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# 1 Quartz Stressing and Fracturing by Pore Pressure Dropping Down to 2 Negative Pressure

3 Lionel Mercury,\* Emmanuel De Bilbao, Patrick Simon, Hugues Raimbourg, Isabelle Bergonzi,  
4 Claudie Hulin, Aurélien Canizarès, and Kirill I. Shmulovich



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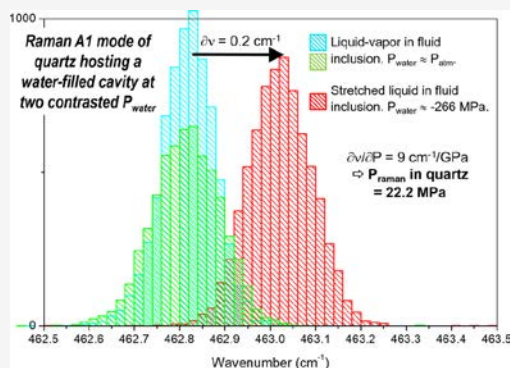
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5 **ABSTRACT:** In water-bearing porous rocks, pore pressure variations play a  
6 major role in deformation, through dissolution–precipitation and fracturing  
7 processes. An often-overlooked variation where pressure falls to negative  
8 pressure or tension can operate whenever aquifer formations dry out, for  
9 instance, in deep storage (nuclear or industrial wastes, long-term CO<sub>2</sub> mitigation,  
10 short-term energetic resources, etc.). This can generate capillary tension within  
11 the aquifers. This study investigates the mechanical effect of such in-pore tension  
12 in the surrounding crystal field, through laboratory experiments at the one-pore  
13 scale. Microthermometric procedures were carried out on synthetic fluid  
14 inclusions to generate large tensile stress and were combined with Raman  
15 microspectrometry to visualize the resulting stress fields in the host quartz. For  
16 comparison, we numerically modeled the stress field by linear elasticity theory.  
17 The experiments demonstrate that significant damage is produced in crystalline  
18 materials by the pore tension. Despite the induced stress measured by micro-  
19 Raman spectrometry to remain moderate, it is able to fracture the quartz. The volume of the cavity is a prominent controlling  
20 parameter for the stress amplitude. The crystalline heterogeneities of the solid are another major parameter for localizing the mean  
21 weak stress and accumulating overstress. Our results call for bringing pore-scale micromechanics into the safety assessment of the  
22 geological storage of various wastes inside depleted aquifers. They also show the magnifying effect of heterogeneities on propagating  
23 stress and localizing it along certain directions, promoting the final failure of water-bearing minerals, rocks, or pore networks.



24 **KEYWORDS:** *tensile strength, pore rock damage, storage safety, Raman scattering, quartz weakening, fluid inclusions*

## 1. INTRODUCTION

25 Modern societies have growing interest in water-depleted  
26 aquifers for various storage operations, which are often  
27 accompanied by enhanced drying and increasing water tension  
28 (liquid negative pressure) in the liquid infilling the pores.  
29 Water tension in pores does induce a stress in the solid lattice  
30 around the fluid-bearing cavity, which is largely overlooked  
31 while possibly conducive to crystal failure. Even in the  
32 subcritical cracking regime, low stresses, possibly amplified at  
33 the tip of microcracks because of pre-existing flaws in the rock,  
34 and slow processes, persisting in the long term, can result in  
35 rock failure (e.g., refs.<sup>1,2</sup>).

36 The micromechanics of such situations can be treated  
37 similarly to the drying-driven damage occurring in rocks at  
38 variable humidities (e.g., refs.<sup>3,4</sup>). The theory involves the role  
39 of variable water saturation, of capillary bridging forces  
40 crossing the micro/nanopores, and of disjoining forces that  
41 hinder adsorption of water in nanopores, all processes that  
42 cause strain softening and microcracking. In all these studies, it  
43 is difficult to distinguish at the relevant scale the mechanical  
44 role of field stress created by pore tension from stress corrosion

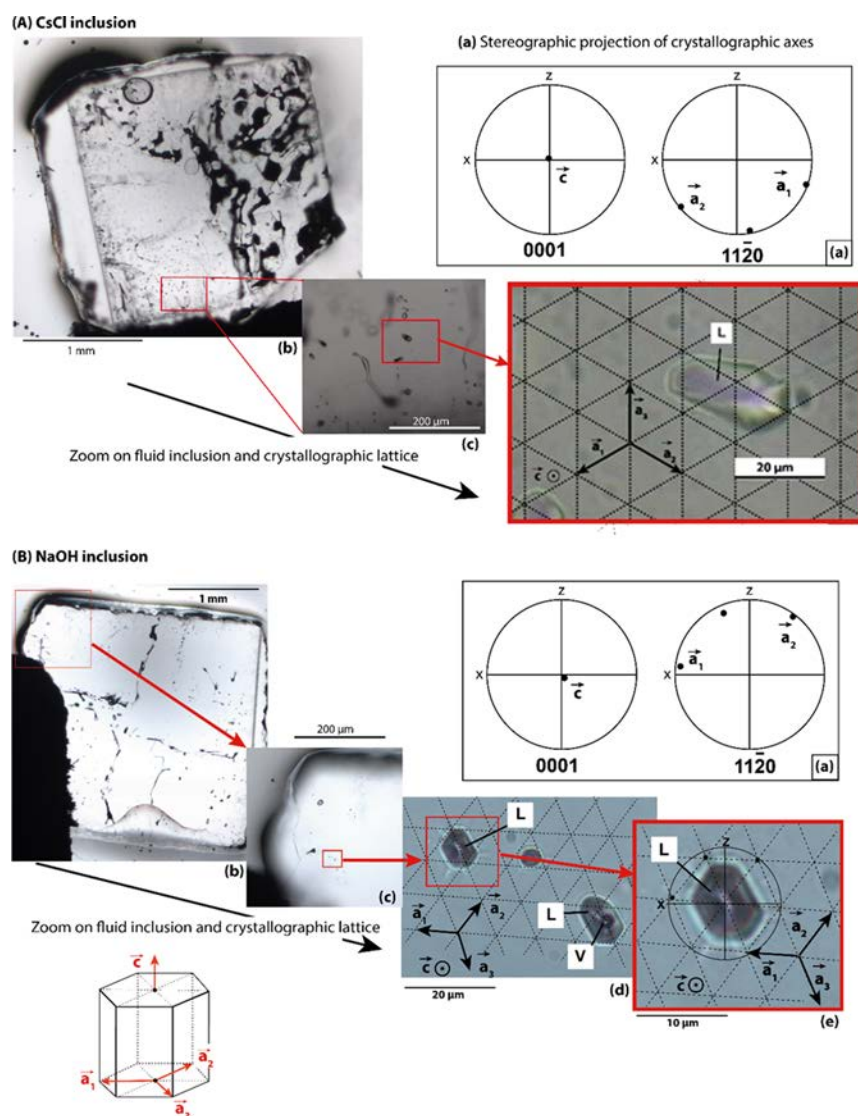
of chemical origin, which contributes to water weakening.<sup>5,6</sup> In  
particular, imaging and quantification of the microstress in the  
solid network, before and after fluid tension sets up in the  
pores, have been missing until now.

The challenges associated with this area of research are first  
in materials science in which several examples of tension-  
driven fracture processes still require mechanistic explanations  
or quantification. While sol–gel processing explains how  
drying-driven stress causes bodies to crack, how nanoparticle  
suspensions dry is much less understood, depending  
appreciably on molecular-scale physics combining capillary  
and viscous forces (e.g., refs.<sup>7,8</sup>). How cementitious materials  
dry is also of interest. There is little doubt there, ever since the  
pioneering work<sup>9,10</sup> showing that the main driving force is 58

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**Figure 1.** Photomicrographs and EBSD measurements of the two inclusions of interest (L = liquid aqueous solution; V = vapor). A. CsCl inclusion entirely filled by aqueous solution. B. NaOH inclusion. For each inclusion, two stereoplots show the orientation of the  $[0001]$  and  $[11\bar{2}0]$  axes within the host quartz, located perpendicular and parallel to the polishing plane, respectively. The redundant coordinate system ( $a_1$ ,  $a_2$ ,  $a_3$ ,  $c$ ) is used (hexagonal lattice).

59 capillary tension, possibly relayed in the smallest spaces by  
 60 disjoining pressure effects (e.g., refs<sup>11–14</sup>). However, the main  
 61 challenges are the role these processes may play in crystalline  
 62 natural rocks, as for hydrosystems subjected to drying  
 63 operations. The issue is understanding if and how these  
 64 processes are able to generate new pore-scale stress fields and  
 65 modify the cracking network of a rock as well as the air/water  
 66 permeability throughout the aquifer. For illustration, nuclear  
 67 waste storage in low-permeability rocks requires shaft and drift  
 68 mining that dries out the rocks, expected over a few meters  
 69 around galleries (e.g., refs<sup>15–19</sup>). On the one hand, ventilation  
 70 of the tunnels promotes high tensions that can reach  $-100$   
 71 MPa or more.<sup>19</sup> On the other hand, geochemical traces of air  
 72 introduction are recorded up to 21 meters from the ventilated  
 73 tunnel, whereas the formation is assumed to be water-saturated  
 74 at such a distance (e.g., refs<sup>18,20</sup>). The second illustration is the  
 75 injection of (supercritical)  $\text{CO}_2$  into deep aquifers. This  
 76 provokes intense drying in the near field of the wellbore with  
 77 strong and counterintuitive capillary effects.<sup>21–23</sup> Third,  
 78 enhanced-oil recovery operations play with successive

sequences of various fluid injections (air, liquid, and oil). 79  
 The water invasion in dried rocks is known to induce 80  
 weakening effects without a clear viewpoint on the active 81  
 mechanisms (e.g., refs<sup>24,25</sup>). Fourth, salt damage to cultural 82  
 heritage stones is mostly interpreted as the role of 83  
 crystallization pressure but is accompanied by significant 84  
 desaturation and capillary effects (e.g., refs<sup>14,26</sup>). 85

The key objective of this contribution is therefore to address 86  
 drying-driven microcracking mechanisms, which may down- 87  
 grade the material's quality and impact the physical properties 88  
 (transmissivity and safety storage) of the damaged rock. Two 89  
 experiments were designed with fluid inclusions synthesized in 90  
 monocrystalline quartz and filled with aqueous solutions. As 91  
 such, they stand for pores in crystalline and cemented materials 92  
 but cannot be directly used to draw conclusions on natural 93  
 fluid inclusions that contain less structural water and lower 94  
 dislocation densities than synthetic fluid inclusions (SFIs). The 95  
 occluded liquid was put under variable high tensions with 96  
 various time frames, according to a microthermometric 97  
 procedure (closed univariant system) (e.g., refs<sup>27–31</sup>). The 98

99 Raman shift of the quartz was mapped and shown to vary as a  
100 function of the in-pore tension, therefore visualizing the  
101 internal stress fields in the host crystal.

102 Two levels of damage occurred during the course of these  
103 experiments: optically invisible damage at the microscale and  
104 visible fracturing of the host quartz. The experimental  
105 investigations were compared to a numerical simulation  
106 based on isotropic linear elasticity. The distance of influence  
107 of the in-pore tension inside the host quartz appears strikingly  
108 larger than expectable, while the simulated and measured  
109 distributions of stress in the crystal match.

## 2. MATERIALS AND METHODS

110 **2.1. Samples.** SFIs have been synthesized in two  
111 monocrystalline pieces of hydrothermal quartz. After thermal  
112 fracturing, the quartz pieces were healed at high pressure and  
113 temperature ( $P, T$ ) by  $\text{SiO}_2$  overgrowth, in the presence of an  
114 aqueous solution of known composition.<sup>30</sup> One quartz piece  
115 was healed in the presence of a CsCl 13.6 M (69.6 wt %) brine,  
116 at 630 MPa and 480 °C for 20 days. Under ambient  
117 conditions, CsCl inclusions contain either two phases (a  
118 bubble of gas and a liquid phase) or a monophasic liquid-only  
119 phase (Figure 1). This trapped solution is known to sustain the  
120 most extreme tensile strength ever recorded in aqueous fluids<sup>30</sup>  
121 and therefore will serve to install super-high tensile stress. In  
122 addition, the decreasing water activity associated with the CsCl  
123 electrolyte (0.57 from Pitzer calculations at 25 °C<sup>32</sup>) may  
124 contribute to water weakening by enhancing solubility,  
125 especially at the stress concentration zones.

126 The other quartz piece was hydrothermally treated at 500  
127 °C, 600 MPa for 45 days, in the presence of a 0.2 M NaOH  
128 dilute solution. Under ambient conditions, these NaOH  
129 inclusions also contain either two phases—a bubble of gas  
130 and a liquid phase—or a monophasic liquid-only phase (Figure  
131 1). The dilute NaOH solution trapped under high-density  
132 conditions is prone to install liquid tension at room  
133 temperature (RT)<sup>30</sup> and so serves to exhibit long-term tensile  
134 stress.

135 These two electrolytes make the quartz more soluble,  
136 especially under the synthesis conditions (0.63 GPa, 480 °C,  
137 and 20 days for the first; 0.6 GPa, 500 °C, and 45 days, for the  
138 second), so they may produce inclusions with very good inner  
139 surfaces well prone to hosting superheating processes.  
140 According to previous datasets,<sup>30</sup> and as mentioned above,  
141 CsCl solutions can sustain the most extreme tensile strength  
142 ever recorded in aqueous fluids, while dilute NaOH solutions  
143 are efficiently superheated at RT or below (high-density  
144 samples). Additionally, the role of both electrolytes during  
145 these experiments should have enforced the tensile stress by a  
146 chemical “weakening” effect. However, considering the slow  
147 kinetics of the dissolution–precipitation process under the  
148 thermometric cycle conditions, this effect is certainly of  
149 secondary importance.

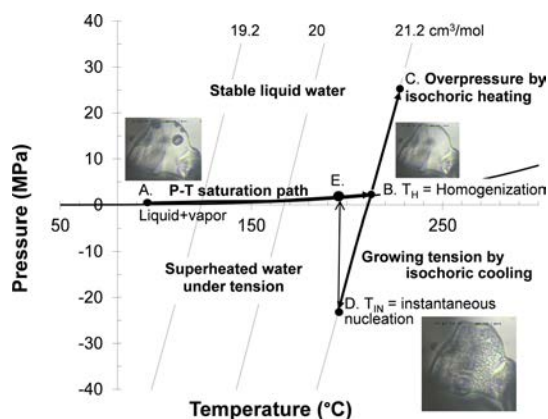
150 Electron back-scattered diffraction (EBSD) was used to  
151 determine the crystallographic orientation of the quartz  
152 samples around the fluid inclusions, after the microthermo-  
153 metric studies, to prevent any electron-driven defects. To do  
154 so, thin sections were chemically polished with a colloidal silica  
155 suspension (0.04  $\mu\text{m}$  colloidal silica suspension, Struers) and  
156 then carbon-coated to prevent charging effects. All sections  
157 were tilted by 70° to the electron beam to produce clear  
158 diffraction patterns. Data were collected using an EDAX  
159 PEGASUS EDS/EBSD system and processed with OIM DC

6.4 software (manufacturer EDAX, Mahwah, USA), available at  
BRGM (Orléans, France). The working distance was of about  
18 mm, at an accelerating voltage of 25 kV.

The samples are platelets containing the  $a$ - and  $b$ -axes and  
thus perpendicular to the crystallographic  $c$ -axis (Figure 1).

**2.2. Method 1: Establishing Tensile Conditions in the Pore Fluid.** High tension can be produced in a liquid  
occluded inside a closed cavity, by making it monophasic  
through increasing temperature and then cooling down this  
monophasic liquid below the saturation curve along a constant  
volume trajectory. This procedure was largely used in the past  
to study the phase diagram of tensile water (e.g., refs.<sup>27–31</sup>)  
and the corresponding changes of phase equilibria (e.g.,  
refs.<sup>33,34</sup> using fluid inclusions; refs.<sup>35,36</sup> using Berthelot tubes).

The starting pore material generally contains a biphasic  
liquid + vapor assemblage (L + V). With progressive heating,  
the liquid density and bubble pressure change, and the trapped  
liquid progressively invades the whole inclusion space (A to B  
path, Figure 2) up to a particular density where there is no



**Figure 2.** Phase diagram of pure water in the  $P$ – $T$  space, calculated with the IAPWS-95 equation of state.<sup>37</sup> Each isochore is labeled with the molar volume in  $\text{cm}^3 \cdot \text{mol}^{-1}$ . The CsCl inclusion micrographs illustrate the fluid content present in the cavity at each characteristic step.

more vapor (point B, Figure 2). The inclusion is then  
recognized to be homogenized at the corresponding  
“homogenization temperature” ( $T_H$ ). Further heating drives  
the  $P$ – $T$  conditions in the inclusion along the isochore curve  
inside the stable domain of liquid (B to C path, Figure 2). The  
second step is the progressive cooling of the sample, which  
follows the isochoric path as long as the inclusion remains  
homogeneously filled with liquid (C to D path without  
nucleation at B, Figure 2). Once  $T_H$  is crossed without bubble  
nucleation, the monophasic liquid becomes metastable; that is,  
it is less stable than the liquid–vapor assemblage. The  
nucleation does not occur as long as the energy cost of the  
vapor–liquid interface fabrication is higher than the gain  
afforded by the bulk energy of the most stable phase.<sup>31,38</sup> Such  
a monophasic liquid is superheated (located to the right of the  
saturation curve) and follows an isochoric cooling down to a  
certain temperature at which a bubble appears suddenly. This  
is the instantaneous nucleation temperature ( $T_{IN}$ ), which is  
always located within the tensile domain: nucleation in fluid  
inclusions disobeys the saturation conditions. After nucleation,  
the newly formed LV assemblage moves instantaneously back  
to the saturation curve conditions (D to E path, Figure 2). This

201 procedure fabricates tensile water similar to that retrieved at  
202 the high capillary degree that forms under drying conditions.  
203 All thermal sequences were carried out on a Linkam  
204 heating–cooling stage THMS600, at a slow rate (2 °C/min) to  
205 avoid any temperature overshoot and guarantee a thermal  
206 equilibrium at each set point.

### 207 2.3. Method 2: Measuring the Stress in the Container.

208 In situ Raman spectrometry can be used to record the  
209 temperature/pressure shift of a solid material because of the  
210 anharmonicity of a Raman-active vibration mode.<sup>39</sup> Anhar-  
211 monicity is generally considered to have two contributions:  
212 explicit ones (as phonon–phonon interactions) and implicit  
213 ones coming from changes in bond lengths (under  $P$  or  $T$   
214 variations) (e.g., refs.<sup>40,41</sup>). Both will lead to the wavenumber  
215 shift of vibration modes upon external solicitations such as  
216 temperature or hydrostatic pressure. A previous study on  
217 quartz<sup>42</sup> investigated the changes in wavenumber and line-  
218 width of the 206 and 464  $\text{cm}^{-1}$   $A_1$  Raman modes of  $\text{SiO}_2$  from  
219 23 to 800 °C and from 0.1 MPa to 2.1 GPa. It was observed  
220 that, under hydrostatic stress, the wavenumber shift of the 464  
221  $\text{cm}^{-1}$  peak at RT (23 °C) depends linearly on pressure up to  
222 0.5 GPa:  $d/dP = 8.7 \text{ cm}^{-1}/\text{GPa}$ . The wavenumber shift for the  
223 206  $\text{cm}^{-1}$  mode also has linear pressure dependency, twice as  
224 much at  $d/dP = 20 \text{ cm}^{-1}/\text{GPa}$ . Schmidt and Ziemann<sup>42</sup>  
225 considered an isotropic stress according to the Grüneisen  
226 formalism, with a linear dependence between stress and Raman  
227 wavenumber. This linear approach is certainly the most reliable  
228 to treat the complex case of a noncubic crystalline symmetry,  
229 noninfinite crystal because of the inclusion vicinity, and  
230 nonuniform force field and is the method used here, assuming  
231 that the stress field induced by pressure change in the fluid  
232 inclusion is similar to hydrostatic stress and considering the  
233 isotropy in (a,b)-plane. As no resonant Raman scattering effect  
234 occurs here, the stress/Raman shift relation obtained by  
235 Schmidt and Ziemann<sup>42</sup> with a 514.5 nm laser can be used for  
236 any other nonresonant Raman excitation laser line.

237 The measurements were performed on a Renishaw inVia  
238 Reflex spectrometer, using the 633 nm excitation line of a He–  
239 Ne laser (less than 10 mW on the sample). The grating was  
240 1800 grooves/mm, giving a wavenumber step between two  
241 adjacent pixels of the charge-coupled device equal to 0.97  
242  $\text{cm}^{-1}$ . Each mapping measurement was performed after a  
243 wavenumber calibration procedure of the spectrometer on its  
244 internal silicon reference sample (520.5  $\text{cm}^{-1}$ ), without moving  
245 the quartz sample, which ensures the calibration state and  
246 promotes the best possible reproducibility. The calibration was  
247 systematically checked after map acquisitions and was stable  
248 within an accuracy much better than  $\pm 0.1 \text{ cm}^{-1}$  over 24 h (no  
249 detectable change of the 520.5  $\text{cm}^{-1}$  position). The micro-  
250 scope (DM2500 Leica) lens compatible with this configuration  
251 was a Leica 50X long front distance (NA = 0.50). Each  
252 individual Raman spectrum was obtained with an accumulation  
253 time of 10 s. Because of the small diameter of the Raman spot  
254 ( $\approx 2 \mu\text{m}$ ) and the size of the inclusions, maps of around 7600  
255 points were acquired, with an acquisition total time reaching  
256 20 h. The map acquisitions were performed in the Renishaw  
257 StreamlineHR mode, optimizing the acquisition time and the  
258 vertical resolution (equivalent to a confocal mode), here  
259 estimated to be better than 2  $\mu\text{m}$ .

260 Spectra were treated with Renishaw Wire 3 software. The  
261 Raman spectra were not baseline-corrected but directly fitted  
262 with a Gauss–Lorentz (G/L hereafter) profile, to involve even  
263 the tiniest distortions in the analysis. Very small differences

between mono- and biphasic conditions could thus be probed  
264 because the spectra were acquired with strictly identical  
265 conditions (optical configuration and temperature), apart from  
266 the pressure inside the inclusion. No Bose–Einstein thermal  
267 correction was performed<sup>43</sup> because Raman shifts were  
268 compared at identical temperatures under two different  
269 pressure conditions (monophasic and biphasic regimes).<sup>39</sup> 270

### 271 2.4. Method 3: Super-Stressing the Container toward

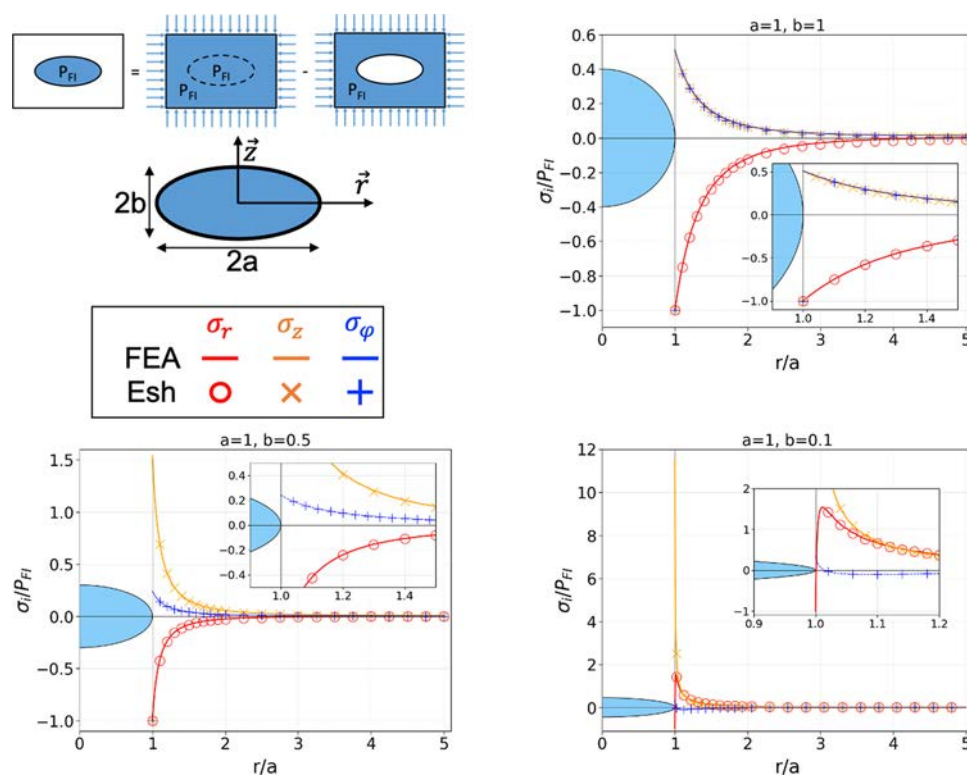
**272 Failure.** Two methods were used to establish whether the  
273 stress induced in quartz by the in-pore tension was able to  
274 provoke the quartz failure. First, the characteristics of the CsCl  
275 fluid inclusion allowed us to subject it to high tension  
276 cyclically. The procedure was simply to put the inclusion at  
277 various temperatures of measurements ( $T_{\text{MEAS}}$ ) corresponding  
278 to different high tensions and leave the inclusion in this  
279 monophasic metastable state until cavitation occurs, bringing  
280 back the inclusion to the LV equilibrium state. Then, the  
281 inclusion was homogenized and again cooled down to a certain  
282  $T_{\text{MEAS}}$  pursuing the cycle. From a mechanical point of view,  
283 these repeated stress conditions can damage the solid  
284 depending on the lattice's defaults, the intensity of the stress,  
285 and the number of cycles.

286 Second, the NaOH fluid inclusions allowed us to install  
287 high-tension conditions at RT, so the liquid tension could be  
288 readily maintained over a long time. Therefore, stress is  
289 accumulated within the sample over time, as long as bubbles  
290 are absent (easily verified by optical observations) in the  
291 superheated inclusions: this was a permanent or “enduring”  
292 tension experiment, corresponding to purely static stress  
293 conditions.

### 294 2.5. Method 4: Simulating the Stress in the Host

**295 Crystal as a Function of in-Pore Fluid Tension.** Numerical  
296 simulations of the experiments were performed by finite  
297 element analysis (FEA hereafter) using Comsol Multiphysics  
298 software for a deeper understanding of the stress change  
299 observed by Raman spectroscopy. In the first approach, the  
300 sample was modeled as a 2D axisymmetric solid containing an  
301 oblate spheroidal inclusion.<sup>44</sup> The stress field around a cavity  
302 has been studied many times. In particular, Eshelby<sup>45</sup> studied  
303 how an applied stress, uniform at large distances, is disturbed  
304 by a cavity. From this early work, many analytical or closed-  
305 form analytical solutions have been proposed for spherical or  
306 spheroidal inclusions and considering isotropic or anisotropic  
307 materials.<sup>46–54</sup> The problem becomes more complicated for a  
308 spheroidal cavity hosted in an anisotropic solid. On the other  
309 hand, FEA has proved its reliability for solving mechanical  
310 problems especially in the case of linear elastic problems but  
311 also in the case of geometric nonlinearity and with nonlinear  
312 isotropic elastic materials.<sup>55</sup> Actually, FEA can be applied  
313 whatever the geometry of the inclusion.

314 In a first approach, the sample was modeled as a 2D  
315 axisymmetric solid containing an oblate spheroidal inclusion,<sup>44</sup>  
316 and the finite-element-based results were compared with  
317 theoretical results obtained using the code recently developed  
318 by Meng et al.<sup>51–53</sup> which gives quasianalytical strain/stress  
319 fields following Eshelby's solution, with the elliptic integral  
320 approximated through a numerical routine. The purpose of this  
321 comparison was to determine the size of the solid surrounding  
322 the cavity to avoid boundary effects and define the meshing  
323 strategy to avoid numerical artifacts or errors and to better  
324 understand the stress field building around the inclusion. An  
325 isotropic elastic material was defined in the solid part with  
326 Young's modulus of 100 GPa and Poisson's coefficient of 0.326



**Figure 3.** Normalized stress along the radial axis. The normalized stresses are calculated by dividing the stresses by the pressure applied onto the inclusion wall. The normalized radial coordinate is the radial coordinate divided by the half-length of the spheroid,  $r^* = r/a$ . The stresses denoted “Esh” were calculated following Eshelby’s theory<sup>45</sup> by applying script developed by Meng et al.<sup>31–53</sup> and according to the superposition principle for linear elastic mechanics (top-left of the figure). Stresses that were noted by FEA were calculated using Comsol Multiphysics software. For all the calculations, Young’s modulus and Poisson’s coefficient were 100 GPa and 0.06, respectively, according to ref.<sup>56</sup>

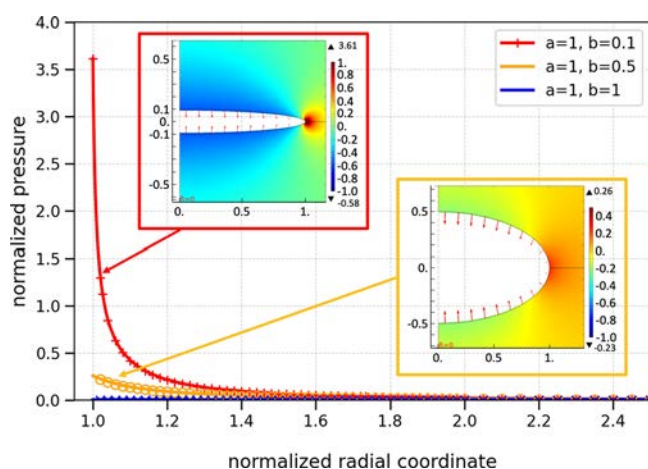
327 0.06.<sup>56</sup> These elastic properties correspond to equivalent quasi-  
 328 isotropic quartz obtained by Voigt–Reuss–Hill averaging.<sup>56</sup>  
 329 The inclusion was defined with null elastic constants, and a  
 330 negative pressure  $P_{FI}$  (e.g.,  $P_{FI} = -1$  MPa) was applied on the  
 331 cavity wall. For the theoretical solution, the superposition  
 332 principle was applied as the code because it does not directly  
 333 apply pressure on the cavity wall (Figure 3, top, left).  
 334 Unstructured triangular quadratic elements were applied for  
 335 the FEA, and zero displacement was applied to the symmetry  
 336 plane (horizontal) perpendicular to the revolution axis  
 337 (vertical). The stresses  $\sigma_{ii}/P_{FI}$  lying along the radial direction  
 338 were compared (Figure 3). For the sake of simplicity, the stress  
 339 sign convention commonly used in mechanics has been  
 340 changed in this paper, and a positive stress refers to a  
 341 compressive state. The pressure has also been changed  $P_T =$   
 342  $Tr(\bar{\sigma})/3$  instead of  $P_T = -Tr(\bar{\sigma})/3$  to keep its usual meaning,  
 343 namely, a positive value refers to a compressive state. The  
 344 stresses were normalized by dividing each of them by  $P_{FI}$  (  
 345  $\sigma_{ii}^* = \sigma_{ii}/P_{FI}$ ), and the radial coordinate was divided by the half-  
 346 length of the ellipse  $a$  ( $r^* = r/a$ ).

347 We considered three shapes defined by the semiaxis ratio  $b/a$   
 348  $a$  (hereafter called shape factor), where  $a$  and  $b$  are the  
 349 semi-axes in the radial and axial directions, respectively. The  
 350 third semi-axis  $c$  is equal to the radial axis in the oblate  
 351 spheroid. Simulated results are in very good agreement with  
 352 theoretical results for all the stresses, proving that the solid  
 353 model size was large enough and the meshing strategy was  
 354 suitable. The FEA model was validated. The results show  
 355 clearly the stress concentration effect induced by the cavity and  
 356 the dependence of the concentration amplitude on the shape

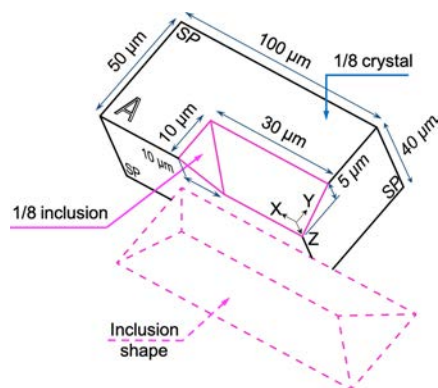
factor  $b/a$ . For a sphere,  $b/a = 1$ , the axial and tangent stresses  
 357 are equal and compensate the radial stress, and the resulting  
 358 pressure is null. Each stress does not exceed the pressure, and  
 359 no stress concentration effect occurs. On the contrary, when  
 360 the spheroid is flattened, the axial and tangent stresses are not  
 361 equal any longer, and they do not compensate the radial stress.  
 362 The axial stress largely predominates the other stresses and  
 363 reaches up to 12 times the fluid inclusion pressure. The  
 364 positive values of the axial stress and pressure indicate a  
 365 compressive state in equatorial plane although a tensile stress is  
 366 applied on the cavity wall (negative pressure  $P_{FI}$ ) (Figure 4).  
 367 This effect is due to the flattening of the spheroid and is  
 368 magnified when the shape factor decreases.  
 369

Once validated, the ellipsoid-based model was used to  
 370 simulate the experiments. A negative (tensile) pressure was  
 371 applied on the 2D elliptical edge to simulate the in-pore  
 372 pressure change. No gradient or interfacial effects of any sort  
 373 that may “buffer” the liquid-to-solid pressure transmission were  
 374 taken into account. The anisotropy of  $\alpha$ -quartz was considered,  
 375 and the elastic moduli were defined according to Calderon et  
 376 al.<sup>57</sup>  
 377

Second, the sample was modeled with a 3D prismatic solid  
 378 containing a faceted inclusion to look like the inclusion  
 379 observed with Raman spectroscopy (Figure 5). Only an eighth  
 380 of the sample was modeled considering symmetry conditions,  
 381 and the dimensions were defined to match the inclusion  
 382 actually considered. Zero displacement was applied to the  
 383 three symmetry planes (SP), and a negative pressure was again  
 384 applied on the inner surfaces of the inclusion. The same  
 385



**Figure 4.** Simulation of a host with a spherical or spheroidal inclusion with a negative (tensile) pressure applied on the wall cavity. See Figure 1 for more details on the model. Normalized pressure simulated with FEA and depending on shape factor  $b/a$ , maps, and values along the radial axis. For each shape factor, the continuous line and marks represent the FEA-based pressure and the Eshelby-based pressure, respectively.



**Figure 5.** Geometry of the 3D mechanical model of the inclusion for the FEA. Because of symmetries (SP), only an eighth of the solid is modeled. The image size is not scaled with the prism size for visibility purposes.

386 anisotropic elastic moduli as for the previous simulation were  
387 used.

### 3. EXPERIMENTAL RESULTS AND INTERPRETATION

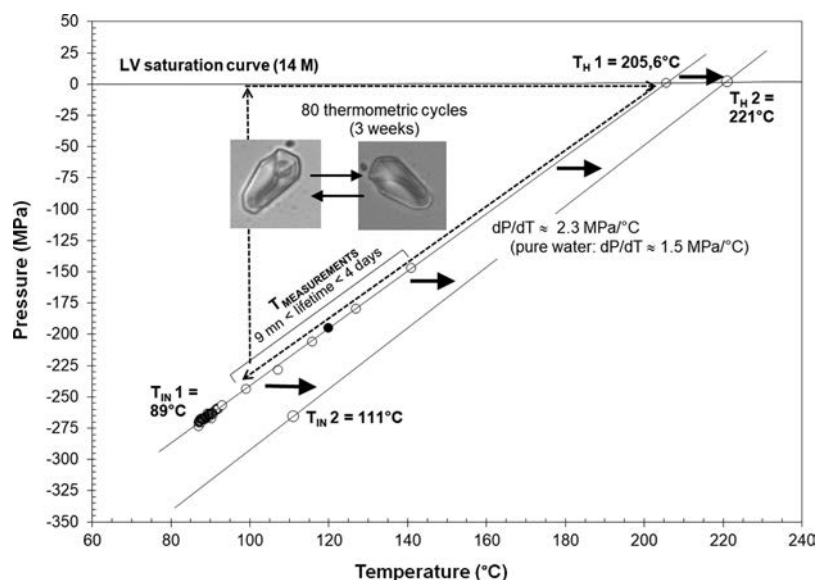
388 **3.1. Stressing the Container (CsCl Inclusion).** The CsCl  
389 fluid inclusion has a  $T_H$  of  $205.6 \pm 0.4$  °C and  $T_{IN}$  of  $89 \pm 1.4$   
390 °C. Drawing a straight line from the synthesis conditions (630  
391 MPa and 480 °C) to the  $(T_{lv}, P_H)$  pair ( $dP/dT = 2.3$  MPa/°C),  
392 and extrapolating this line to the  $T_{IN}$  value, gives the liquid  
393 tension existing in the inclusion just before the nucleation, at  
394  $-266 \pm 3$  MPa (Figure 6).

395 First, the Raman maps all around a CsCl inclusion were  
396 recorded at 120 °C while the internal pressure in the liquid was  
397 either 0.12 MPa, corresponding to biphasic liquid–vapor  
398 assemblage, or  $-194$  MPa, corresponding to the metastable  
399 monophasic state with liquid under tension. Each mapping  
400 took 20 h. The chosen temperature of 120 °C was sufficiently  
401 above the  $T_{IN}$  to avoid any nucleation during the Raman  
402 measurement time. Indeed, the metastable lifetime depends  
403 exponentially upon the distance to  $T_{IN}$ .<sup>58–60</sup>

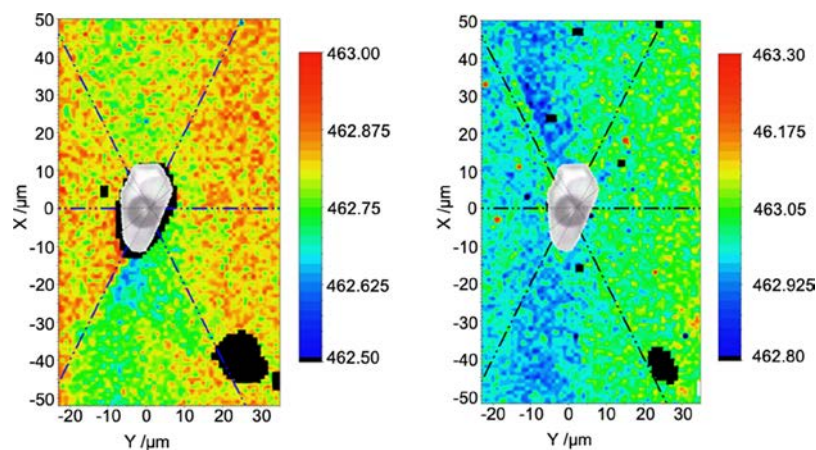
Two  $A_1$  Raman modes of  $\text{SiO}_2$  with highest wavenumbers 404  
were studied: the mode at  $464$   $\text{cm}^{-1}$  and the mode at  $206$  405  
 $\text{cm}^{-1}$ . The signal was mapped in the quartz around the  
inclusion (width  $70$   $\mu\text{m}$   $\times$  height  $110$   $\mu\text{m}$ ) that contained the 406  
fluid. A G/L profile was fitted with the recorded spectrum at 407  
each point, and the characteristic wavenumber of the G/L 408  
profile was used to build the map. The map obtained with the 409  
 $464$   $\text{cm}^{-1}$  mode in the stable state (biphasic liquid–vapor 410  
assemblage) shows actual wavenumbers ranging from  $462.5$  to 411  
 $463.1$   $\text{cm}^{-1}$  with a mean value of  $462.8$   $\text{cm}^{-1}$  (Figure 7). 412  
Black spots correspond to regions where the Raman line intensity 413  
decreases below a threshold and were used to locate the 414  
inclusions. The barycenter of the black spot corresponding to 415  
the inclusion of interest was used as the origin of the map. 416  
Finally, a micrograph of the inclusion of interest has been 417  
superimposed by aligning the lattice directions determined 418  
with EBSD with the Raman map with a perfect match. The 419  
dark spot is slightly bigger than the inclusion image because of 420  
the empirical determination of the threshold. 421  
422

Applying the Schmidt and Ziemann<sup>42</sup> relation at  $120$  °C 423  
gives an expected wavenumber of  $462.4$   $\text{cm}^{-1}$ , which can 424  
favorably be compared with our mean measured wavenumber 425  
 $462.8$   $\text{cm}^{-1}$ . Because of uncertainties (absolute calibration of 426  
two different spectrometers, accuracy on the wavenumber of a 427  
“reference” quartz totally stress-free at RT), these values look 428  
similar. Though the wavenumbers of the map seem to follow a 429  
rather narrow spread, their spatial distribution is well organized 430  
around the inclusion. Four zones aligned with the crystal axes 431  
show a remarkable symmetry (Figure 7, left). In the upper and 432  
lower triangular zones (where green predominates), the 433  
wavenumber is close to  $462.75$   $\text{cm}^{-1}$  while it is close to  $463$  434  
 $\text{cm}^{-1}$  in the lateral zones (orange/red pixels). The sharp 435  
variation in internal pressure between these domains leads us 436  
to think of some localized strains on planar defects, presumably 437  
connected with how the inclusion formed (thermal fracturing 438  
followed by  $\text{SiO}_2$  overgrowth). 439

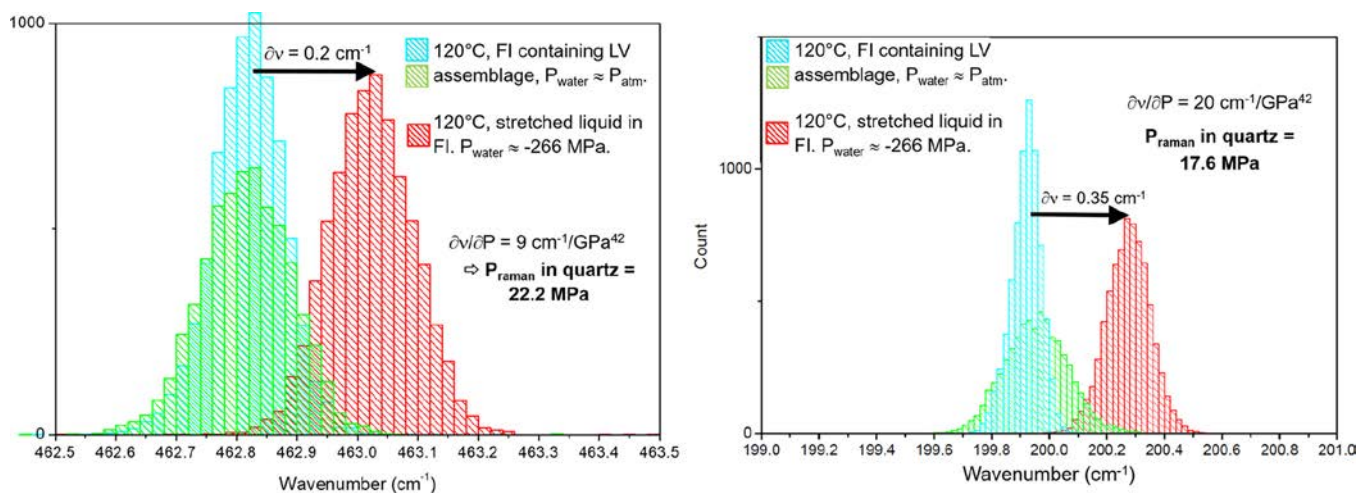
The map obtained from inclusion in the monophasic state 440  
for the same  $A_1$  Raman mode is presented in Figure 7 on the 441  
right. Again, the micrograph of the inclusion of interest has 442  
been superimposed. In this figure, the dark spot is hidden by 443  
the inclusion image, indicating that the dark spot is smaller 444  
than that of the biphasic state map. That is also the case for the 445  
other spot located at the bottom-right of each map. This shows 446  
that the confocal  $z$  plane slightly changed. The mean 447  
wavenumber is  $463.0$   $\text{cm}^{-1}$ , ranging from  $462.8$  to  $463.3$  448  
 $\text{cm}^{-1}$ . Again, the temperature-corrected wavenumber calcu- 449  
lated with the Schmidt and Ziemann<sup>42</sup> relationship compares 450  
favorably with the “monophasic” average value. However, it is 451  
the gap between the “biphasic” and “monophasic” values which 452  
is of special interest. It is very small ( $0.25$   $\text{cm}^{-1}$  between  $462.75$  453  
and  $463$   $\text{cm}^{-1}$ ), but both measurements were performed on the 454  
same spectrometer with the same calibration procedure, and 455  
on the same points of one quartz sample. Only the 456  
spectrometer stability is involved here. It is worth noting 457  
that the color scale for the monophasic state map slightly 458  
differs from the LV state one. The color scale of each map has 459  
been chosen to emphasize the similarities between the spatial 460  
distributions of the colors and consequently of the wave- 461  
numbers. Globally, the increase of the Raman wavenumbers of 462  
the monophasic state map indicates the development of 463  
compressive stress although no optical evidence of quartz 464  
failure was recorded during this experiment, which therefore 465  
follows a purely elastic behavior. 466



**Figure 6.** Thermal procedure, microthermometric features, and schematics of the cyclic tension applied to the sample, before (label 1, Section 3.1) and after (label 2, Section 3.2) the stretching irreversible failure of the inclusion.



**Figure 7.** Raman map of the wavenumber of the high wavenumber  $A_1$  quartz mode, with infilling fluid at the liquid–vapor saturation state (left) and monophasic liquid state (right). The wavenumber values are given by the color scale. The inclusion of interest has been superimposed as well as the crystal axes determined with EBSD.



**Figure 8.** Raman line center histograms at 120 °C of the 464 (left) and 206 (right)  $\text{cm}^{-1}$  bands of quartz around a fluid inclusion filled with either a biphasic liquid–vapor stable mixture (green, blue = repetition to test for reproducibility) or a monophasic tensile liquid (red).



To extract the mean Raman shift provoked by the in-pore tension in the actual sample over the experimental area, the whole data set collected with each map was redrawn as the histogram of the number of occurrences in each wavenumber range, for the two Raman mode maps (464 and 206  $\text{cm}^{-1}$ ) under the two stressed conditions (Figure 8). This shows how the wavenumbers measured vary within the experimental area for the two Raman modes and also shows how regular the datasets are.

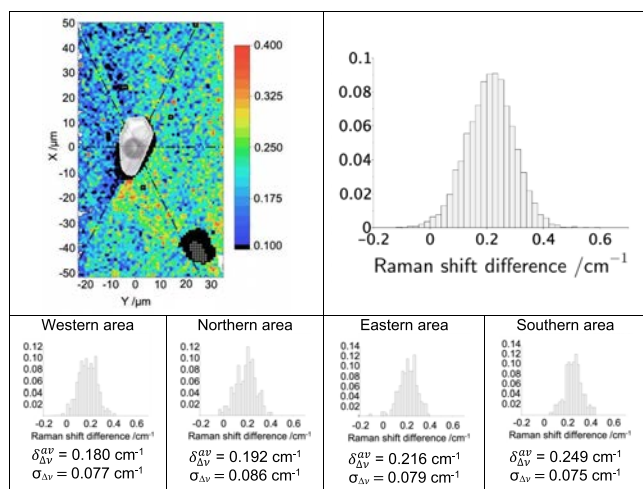
The liquid–vapor series gives the Raman modes at saturation pressure: the Gaussian maxima are at 462.8 and 199.9  $\text{cm}^{-1}$ . These measurements were double-checked to test the reproducibility of the recorded values (blue and green histograms), and both datasets match well. The match is strictly perfect for the high wavenumber mode (same main wavenumber and same width) while the low wavenumber  $A_1$  mode gave a 0.015  $\text{cm}^{-1}$  change for wavenumber (showing the high stability of the experiment) with the total width varying by a maximum of 0.1  $\text{cm}^{-1}$ . The main information we take from these graphs is the Raman gap that exists between the two 120 °C datasets at different pressures. Each mode (464 and 206  $\text{cm}^{-1}$ ) has a specific gap, quite moderate with respect to the precision of the spectrometer, but largely beyond any instrumental effect. Note that here the key factor of the spectrometer is its stability, not its spectral resolution. Specific care was taken to improve stability by avoiding thermal fluctuations and then any human presence in the experimental room. Now, using the calibration of the Raman shift with pressure,<sup>42</sup> it is possible to estimate the level of strain involved. The two modes agreed remarkably well for the resulting stress: 20 MPa  $\pm$  2.5 MPa (Figure 8). The small difference between the values (22.2 MPa for 464  $\text{cm}^{-1}$  mode and 17.6 for 206  $\text{cm}^{-1}$  mode) can be related to the wavenumber measurement uncertainty, and by the application of only one parameter on a noncubic structure, which is, moreover, not subjected to a hydrostatic pressure but to a complex stress field.

The Raman shift difference of the 464  $\text{cm}^{-1}$  mode between the biphasic and monophasic modes was plotted as a map (Figure 9). This plot is a spatial representation of the Raman

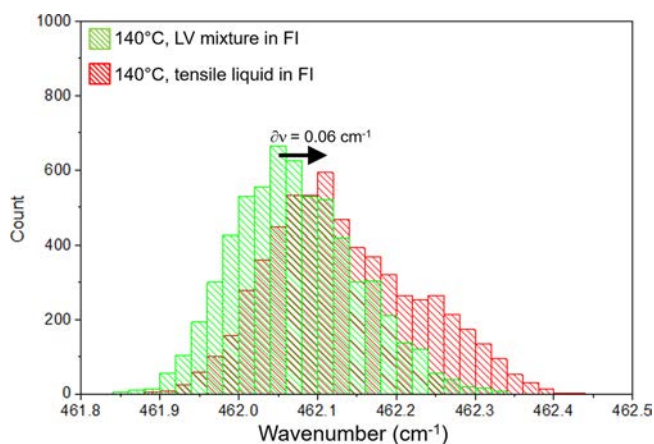
wavenumber change, that is to say the stress distribution induced by the in-pore pressure change. The difference is positive or zero, except for very rare occurrences. In addition, the average wavenumber shift and standard deviation were evaluated in four zones surrounding the inclusion. The area above the inclusion in the map is called “North,” and so on. The statistics are very close in the three zones West, North, and East (see Figure 9) with a mean wavenumber shift  $\delta_{\Delta\nu}^{\text{av}}$  close to the 0.2  $\text{cm}^{-1}$  overall shift (Figure 8) and a very constant standard deviation. This proves that the stress field produced by the in-pore pressure change is superimposed on an initial spatial stress/strain distribution observable in the Raman map under LV conditions (Figure 7, left). The southern zone shows a different behavior with a higher Raman shift difference (0.249  $\text{cm}^{-1}$ ) corresponding to a Raman pressure of 28 MPa. It is worth noting that the highest shift difference represented by the red/orange pixels in Figure 9 follows the crystallographic axis.

**3.2. Nonvisible Failure of the Container (CsCl Inclusion).** The experiment was carried out repeatedly (see Section 2.4 with the cyclical procedure). After around 80 cycles carried out over 3 weeks, with tension lasting from some minutes to some days during each cycle, a brutal change of  $T_{\text{H}}$  was observed, expressing an internal failure (usually called “inclusion stretching” in the inclusionist’s glossary; see ref.<sup>61</sup> for a review about the different types of damage in inclusions) and a change of the cavity volume.  $T_{\text{H}}$  was then upshifted by 16 °C, and logically, the  $T_{\text{IN}}$  changed by a similar value, at  $T_{\text{IN}} = 111$  °C (Figure 6). Despite this thermometric evidence, the change in the cavity shape or volume was so small that it could not be observed optically (this is usual with this “inclusion stretching”), leading us to infer that the volume change resulted from the formation of damage at the microscale as a network around the inclusion, below the optical limit.

The Raman maps were then measured at 140 °C, that is to say, for the same  $T - T_{\text{IN}}$  difference as for the previous data sets. They showed a very weak Raman shift between the biphasic and the monophasic situations (Figure 10), much weaker than in the precracked state (Figure 8). This fact matches very well with the presence of a dense network of microcracks, diminishing the lattice stress detectable with Raman spectroscopy.



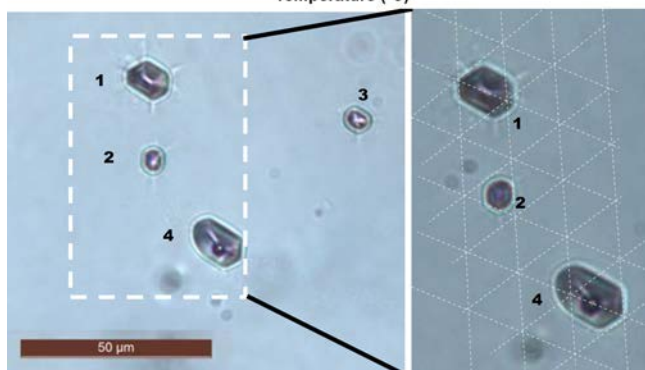
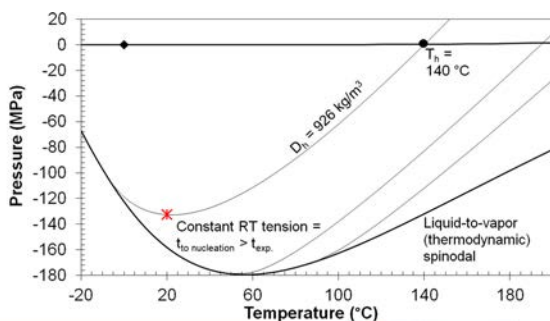
**Figure 9.** Shift difference between biphasic and monophasic modes for the 464  $\text{cm}^{-1}$  Raman mode. Top-left: Map of the shift difference. Top-right: global histogram of this map. Bottom: Histograms of the four regions indicated by the red rectangles on the map, with a geographic-like denomination.



**Figure 10.** Histograms of the line center of the high wavenumber band, at 140 °C, along the equatorial plane of the inclusion, after the  $T_{\text{H}}$ -recorded damage.

548 It means that, despite the low stress thus registered, the  
549 cyclical procedure led to a real damage all around the cavity  
550 materialized by a brutal increase of  $T_{\text{H}}$ . The local damage is  
551 also evidenced by the Raman maps recorded after the damage  
552 of the inclusion, which show much lower values of the peak  
553 stress (i.e., for the largest tension in the inclusion), +6.7 MPa  
554 (Figure 10), compared to the precracked state (+20 MPa in  
555 the plane, Figure 8). This large drop of the in-plane stress is  
556 interpreted as the presence of a dense network of microcracks,  
557 able to adjust the liquid tensile stress by a multitude of  
558 microdisplacements inside the crack, instead of provoking a  
559 lattice stress detectable with Raman spectroscopy.

560 **3.3. Fracturing the Container (NaOH Inclusion).** The  
561 NaOH sample contains four inclusions shaped as “negative  
562 quartz crystals” (Figure 11), numbered 1 to 4.  $T_{\text{H}}$  is revolving



**Figure 11.** Upper panel, installing the “enduring tension” situation by isochoric cooling of a high-density SFI. Bottom left, observation of three fluid inclusions numbered (1–3) with microcracking in the quartz at each corner of the negatively shaped cavity. The fourth (num. 4), which does not tolerate tensile stress (see the bubble), is intact. Bottom-right, crystallographic axes measured by EBSD are reported on the right micrograph.

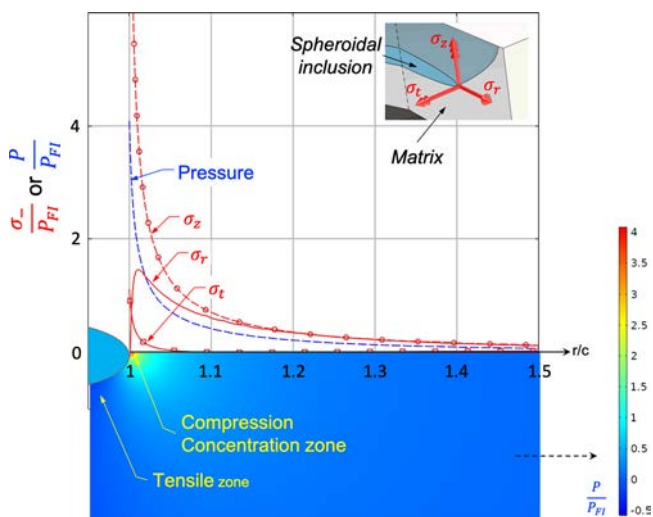
563 around 140 °C, corresponding to a mean water density of  $D \approx$   
564 926 kg/m<sup>3</sup> according to IAPWS EoS (pure water approx-  
565 imation<sup>37</sup>) (Figure 11). Inclusions 1–3 did not show any  
566 instantaneous nucleation in the positive (Celsius) temperature  
567 area. At RT and after isochoric cooling from  $T_{\text{H}}$ , the liquid  
568 tension in the three monophasic inclusions 1–3 was –132  
569 MPa (Figure 11). Inclusion 4 had  $T_{\text{IN}}$  equal to 44 °C so this  
570 inclusion was never under tension under ambient conditions  
571 while the three others were, giving us a “reference” inclusion  
572 without a fluid pressure effect on the nearby surroundings.

573 With this RT superheating installed in inclusions 1–3, we  
574 started observing the inclusions subjected to a permanent  
575 tension from the in-pore liquid. Surprisingly, after only some  
576 weeks and before any Raman records or accumulation of data  
577 on the inclusions of interest, the host quartz cracked all around

the three inclusions hosting tensile liquid, consistent with the  
crystallographic axis (Figure 11, bottom-right panel).

The quartz failure occurred with optically visible cracks  
appearing at the edge of the three inclusions 1–3. The bright  
border is underlined by a similar black edge when zooming:  
the cracks cannot be due to an optical artifact. Inclusion 4,  
which was never subjected to long tension ( $T_{\text{IN}} > RT$ ), was not  
damaged. The coexistence between the two mechanical  
behaviors, so well correlated with the microthermometric  
features, is a clear indication that the liquid tension is able to  
fracture the surrounding quartz.

**3.4. Numerical Models of Stress Concentration and Fracturing.** **3.4.1. Ellipsoidal Model and Pressure in the Equatorial Plane.** The simulated stresses and pressure resulting from FEA simulation based on oblate spheroids with a shape factor  $b/a = 0.1$  are represented in Figure 12. The



**Figure 12.** 2D axisymmetric mechanics model of an ellipsoidal-shaped inclusion. Bottom: Normalized pressure map around an inclusion. The vertical symmetry axis is the revolution axis. Top: Stresses and pressure magnitude along the radial axis in the optical plane.

pressure is highly concentrated close to the inclusion edge  
where it reaches four times the fluid inclusion pressure and  
decreases sharply along the radial axis. The pressure  
distribution corroborates the Raman observations (Figure  
10): a compressive stress (positive) lies within the equatorial  
plane around the cavity (red color). This can be explained by  
the flattening of the spheroid, like what occurred with the  
remote stress above. The simulation indicates that the principal  
stresses are aligned with the geometrical axes, that is, the radial,  
tangent, and axial directions of the ellipsoid (see the  $r$ ,  $t$ , and  $z$   
directions, respectively, in the inset top-right in Figure 12). In  
the equatorial plane, the compressive axial stress  $\sigma_z$  is the  
largest contribution to the total pressure while the magnitudes  
of the tangent and radial stresses  $\sigma_t$  and  $\sigma_r$  are much smaller.  
The tangent stress  $\sigma_t$  is compressive as well and contributes to  
a lesser extent to the total pressure. On the other hand, radial  
stress  $\sigma_r$  does not have a monotonous change. It has a negative  
value in the very vicinity of the edge, quickly inhibited by the  
global flattening of the inclusion yielding a compressive stress.

**3.4.2. Real Inclusion Shape and the Stress Concentration in the CsCl Inclusion.** The Raman shift can be evaluated from either from Grüneisen’s constant as shown above or from the deformation phonon potentials, usually noted  $p$ ,  $q$ , and  $r$ , 616

617 which are the components of the fourth rank tensor relating  
618 the changes of the spring constants of the lattice and the  
619 deformation tensor.<sup>62</sup> They generally are determined from  
620 hydrostatic pressure Raman experiments using diamond anvil  
621 cells, uniaxial stress experiments, or strained thin film grown by  
622 strained-layer epitaxy. It is worth noting that the third potential  
623  $r$  relates the shear strain components of the tensor. Briggs and  
624 Ramdas<sup>63</sup> determined the deformation potential constants of  
625 the zone-center optical phonons of  $\alpha$ -quartz under uniaxial  
626 stress experiments. Finally, the Raman shift can also be  
627 evaluated from the stresses using the components of the fourth  
628 rank elastic tensor relating stress and strain.

629 In the present case, the radial, tangent, and axial stresses are  
630 also the principal stresses because of the symmetry of the  
631 geometry and the loading, and it is therefore possible to derive  
632 the expected Raman shift from either the principal stresses or  
633 the radial, tangent, and axial stresses. Here, the constants  
634 determined by Briggs and Ramdas<sup>63</sup> were used to calculate the  
635  $464\text{ cm}^{-1}$  Raman shift from the stresses considering that the  $z$ -  
636 axis of the model coincides with the crystallographic  $c$ -axis as  
637 shown in Section 2.1:

$$\delta\nu_{A_{1,464\text{cm}^{-1}}} = 0.21 \cdot 10^{-2} \times (\sigma_t + \sigma_r) + 0.38 \cdot 10^{-2} \times \sigma_z$$

638 where the stresses are in MPa and  $\delta\nu$  in  $\text{cm}^{-1}$ . The Briggs'  
639 potentials were determined with an uncertainty of  $\pm 0.02 \cdot 10^{-2}$   
640  $\text{cm}^{-1}/\text{MPa}$ . Note that they are here positive because of the  
641 change in the sign of the stresses. The uncertainty of the  
642 Raman shift evaluated from uncertainty propagation depends  
643 on the stresses and reaches a maximum value of  $0.5\text{ cm}^{-1}$ .

644 The Raman shift was also calculated following the Grüneisen  
645 formalism:

$$\delta\nu_{A_{1,464\text{cm}^{-1}}} = 8.7 \cdot 10^{-3} \times P$$

646 where  $P$  is in MPa and  $\delta\nu$  in  $\text{cm}^{-1}$ .

647 Both Raman shifts were evaluated along with the radial axis  
648 (Figure 13). The very good agreement between Briggs and

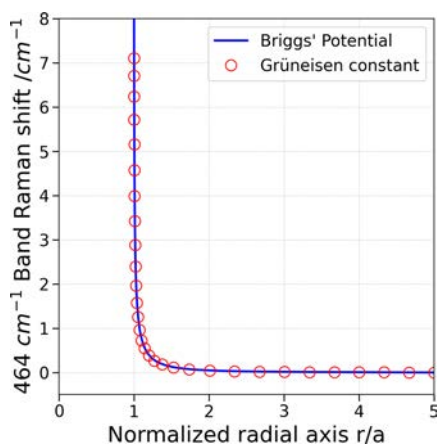


Figure 13. Raman shift evaluation along the radial axis.

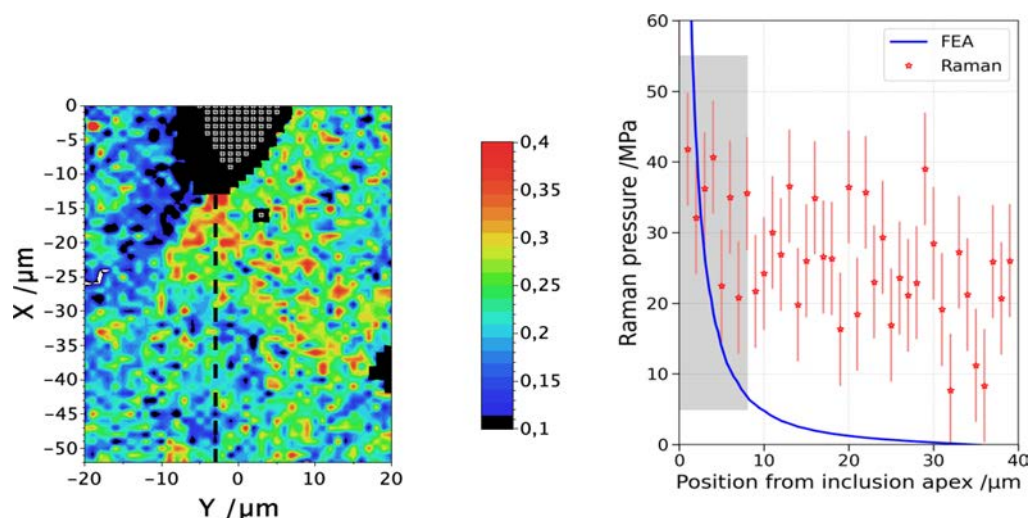
649 Grüneisen formalisms confirms that the Grüneisen's constant-  
650 based approach was really reliable in this study, as proposed in  
651 Section 2.3.

652 Focusing on the inclusion described in Section 3.1, the  
653 Raman pressure at the bottom-right corner of the inclusion  
654 (Figure 9) was compared with the simulation of the oblate  
655 cavity with a shape factor  $b/a = 0.1$  and anisotropic properties

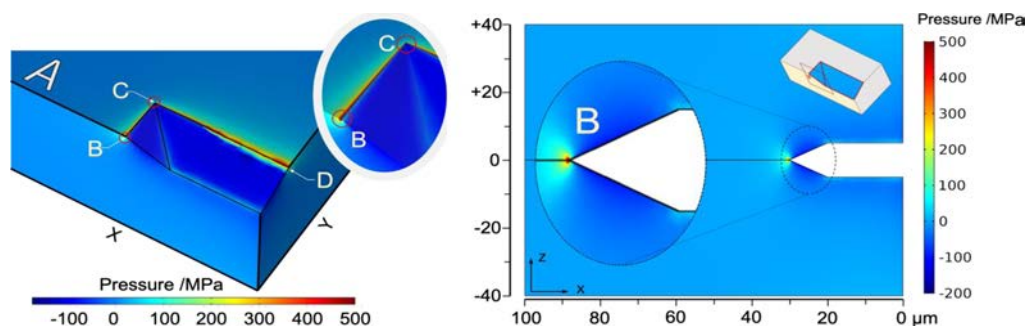
(Figure 14). The simulated pressure (blue line FEA) quickly  
tends asymptotically to zero upon moving away from the  
inclusion, as expected from a direct application of the theory of  
solid mechanics. In the meantime, the experimental values  
showed that the sample is under stress over the total area (red  
stars, Figure 14; see also the green and blue pixels, Figure 9).  
The pressure derived from the Raman measures shows a slight  
decrease, especially close to the inclusion (gray area), where  
the values are in the same order of the simulation. Considering  
the difficulty in localizing the edge of the Raman map and the  
assumptions for the Raman pressure calculation and the  
simplified geometry for the simulation and despite the  
dispersion of the measured values, measurements and  
simulation can be estimated as consistent at least from a  
qualitative point of view. However, the Raman pressure seems  
to remain constant around 25 MPa when looking over the  
whole map even farther from the inclusion. This asymptotic  
mean pressure is not at all expectable and constitutes one of  
the main surprises of this experimental study. Although we do  
not have explanations for this bias, it may be compared with  
the Raman gap averaged over the whole map ( $0.212\text{ cm}^{-1}$ , i.e.,  
24 MPa). Another point to be considered is the presence of  
another cavity, which might not be alone, close to the studied  
inclusion. The stress fields induced by these surrounding  
cavities might produce such a general overstress. Finally, the  
general overstress may also be related to the localized strain/  
stress induced by the inclusion synthesis procedure.

The Raman pressure appears to be a good probe of the  
stress fields around the water-bearing cavity, and a highly  
resolved measurement of the instantaneous/local stress is  
certainly possible according to our preliminary results. It is also  
clear that any change in the in-pore pressure drives a significant  
modification in the poromechanical stress field, over an  
unexpected long-range scope. To address these findings,  
further studies should involve the anisotropic strain prop-  
agation in the matrix along preferential axes (crystallography,  
dislocations, etc.) by carefully plotting how the quartz band  
varies from place to place, at saturation pressure. It was already  
clear (Figure 7 left) that our hydrothermal monocrystalline  
quartz was not uniform in terms of Raman shift.

3.4.3. Real Inclusion Shape and the Fracturing of the  
NaOH Inclusion. The objective of the FEA simulation  
performed on the 3D faceted cavity (Figure 5) was to model  
the fracturing of the NaOH hexagonal shaped inclusions as a  
result of tensile liquid in the cavity (Figure 11). As a preamble,  
it is well known that geometrical singularities yield artificially  
increased stress in finite elements depending on the meshing.  
In addition, the real interface between the inclusion and the  
contained liquid is not as clear as in the geometrical model  
where the interface corresponds to a wall. Therefore, values of  
the simulated pressure must be carefully considered. The main  
purpose is to obtain tendencies that give us a better  
understanding of crack formation. As expected, the (negative)  
tensile pressure applied on the inner wall of the cavity ( $-200$   
MPa) yields a tensile state within the major part of the solid  
domain proved by the negative value of the simulated pressure  
(Figure 15, left). Like for the oblate spheroid model, the shape  
factor effect is observed as the pressure increase concentrates  
around the inclusion, reaching positive values along the cavity  
edges lying in the symmetry plane A, significantly higher than  
the applied inner pressure and indicating a compressive state in  
the plane induced by the predominant flattening of the cavity.  
The pressure reaches its highest values rather in the middle of



**Figure 14.** Left, Zooming in the southern area having the larger average wavenumber Raman shift (i.e., Figure 9). Right, Raman pressure (red stars) vs simulation (blue curve). The behavior close to the interface is highlighted as a gray area.



**Figure 15.** Pressure field showing (left) stress concentration along the longest edge lying in the symmetry plane XY (see Figure 5) near inclusion wall angles and (right) domains of negative/positive stress in the XZ symmetry plane.

719 the equatorial edges (e.g., points B and D) instead of the apex  
720 (e.g., point C) where the cracks form.

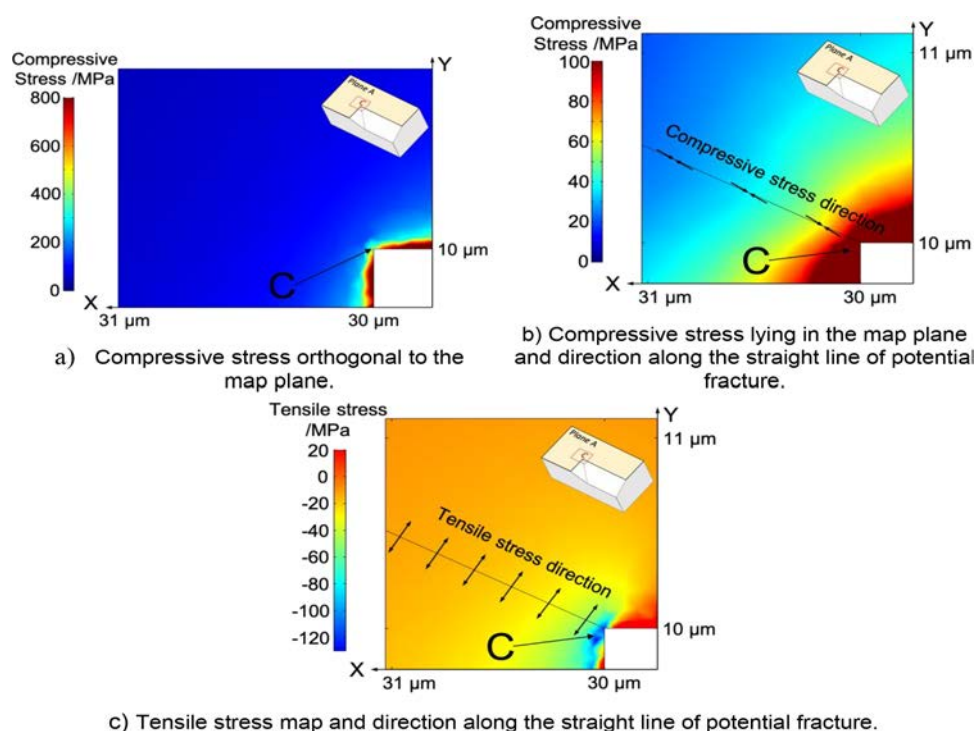
721 Focusing on the symmetry plane A (equatorial plane) that  
722 contains edges B-C-D of the inclusion, we observe that two  
723 principal stresses lie in plane A and that last one is  
724 perpendicular to the plane. This can be explained by the  
725 geometrical symmetry, quartz trigonal symmetry, and the  
726 orientation of the inclusion with respect to the crystallographic  
727 axes. The highest compressive stress is perpendicular to the  
728 equatorial plane aligned with crystallographic  $c \rightarrow$  axis and is  
729 very concentrated along the cavity edges (Figure 16). The  
730 second compressive stress lies in the equatorial plane with  
731 lower magnitude (Figure 16b, compare the color scale with  
732 that of Figure 16a). The third principal stress also lies in the  
733 equatorial plane and shows negative values corresponding to  
734 tensile stress. It reaches its maximum magnitude around the  
735 apex C (Figure 16c, tensile stress). The tensile stress direction  
736 being along the line with the same origin and orientation as  
737 experimentally observed in the studied inclusions (Figure 11)  
738 confirms the possibility of crack formation along this line.

## 4. DISCUSSION

739 **4.1. The Raman Pressure.** Micro-Raman was here used to  
740 dynamically follow the internal pressure in a crystal hosting a  
741 variable pore tension. It is assumed that the applicability of the  
742 Grüneisen formalism allows us to translate the Raman shift  
743 into pressure. The anisotropy of monocrystalline quartz and

the imperfections of the crystal lattice even under room 744  
conditions (see the Raman “irregularities” in Figure 7 left) 745  
limit this applicability. However, our study relies on the 746  
comparison of two datasets obtained at two different pore 747  
pressures, with all other parameters being constant. In 748  
addition, the shift is observed for two different Raman 749  
vibration modes, and it is very comparable. In that sense, the 750  
recorded Raman shift cannot be related to mechanisms other 751  
than lattice deformation and can be interpreted with 752  
confidence using the solid’s linear elasticity. 753

Raman microspectrometry of silica minerals is commonly 754  
used to determine the pressure conditions of polymineralic 755  
assemblages containing various solid inclusions in minerals 756  
(e.g., refs<sup>64–70</sup>). The dominant compression mechanism is 757  
considered to be the reduction of (Si-O-Si) (e.g., ref.<sup>71</sup>). A 758  
similar Raman barometry is used for the  $P$ - $T$  conditions of the 759  
diamonds’ source regions, based on determination of the 760  
internal pressure in olivine inclusions and the stresses in the 761  
surrounding diamond (e.g., refs.<sup>72,73</sup>). More recently, the 762  
Raman shifts of sapphires around a zircon inclusion were 763  
converted to hydrostatic pressure and deviatoric components 764  
of the stress tensor, combining micro-Raman and photo- 765  
luminescence imaging techniques, linked by the piezospectro- 766  
scopic effects on Raman and photoluminescence spectra.<sup>74</sup> 767  
The internal stress was highly concentrated at the tips of the 768  
zircon crystal, resulting in a compressive stress of several 769  
hundreds of MPa and leading to most inclusions in radial 770



**Figure 16.** Principal stress magnitude map near the corner of the symmetry plane XY (see Figure 5, plane noted A). (a) Principal compressive stress ( $\sigma_{\perp}$ ) perpendicular to the plane. (b) Second principal compressive stress ( $\sigma_{\parallel}$ ) field near the corner of the symmetry plane XY (Figure 5, plane noted A). The double black arrows indicate the direction of  $\sigma_{\parallel}$  along the line corresponding to the potential crack direction. (c) Principal tensile stress ( $\sigma_{\perp}$ ) field near the corner of the symmetry plane XY (see Figure 9, plane noted A). The double black arrows indicate the direction of  $\sigma_{\perp}$  along the line corresponding to the potential crack direction. Note that negative/positive values indicate tensile/compressive stress.

771 cracks propagating in the host sapphire crystal from the apex of  
 772 the hexagonal zircon. The present paper affords evidence that  
 773 cracking can be invisible while leading to significant variation  
 774 of the residual pressure. It could explain the growing  
 775 observations in natural samples of a wide scattering of residual  
 776 pressure sealed in inclusions (e.g., refs.<sup>75–78</sup>).

777 **4.2. Crystal Host Stress Field.** The comparison between  
 778 simulation and Raman measurements is to some extent  
 779 hindered by the heterogeneity displayed by the sample.  
 780 When recording the spectroscopic signatures at RT, namely,  
 781 the reference state without any external constraint, the data set  
 782 showed significant variations of the Raman peaks across the  
 783 whole map. Raman peaks showed a distribution into four  
 784 quadrants, which remained almost unchanged whichever the  
 785 fluid pressure (Figure 5). These measurements demonstrate  
 786 that the host crystal is not the perfect, stress-free monocrystal  
 787 assumed in the simulations. Experiments confirm the idea that  
 788 the elastic deformations induced by the growing fluid pore  
 789 tension retain and even magnify the initial imperfections. The  
 790 Raman maps clearly show that the tension-driven shifts are  
 791 amplified along the crystallographic axes. Therefore, both the  
 792 Grüneisen formalism to convert Raman signatures into  
 793 pressure and a direct comparison of such values to FEA  
 794 simulations done through isotropic elastic theory can only  
 795 approximately describe the complex mechanical behavior of  
 796 quartz.

797 In spite of these limitations, the Raman measurements do  
 798 retrieve features expected from elastic theory: (i) a  
 799 compressive stress develops within the equatorial plane and  
 800 (ii) the stress concentration is maximal in the vicinity of the  
 801 cavity tip (Figure 14). Furthermore, the shape of the pore  
 802 cavities plays a role in the stress field to build up a potentially

complex 3D result (Figures 15 and 16). This complexity is  
 certainly increased by the pre-existence, before installing any  
 new constraints, of a certain degree of heterogeneity that is  
 visible in the Raman maps at RT (Figure 7 left).

**4.3. Stress Accumulation and Fracturing Threshold.** It  
 is difficult to be quantitative here; however, the stress  
 generated around the water-bearing cavity appears moderate,  
 especially compared to the observations of the damage ( $T_{\text{H}}$   
 variations, apex fractures) in the host quartz. One proposition  
 for reconciling low stress and evidence of cracking is the role  
 played by fatigue effects in the resistance of materials. Stresses  
 that vary with time and in intensity are able to cause the rock  
 failure while below the yield strength, and even in the linear  
 elastic domain (e.g., refs.<sup>5,79–81</sup>). The best illustration is what is  
 known as “reequilibrium” in fluid inclusions studies, which is  
 a modification of the inclusion shape and/or a fluid leakage  
 because of the effective stress, namely, the pressure difference  
 between host mineral stress and cavity-filling fluid pressure  
 (e.g., refs.<sup>82–86</sup>). One strong hypothesis, often claimed to infer  
 various deep fluid conditions from fluid inclusions, is their  
 isochoric behavior along the rock pathway throughout the  
 Earth’s crust (burial and/or uplift). To validate it, the  
 resistance of quartz to differential stresses was measured on  
 SFIs for internal under- or overpressure (respectively  $P_{\text{solid}} >$   
 $P_{\text{fluid}}$  or  $P_{\text{solid}} < P_{\text{fluid}}$ ). Overpressure causes reequilibration from  
 reaching 100 MPa.<sup>82,85</sup> Underpressure caused visible cracks  
 from around 200 MPa, while reequilibration proceeded by  
 dissolution–precipitation in the range of 100–200 MPa (e.g.,  
 ref.<sup>83</sup>). In a later study, cracking was observed when internal  
 underpressure only exceeded 270 MPa.<sup>85</sup>

In our case, the amplitude of tensile stress in the inclusion,  
 analogous to an underpressure stress, is either  $\sim 200$  MPa

(CsCl sample) or  $\sim 140$  MPa (NaOH sample). In spite of internal underpressure lower than [82–83]'s, we observed the formation of cracks with the lower differential stress. The simplest explanation for the difference is the effect of confining pressure, absent in our present study, while it is known to inhibit cracking.<sup>85</sup> An additional effect lies in the geometrical shape of the fluid inclusion, commonly spheroidal for natural inclusions. Our FEA modeling shows that the stress concentration at the tip of the inclusion reached a larger amplitude for the negative crystal shape (as displayed by the SFIs we used) than the spheroidal one. The geometry thus promotes the concentration of stress in the very limited area of the apex, which may facilitate crack initiation.

Furthermore, we can speculate a little more about the micromechanical mechanisms that underlie the development of cracks at low levels of tension. For instance, the microprestress theory<sup>4</sup> offers a comprehensive view of how capillary and disjoining pressures can drive the nucleation and growth of tensile microcracks in the complex pore network of an aging cement. In particular, hindered adsorption inside the nanoscale pores (1 to 10 molecular width and 0.3 to 3 nm) within hardened cement paste plays a pivotal role. It is appealing to hypothesize, for our experiments, the existence of tiny quantities of water present along the quartz dislocations comparable to the gel pores for cement. The liquid tension existing in the cavity might therefore spread over the nearby crystal lattice owing to minute water-bearing dislocations, propagating the tensile stress farther from the cavity and concentrating the constraints.

## 5. CONCLUSION AND PERSPECTIVES

The tension of water occluded in a crystalline cavity has a pore-scale micromechanical effect, as exemplified by the visible cracking for the NaOH sample, and the microthermometric features change ( $T_{\text{H}}$  increasing) for the CsCl sample. We demonstrated here that Raman spectroscopy is able to monitor in space and time the pressure in the quartz crystal around a fluid inclusion. The Raman maps revealed that the stress fields induced by the pore tension within the crystalline host rock are nonuniform and concentrated along the crystallographic orientations and, probably, crystal defects. The exact value of stress at these overstressed sites cannot be ascertained by the Raman technique because they may operate at a much smaller scale than the Raman scattering volume. The numerical-model simulated stress field and stress concentration match the measured 3D distribution of stress well and outline the role of geometry in terms of stress concentration in the region where fracturing was observed. On the contrary, the Raman estimates of how stress changes with distance from the inclusion do not match the elastic theory, showing that the crystal defects probably play a role in the stress distribution. Technically, micro-Raman associated with SFI microthermometry appears to be a powerful tool for deciphering the micromechanical mechanisms involved in complex field stress in rocks and porous media.

To summarize, our study demonstrates unambiguously that a permanent low stress as well as repeated cyclic stresses established in a crystal lattice by reducing the in-pore pressure in an occluded water-bearing cavity (related to capillary-type effects) is able to damage the hosting quartz despite its high resistance. The mechanical role pressurized pore fluids can play in weakening and embrittling rocks has long been known (e.g., refs.<sup>87,88</sup>), and this paper is a first step in envisioning the role of

tensile pore fluids. Furthermore, this result poses the question of the mid/long-term safety of geological storage ( $\text{CO}_2$ , nuclear wastes, energy) wherever the geological formations are subjected to drying operations that make it possible to install liquid tension in large masses of unsaturated hydrosystems. In particular, the use of clayey formations to guarantee the confinement of the nuclear species owing to this impermeable barrier must be questioned if the consequent tension of tunnel ventilation was able to enhance permeability in the massif by creating fissures. In the same way, the integrity of the caprocks in  $\text{CO}_2$  storage is a crucial property that prevents any leakage from occurring. However, the injection of supercritical  $\text{CO}_2$  severely dries out the formation, especially at the highest part where the  $\text{CO}_2$  bubble accumulates at the very contact with the caprock, establishing the right conditions for tension-driven processes.

During the course of the study, the initiation of microcracking and brittle failure was also discussed in association with the water distribution in rock. This aspect is of great significance in natural systems, beyond the question of storage safety. At high pressure and temperature, where deformation proceeds mainly as a result of temperature-dependent viscous creep processes (dislocation- or diffusion creep), fracturing is still present. These brittle precursors promote grain-size reduction and therefore the fluid flow and chemical reactions that activate water corrosion.<sup>89–91</sup> High fluid pressures, up to confining pressure values, are necessary to open cracks, but the mechanisms are not well understood, even if we know that the physical state of the water present in mineral assemblages with very low porosity is often involved as a triggering mechanism.<sup>92,93</sup> This study demonstrates that reducing fluid pressure also induces cracking mechanisms rooted at the small scale, even if the generality *versus* specificity of such mechanisms in the various pressure contexts is still to be explored.

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