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## Bridging the shocked monazite gap- deformation microstructures in natural and laser shock-loaded samples

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

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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, two main plastic  
31 deformation structures were found in experimentally shocked monazite: mosaicism, and deformation  
32 bands. In contrast, the naturally shocked monazite sample, contained only deformation twins with  
33 elemental enrichment along host-twin boundaries. Both mosaicism and deformation bands,  
34 expressed in SAED patterns as streaking of spots, and the presence of extra spots (more or less  
35 pronounced), are proposed as nano-scale signatures of shock metamorphism in monazite.  
36 Experimentally calibrated deformation features, such as those documented here at TEM-scale,  
37 provide new tools for identifying evidence of shock deformation in natural samples.

38

## 39 **1. INTRODUCTION**

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

47 Impact-related damage in minerals and rocks provides key evidence to identify impact  
48 structures (*French and Koeberl, 2010*). Shock deformation microstructures have been intensively  
49 studied in some minerals, especially quartz, down to the nanometer scale with transmission electron  
50 microscopy (TEM), and include formation of dislocations, planar deformation features (PDF),  
51 mosaicism (i.e. a mosaic texture with small domains of crystalline blocks slightly misoriented to each

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

74 Published studies show that evidence of impact age resetting in U-Pb geochronometers can  
75 be highly heterogeneous due to complex microstructures at the grain scale (*e.g.* *Cavosie et al., 2018*  
76 *and 2021*). Shock-deformation in monazite has previously been described (*Schärer and Deutsch,*  
77 *1990*), however its microstructure has only been systematically described at the micrometer scale

78 recently using electron backscatter diffraction (EBSD) (*Erickson et al., 2016, 2017, 2020; Cavosie et al.,*  
79 *2018*). No nanometer-scale investigations using TEM to describe shock deformation features in  
80 monazite have been conducted previously.

81 Experimental approaches have been applied to address formation of shock deformation  
82 microstructures in monazite (*Deutsch and Schärer, 1990; Huang et al., 2010; Lacomba-Perales et al.,*  
83 *2010; Seydoux-Guillaume et al., 2010; D'Abzac et al., 2012; Heuser et al., 2018*), and some propose  
84 the existence of high-pressure monazite polymorphs which have thus far not been discovered in  
85 nature (*Erickson et al., 2019*). Laser-driven experiments have previously demonstrated the ability to  
86 simulate conditions of impact events (e.g. in olivine; *Langenhorst et al., 1999*). Here we compare  
87 nanoscale deformation structures formed in shocked monazite from the Vredefort impact structure  
88 in South Africa (*Cavosie et al., 2018*) with experimentally shocked monazite, in order to identify which  
89 features can be used as shock indicators, and also enhance the validity of laser-driven shock-  
90 experiments.

91

## 92 **2. MATERIALS AND METHODS**

### 93 *2.1. Starting material*

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

101 A shocked monazite grain from the Rietputs Formation in South Africa (Sample Sec-03D, grain  
102 9) was also investigated to evaluate if laser-driven shock experiments are able to reproduce impact  
103 damage found in nature. This monazite is a detrital grain that eroded from shocked bedrock at the

104 Vredefort impact structure, and was transported ~500 km downstream in the Vaal River (*Cavosie et*  
105 *al., 2018*). It was previously characterized with BSE and EBSD, and shown to contain an anomalously  
106 high density of deformation twins, as well as localized areas that have recrystallized into neoblastic  
107 domains (*Cavosie et al., 2018*). The original host rock is unknown, however, it is assumed that the  
108 detrital shocked monazite originated from between the 20 and 30 GPa isobars at the Vredefort impact  
109 structure, as it is not fully neoblastic (e.g., *Erickson et al., 2017*), and is similar to other detrital shocked  
110 monazite grains that host shock-twinned zircon inclusions (*Erickson et al., 2016*).

111

## 112 2.2. Laser-driven shock loading

113 The laser shock experiment was carried out at the “nano2000” facility of the *Laboratoire pour*  
114 *l’Utilisation des Lasers Intenses* (LULI, UMR CNRS 7605, Ecole Polytechnique, Palaiseau, France). The  
115 target consisted of a 20 µm-thick Al foil glued on top of the monazite crystal (Fig. 1a). A high-power  
116 laser pulse of 1.06 µm-wavelength, 5 ns-duration, 765 J-energy, was focused onto a 3.2 mm-diameter  
117 spot on the target surface. The resulting laser intensity was about  $1.9 \times 10^{12}$  W/cm<sup>2</sup>. A thin absorbing  
118 layer of Al (~µm-order) is ablated into a plasma cloud, whose expansion drives a short compressive  
119 pulse. The amplitude (50 GPa) of this pressure pulse and its temporal shape (about 6 ns-duration at  
120 half maximum) were inferred from a simulation of laser-matter interaction, using the measured profile  
121 of laser intensity as an input boundary condition. Shock pressure transmitted to the monazite sample  
122 across the Al-monazite interface was estimated by accounting for the impedance mismatch between  
123 both materials, using data reported for CePO<sub>4</sub> monazite (*Feng et al., 2013; Du et al. 2009*). Peak loading  
124 pressure applied on the monazite crystal was thus calculated at 56.7 GPa. The post-shock temperature  
125 computed in Al is about 1300 K, which agrees with calculated thermodynamic data for a 50 GPa mean  
126 shock pressure (*Kinslow, 1970*). The subsequent post-release temperature in Al after pressure  
127 unloading is about 700 K. In the monazite crystal however, shock-induced heating cannot be assessed  
128 without an equation of state for this material, but it should be similar in a natural impact event for an

129 analogous loading pressure, as temperature only depends on shock pressure. Nevertheless, the much  
130 shorter duration of both pressure and temperature under laser-driven compression may result in  
131 differences in shock-induced transformations, due to (i) possible kinetic inhibition of time-consuming  
132 processes (e.g. diffusion, conduction), and (ii) faster pressure decay with propagation distance which  
133 would strongly restrict the size of the shock-heated region and possibly hinder neighbourhood effects  
134 within heterogeneous samples. One goal of this study is thus to address both relevance and limitations  
135 of the impact/laser analog.

### 136 2.3. Analytical methods.

137 Raman spectra were collected directly on the shocked surface of the monazite crystal in clean  
138 areas (Fig. 1d-g) with a Horiba micro-Raman spectrometer LabRam HR800 evolution. Groups of 10  
139 spectra were collected respectively on starting material, shocked samples C1 and C2, with two  
140 accumulations of 10 s exposure (Fig. 2a). Raman peaks were fitted with Gauss-Lorentz spectral models  
141 in the spectral range from 800 to 1200  $\text{cm}^{-1}$ , with the Matlab application tool PeakFit to extract the  
142 position and full width at half maximum (FWHM) of the  $\nu_1$  peak (Fig. 2b, Table S1). FWHM values are  
143 corrected for the apparatus function of the Raman instrument (*Nasdala et al., 2001*).

144 The TEM foils were prepared using a Thermo Fisher Scientific FEI 125 Helios Nanolab 600i  
145 focused-ion beam scanning electron microscope (FIB/SEM) hosted by MANUTECH USD platform, at  
146 Hubert Curien laboratory, Saint-Etienne (France). Nanoscale characterization was performed with a  
147 Cs-corrected TEM (NeoARM200F Cold FEG) at 200 kV, operated by the CLYM and hosted within the  
148 Hubert Curien Laboratory, Saint-Etienne (France). A Gaussian low-pass filter for noise reduction was  
149 applied to high-magnification STEM images (Figures 5c-d, 8d-f and 9d).

150

151 For further details see Supplementary Materials.

152

## 153 3. RESULTS

154 3.1. Optical and SEM observations

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

163

164 3.2. Raman observations

165 Raman measurements were performed on both unshocked areas of the monazite crystal and  
166 in the central shocked zone (C1 and C2; Fig. 1). The first result is that only monazite was identified; no  
167 peaks associated with other phases were present. As described in *Heuser et al. (2018)*, bands between  
168 900 and 1100  $\text{cm}^{-1}$  can be assigned to antisymmetric ( $\nu_3$ ) and symmetric ( $\nu_1$ ) stretching modes,  
169 respectively, and peaks between 400 and 700  $\text{cm}^{-1}$  to antisymmetric ( $\nu_4$ ) and symmetric ( $\nu_2$ ) bending  
170 modes of the  $\text{PO}_4$  group of monazite. Differences between the three areas are apparent only in the  
171 position and shape of the peaks. As previously shown (*Seydoux-Guillaume et al., 2002; Ruschel et al.,*  
172 *2012*) the FWHM of the  $\nu_1$  Raman band is suitable to estimate the degree of short-range order of  
173 monazite (Fig. 2b). Mean values for the position vary from 969.40  $\text{cm}^{-1}$  for unshocked monazite to  
174 968.81 and 968.34  $\text{cm}^{-1}$  for shocked monazite (C1 and C2 zones respectively), and for FWHM from  
175 18.34 (unshocked monazite) to 21.52 and 21.45  $\text{cm}^{-1}$  (C1 and C2 respectively). The positions and  
176 FWHM are more variable in shocked areas (968.62-968.93/21.20-21.94  $\text{cm}^{-1}$  for C1, 968.13-  
177 968.57/21.09-21.93  $\text{cm}^{-1}$  for C2) than unshocked areas (969.30-969.51/18.10-18.73  $\text{cm}^{-1}$ ) of the  
178 crystal, indicating a higher local variability of microstructure.

179



### 180 3.3. Transmission Electron Microscopy

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

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

195

#### 196 3.3.1. TEM foil C1 (FIB1) – Figures 3 to 5

197 Deformation features in foil FIB1-C1 vary spatially depending on the depth of observation  
198 within the foil relative to the polished surface (Figures 3-5). From the surface of the sample down to  
199 approximately 3  $\mu\text{m}$  (Fig. 3b), FIB1 is characterized by mosaïcism, which consists of a high density of  
200  $\sim 50$  nm sized irregularly shaped domains that are slightly misoriented ( $1\text{-}2^\circ$ ) with respect to each  
201 other, resulting in a mottled diffraction contrast in BF-TEM (Fig. 3) and a slight streaking of spots in  
202 the selected area electron diffraction patterns (SAED; Fig. 3a). Mosaïcism indicates the presence of  
203 misoriented subgrains, which are  $\sim 50$  nm-size bright domains visible in Dark-Field (DF) TEM mode (Fig.  
204 3c). When the FIB1 foil is oriented parallel to the [100] zone axis (Fig. 3a), extra spots compatible with  
205 the monazite structure are visible (DF1 at  $3.26\text{\AA}$  and DF2 at  $1.81\text{\AA}$ ). At depths below 3  $\mu\text{m}$  from the

206 surface within foil FIB1 (Fig. 4) the structure is dominated by bands that are subparallel to the surface  
207 (Fig. 4a-b), and they are also visible as a SW-NE fabric in the Dark-Field (DF) image (Fig. 4d). The bands  
208 are 100-300 nm long and about 50 nm wide, and form a wavy pattern within the sample. Contrast  
209 within the bands is quite homogeneous, with a grey color and almost no Bragg contrast, consistent  
210 with diminished crystallinity relative to other areas. An SAED pattern (Fig. 4c) across one band in the  
211 [100] zone axis shows streaking of some spots, more pronounced than in Fig. 3a, and extra spots (DF1:  
212 3.26Å, DF2: 1.81Å, DF3: 2.06Å). The SAED data are compatible with a monazite structure, and provide  
213 evidence of highly disoriented domains (misoriented subgrains are visible in DF-TEM in Fig. 4d-f).  
214 Moiré fringes are also observed and provide further evidence of misorientation of the nano-domains  
215 (arrows in Fig. 4b). Annular dark field (ADF) scanning TEM (STEM) images across band domains (Fig. 5)  
216 show that Bragg contrasts are strongly reduced inside bands (darker areas), resulting from the lower  
217 density of the material within the deformation band (Fig. 5a-b). At very high magnification (Fig. 5c-d)  
218 the atomic arrangement within the monazite structure is revealed. In ADF mode, only the heaviest  
219 atoms are visible (i.e. rare earth elements like Ce in CePO<sub>4</sub> monazite structure); in Figure 5f the pattern  
220 matches the arrangement of Ce atoms in monazite along the [100] direction. In contrast, within the  
221 deformation bands (upper parts in Fig. 5c-d) the atomic arrangement almost disappears, and instead  
222 consists of highly disoriented nano-crystals of monazite (some fringes can be observed within these  
223 bands).

224

### 225 3.3.2. TEM foil C2 (FIB5) – Figures 6 to 8

226 In this sample two kinds of deformation features were observed, depending on depth of  
227 observation within the foil. From the surface down to approximately 4 µm (Fig. 6a), the sample  
228 revealed a high density of 10-20 nm domains that are slightly misoriented with respect to each other,  
229 resulting in mottled diffraction contrasts in BF-TEM (Fig. 6a-b). Selected area electron diffraction  
230 patterns (SAED) show a slight stretching of diffraction spots (Fig. 6c and e), indicative of a small  
231 misorientation of domains (<2 degrees). When the crystal is oriented parallel to the [100] zone axis,

232 the most intense stretching is seen along the (012) plane. Additional diffuse spots are also visible  
233 (arrows in Fig. 6e) and are measured at a distance of 3.16 Å, compatible with the monazite structure.  
234 At higher magnification moiré fringes (arrows in Fig. 6d) are observed and provide further evidence of  
235 misorientation of the nano-domains. From 4 μm depth to the bottom of the foil (Fig. 7a), the structure  
236 is dominated by bands subparallel to the shock-loaded surface (Fig. 7b). The bands are 300 ± 50 nm  
237 long and about 50 nm wide, are relatively regular, and form a wavy pattern within the sample (Fig. 7  
238 c-d). Contrast within the bands is homogeneous, with a grey color, and almost no Bragg contrast,  
239 consistent with a low crystallinity, almost glassy structure. An SAED pattern parallel to the [100] zone  
240 axis that overlaps a deformation band and the adjacent monazite confirms the presence of a diffuse  
241 ring, characteristic of amorphous material that is superimposed on the monazite diffraction signature.  
242 The same SAED pattern also revealed the appearance of additional spots, some close to the principal  
243 spots from the [100] zone axis (Fig. 7e). The most visible additional spots in the SAED pattern, with the  
244 shortest distance, are indicated by arrows in Figure 7e, and correspond to a  $d_{hkl}$  of 3.58 Å, close to the  
245 distance measured in the part of foil closer to the polished surface (Fig. 6e). Additional spots at 2.59,  
246 2.17, 2.01, 1.80 Å are all compatible with the monazite lattice. The same region was observed using  
247 scanning TEM (STEM) with an annular dark field (ADF) detector (Fig. 8). In this mode, Bragg contrasts  
248 are strongly reduced and contrast arises from atomic number and density. The bands appear darker  
249 (Fig. 8a-e) due to the lower density of the glassy material within the deformation band (Fig. 8a-b). At  
250 very high magnification (Fig. 8e-f) the atomic arrangement within the monazite structure is revealed,  
251 and in Figure 8f the pattern matches the arrangement of Ce atoms in monazite along the [100]  
252 direction. High resolution STEM imaging and associated Fast Fourier Transform (FFT; Fig. 8c-e) show  
253 that the deformation bands are not completely amorphous, and contain highly disoriented nano-  
254 crystals of monazite; in Figures 8d and 5e some fringes can be observed within these bands. FFT of  
255 different areas in Figure 8c show the strong disorientation from the [100] direction (FFT1) depending  
256 on position in the band (compare FFT2 and 3 in Fig. 8c). In FFT3 the area is strongly disoriented with

257 only a faint (0-11) reflection visible. Extra spots observed at 3.58 Å in SAED in TEM mode (Fig. 7e) are  
258 also visible (arrows in FFT2), and appear when crossing the band (see arrows in FFT2).

259

260 *3.3.3. TEM foil of naturally shocked Vredefort monazite – Figure 9 (and Supplementary Data S2; Figures*  
261 *S9)*

262 One FIB-foil located across deformation twins (FIB4 in S9a) was prepared from one area of  
263 Vredefort monazite Sec-03D, grain 9 (Cavosie *et al.*, 2018). Only deformation twins (Fig. 9), have been  
264 observed. Some twins are visible along the (001) plane (Fig. 9a-b). The (001) deformation twins are  
265 consistent with those reported from prior EBSD analysis (Cavosie *et al.*, 2018). Twins along the (001)  
266 plane range from 250 nm to 1.1 µm in width, and contain an enrichment in Ca along the twin-host  
267 boundary but no enrichment nor depletion of Pb (Fig. 9c-d and S9b in Supplementary data).

268

## 269 **4. DISCUSSION**

270 *4.1. Experimental shock-deformation features up to the nanoscale.*

271 Early shock experiments on monazite (up to 59 GPa) used the shock-wave reverberation  
272 technique and high explosives for planar shock-wave generation (Deutsch and Schärer, 1990); the  
273 shocked monazite grains exhibited lower birefringence, decolorization, intense mosaicism and the  
274 presence of fractures. Laser shock experiments on monazite by femtosecond laser ablation show the  
275 effect of high-pressure shock waves caused by plasma expansion, revealing nanostructural  
276 deformation features below the ablation crater, including fractures, mosaicism, and deformation  
277 twins (Seydoux-Guillaume *et al.*, 2010; D'Abzac *et al.*, 2012). Static experimental data (using diamond  
278 anvil cell) focused on high-pressure transformation of monazite with various compositions (CePO<sub>4</sub>-  
279 Huang *et al.*, 2010; SmTbPO<sub>4</sub>-Heuser *et al.*, 2018; La, Nd, Eu, GdPO<sub>4</sub>-Lacomba-Perales *et al.*, 2010).  
280 Huang *et al.* (2010) revealed only structural lattice distortion at around 11 GPa, with no phase  
281 transition up to 20 GPa. In contrast, Lacomba-Perales *et al.* (2010) identified a non-reversible high-

282 pressure phase with barite-type structure at 26 GPa for LaPO<sub>4</sub> but no phase transition up to 30 GPa  
283 for other compositions (Gd, Eu, NdPO<sub>4</sub>).

284 In the present study, no significant difference between Raman spectra was observed between  
285 unshocked and shocked monazite samples, except for the structural distortion responsible for both  
286 Raman-band broadening and data spreading; hence no evidence for formation of a high-pressure  
287 phase was found (Fig. 2). Raman-band broadening of natural monazite is due to the combination of  
288 two effects: chemical composition (mostly Th, U, Ca and Pb) and lattice distortion caused by radiation  
289 damage (e.g. *Nasdala et al., 2002; Seydoux-Guillaume et al., 2002; Ruschel et al., 2012*). *Ruschel et al.*  
290 (2012) proposed an empirical formula for estimating the degree of radiation damage if the chemical  
291 composition is known:

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

293 where FWHM is the full width at half maximum of the most intense Raman band of monazite (i.e., the  
294  $\nu_1$  symmetric PO<sub>4</sub> stretching mode near 970 cm<sup>-1</sup>; Fig. 2). The monazite used for our experiments  
295 contains 0.12, 0.002, 0.045, and 0.003 apfu (based on 4O) for Th, U, Ca and Pb respectively, which  
296 gives a  $\Sigma(\text{Th+U+Ca+Pb})$  of 0.17 apfu (*Seydoux-Guillaume et al., 2004*). The expected FWHM is then 8.5  
297 cm<sup>-1</sup> for monazite with the same composition and no radiation damage. The FWHM of the unshocked  
298 monazite is 18.3 cm<sup>-1</sup>. Interestingly, the monazite used in the present study corresponds closely to the  
299 F6 monazite described in *Ruschel et al. (2012)*, with a  $\Sigma(\text{Th+U+Ca+Pb})$  of 0.15, a FWHM<sub>unannealed</sub> of 18.1  
300 cm<sup>-1</sup> and a FWHM<sub>annealed</sub> of 7.9 cm<sup>-1</sup>. The difference in width of Raman peaks between  
301 FWHM<sub>unannealed/unshocked</sub> (18.1 and 18.3 cm<sup>-1</sup>) values to FWHM<sub>annealed</sub> (7.9 and 8.5 cm<sup>-1</sup>) values is  
302 attributed to the “radiation damage component” (~10 cm<sup>-1</sup>). The FWHM of Raman-bands from the  
303 shocked monazite domains C1 and C2 are ~21.5 cm<sup>-1</sup> (Fig. 2). The ~3 cm<sup>-1</sup> difference in the FWHM of  
304 the Raman band between the unshocked and shocked monazite is attributed to shock-induced  
305 distortion of the lattice. The FWHM increase is expected when grain size is reduced, as broadening is  
306 inversely proportional to grain size in CeO<sub>2</sub> ceramics (e.g., *Gouadec and Colomban, 2007*). In ceria,

307 band broadening of  $3 \text{ cm}^{-1}$  is observed for grain size of about 40 nm, thus the observed broadening of  
308  $3 \text{ cm}^{-1}$  is consistent with the TEM observation of mosaicism at a similar scale (Fig. 3 and 6).

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

322 The deformation bands (Figs. 4 and 7) have not been observed in monazite before, even in  
323 shocked samples from femtosecond-laser experiments (*Seydoux-Guillaume et al., 2010; d’Abzac et al.*  
324 *2012*); this microstructure unambiguously formed in response to the shock experiment. The  
325 orientation of the deformation bands is parallel to the direction of shock wave propagation into the  
326 crystal (Figs. 4a-b and 7). They are different from typical planar deformation features (PDF) classically  
327 observed in shocked silicates by TEM like quartz (*Langenhorst and Deutsch, 2012*) or zircon (*Reimold*  
328 *et al., 2002; Leroux et al., 1999*), which are straight, sharp and continuous planes, filled with  
329 amorphous material, and sometimes decorated by bubbles formed during post-shock processes, such  
330 as annealing or alteration (*Langenhorst and Deutsch, 2012*). In the studied shocked monazite, the band  
331 structures are shorter (hundreds of nm long) and are not filled with an entirely amorphous material  
332 but instead are defined by nanometer sized domains with a highly different orientation, as shown in

333 STEM-ADF images (Fig. 8c-e and in the various FFT from Fig. 8c). This observation is also confirmed by  
334 the presence of diffraction contrasts in BF-TEM (Fig. 7c-d), a SAED pattern which shows almost no  
335 diffuse diffraction ring (Fig. 7e) but instead contains extra spots characteristic of a monazite lattice,  
336 and streaking of spots corresponding to high misorientation of nanodomains to each other and from  
337 orientation of the monazite host. We suggest that such features may represent precursor  
338 microstructural damage that leads to formation of more typical features found in shocked monazite,  
339 such as planar deformation bands (e.g. *Erickson et al., 2016*). Another possibility is that they represent  
340 partly annealed PDFs, similar to those described in various shocked minerals (e.g. *Leroux et al., 2001*),  
341 which do not remain amorphous after shock due to the ability of monazite to recrystallize in response  
342 to thermal and/or ionization processes (*Seydoux-Guillaume et al., 2004 and 2018*). These highly  
343 misoriented deformation band structures could also represent domains from which either neoblasts  
344 or a high-pressure phase could crystallize in natural shocked monazite. Additional diffraction spots  
345 observed within these domains can all be attributed to the monazite lattice (Figs. 7d-e), and thus might  
346 also represent incipient formation of neoblasts.

347

#### 348 4.2. Laser-shock experiments as analogues for naturally-shocked samples

349 One of the main objectives of the present study is to evaluate if laser-driven shock  
350 experiments reproduce the types of impact damage previously characterized in naturally shocked  
351 monazite. Shocked monazite has been reported both in bedrock of the Vredefort impact structure,  
352 South Africa (*Moser, 1997, Erickson et al., 2017*), the Nördlinger Ries crater, Germany, the Houghton  
353 dome, Canada (*Erickson et al., 2019*), the Araguinha crater, Brazil (*Erickson et al., 2017*), the  
354 Woodleigh impact structure in Australia (*Fougerouse et al., 2021a*), the Yarrabubba monzogranite and  
355 Barlangi granophyre impact melt (*Erickson et al., 2020*), and in both modern and Pleistocene alluvial  
356 deposits of the Vaal River in South Africa as detrital grains (*Cavosie et al., 2010; Erickson et al., 2013;*  
357 *Cavosie et al., 2018*). *Erickson et al. (2019)* reported shocked monazite grains from Ries Crater and  
358 Houghton dome with complex yet systematic twin relations produced by reversion from an

359 unquenchable high-pressure tetragonal polymorph, a phase not previously known. No studies have  
360 investigated shock-deformation structures in monazite at a nanometer scale, except a recent study by  
361 *Fougerouse et al. (2021a)* that focused on Pb mobility as determined from atom probe tomography, a  
362 method shown previously to demonstrate atom-scale element mobility or segregation on twin  
363 boundaries triggered by tectonic deformation (*Fougerouse et al., 2021b*).

364         The results presented here demonstrate the ability of laser-driven experiments to produce  
365 shock deformation microstructures previously described in the literature,, specifically mosaïcism, and  
366 deformation bands. Additional microstructures described by *Cavosie et al. (2018)* and *Erickson et al.*  
367 *(2017)* include deformation twinning (Fig. 9) and neoblastic domains.. We suggest that the highly-  
368 deformed bands may represent either precursor microstructural damage that leads to formation of  
369 more typical features found in naturally shocked monazite, such as planar deformation bands (e.g.  
370 *Erickson et al., 2016*) or deformation twins, which failed to form during the experiment, likely because  
371 of insufficient duration of pressure application. The presence of neoblastic domains provides evidence  
372 of localized recrystallisation of monazite during, or more likely, immediately following shock  
373 deformation. The absence of neoblasts in the laser shock-loaded monazite crystal may be explained  
374 by either (i) lower shock conditions, too low to induce recrystallization, in contrast to what can be  
375 observed in naturally shocked monazite (e.g. *Erickson et al., 2017; 2020*), or by (ii) insufficient duration  
376 of the thermomechanical load, shorter by many orders of magnitude in the experiment (~6 ns-  
377 pressure pulse, see Section 2.2), which may be below the characteristic time required to form  
378 neoblasts.

379

#### 380 *4.3. Role of radiation damage in formation of shock-deformation features?*

381         In order to ascertain shock conditions of minerals during impact events, the structural state  
382 of the mineral at the time of impact must be estimated. In the case of zircon, a mineral highly sensitive  
383 to radiation damage, formation of the high-pressure polymorph reidite is inhibited in partially  
384 metamict zircon due to the general reduction in longitudinal and shear stiffness with radiation damage



385 (*Erickson et al., 2017; Timms et al., 2018*). Extrapolation of impact conditions in natural shocked zircon  
386 can thus be complicated due to lack of knowledge of pre-impact intrinsic properties. In contrast,  
387 monazite has the ability to remain crystalline over geological time due to self-annealing of radiation  
388 damage (*Seydoux-Guillaume et al. 2004; 2018b*), however it is not known if the presence of radiation  
389 damage influences formation of shock-deformation features or high-pressure polymorphs (e.g.,  
390 *Erickson et al., 2019*). Further shock-experiments using monazite free of radiation damage as a starting  
391 material may be able to elucidate such behavior.

392           It is also worth considering that monazite samples older than 1 Ga may have accumulated a  
393 high amount of radiogenic Pb in the lattice and received intensive radiation doses. Even if clear  
394 evidence for radiation damage is limited to nm-isolated domains within monazite resulting in lattice  
395 distortion (*Seydoux-Guillaume et al., 2004*), these effects induce Raman broadening and mottled  
396 diffraction contrasts visible in TEM. At the micrometer scale, peak broadening of Raman spectra  
397 provides one indication that monazite crystals were affected by a shock event. This requires, however,  
398 knowledge of both composition and FWHM of Raman spectra of unshocked monazite samples, in  
399 order to evaluate the radiation damage component, which produces the same broadening effect  
400 (*Nasdala et al., 2002; Seydoux-Guillaume et al., 2002; Ruschel et al., 2012*). More investigations using  
401 TEM are needed to confirm a primary (shock) interpretation, and to describe in detail shock  
402 deformation features. Analysis of shocked monazite by TEM revealed intense lattice distortion in the  
403 form of mosaicism, deformation bands, and the presence of intense streaking and extra spots in the  
404 SAED pattern; these features can unambiguously be attributed to deformation that occurred during  
405 the experimental shock loading experiment. Unshocked monazite crystals (e.g. *Seydoux-Guillaume et*  
406 *al., 2004 and 2018a*) and tectonically deformed grains (*Fougerouse et al., 2021b*), did not display Bragg  
407 diffraction contrasts in bright field mode (with their corresponding SAED patterns) as pronounced as  
408 those described here that correspond to mosaicism and deformation bands. Inside the twinned areas  
409 (Fig. 9) it is almost impossible to distinguish contrasts in shocked monazite from those of tectonically  
410 deformed monazite, except in the case where twin orientations are specifically characteristic of shock

411 deformation (*Erickson et al., 2016; Fougereuse et al., 2021a*). However, in the case of common twin  
412 orientations, this criterion is not sufficient.

413

#### 414 **CONCLUSIONS**

415 This study demonstrated the ability of laser-driven shock experiments using a high-energy  
416 laser pulse of ns-order duration to produce shock-deformation microstructures observed in natural  
417 shocked monazite. We describe two main microstructural features at the nanoscale: mosaïcism, and  
418 deformation bands. Both mosaïcism and deformation bands, expressed in SAED patterns with  
419 streaking of spots, and the presence of extra spots, more or less pronounced, provide evidence to  
420 identify shocked monazite grains. Other shock-deformation features reported in naturally shocked  
421 monazite, such as deformation twins, high-pressure polymorphs and neoblastic domains, were not  
422 observed in the experimental charges. Further study is needed to evaluate the possibility of forming  
423 such features with laser-driven shock experiments. Furthermore, as the presence of radiation damage  
424 may also modify the formation of shock-deformation features, use of monazite crystals free of  
425 radiation damage may help to answer this question.

426

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437

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587

588 **Figure captions**

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

593 **Figure 2** – Raman spectra performed in unshocked and shocked (C1 and C2) domains from monazite  
594 crystal. a- average and standard deviation of the Raman spectra per group. b- diagram showing the  
595 FWHM (full width at half maximum) of the  $\nu_1$  peak as a function of its spectral position (in  $\text{cm}^{-1}$ ). These  
596 values were corrected for the apparatus function of the Raman instrument (*Nasdala et al. 2001*). The  
597 peak positions and FWHM were determined without smoothing spectra and a linear baseline was used  
598 in the spectral range  $800\text{-}1200\text{ cm}^{-1}$ . The reproducibility is better than  $\pm 0.01\text{ cm}^{-1}$  and our  
599 uncertainties on data are two magnitude lower than  $1\text{ cm}^{-1}$ .

600 **Figure 3** – Transmission Electron Microscope (TEM) images performed in C1 (FIB1). a- Selected Area  
601 Electron Diffraction (SAED) from area in b. b- Bright-Field (BF) TEM image. c- Dark-Field (DF) TEM  
602 image using spot 2 (SAED in a). Note mottled diffraction contrasts (b), streaking of diffraction spots  
603 (a), and extra spots DF1 ( $3.26\text{\AA}$ ) and DF2 ( $1.81\text{\AA}$ ) in  $[100]$  oriented SAED (a), characteristic features  
604 from mosaïcism (misoriented subgrains visible in DF-TEM in c).

605 **Figure 4** – Bright (a-b) and Dark Field (d-f) TEM images, and Selected Area Electron Diffraction (SAED -  
606 c) pattern from FIB-foil (FIB1-C1). Note the presence of band features almost parallel to each other (a-  
607 b), and moiré fringes (arrows in b), in a domain that is deeper in the FIB foil than in Figure 3. The  
608 crystallinity is very reduced inside these bands, with almost no Bragg contrasts (homogeneous grey –  
609 e). SAED pattern (c) realized across one band and the monazite (inset in e) in zone axis  $[100]$ , shows  
610 streaking of some spots and a lot of extra spots (DF1:  $3,26\text{\AA}$ , DF2:  $1,81\text{\AA}$ , DF3:  $2,06\text{\AA}$ ) proof for highly  
611 disoriented domains (misoriented subgrains visible in DF-TEM in d-f).

612 **Figure 5** – Annular Dark Field Scanning TEM (STEM) images from FIB-foil (FIB1-C1) zoom in the band  
613 domains. a-b Lower magnification images: band domains appear darker (less diffracting regions). c-d-  
614 High resolution images. Note the crystallographic fringes still visible in the dark band domain (d and  
615 e). The perfectly ordered ADF-STEM image in d shows arrangements of heavy atoms (e.g. Ce) in [100]  
616 zone axis, in agreement with the crystallographic model. A Gaussian low-pass filter for noise reduction  
617 was applied to high-magnification STEM images (c-d).

618 **Figure 6** – Bright Field Transmission Electron Microscope (BF-TEM) images (a-b and d) and Selected  
619 Area Electron Diffraction (SAED – c and e) from FIB-foil (FIB5) prepared from C2 area - Mosaicism.  
620 Note mottled diffraction contrasts (a-b), streaking of diffraction spots (c), moiré fringes (arrows in d),  
621 and extra spots in [100] oriented SAED (arrows in e), characteristic features from mosaicism  
622 (misoriented subgrains).

623 **Figure 7** – Bright Field Transmission Electron Microscope (BF-TEM) images (a-d) and Selected Area  
624 Electron Diffraction (SAED - e) from FIB-foil (FIB5) prepared from C2 area - Highly-disoriented bands.  
625 Note the presence of band features almost parallel to each other (a and b), in a domain that is deeper  
626 in the FIB foil (a). Note a very reduced crystallinity inside these bands, with almost no Bragg contrasts  
627 (homogeneous grey – c and d). SAED pattern (e) realized across one band and the monazite (inset in  
628 d) in zone axis [100], shows streaking of some spots and a lot of extra spots (arrows in e) proof for  
629 highly disoriented domains.

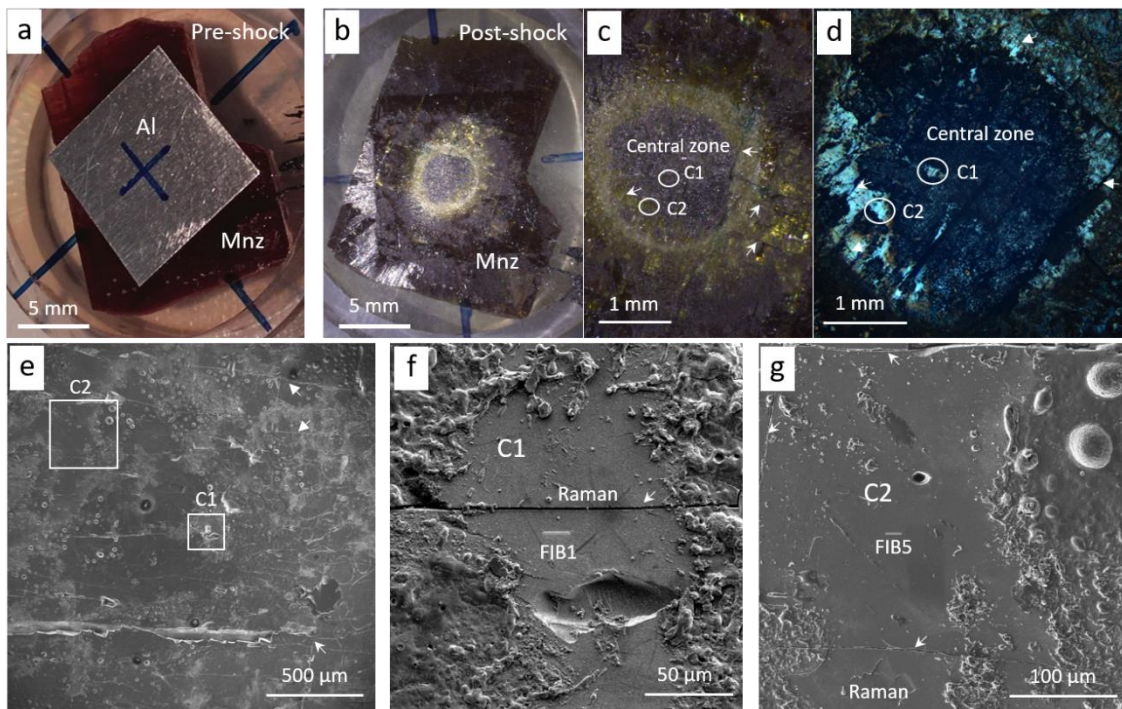
630 **Figure 8** – Annular Dark Field Scanning TEM (STEM) images from FIB-foil (FIB5) prepared from C2 area  
631 in the highly-deformed bands domain. a- Low magnification ADF-STEM image showing the presence  
632 of bands domains appearing darker (less diffracting regions). b- zoom in one band domain. c- Zoom in  
633 area inset in b and three Fast Fourier Transform (FFT) from different domains in c showing contrasts  
634 between the bright perfectly ordered domain (FFT1) and dark highly disoriented (FFT2 and 3) domains  
635 (bands). Note arrow indicating extra spot in FFT2 (measured at 3.2 Å). d-e: zoom from image in c. Note  
636 the crystallographic fringes still visible in the dark band domain (d and e). The perfectly ordered ADF-

637 STEM image in f shows arrangements of heavy atoms in [100] zone axis, in agreement with the  
638 crystallographic model (see Supp data S2).

639 **Figure 9** - Bright Field TEM images (a), SAED patterns (b), and High Resolution ADF-STEM images (c-d)  
640 from one FIB-foil prepared in one naturally shocked monazite grain (Mnz9-FIB4) from Rietputs  
641 formation (South-Africa; *Cavosie et al., 2018*). Deformation twins in (001) with Ca enrichment within  
642 the boundary (Ca map from inset in c). Details on location of FIB foil and on chemical mapping are  
643 given in Supp. Data S2.

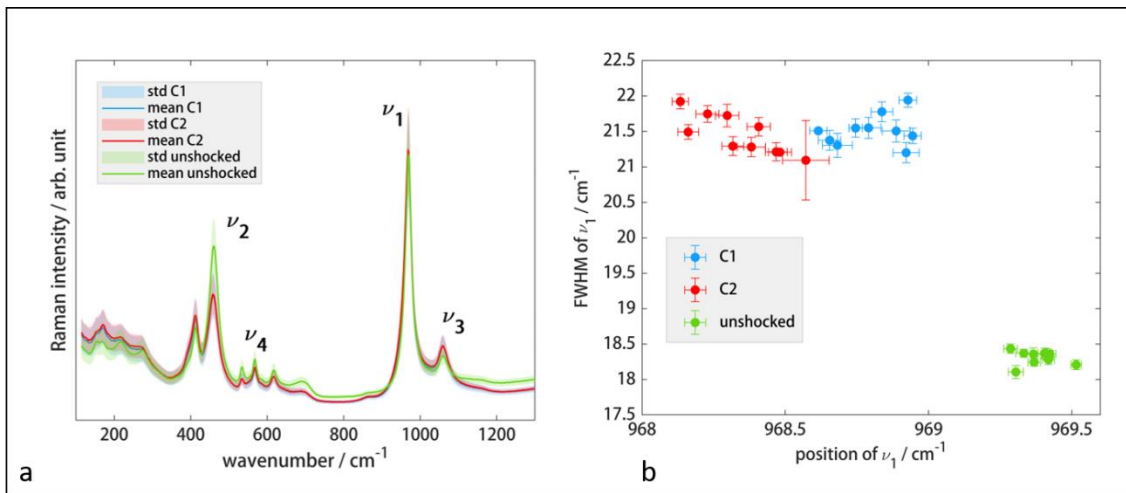
644 **Figures**

645 **Figure 1:**



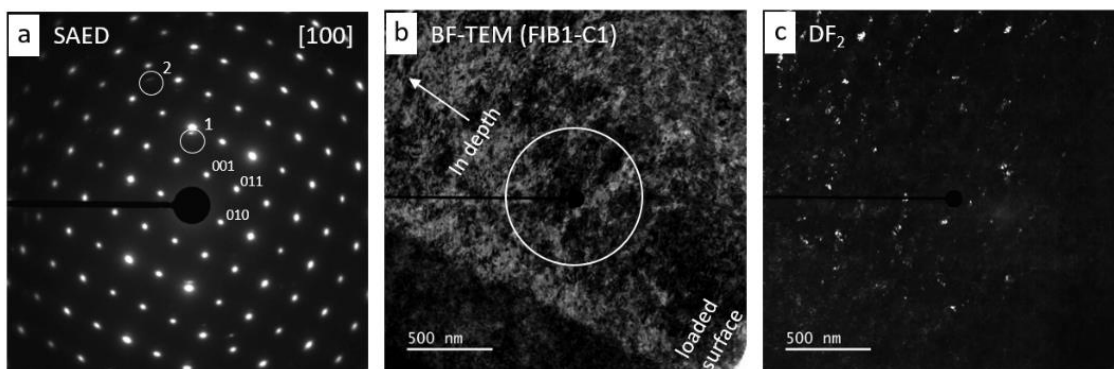
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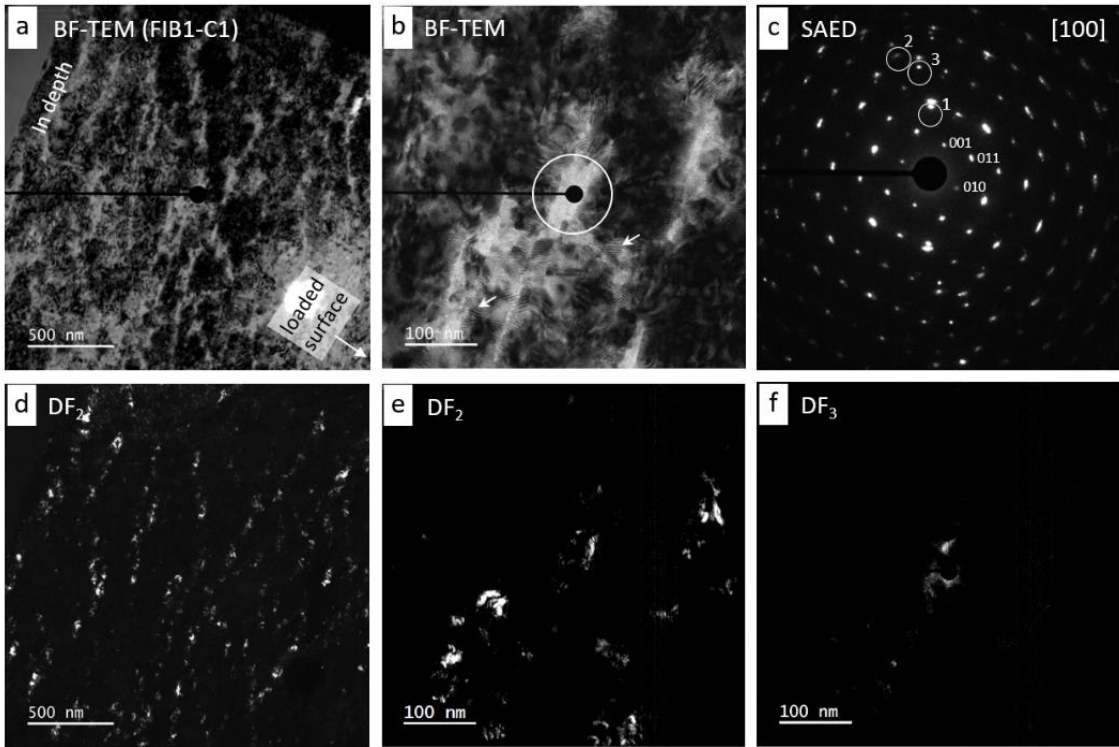
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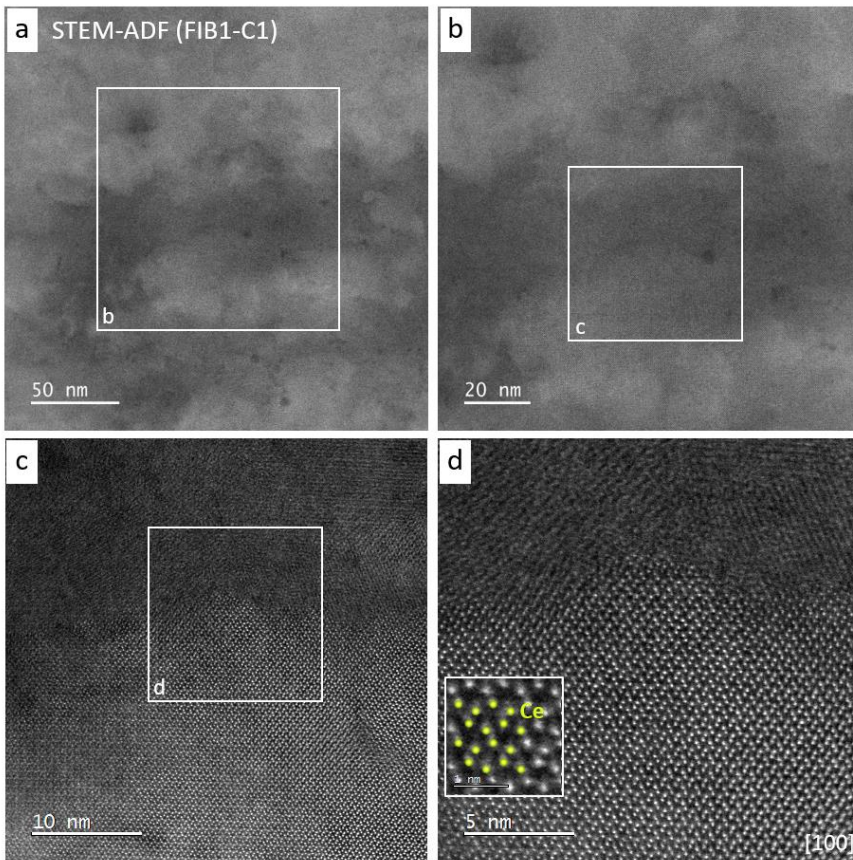
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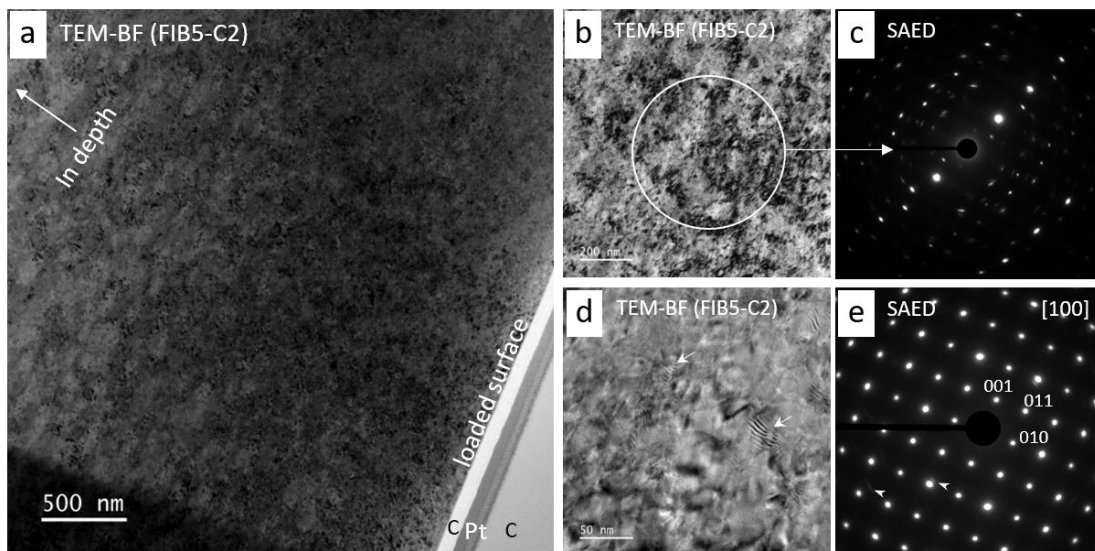
653 **Figure 5:**



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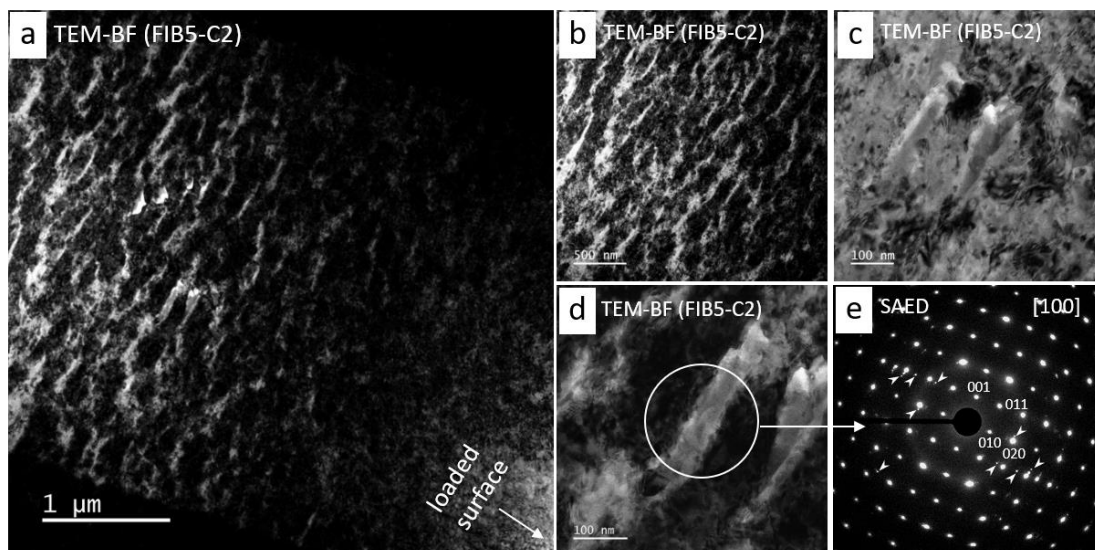
655 **Figure 6:**





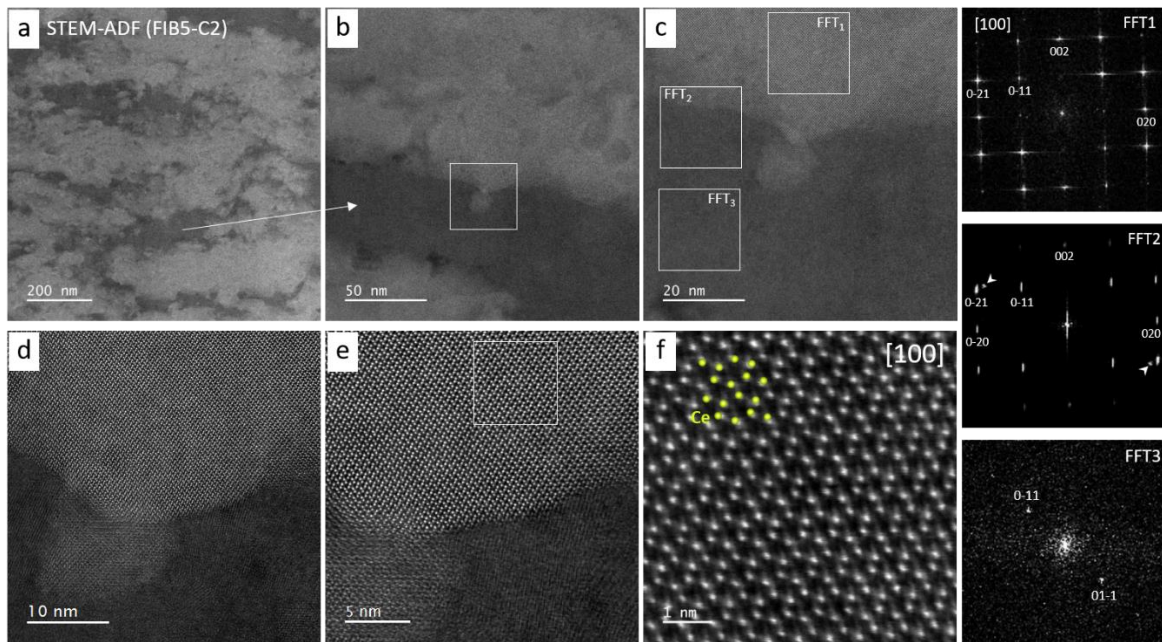
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657 **Figure 7:**



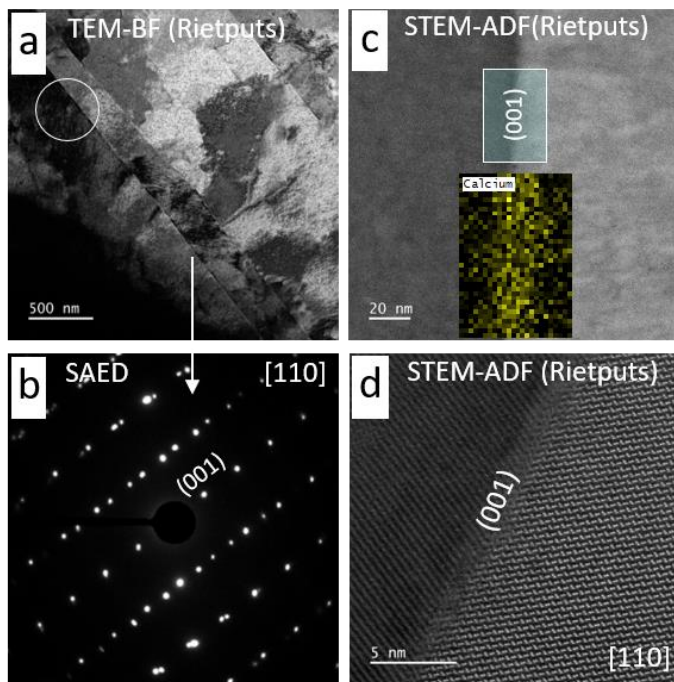
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659 **Figure 8:**



660

661 **Figure 9:**



662