competition between shock-
30 induced distortion of the lattice, and post-shock annealing. At nanoscale, three main plastic
31 deformation structures were found in both naturally and experimentally shocked monazite:
32 deformation twins, mosaïcism, and deformation bands. The element Ca is enriched along host-twin
33 boundaries, which further confirms that the laser shock loading experiment produced both
34 comparable styles of crystal-plastic deformation, and also localized element mobility, as that found in
35 natural shock-deformed monazite. Deformation twins form in the experiment were only along the
36 (001) plane, an orientation which is not considered diagnostic of shock deformation. However, both
37 mosaïcism and deformation, expressed in SAED patterns as streaking of spots, and the presence of
38 extra spots (more or less pronounced), are interpreted as unambiguous nano-scale signatures of shock
39 metamorphism in monazite. Experimentally calibrated deformation features, such as those
40 documented here at TEM-scale, provide new tools for identifying evidence of shock deformation in
41 natural samples.

42

43 **1. INTRODUCTION**

44 The formation of meteorite impact craters is a ubiquitous process on planetary surfaces
45 (*French and Koeberl, 2010*). On Earth, few impact craters are accurately and precisely dated due to
46 the lack of suitable age geochronometers (*Schmieder and Kring, 2020*), which makes it difficult to link
47 meteorite impacts to significant events in the geological record (*Jourdan et al., 2012*). As a result,
48 fundamental questions regarding possible links between impact events, changes in the geosphere and
49 biosphere, and the origin of life, all of which rely on the acquisition of both accurate impact conditions
50 and timing, remain debated (*Moser et al., 2019*).

51 Impact-related damage in minerals and rocks provides key evidence to identify impact
52 structures (*French and Koeberl, 2010*). Shock deformation microstructures have been intensively
53 studied in some minerals, especially quartz, down to the nanometer scale with transmission electron
54 microscopy (TEM), and include formation of dislocations, planar deformation features (PDF),
55 mosaïcism (i.e. a mosaic texture with small domains of crystalline blocks slightly misoriented to each
56 other), twins, high-pressure phases, decomposition, recrystallization, and melting (*e.g., Leroux et al.,*
57 *1994*). Their formation initially depends on pressure conditions, often above 10 GPa, are attained
58 within nanoseconds to seconds (*Langenhorst and Deutsch, 2012*), and can be modified by subsequent
59 heating. Over the past decade, with the advent of high-spatial resolution techniques, resolving
60 deformation of U-Th-minerals in target rocks (e.g. zircon, monazite, apatite, xenotime, titanite) makes
61 possible precise dating and determination of pressure-temperature conditions (P,T) for impact events.
62 Zircon is the most widely studied geochronometer for shock deformation and forms various shock
63 microstructures (*e.g. Wittmann et al., 2006; Moser et al., 2011; Timms et al. 2017*). In contrast,
64 shocked monazite is less studied; neoblasts (*Erickson et al., 2017; Erickson et al., 2020*), deformation
65 twins (*Fougerouse et al., 2021a*), and a high-pressure phase (*Erickson et al., 2019*) can form during
66 shock metamorphism, all of which offer the potential for dating impacts. One important drawback of
67 zircon concerns self-irradiation damage that can lead to complete amorphization (*Ewing et al., 2003*).
68 This has consequences both on the disturbance of the U-Pb geochronological systems (e.g. *Seydoux-*
69 *Guillaume et al., 2015; Peterman et al., 2016*), and also on formation and retention of deformation
70 microstructures. For example, radiation damage can inhibit the formation of the high-pressure phase
71 reidite (*Lang et al., 2008; Timms et al., 2018*), and obliterate shock microstructures at atom scale over
72 time (*Reimold et al., 2002*). In contrast, despite a much higher radionuclide incorporation rate,
73 monazite is much more resistant to irradiation. Monazite has the ability to remain crystalline over
74 geological time due to self-annealing of radiation damage (*Seydoux-Guillaume et al. 2004; 2018*), and
75 will therefore preserve more or less the same structural state upon impact. In this regard, reliable
76 impact conditions may be more readily extracted from shock-features in monazite.

77 Published studies show that evidence of impact age resetting in U-Pb geochronometers can
78 be highly heterogeneous due to complex microstructures at the grain scale (e.g. *Cavosie et al., 2018*
79 *and 2021*). Shock-deformation in monazite has previously been described (*Schärer and Deutsch,*
80 *1990*), however its microstructure has only been systematically described at the micrometer scale
81 recently using electron backscatter diffraction (EBSD) (*Erickson et al., 2016, 2017, 2020; Cavosie et al.,*
82 *2018*). No nanometer-scale investigations using TEM to describe shock deformation features in
83 monazite have been conducted previously.

84 Experimental approaches have been applied to address formation of shock deformation
85 microstructures in monazite (*Deutsch and Schärer, 1990; Huang et al., 2010; Lacomba-Perales et al.,*
86 *2010; Seydoux-Guillaume et al., 2010; D'Abzac et al., 2012; Heuser et al., 2018*), and propose the
87 existence of high-pressure monazite polymorphs which have thus far not been discovered in nature
88 (*Erickson et al., 2019*). Laser-driven experiments have previously demonstrated the ability to simulate
89 conditions of impact events (e.g. in olivine; *Langenhorst et al., 1999*). Here we compare nanoscale
90 deformation structures formed in shocked monazite from the Vredefort impact structure in South
91 Africa (*Cavosie et al., 2018*) with experimentally shocked monazite, in order to identify which features
92 can be used as shock indicators, and also enhance the validity of laser-driven shock-experiments.

93

94 **2. MATERIALS AND METHODS**

95 *2.1. Starting material*

96 A piece of a centimeter-sized single monazite crystal from Manangotry (Madagascar) was cut
97 in a random orientation, embedded in epoxy and polished (Fig. 1). The sample was previously
98 structurally characterized at the nanoscale by TEM (*Seydoux-Guillaume et al., 2004; Grand'Homme et*
99 *al., 2018*), particularly with regards to structural defects induced by radiation damage; no twins were
100 observed in previous studies. This monazite crystal is also chemically homogenous, with negligible
101 inclusions and porosity, and has a well-resolved age (555 ± 2 Ma, ID-TIMS; *Paquette and Tiepolo,*
102 *2007*).

103 A shocked monazite grain from the Rietputs Formation in South Africa (Sample Sec-03D, grain
104 9) was also investigated to evaluate if laser-driven shock experiments are able to reproduce impact
105 damage found in nature. This monazite is a detrital grain that eroded from shocked bedrock at the
106 Vredefort impact structure, and was transported ~500 km downstream in the Vaal River (*Cavosie et*
107 *al., 2018*). It was previously characterized with BSE and EBSD, and shown to contain an anomalously
108 high density of deformation twins, as well as localized areas that have recrystallized into neoblastic
109 domains (*Cavosie et al., 2018*). The original host rock is unknown, however, it is assumed that the
110 detrital shocked monazite originated from between the 20 and 30 GPa isobars at the Vredefort impact
111 structure, as it is not fully neoblastic (e.g., *Erickson et al., 2017*), and is similar to other detrital shocked
112 monazite grains that host shock-twinned zircon inclusions (*Erickson et al., 2016*).

113

114 2.2. Laser-driven shock loading

115 The laser shock experiment was carried out at the “nano2000” facility of the *Laboratoire pour*
116 *l’Utilisation des Lasers Intenses* (LULI, UMR CNRS 7605, Ecole Polytechnique, Palaiseau, France). The
117 target consisted of a 20 µm-thick Al foil glued on top of the monazite crystal (Fig. 1a). A high-power
118 laser pulse of 1.06 µm-wavelength, 5 ns-duration, 765 J-energy, was focused onto a 3.2 mm-diameter
119 spot on the target surface. The resulting laser intensity was about 1.9×10^{12} W/cm². A thin absorbing
120 layer of Al (~µm-order) is ablated into a plasma cloud, whose expansion drives a short compressive
121 pulse. The amplitude (50 GPa) of this pressure pulse and its temporal shape (about 6 ns-duration at
122 half maximum) were inferred from a simulation of laser-matter interaction, using the measured profile
123 of laser intensity as an input boundary condition. Shock pressure transmitted to the monazite sample
124 across the Al-monazite interface was estimated by accounting for the impedance mismatch between
125 both materials, using data reported for CePO₄ monazite (*Feng et al., 2013; Du et al. 2009*). Peak loading
126 pressure applied on the monazite crystal was thus calculated at 56.7 GPa. The post-shock temperature
127 computed in Al is about 1300 K, which agrees with calculated thermodynamic data for a 50 GPa mean

128 shock pressure (*Kinslow, 1970*). The subsequent post-release temperature in Al after pressure
129 unloading is about 700 K. In the monazite crystal however, shock-induced heating cannot be assessed
130 without an equation of state for this material, but it should be similar in a natural impact event for an
131 analogous loading pressure, as temperature only depends on shock pressure. Nevertheless, the much
132 shorter duration of both pressure and temperature under laser-driven compression may result in
133 differences in shock-induced transformations, due to (i) possible kinetic inhibition of time-consuming
134 processes (e.g. diffusion, conduction), and (ii) faster pressure decay with propagation distance which
135 would strongly restrict the size of the shock-heated region and possibly hinder neighbourhood effects
136 within heterogeneous samples. One goal of this study is thus to address both relevance and limitations
137 of the impact/laser analog.

138 2.3. Analytical methods.

139 Raman spectra were collected directly on the shocked surface of the monazite crystal in clean
140 areas (Fig. 1d-g) with a Horiba micro-Raman spectrometer LabRam HR800 evolution. Groups of 10
141 spectra were collected respectively on starting material, shocked samples C1 and C2, with two
142 accumulations of 10 s exposure (Fig. 2a). Raman peaks were fitted with Gauss-Lorentz spectral models
143 in the spectral range from 800 to 1200 cm^{-1} , with the Matlab application tool PeakFit to extract the
144 position and full width at half maximum (FWHM) of the ν_1 peak (Fig. 2b, Table S1). FWHM values are
145 corrected for the apparatus function of the Raman instrument (*Nasdala et al., 2001*).

146 The TEM foils were prepared using a Thermo Fisher Scientific FEI 125 Helios Nanolab 600i
147 focused-ion beam scanning electron microscope (FIB/SEM) hosted by MANUTECH USD platform, at
148 Hubert Curien laboratory, Saint-Etienne (France). Nanoscale characterization was performed with a
149 Cs-corrected TEM (NeoARM200F Cold FEG) at 200 kV, operated by the CLYM and hosted within the
150 Hubert Curien Laboratory, Saint-Etienne (France). A Gaussian low-pass filter for noise reduction was
151 applied to high-magnification STEM images (Figures 5d-f, 7a-c and 8g and i).

152

153 For further details see Supplementary Materials.

154

155 **3. RESULTS**

156 *3.1. Optical and SEM observations*

157 After the shock experiment the Al-foil was removed but some glue remained on the surface
158 (dark areas in Figure 1d and also SEM images in figures 1f and g, rough zones on the surface). Only
159 domains free of glue were targeted for analysis (Raman and TEM), i.e. zones C1 and C2. In optical light
160 the central zone is a rounded area where the shock was most intense (Fig. 1b-d); it is approximately 3
161 mm in diameter, which matches the 3.2 mm-diameter of the irradiated spot in the Al foil (Fig. 1b).
162 Numerous planar fractures in monazite are visible in this area, with at least two directions nearly
163 perpendicular to each other (arrows in Fig. 1 c-g). Some of the planar microstructures appear open
164 (Fig. 1c and g), and thus may be tensile fractures.

165

166 *3.2. Raman observations*

167 Raman measurements were performed on both unshocked areas of the monazite crystal and
168 in the central shocked zone (C1 and C2; Fig. 1). The first result is that only monazite was identified; no
169 peaks associated with other phases were present. As described in *Heuser et al. (2018)*, bands between
170 900 and 1100 cm^{-1} can be assigned to antisymmetric (ν_3) and symmetric (ν_1) stretching modes,
171 respectively, and peaks between 400 and 700 cm^{-1} to antisymmetric (ν_4) and symmetric (ν_2) bending
172 modes of the PO_4 group of monazite. Differences between the three areas are apparent only in the
173 position and shape of the peaks. As previously shown (*Seydoux-Guillaume et al., 2002; Ruschel et al.,*
174 *2012*) the FWHM of the ν_1 Raman band is suitable to estimate the degree of short-range order of
175 monazite (Fig. 2b). Mean values for the position vary from 969.40 cm^{-1} for unshocked monazite to
176 968.81 and 968.34 cm^{-1} for shocked monazite (C1 and C2 zones respectively), and for FWHM from
177 18.34 (unshocked monazite) to 21.52 and 21.45 cm^{-1} (C1 and C2 respectively). The positions and
178 FWHM are more variable in shocked areas (968.62-968.93/21.20-21.94 cm^{-1} for C1, 968.13-

179 968.57/21.09-21.93 cm^{-1} for C2) than unshocked areas (969.30-969.51/18.10-18.73 cm^{-1}) of the
180 crystal, indicating a higher local variability of microstructure.

181

182 3.3. Transmission Electron Microscopy

183 Nanoscale characterization was conducted on two TEM foils extracted from the central part
184 of the shocked monazite sample: one in area C1 (FIB1), and one in area C2 (FIB5), a little further from
185 the center of the shocked zone (Fig. 1). Both foils allow observations to be made over approximately
186 8 μm of depth, from the surface to the interior of the monazite crystal. In the following sections (3.3.1
187 and 3.3.2) different deformation structures induced by laser-driven shock loading are described. Two
188 TEM foils were also prepared from the naturally shocked monazite grain from Vredefort for
189 comparison (Fig. 8), and deformation structures are described in section 3.3.3.

190 Each monazite sample reveals typical contrasts in bright-field (BF) TEM mode due to radiation
191 damage (*Seydoux-Guillaume et al., 2004*). The starting (i.e. unshocked) monazite sample as well shows
192 typical mottled diffraction contrasts due to the presence of a distorted lattice (*Seydoux-Guillaume et*
193 *al., 2002*). The diffraction contrasts are a consequence of the competition between defect formation
194 and annealing of radiation damage (*Seydoux-Guillaume et al., 2018*). However, the distortion is not
195 sufficient to induce visible stretching of diffraction spots (see *Seydoux-Guillaume et al., 2004*), and
196 therefore implies an absence of mosaïcism.

197

198 3.3.1. TEM foil C2 (FIB5) – Figures 3 to 5

199 In this sample two kinds of deformation features were observed, depending on depth of
200 observation within the foil. From the surface down to approximately 4 μm (Fig. 3a), the sample
201 revealed a high density of 10-20 nm domains that are slightly misoriented with respect to each other,
202 resulting in mottled diffraction contrasts in BF-TEM (Fig. 3a-b). Selected area electron diffraction
203 patterns (SAED) show a slight stretching of diffraction spots (Fig. 3c and e), indicative of a small
204 misorientation of domains (<2 degrees). When the crystal is oriented parallel to the [100] zone axis,

205 the most intense stretching is seen along the (012) plane. Additional diffuse spots are also visible
206 (arrows in Fig. 3e) and are measured at a distance of 3.16 Å, compatible with the monazite structure.
207 At higher magnification moiré fringes (arrows in Fig. 3d) are observed and provide further evidence of
208 misorientation of the nano-domains. From 4 µm depth to the bottom of the foil (Fig. 4a), the structure
209 is dominated by bands subparallel to the shock-loaded surface (Fig. 4b). The bands are 300 ± 50 nm
210 long and about 50 nm wide, are relatively regular, and form a wavy pattern within the sample (Fig. 4
211 c-d). Contrast within the bands is homogeneous, with a grey color, and almost no Bragg contrast,
212 consistent with a low crystallinity, almost glassy structure. An SAED pattern parallel to the [100] zone
213 axis that overlaps a deformation band and the adjacent monazite confirms the presence of a diffuse
214 ring, characteristic of amorphous material that is superimposed on the monazite diffraction signature.
215 The same SAED pattern also revealed the appearance of additional spots, some close to the principal
216 spots from the [100] zone axis (Fig. 4e). The most visible additional spots in the SAED pattern, with the
217 shortest distance, are indicated by arrows in Figure 4e, and correspond to a d_{hkl} of 3.58 Å, close to the
218 distance measured in the part of foil closer to the polished surface (Fig. 3e). Additional spots at 2.59,
219 2.17, 2.01, 1.80 Å are all compatible with the monazite lattice. The same region was observed using
220 scanning TEM (STEM) with an annular dark field (ADF) detector (Fig. 5). In this mode, Bragg contrasts
221 are strongly reduced and contrast arises from atomic number and density. The bands appear darker
222 (Fig. 5a-e) due to the lower density of the glassy material within the deformation band (Fig. 5a-b). At
223 very high magnification (Fig. 5e-f) the atomic arrangement within the monazite structure is revealed.
224 In ADF mode, only the heaviest atoms are visible (i.e. rare earth elements like Ce in CePO₄ monazite
225 structure); in Figure 5f the pattern matches the arrangement of Ce atoms in monazite along the [100]
226 direction. High resolution STEM imaging and associated Fast Fourier Transform (FFT; Fig. 5c-e) show
227 that the deformation bands are not completely amorphous, and contain highly disoriented nano-
228 crystals of monazite; in Figures 5d and 5e some fringes can be observed within these bands. FFT of
229 different areas in Figure 5c show the strong disorientation from the [100] direction (FFT1) depending
230 on position in the band (compare FFT2 and 3 in Fig. 5c). In FFT3 the area is strongly disoriented with

231 only a faint (0-11) reflection visible. Extra spots observed at 3.58 Å in SAED in TEM mode (Fig. 4e) are
232 also visible (arrows in FFT2), and appear when crossing the band (see arrows in FFT2).

233

234 3.3.2. TEM foil C1 (FIB1) – Figures 6 and 7 (and Supplementary Data S2; Figures S7)

235 The TEM foil in area C1 displays twins over the entire foil. In BF-TEM many twin boundaries
236 can be observed at low resolution (Fig. 6a), all parallel to each other. The twins are relatively thick
237 (280 nm to 1.4 µm), with only one direction oriented about 70° from the surface plane. One fracture
238 propagated from the surface into the crystal parallel to the twin boundaries. The twins are oriented
239 parallel to (001), as indicated in the SAED pattern (Fig. 6g) collected across two twin boundaries shown
240 in Figure 6d. Tilting the sample highlighted the twin boundaries and the mottled Bragg diffraction
241 contrasts resulting from radiation damage (Fig. 6b and c). The contrasts are not as pronounced as
242 those in area C2 (Fig. 3 and 4), which agrees with the absence of streaking of SAED spots or the
243 presence of extra spots (Fig. 6e and g). These contrasts are similar to those found in the same
244 unshocked monazite crystal (see Fig. 3c in *Seydoux-Guillaume et al., 2004* and figures 7 to 10 in
245 *Grand'homme et al., 2018*). One twin was imaged in dark field mode (Fig. 6f) collected with the (11-1)
246 plane (Fig. 6g). Further observations in STEM mode (Fig. 7) were made with the monazite crystal
247 oriented along the [110] zone axis, as shown in the SAED pattern in Figure 6e (area shown in Fig. 6a).
248 One twin boundary is observed at high resolution in ADF (Fig. 7a) and annular BF (ABF) (Fig. 7a) mode.
249 In ADF only heavy atoms are visible whereas in ABF lighter atoms can be observed (mostly P). A high
250 magnification image in ADF mode illustrates the match between the arrangement of the Ce atoms
251 along the [110] direction (Fig. 7c) with the expected crystalline pattern. Energy dispersive
252 spectrometry (EDS) chemical mapping across the twin boundary revealed an enrichment in Ca within
253 the twin boundary (Fig. 7d and Supplementary data S7a); in contrast no enrichment nor depletion of
254 Pb was observed within the boundary (Figure S7b in Supplementary data).

255

256 3.3.3. TEM foils of naturally shocked Vredefort monazite – Figure 8 (and Supplementary Data S2;
257 Figures S8)

258 Two FIB-foils were prepared from different areas of Vredefort monazite Sec-03D, grain 9
259 (Cavosie *et al.*, 2018). One is located across deformation twins; the other is located a few micrometers
260 away from the first one, outside the twin, and did not cross a twin boundary (Figure S8a in
261 Supplementary data). Three kinds of deformation features were observed in the Vredefort grain: the
262 first TEM-foil contains deformation twins (Fig. 8a, d, g and h), and the second foil contains mosaïcism
263 (Fig. 8b and e) and deformation bands (Fig. 8c and f). Some twins are visible along the (001) plane (Fig.
264 8a). The (001) deformation twins are consistent with those reported from prior EBSD analysis (Cavosie
265 *et al.*, 2018); other orientations of twins present within the sample were not encountered in the
266 experimental sample. Twins along the (001) plane range from 250 nm to 1.1 μm in width, and contain
267 an enrichment in Ca along the twin-host boundary but no enrichment nor depletion of Pb (Fig. 8h and
268 S8b in Supplementary data). In the second TEM-foil (Fig. 8b, e, c, f, i), mosaïcism was observed, with
269 the presence of nano-domains (~ 20 nm) slightly misoriented with respect to each other, and a slight
270 stretching of diffraction spots, indicative of a small misorientation (< 2 degrees) of the domains (Fig.
271 8b and e). Additional diffuse spots (arrows in Fig. 8e) are measured at a distance of 3.25 \AA , compatible
272 with the monazite structure. Deeper within the foil, the structure is dominated by deformation bands
273 (~ 300 nm long), in which almost no Bragg contrast is visible. The most visible additional spots in the
274 SAED pattern (arrow in Fig. 8f) that overlaps a deformation band and the adjacent monazite,
275 correspond to a d_{hkl} of 3.26 \AA . High resolution ADF-STEM imaging (Fig. 8i) show that the deformation
276 band is not completely amorphous (see fringes in the upper part of the image 8i).

277

278 4. DISCUSSION

279 4.1. Experimental shock-deformation features up to the nanoscale.

280 Early shock experiments on monazite (up to 59 GPa) used the shock-wave reverberation
281 technique and high explosives for planar shock-wave generation (Deutsch and Schärer, 1990); the

282 shocked monazite grains exhibited lower birefringence, decolorization, intense mosaicism and the
283 presence of fractures. Laser shock experiments on monazite by femtosecond laser ablation show the
284 effect of high-pressure shock waves caused by plasma expansion, revealing nanostructural
285 deformation features below the ablation crater, including fractures, mosaicism, and deformation
286 twins (*Seydoux-Guillaume et al., 2010; D'Abzac et al., 2012*). Static experimental data (using diamond
287 anvil cell) focused on high-pressure transformation of monazite with various compositions (CePO_4 -
288 *Huang et al., 2010; SmTbPO}_4*-*Heuser et al., 2018; La, Nd, Eu, GdPO}_4*-*Lacomba-Perales et al., 2010*).
289 *Huang et al. (2010)* revealed only structural lattice distortion at around 11 GPa, with no phase
290 transition up to 20 GPa. In contrast, *Lacomba-Perales et al. (2010)* identified a non-reversible high-
291 pressure phase with barite-type structure at 26 GPa for LaPO_4 but no phase transition up to 30 GPa
292 for other compositions (Gd, Eu, NdPO_4).

293 In the present study, no significant difference between Raman spectra was observed between
294 unshocked and shocked monazite samples, except for the structural distortion responsible for both
295 Raman-band broadening and data spreading; hence no evidence for formation of a high-pressure
296 phase was found (Fig. 2). Raman-band broadening of natural monazite is due to the combination of
297 two effects: chemical composition (mostly Th, U, Ca and Pb) and lattice distortion caused by radiation
298 damage (*e.g. Nasdala et al., 2002; Seydoux-Guillaume et al., 2002; Ruschel et al., 2012*). *Ruschel et al.*
299 *(2012)* proposed an empirical formula for estimating the degree of radiation damage if the chemical
300 composition is known:

$$301 \quad \text{FWHM} [\text{cm}^{-1}] = 3,95 + 26,66 \times (\text{Th}+\text{U}+\text{Ca}+\text{Pb}) [\text{apfu}]$$

302 where FWHM is the full width at half maximum of the most intense Raman band of monazite (i.e., the
303 ν_1 symmetric PO_4 stretching mode near 970 cm^{-1} ; Fig. 2). The monazite used for our experiments
304 contains 0.12, 0.002, 0.045, and 0.003 apfu (based on 4O) for Th, U, Ca and Pb respectively, which
305 gives a $\sum(\text{Th}+\text{U}+\text{Ca}+\text{Pb})$ of 0.17 apfu (*Seydoux-Guillaume et al., 2004*). The expected FWHM is then 8.5
306 cm^{-1} for monazite with the same composition and no radiation damage. The FWHM of the unshocked
307 monazite is 18.3 cm^{-1} . Interestingly, the monazite used in the present study corresponds closely to the

308 F6 monazite described in *Ruschel et al. (2012)*, with a $\Sigma(\text{Th}+\text{U}+\text{Ca}+\text{Pb})$ of 0.15, a $\text{FWHM}_{\text{unannealed}}$ of 18.1
309 cm^{-1} and a $\text{FWHM}_{\text{annealed}}$ of 7.9 cm^{-1} . The difference in width of Raman peaks between
310 $\text{FWHM}_{\text{unannealed/unshocked}}$ (18.1 and 18.3 cm^{-1}) values to $\text{FWHM}_{\text{annealed}}$ (7.9 and 8.5 cm^{-1}) values is
311 attributed to the “radiation damage component” ($\sim 10 \text{ cm}^{-1}$). The FWHM of Raman-bands from the
312 shocked monazite domains C1 and C2 are $\sim 21.5 \text{ cm}^{-1}$ (Fig. 2). The $\sim 3 \text{ cm}^{-1}$ difference in the FWHM of
313 the Raman band between the unshocked and shocked monazite is attributed to shock-induced
314 distortion of the lattice. The FWHM increase is expected when grain size is reduced, as broadening is
315 inversely proportional to grain size in CeO_2 ceramics (e.g., *Gouadec and Colomban, 2007*). In ceria,
316 band broadening of 3 cm^{-1} is observed for grain size of about 40 nm, thus the observed broadening of
317 3 cm^{-1} is consistent with the TEM observation of mosaicism at a similar scale (Fig. 3).

318 Raman band broadening is essentially related to two nano-features identified using TEM:
319 mosaicism (Fig. 3) and the presence of planar band structures (Fig. 4). As the unshocked monazite
320 crystal already contains radiation damage, expressed as typical mottled diffraction contrasts in BF-
321 TEM mode (Fig. 6a-c) and corresponding to small lattice distortion and the presence of strain
322 (*Seydoux-Guillaume et al., 2002; 2004; 2018*), it is not obvious how to isolate the “radiation damage
323 component” from the “shock component”, as done in the previous paragraph with Raman. The role
324 of radiation damage, and therefore the role of “initial structural state” of monazite at time of impact,
325 and formation of shock-deformation features, is discussed below. As the unshocked monazite was
326 previously well-characterized, it is here possible to distinguish some of the shock effects. Note
327 especially BF-TEM images in *Grand’homme et al. (2018)*, Figures 7, 9 and 10 (Mnz1). Mosaicism was
328 absent in the pristine monazite crystal (*Seydoux-Guillaume et al., 2004*). Obvious streaking in the
329 diffraction spots (Fig. 3c), moiré fringes (Fig. 3d), and the presence of extra diffraction spots in the
330 SAED pattern (Fig. 3e), are all evidence that the monazite nanodomains are misorientated by a few
331 degrees, i.e. mosaicism.

332 The deformation bands (Fig. 4) have not been observed in monazite before, even in shocked
333 samples from femtosecond-laser experiments (*Seydoux-Guillaume et al., 2010; d’Abzac et al. 2012*);

334 this microstructure unambiguously formed in response to the shock experiment. The orientation of
335 the deformation bands is parallel to the direction of shock wave propagation into the crystal (Fig. 4a-
336 b). They are different from typical planar deformation features (PDF) classically observed in shocked
337 silicates like quartz (*Langenhorst and Deutsch, 2012*) or zircon (*Reimold et al., 2002; Leroux et al.,*
338 *1999*), which are straight, sharp and continuous planes, filled with amorphous material, and
339 sometimes decorated by bubbles formed during post-shock processes, such as annealing or alteration
340 (*Langenhorst and Deutsch, 2012*). In the present shocked monazite, the band structures are shorter
341 (hundreds of nm long) and are not filled with an entirely amorphous material but instead are defined
342 by nanometer sized domains with a highly different orientation, as shown in STEM-ADF images (Fig.
343 5c-e and in the various FFT from Fig. 5c). This observation is also confirmed by the presence of
344 diffraction contrasts in BF-TEM (Fig. 4c-d), a SAED pattern which shows almost no diffuse diffraction
345 ring (Fig. 4e) but instead contains extra spots characteristic of a monazite lattice, and streaking of
346 spots corresponding to high misorientation of nanodomains to each other and from orientation of the
347 monazite host. We suggest that such features may represent precursor microstructural damage that
348 leads to formation of more typical features found in shocked monazite, such as planar deformation
349 bands (e.g. *Erickson et al., 2016*). Another possibility is that they represent partly annealed PDFs,
350 similar to those described in various shocked minerals (e.g. *Leroux et al., 2001*), which do not remain
351 amorphous after shock due to the ability of monazite to recrystallize in response to thermal and/or
352 ionization processes (*Seydoux-Guillaume et al., 2004 and 2018*). These highly misoriented deformation
353 band structures could also represent domains from which either neoblasts or high-pressure phase
354 crystallize. Additional diffraction spots observed within these domains can all be attributed to the
355 monazite lattice (Figs. 4d-e and 8 c and f), and thus might also represent incipient formation of
356 neoblasts.

357 Mechanical twins, formed in response to plastic deformation, are commonly observed in
358 shocked monazite from nature (*Cavosie et al., 2018; Erickson et al., 2017, 2019; Fougereuse et al.,*
359 *2021a*) and in experiments (*Seydoux-Guillaume et al., 2010*). However, twins in (100), (001) and (120),

360 are commonly formed during deformation, including indentation experiments (*Hay and Marshall,*
361 *2003*) and tectonically deformed monazite (*Erickson et al., 2015; Fougereuse et al., 2021b*). Such twin
362 orientations therefore cannot be used as diagnostic evidence to identify a shock event (see *Erickson*
363 *et al., 2016*). In the present study (Fig. 6), only twins in (001) were formed in the experimentally
364 shocked monazite; these are obtained with a glide plane at the interface, with displacement vector
365 $\frac{1}{2}[010]$, and are exactly the same configuration as that found in indentation experiments (*Hay and*
366 *Marshall, 2003*). Such twins were not present in the original crystal and were not detected outside the
367 shocked region. Considering the mottled diffraction contrasts revealed in BF-TEM mode (Fig. 6b-c),
368 they are very different from those observed in the other FIB-foil (Figs. 3 and 4) but are very similar to
369 the typical Bragg contrasts commonly observed in natural monazite samples, and correspond to
370 radiation damage (*Seydoux-Guillaume et al., 2002; 2018*). Therefore, in the area of C1, energy involved
371 during the shock event was used to form twins and not highly disoriented domains, as in area C2. Such
372 a contrasting response might be due to possible differences in the loading conditions, with some edge
373 effects (lateral release, shear deformation) at the periphery (area C2) vs. uniaxial strain under planar
374 shock propagation in the central region (area C1). However, further observations are needed to
375 address the distribution of deformation twins in the experimental sample. Furthermore, either the
376 temperature was too low to completely heal defects ($< 900^{\circ}\text{C}$; *Seydoux-Guillaume et al., 2002*), or the
377 kinetics of the shock experiment were too fast (few nanoseconds duration) to allow complete healing
378 of the monazite lattice.

379 Finally, an interesting observation here concerns the enrichment in Ca within the twin
380 boundary (Fig. 7d and S7a and b). Segregation of Ca during such a very short (ns) process is difficult to
381 attribute to volume diffusion, which is slow in monazite; it takes 25 s for Ca to diffuse 1 nm at 1300°C
382 and 48 h at 1000°C (*Gardès et al., 2007*). Diffusivities used for these calculations were obtained from
383 $\text{Pb} \leftrightarrow \text{Ca}$ interdiffusion experiments, and are controlled by the slower species, in this case Pb. Here,
384 the mobility of Ca during the shock experiment may be enhanced by the presence of dislocations
385 formed in response to the shock, and could explain its enrichment over ~ 2 nm along a twin boundary.

386 In natural monazite crystals (e.g. *Seydoux-Guillaume et al., 2003; 2019; Fougrouse et al., 2018; 2021a*
387 *and b*), Ca-Pb-rich nanoclusters are often found in old (>1 Ga) samples, and may explain the
388 segregation of Ca along twin boundaries or dislocations during a deformation event; however, the
389 monazite crystal used in the present study is relatively young (550 Ma) and nanoclusters were not
390 observed. Monazite forms chains along [001] of alternating phosphate tetrahedra and REE polyhedra
391 (9-fold coordinated). In the monazite lattice, Ca has no “structural” position; it is only incorporated by
392 exchange of 2REE^{3+} for $\text{Ca}^{2+} + (\text{Th}, \text{U})^{4+}$ as cheralite substitution in the REE polyhedra. Furthermore, as
393 REE-O bonds are more likely to break than P-O bonds during twinning (*Hay and Marshall, 2003*), this
394 would first affect the Ca-O bonds and potentially expel Ca along the twin boundary during its
395 formation. This idea was suggested by *Fougrouse et al. (2021b)*, in a 1700 Ma old tectonically
396 deformed monazite, where Ca is also enriched along the twin boundary.

397

398 4.2. Laser-shock experiments as analogues for naturally-shocked samples

399 One of the main objectives of the present study is to evaluate if laser-driven shock
400 experiments reproduce the types of impact damage previously characterized in naturally shocked
401 monazite. Shocked monazite has been reported both in bedrock of the Vredefort impact structure,
402 South Africa (*Moser, 1997, Erickson et al., 2017*), the Nördlinger Ries crater, Germany, the Houghton
403 dome, Canada (*Erickson et al., 2019*), the Araguinha crater, Brazil (*Erickson et al., 2017*), the
404 Woodleigh impact structure in Australia (*Fougrouse et al., 2021a*), the Yarrabubba monzogranite and
405 Barlangi granophyre impact melt (*Erickson et al., 2020*), and in both modern and Pleistocene alluvial
406 deposits of the Vaal River in South Africa as detrital grains (*Cavosie et al., 2010; Erickson et al., 2013;*
407 *Cavosie et al., 2018*). *Erickson et al. (2019)* reported shocked monazite grains from Ries Crater and
408 Houghton dome with complex yet systematic twin relations produced by reversion from an
409 unquenchable high-pressure tetragonal polymorph, a phase not previously known. No studies have
410 investigated shock-deformation structures in monazite at a nanometer scale, except a recent study by
411 *Fougrouse et al. (2021a)* that focused on Pb mobility as determined from atom probe tomography, a

412 method shown previously to demonstrate atom-scale element mobility or segregation on twin
413 boundaries triggered by tectonic deformation (*Fougerouse et al., 2021b*).

414 Several features observed in the naturally shocked Vredefort monazite analyzed here (Fig. 8)
415 correspond in many aspects to features in our laser-driven experiments (Figs. 3-4), including (a) the
416 streaking of spots, (b) the presence of extra spots in SAED patterns (indicated by arrows in Fig. 8) with
417 d_{hkl} possibly attributed to monazite lattice (3.25 Å and 3.26 Å in Fig. 8e and f respectively), (c)
418 deformation twins formed along the (001) plane with enrichment in Ca along the twin-host boundary,
419 (d) mosaicism, and above all (e) the highly disoriented bands. Comparisons between both samples are
420 easily done, as the reference frame (zone axis) for both sets of observations is exactly the same. The
421 striking similarity shows that the different features observed beneath the laser shock-loaded surface
422 cannot be attributed to possible artefacts of the laser experiment (e.g. annealing upon conductive
423 heating from the Al plasma, or spreading of the compression front upon transmission through the thin
424 glue layer), as the same features are found in naturally shocked monazite.

425 These results demonstrate the ability of laser-driven experiments to produce shock
426 deformation microstructures found in naturally shocked monazite, specifically mosaicism, twinning
427 and deformation bands. One additional microstructure described by *Cavosie et al. (2018)* and *Erickson*
428 *et al. (2017)* is the formation of neoblastic domains, which were not observed in the experimental
429 products. The presence of neoblastic domains provides evidence of localized recrystallisation of
430 monazite during, or more likely, immediately following shock deformation. The absence of neoblasts
431 in the laser shock-loaded monazite crystal may be explained by either (i) lower shock conditions
432 (essentially temperature), too low to induce recrystallization, in contrast to what can be observed in
433 naturally shocked monazite (e.g. *Erickson et al., 2017; 2020*), or by (ii) insufficient duration of the
434 thermomechanical load, shorter by many orders of magnitude in the experiment (~6 ns-pressure
435 pulse, see Section 2.2), which may be below the characteristic time required to form neoblasts.

436 Finally, the fact that in both cases Ca is significantly enriched within host-twin boundaries over
437 a few nm (compare figures 7d and 8h and S7a-b and S8b), which has been reported previously in

438 shocked monazite (see Ca segregation in Figure 5a of *Fougerouse et al., 2021a*) further confirms that
439 laser shock loading produced both comparable styles of crystal-plastic deformation, and also localized
440 element mobility, thus reproducing shock microstructures found in nature. Even if the mechanism of
441 Ca-segregation is not completely understood, shock conditions of our laser-driven experiments seem
442 sufficient to induce atomic segregation during twin formation. Future studies will evaluate the
443 mobility mechanism and the ability of such experiments to reset geochronological systems by
444 liberating Pb from the structure during twin formation, as suggested by *Fougerouse et al. (2021a)* for
445 shock twins and also in tectonically deformed monazite samples by *Fougerouse et al. (2021b)*. In this
446 study, however, no segregation of Pb was observed in the investigated TEM foils (See Supplementary
447 Data S2; Figures S7b).

448

449 4.3. Role of radiation damage in formation of shock-deformation features?

450 In order to ascertain shock conditions of minerals during impact events, the structural state
451 of the mineral at the time of impact must be estimated. In the case of zircon, a mineral highly sensitive
452 to radiation damage, formation of the high-pressure polymorph reidite is inhibited in partially
453 metamict zircon due to the general reduction in longitudinal and shear stiffness with radiation damage
454 (*Erickson et al., 2017; Timms et al., 2018*). Extrapolation of impact conditions in natural shocked zircon
455 can thus be complicated due to lack of knowledge of pre-impact intrinsic properties. In contrast,
456 monazite has the ability to remain crystalline over geological time due to self-annealing of radiation
457 damage (*Seydoux-Guillaume et al. 2004; 2018b*), however it is not known if the presence of radiation
458 damage influences formation of shock-deformation features or high-pressure polymorphs (e.g.,
459 *Erickson et al., 2019*). Further shock-experiments using monazite free of radiation damage as a starting
460 material may be able to elucidate such behavior.

461 It is also worth considering that monazite samples older than 1 Ga may have accumulated a
462 high amount of radiogenic Pb in the lattice and received intensive radiation doses. Even if clear
463 evidence for radiation damage is limited to nm-isolated domains within monazite resulting in lattice

464 distortion (*Seydoux-Guillaume et al., 2004*), these effects induce Raman broadening and mottled
465 diffraction contrasts visible in TEM. At the micrometer scale, peak broadening of Raman spectra
466 provides one indication that monazite crystals were affected by a shock event. This requires, however,
467 knowledge of both composition and FWHM of Raman spectra of unshocked monazite samples, in
468 order to evaluate the radiation damage component, which produces the same broadening effect
469 (*Nasdala et al., 2002; Seydoux-Guillaume et al., 2002; Ruschel et al., 2012*). More investigations using
470 TEM are needed to confirm a primary (shock) interpretation, and to describe in detail shock
471 deformation features. Analysis of shocked monazite by TEM, away from twinned domains (Figs. 3 to
472 5), revealed intense lattice distortion in the form of mosaicism, deformation bands, and the presence
473 of intense streaking and extra spots in the SAED pattern; these features can unambiguously be
474 attributed to shock deformation. Unshocked monazite crystals (e.g. *Seydoux-Guillaume et al., 2004*
475 *and 2018a*) and tectonically deformed grains (*Fougerouse et al., 2021b*), did not display Bragg
476 diffraction contrasts in bright field mode (with their corresponding SAED patterns) as pronounced as
477 those described here that correspond to mosaicism and deformation bands. Inside the twinned areas
478 it is almost impossible to distinguish contrasts in shocked monazite from those of tectonically
479 deformed monazite, except in the case where twin orientations are specifically characteristic of shock
480 deformation (*Erickson et al., 2016; Fougerouse et al., 2021a*). However, in the case of common twin
481 orientations, like those in the present study with (001), this criterion is not sufficient. The diffraction
482 contrasts are also not discriminating, as in the twinned domains neither extra spots nor streaking of
483 spots were observed. In this case the diffraction contrasts observed in BF-TEM can be directly
484 attributed almost entirely to radiation damage and not shock metamorphism. Finally, the assumption
485 that the presence of crystal defects (e.g. dislocations) in naturally shocked monazite samples may
486 indicate that these defects were not annealed after an impact event should be considered along with
487 the observation that radiation damage in monazite is continuously created and healed over geological
488 time.

489

490 **CONCLUSIONS**

491 This study demonstrated the ability of laser-driven shock experiments using a high-energy
492 laser pulse of ns-order duration to reproduce shock-deformation microstructures observed in natural
493 shocked monazite. We describe three main microstructural features at the nanoscale: deformation
494 twins, mosaïcism, and deformation bands. The deformation twins formed in (001), an orientation that
495 is not diagnostic of shock deformation. However, both mosaïcism and deformation bands, expressed
496 in SAED pattern with streaking of spots, and the presence of extra spots, more or less pronounced,
497 provide evidence to identify shocked monazite grains. Other shock-deformation features reported in
498 naturally shocked monazite, such as high-pressure polymorphs and neoblastic domains, were not
499 observed in the experimental charges. Further study is needed to evaluate the possibility of forming
500 such features with laser-driven shock experiments. Furthermore, as the presence of radiation damage
501 may also modify the formation of shock-deformation features, use of monazite crystals free of
502 radiation damage may help to answer this question.

503 If Ca segregation along deformation twin boundaries, as revealed in both naturally and
504 experimentally shocked-monazite crystals using TEM, is a consequence of shock-deformation, future
505 studies can similarly evaluate the potential for Pb mobility and the geochronological response to shock
506 events by combining structural and isotopic observations at the nanoscale. *Fougerouse et al. (2021a)*
507 suggested that Pb may be expelled from monazite during shock twin formation, depending on the
508 temperature during the impact event (>900 °C). Work is in progress to see if Pb can be expelled from
509 monazite during such laser-shock experiments, either during twin formation or maybe during
510 formation of these highly disoriented band features, and then reset the U-(Th)-Pb clock.

511

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522

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672

673 **Figure captions**

674 **Figure 1** - Monazite single crystal before and after shock experiment. a-d. Optical views (a-c: binocular
675 and d: reflected light) from the 3 mm shocked area (central zone). e-g: Secondary Electron Microscope
676 images from 2 areas in the central zone where characterizations were performed. Arrows point to
677 cracks induced by shock.

678 **Figure 2** – Raman spectra performed in unshocked and shocked (C1 and C2) domains from monazite
679 crystal. a- average and standard deviation of the Raman spectra per group. b- diagram showing the
680 FWHM (full width at half maximum) of the ν_1 peak as a function of its spectral position (in cm^{-1}). These
681 values were corrected for the apparatus function of the Raman instrument (*Nasdala et al. 2001*). The
682 peak positions and FWHM were determined without smoothing spectra and a linear baseline was used
683 in the spectral range $800\text{-}1200\text{ cm}^{-1}$. The reproducibility is better than $\pm 0.01\text{ cm}^{-1}$ and our
684 uncertainties on data are two magnitude lower than 1 cm^{-1} .

685 **Figure 3** – Bright Field Transmission Electron Microscope (BF-TEM) images (a-b and d) and Selected
686 Area Electron Diffraction (SAED – c and e) from FIB-foil (FIB5) prepared from C2 area - Mosaïcism.
687 Note mottled diffraction contrasts (a-b), streaking of diffraction spots (c), moiré fringes (arrows in d),
688 and extra spots in [100] oriented SAED (arrows in e), characteristic features from mosaïcism
689 (misoriented subgrains).

690 **Figure 4** – Bright Field Transmission Electron Microscope (BF-TEM) images (a-d) and Selected Area
691 Electron Diffraction (SAED - e) from FIB-foil (FIB5) prepared from C2 area - Highly-disoriented bands.

692 Note the presence of band features almost parallel to each other (a and b), in a domain that is deeper
693 in the FIB foil (a). Note a very reduced crystallinity inside these bands, with almost no Bragg contrasts
694 (homogeneous grey – c and d). SAED pattern (e) realized across one band and the monazite (inset in
695 d) in zone axis [100], shows streaking of some spots and a lot of extra spots (arrows in e) proof for
696 highly disoriented domains.

697 **Figure 5** – Annular Dark Field Scanning TEM (STEM) images from FIB-foil (FIB5) prepared from C2 area
698 in the highly-deformed bands domain. a- Low magnification ADF-STEM image showing the presence
699 of bands domains appearing darker (less diffracting regions). b- zoom in one band domain. c- Zoom in
700 area inset in b and three Fast Fourier Transform (FFT) from different domains in c showing contrasts
701 between the bright perfectly ordered domain (FFT1) and dark highly disoriented (FFT2 and 3) domains
702 (bands). Note arrow indicating extra spot in FFT2 (measured at 3.2 Å). d-e: zoom from image in c. Note
703 the crystallographic fringes still visible in the dark band domain (d and e). The perfectly ordered ADF-
704 STEM image in f shows arrangements of heavy atoms in [100] zone axis, in agreement with the
705 crystallographic model (see Supp data S2).

706 **Figure 6** – Bright (a-d) and Dark Field (f) Transmission Electron Microscope (BF/DF-TEM) images, and
707 Selected Area Electron Diffraction (SAED – e and g) from FIB-foil (FIB1) prepared in C1 area - Twinned
708 domain. a-c BF-TEM showing twins almost horizontal in the images. Note the presence of mottled
709 diffraction contrasts however much less pronounced than in other areas described in figures 3 and 4.
710 e- SAED pattern in one twin (inset in a) along [110] zone axis. Note the absence of streaking of spots
711 nor extra spots. f- DF-TEM of a twin with (11-1) diffraction spot. g- SAED pattern realized across one
712 twin boundary showing their (001) directions.

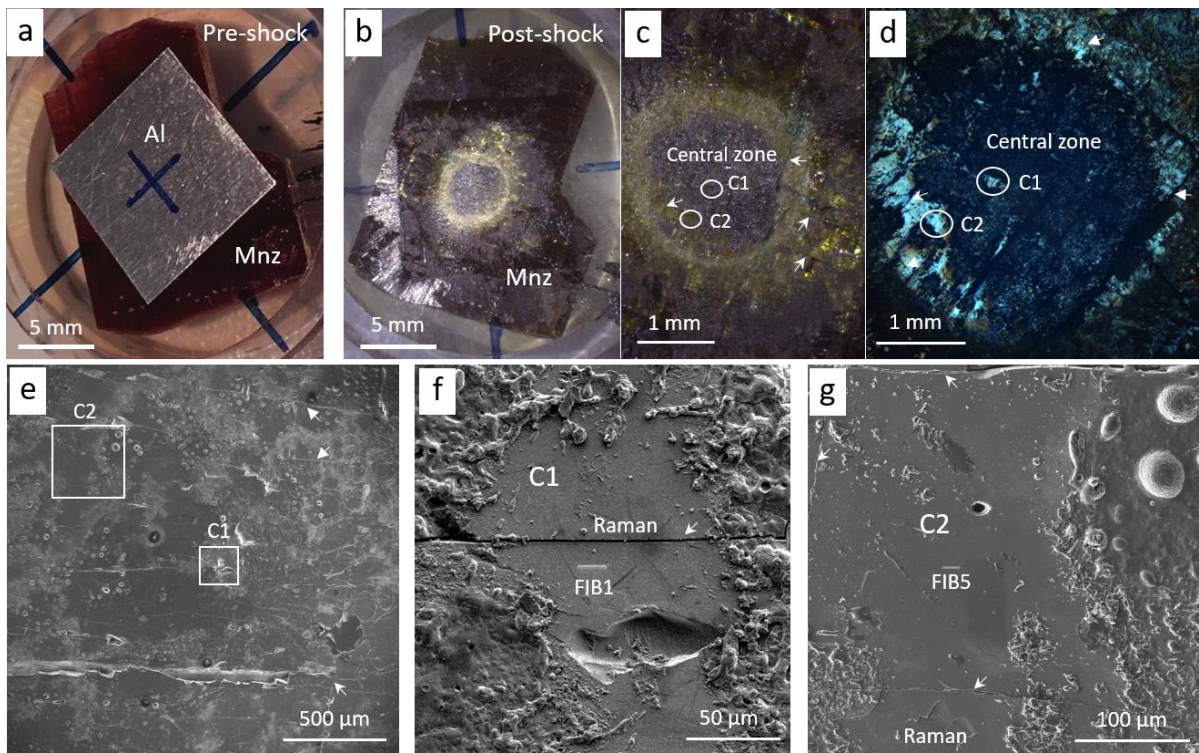
713 **Figure 7** – High Resolution STEM images from FIB-foil (FIB1) prepared from C1 area. Annular Dark Field
714 (a) and Annular Bright Field (b) STEM images across the same twin boundary in (001) with high
715 magnification image (c) in ADF mode from left part of the twin in zone axis [110]. Note only the heavy
716 atoms can be observed with this detector and their arrangements in [110] fit the crystallographic

717 model (CePO_4). $\text{Ca}(\text{K}\alpha)$ distribution in the same area as in a and b with enrichment within the twin
718 boundary (d). Details in Supp. Data S2.

719 **Figure 8** - Bright Field TEM images (a-c), SAED patterns (d-f), and High Resolution ADF-STEM images
720 (g-i) from two FIB-foils prepared in two different areas from one naturally shocked monazite grain
721 (Mnz9) from Rietputs formation (South-Africa; *Cavosie et al., 2018*). Three kinds of deformation
722 features are seen: twins (a, d, g and h) in (001) with Ca enrichment within the boundary (Ca map from
723 inset in h), mosaicism (b and e) and highly deformed band-features (c, f and i). Note streaking of spots
724 (e and f), extra spots in SAED patterns (indicated by arrows, with d_{hkl} of 3.25 Å and 3.26 Å for e and f
725 respectively). Details on location of FIB foils and on chemical mapping are given in Supp. Data S2.

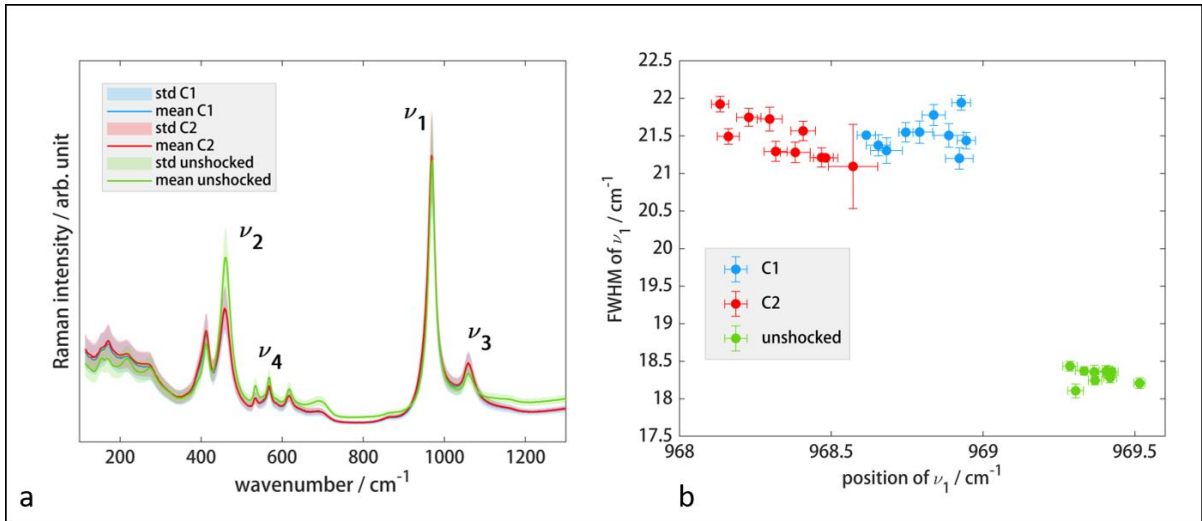
726 **Figures**

727 **Figure 1:**



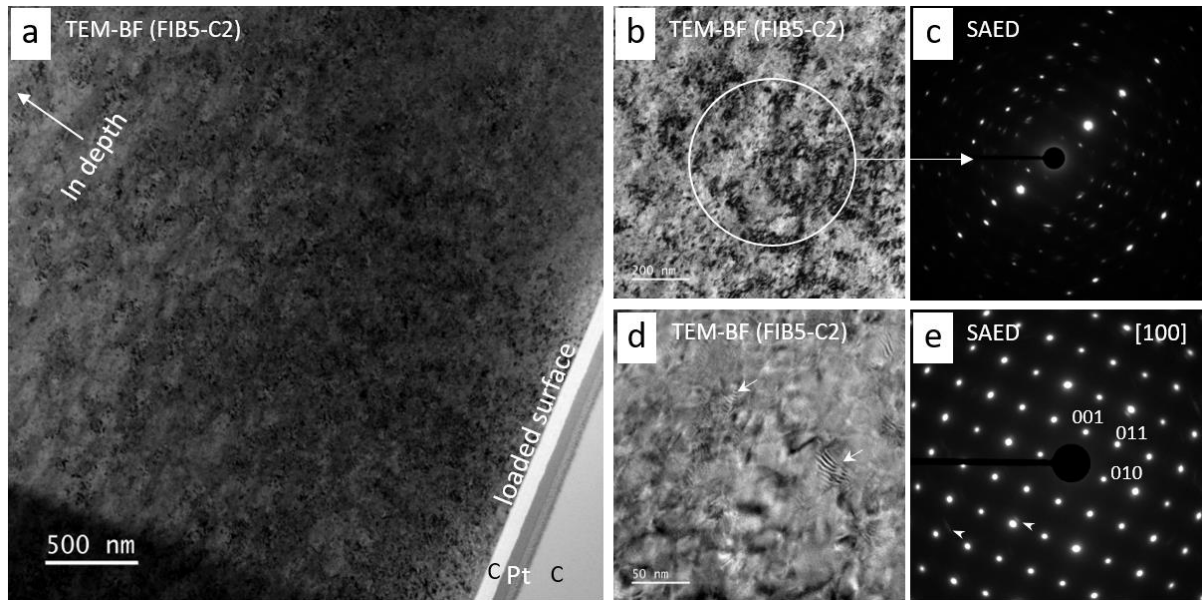
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729 **Figure 2:**



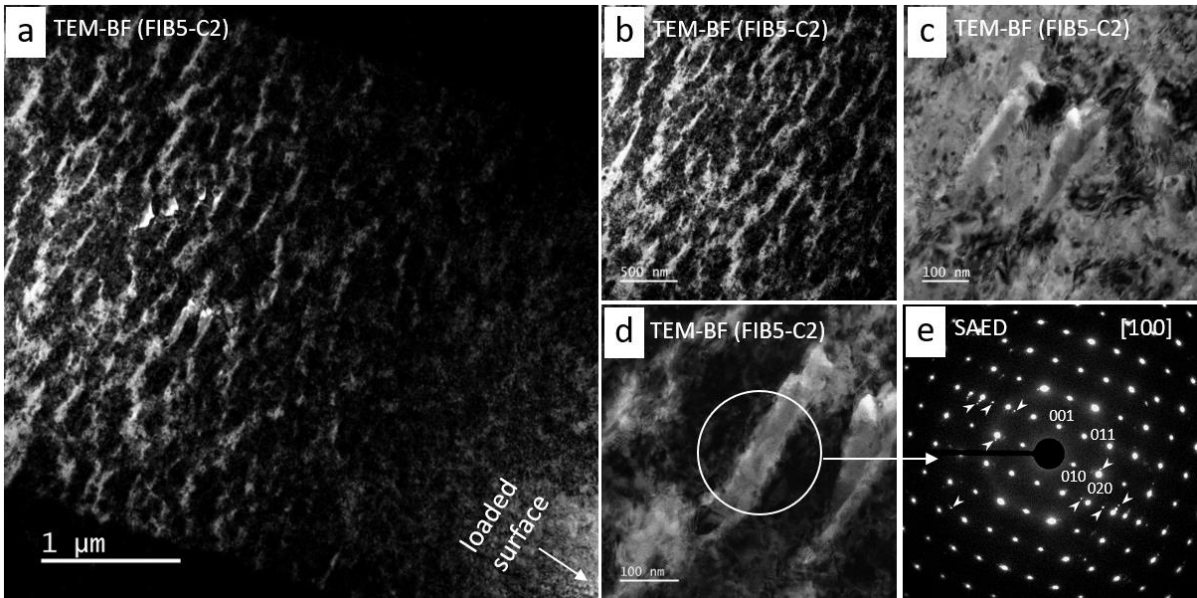
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731 **Figure 3:**



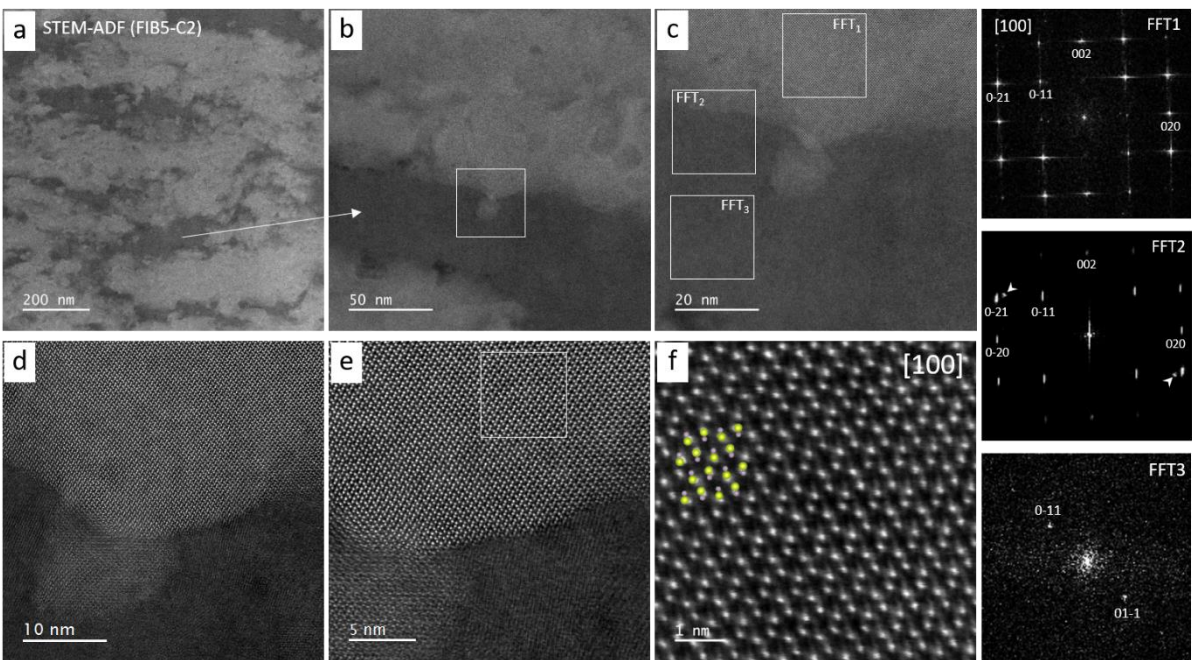
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733 **Figure 4:**



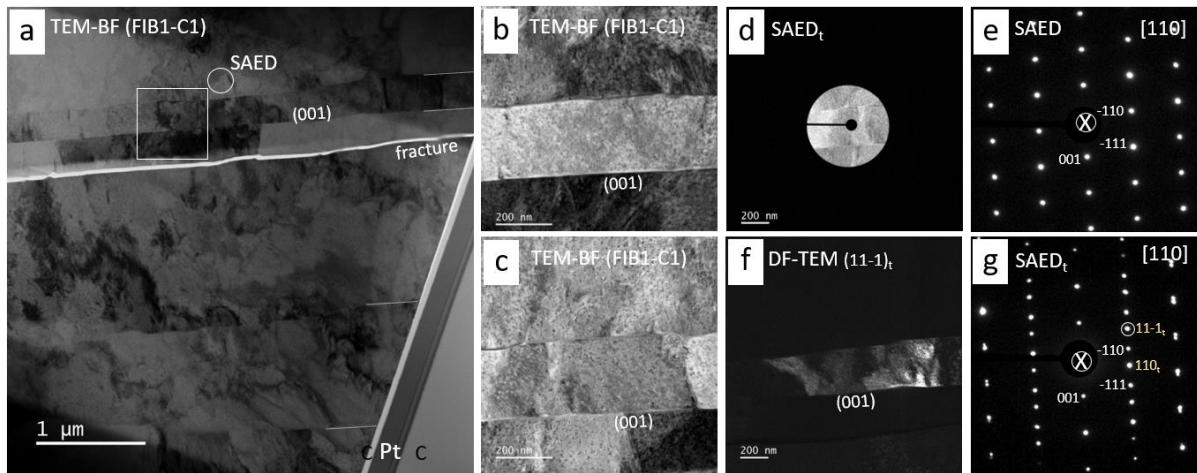
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735 **Figure 5:**



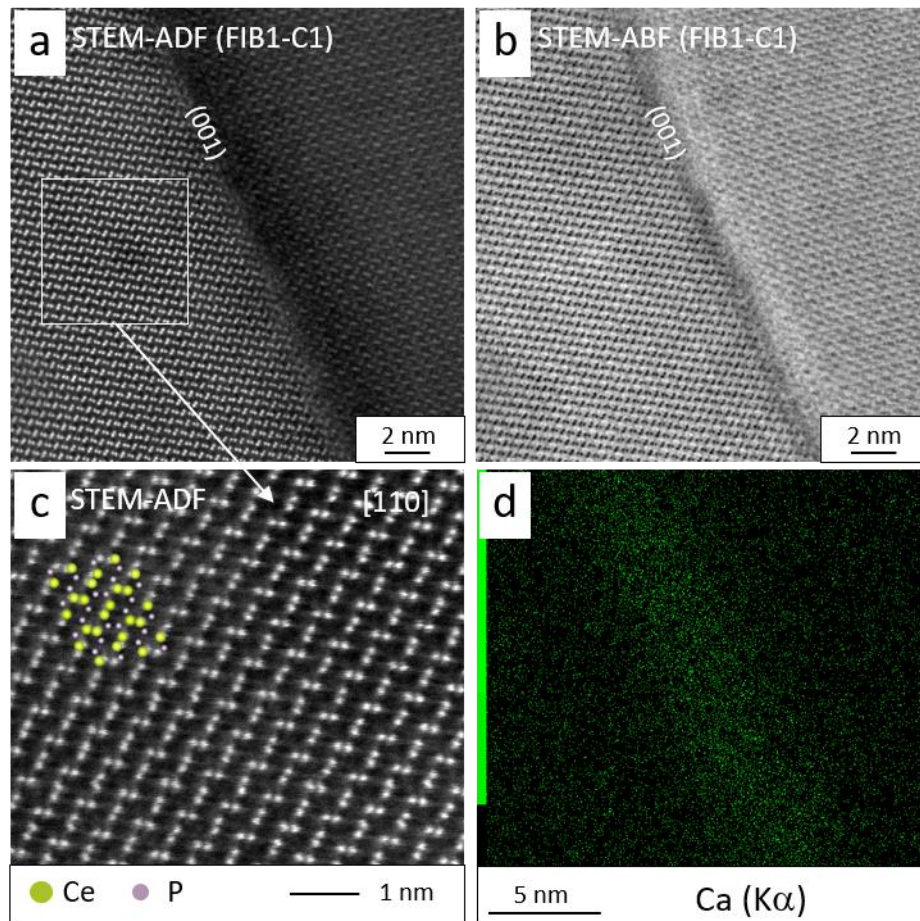
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737 **Figure 6:**



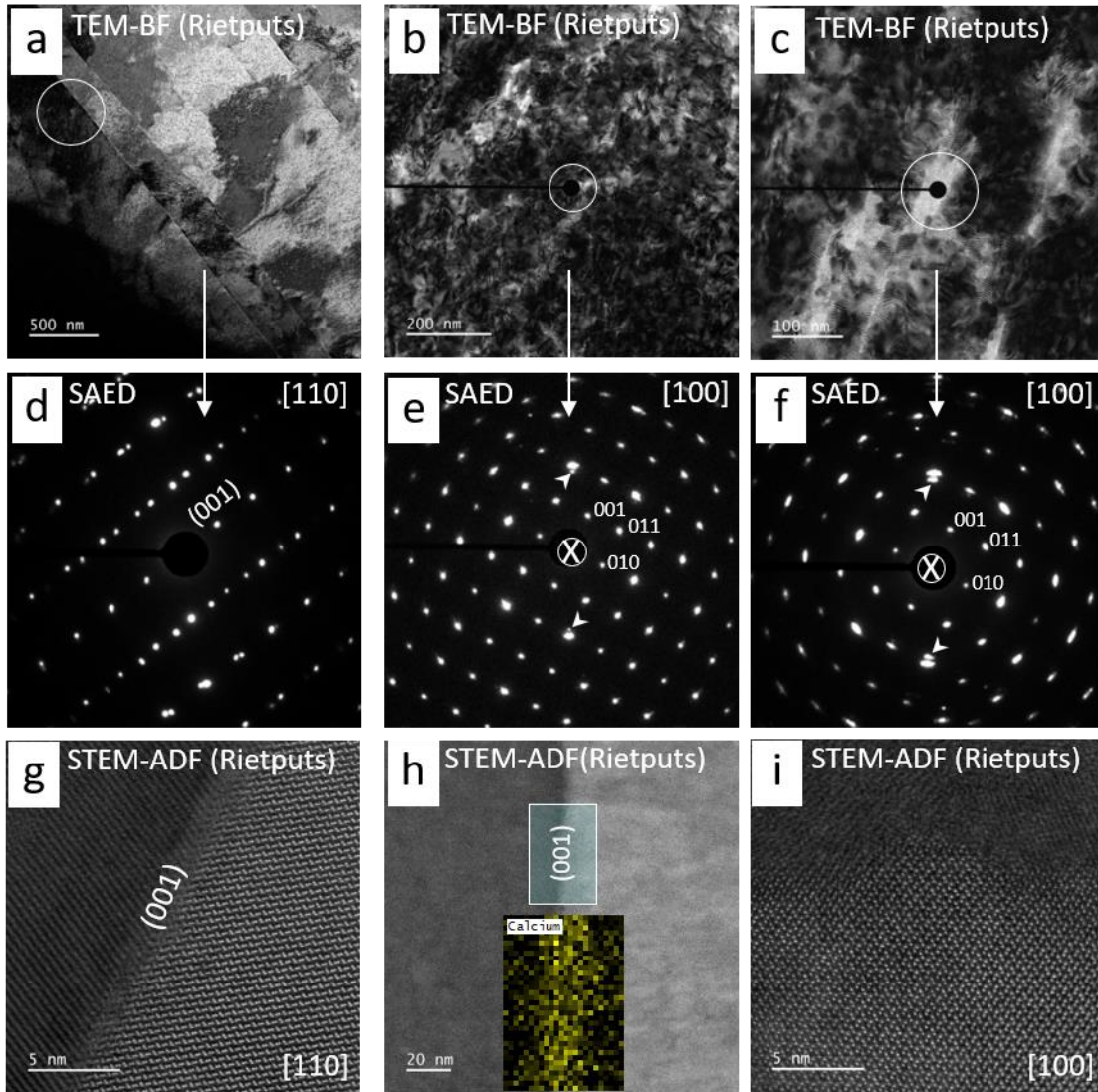
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739 **Figure 7:**



740

741 **Figure 8:**



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