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

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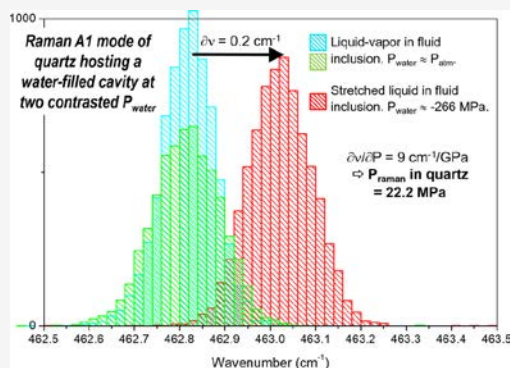
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5 **ABSTRACT:** In water-bearing porous rocks, pore pressure variations play a
6 major role in deformation, through dissolution–precipitation and fracturing
7 processes. An often-overlooked variation where pressure falls to negative
8 pressure or tension can operate whenever aquifer formations dry out, for
9 instance, in deep storage (nuclear or industrial wastes, long-term CO₂ 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.^{1,2}).

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.^{3,4}). 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.^{5,6} 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.^{7,8}). How cementitious materials
dry is also of interest. There is little doubt there, ever since the
pioneering work^{9,10} showing that the main driving force is 58

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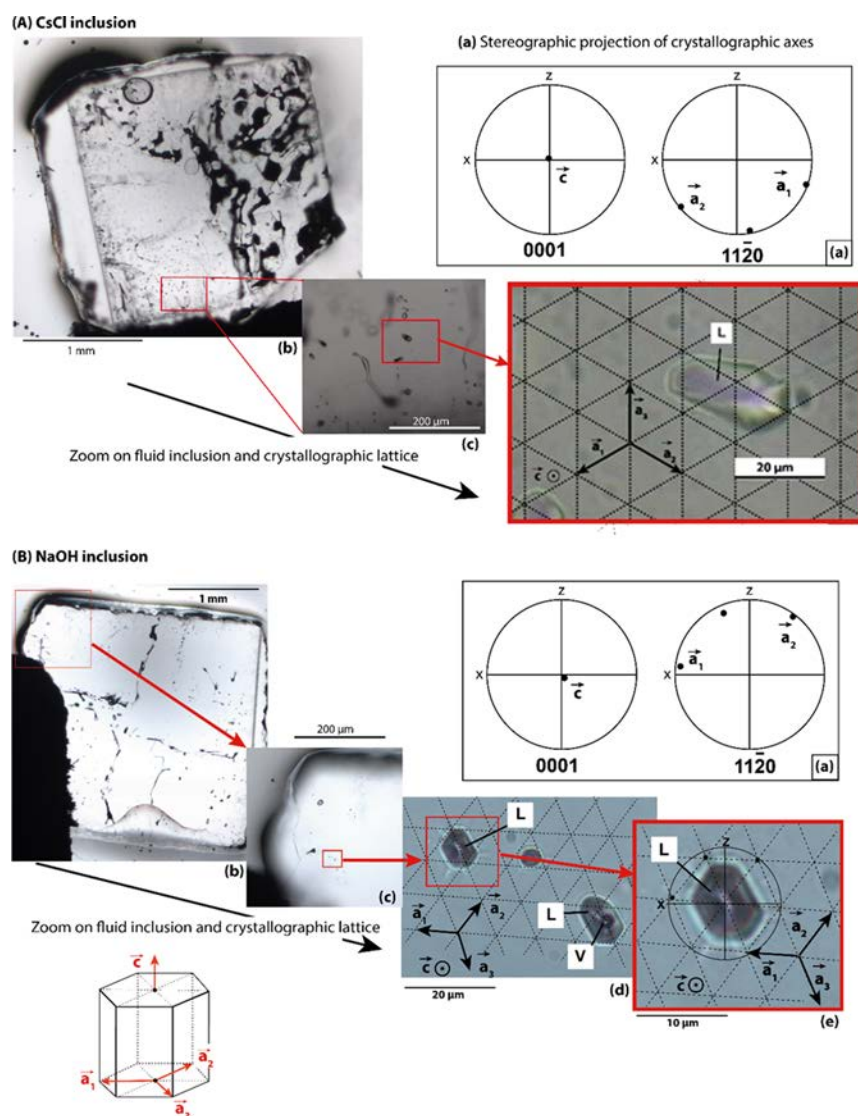


Figure 1. Photomicrographs and EBSD measurements of the two inclusions of interest (L = liquid aqueous solution; V = vapor). A. CsCl inclusion entirely filled by aqueous solution. B. NaOH inclusion. For each inclusion, two stereoplots show the orientation of the $[0001]$ and $[11\bar{2}0]$ axes within 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^{11–14}). 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^{15–19}). On the one hand, ventilation
 70 of the tunnels promotes high tensions that can reach -100
 71 MPa or more.¹⁹ 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^{18,20}). The second illustration is the
 75 injection of (supercritical) CO_2 into deep aquifers. This
 76 provokes intense drying in the near field of the wellbore with
 77 strong and counterintuitive capillary effects.^{21–23} 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^{24,25}). 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^{14,26}). 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^{27–31}). 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 SiO_2 overgrowth, in the presence of an
114 aqueous solution of known composition.³⁰ 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 fluids³⁰
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 °C³²) 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)³⁰ 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,³⁰ 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 μm 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.^{27–31})
and the corresponding changes of phase equilibria (e.g.,
refs.^{33,34} using fluid inclusions; refs.^{35,36} 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

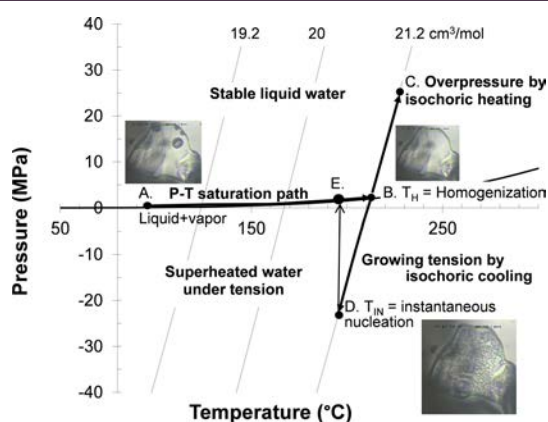


Figure 2. Phase diagram of pure water in the P – T space, calculated with the IAPWS-95 equation of state.³⁷ Each isochore is labeled with the molar volume in $\text{cm}^3 \cdot \text{mol}^{-1}$. The CsCl inclusion micrographs illustrate the fluid content present in the cavity at each characteristic step.

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.^{31,38} 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.³⁹ 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.^{40,41}). 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 quartz⁴² investigated the changes in wavenumber and line-
218 width of the 206 and 464 cm^{-1} A_1 Raman modes of 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 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 cm^{-1} mode also has linear pressure dependency, twice as
224 much at $d/dP = 20 \text{ cm}^{-1}/\text{GPa}$. Schmidt and Ziemann⁴²
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 Ziemann⁴² 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 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 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 cm^{-1} position). The micro-
250 scope (DM2500 Leica) lens compatible with this configuration
251 was a Leica SOX 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 μm .

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 performed⁴³ because Raman shifts were
268 compared at identical temperatures under two different
269 pressure conditions (monophasic and biphasic regimes).³⁹ 270

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_{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_{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.⁴⁴ The stress field around a cavity
302 has been studied many times. In particular, Eshelby⁴⁵ 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.^{46–54} 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.⁵⁵ 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,⁴⁴
316 and the finite-element-based results were compared with
317 theoretical results obtained using the code recently developed
318 by Meng et al.^{51–53} 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

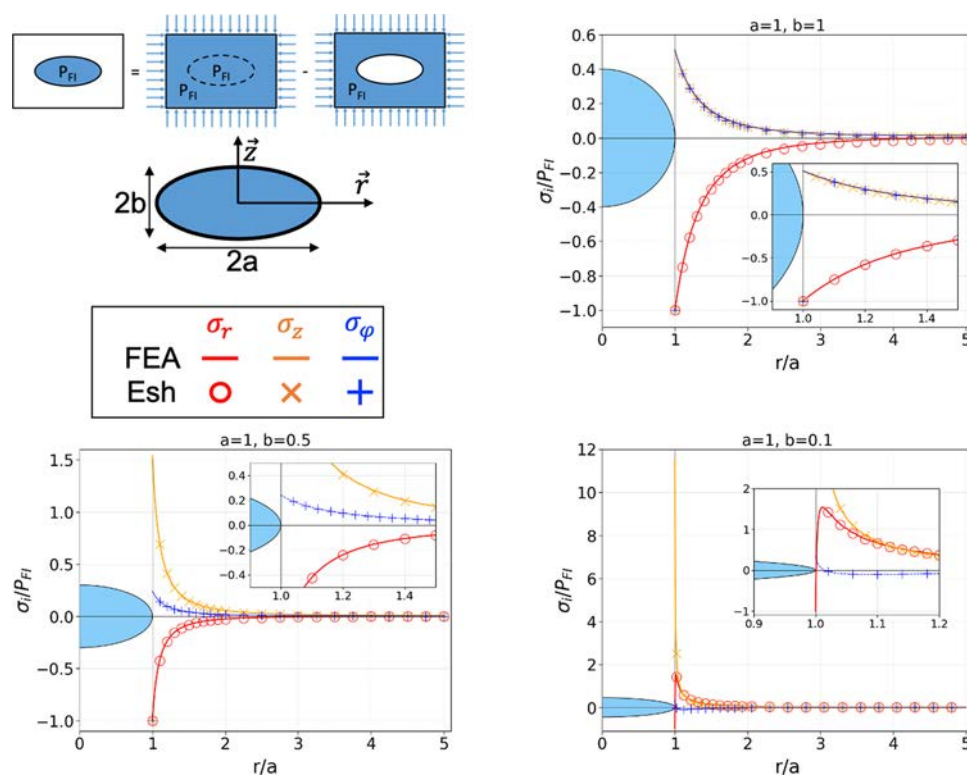


Figure 3. Normalized stress along the radial axis. The normalized stresses are calculated by dividing the stresses by the pressure applied onto the inclusion wall. The normalized radial coordinate is the radial coordinate divided by the half-length of the spheroid, $r^* = r/a$. The stresses denoted “Esh” were calculated following Eshelby’s theory⁴⁵ by applying script developed by Meng et al.^{31–53} 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.⁵⁶

327 0.06.⁵⁶ These elastic properties correspond to equivalent quasi-
 328 isotropic quartz obtained by Voigt–Reuss–Hill averaging.⁵⁶
 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 σ_{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 α -quartz was considered,
 375 and the elastic moduli were defined according to Calderon et
 376 al.⁵⁷
 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

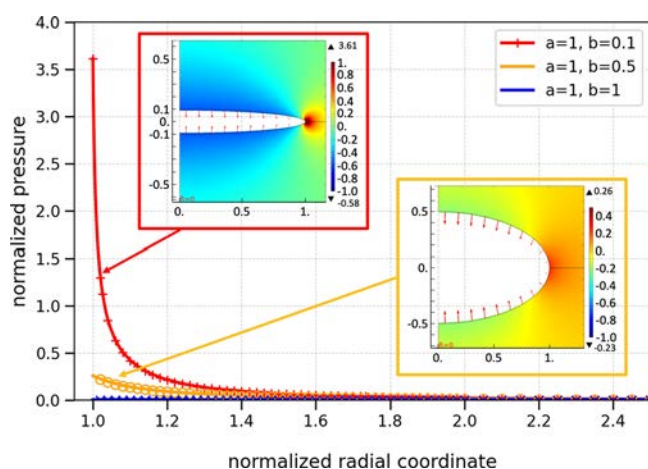


Figure 4. Simulation of a host with a spherical or spheroidal inclusion with a negative (tensile) pressure applied on the wall cavity. See Figure 1 for more details on the model. Normalized pressure simulated with FEA and depending on shape factor b/a , maps, and values along the radial axis. For each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

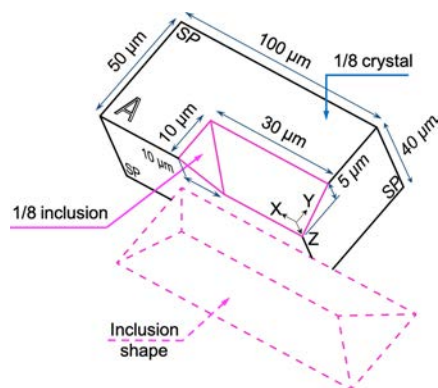


Figure 5. Geometry of the 3D mechanical model of the inclusion for the FEA. Because of symmetries (SP), only an eighth of the solid is modeled. The image size is not scaled with the prism size for visibility purposes.

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 ± 0.4 °C and T_{IN} of 89 ± 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 ± 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} .^{58–60}

Two A_1 Raman modes of SiO_2 with highest wavenumbers 404
were studied: the mode at 464 cm^{-1} and the mode at 206 405
 cm^{-1} . The signal was mapped in the quartz around the
inclusion (width 70 μm \times height 110 μm) 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 cm^{-1} mode in the stable state (biphasic liquid–vapor 410
assemblage) shows actual wavenumbers ranging from 462.5 to 411
 463.1 cm^{-1} with a mean value of 462.8 cm^{-1} (Figure 7). 412
Black spots correspond to regions where the Raman line intensity 413 17
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 Ziemann⁴² relation at 120 °C 423
gives an expected wavenumber of 462.4 cm^{-1} , which can 424
favorably be compared with our mean measured wavenumber 425
 462.8 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 cm^{-1} while it is close to 463 434
 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 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 cm^{-1} , ranging from 462.8 to 463.3 448
 cm^{-1} . Again, the temperature-corrected wavenumber calcu- 449
lated with the Schmidt and Ziemann⁴² 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 cm^{-1} between 462.75 453
and 463 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

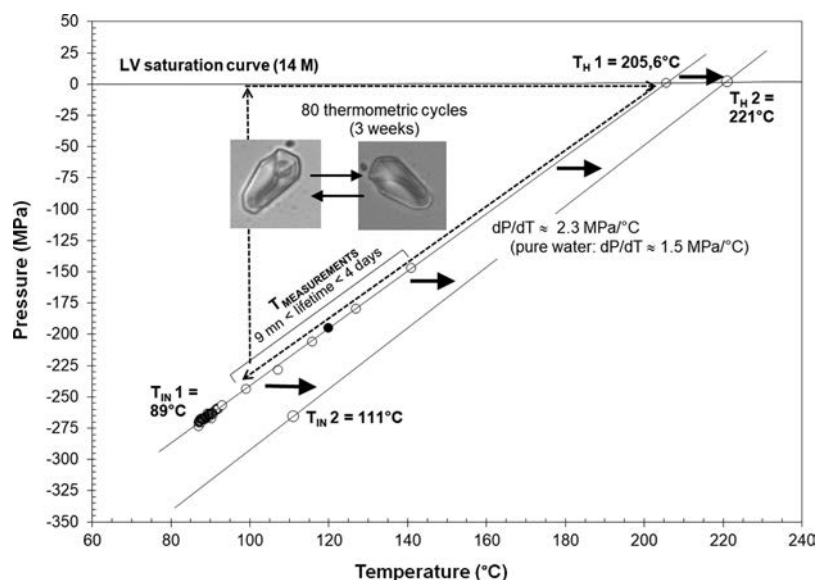


Figure 6. Thermal procedure, microthermometric features, and schematics of the cyclic tension applied to the sample, before (label 1, Section 3.1) and after (label 2, Section 3.2) the stretching irreversible failure of the inclusion.

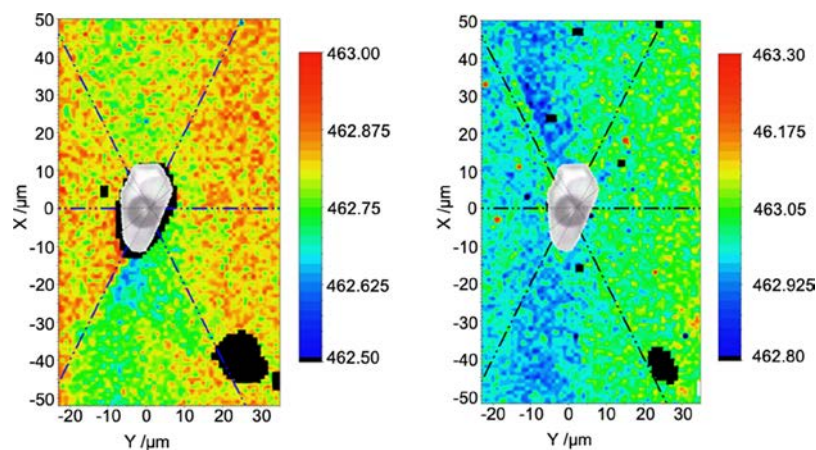


Figure 7. Raman map of the wavenumber of the high wavenumber A_1 quartz mode, with infilling fluid at the liquid–vapor saturation state (left) and monophasic liquid state (right). The wavenumber values are given by the color scale. The inclusion of interest has been superimposed as well as the crystal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

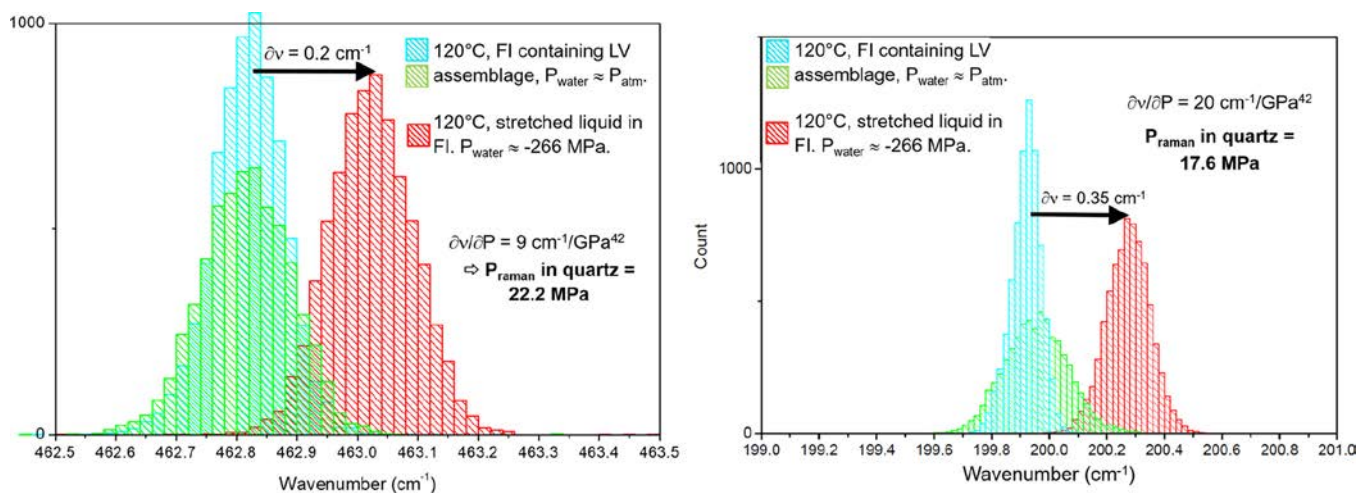


Figure 8. Raman line center histograms at 120 °C of the 464 (left) and 206 (right) cm^{-1} bands of quartz around a fluid inclusion filled with either a biphasic liquid–vapor stable mixture (green, blue = repetition to test for reproducibility) or a monophasic tensile liquid (red).

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 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 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 cm^{-1} change for wavenumber (showing the high stability of the experiment) with the total width varying by a maximum of 0.1 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 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,⁴² 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 cm^{-1} mode and 17.6 for 206 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 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 $\delta_{\Delta v}^{\text{av}}$ close to the 0.2 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 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_{H} was observed, expressing an internal failure (usually called “inclusion stretching” in the inclusionist’s glossary; see ref.⁶¹ for a review about the different types of damage in inclusions) and a change of the cavity volume. T_{H} was then upshifted by 16 °C, and logically, the T_{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.

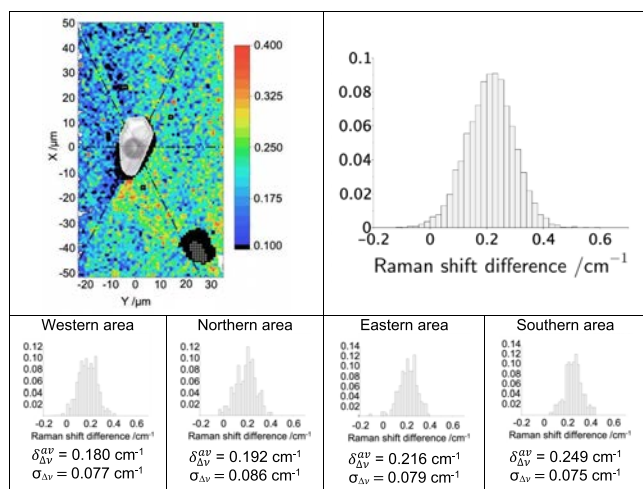


Figure 9. Shift difference between biphasic and monophasic modes for the 464 cm^{-1} Raman mode. Top-left: Map of the shift difference. Top-right: global histogram of this map. Bottom: Histograms of the four regions indicated by the red rectangles on the map, with a geographic-like denomination.

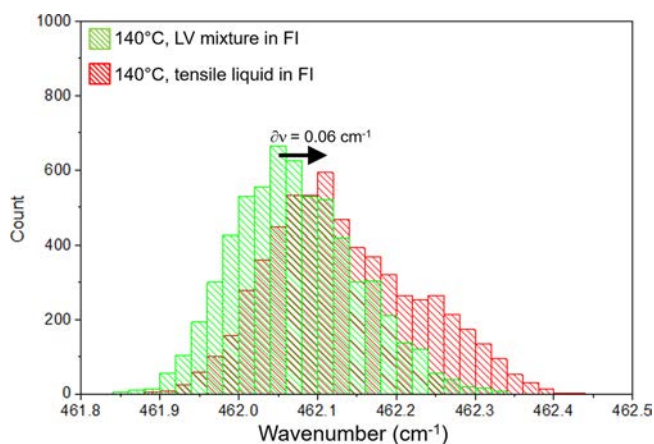


Figure 10. Histograms of the line center of the high wavenumber band, at 140 °C, along the equatorial plane of the inclusion, after the T_{H} -recorded damage.

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_{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_{H} is revolving

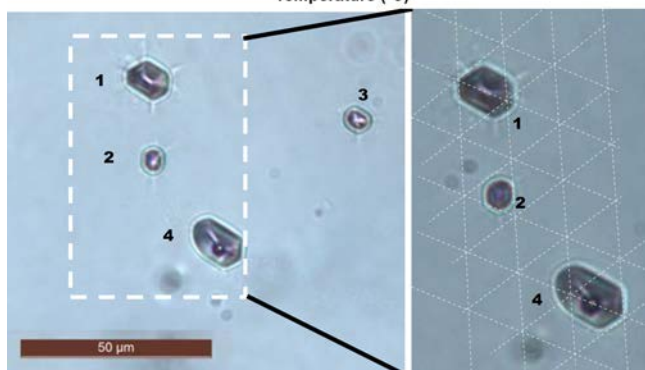
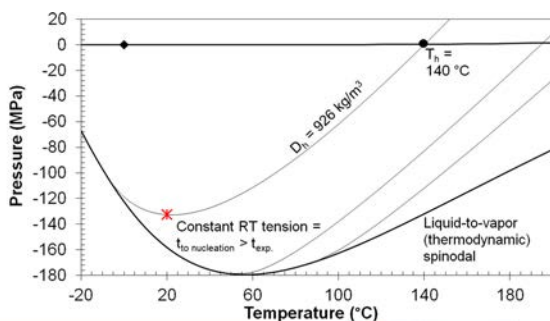


Figure 11. Upper panel, installing the “enduring tension” situation by isochoric cooling of a high-density SFI. Bottom left, observation of three fluid inclusions numbered (1–3) with microcracking in the quartz at each corner of the negatively shaped cavity. The fourth (num. 4), which does not tolerate 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/m³ according to IAPWS EoS (pure water approx-
565 imation³⁷) (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_{H} , the liquid
568 tension in the three monophasic inclusions 1–3 was –132
569 MPa (Figure 11). Inclusion 4 had T_{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
578 crystallographic axis (Figure 11, bottom-right panel). 579

The quartz failure occurred with optically visible cracks
580 appearing at the edge of the three inclusions 1–3. The bright
581 border is underlined by a similar black edge when zooming:
582 the cracks cannot be due to an optical artifact. Inclusion 4,
583 which was never subjected to long tension ($T_{\text{IN}} > \text{RT}$), was not
584 damaged. The coexistence between the two mechanical
585 behaviors, so well correlated with the microthermometric
586 features, is a clear indication that the liquid tension is able to
587 fracture the surrounding quartz. 588

3.4. Numerical Models of Stress Concentration and 589
Fracturing. **3.4.1. Ellipsoidal Model and Pressure in the** 590
Equatorial Plane. The simulated stresses and pressure
591 resulting from FEA simulation based on oblate spheroids
592 with a shape factor $b/a = 0.1$ are represented in Figure 12. The 593 f12

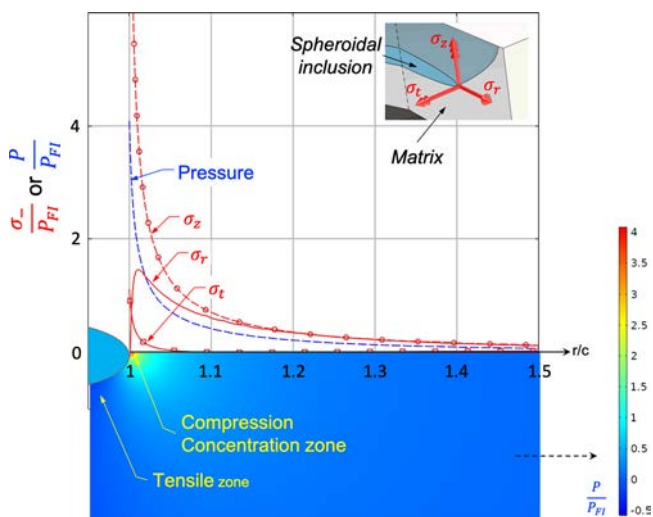


Figure 12. 2D axisymmetric mechanics model of an ellipsoidal-shaped inclusion. Bottom: Normalized pressure map around an inclusion. The vertical symmetry axis is the revolution axis. Top: Stresses and pressure magnitude along the radial axis in the optical plane.

pressure is highly concentrated close to the inclusion edge
594 where it reaches four times the fluid inclusion pressure and
595 decreases sharply along the radial axis. The pressure
596 distribution corroborates the Raman observations (Figure
597 10): a compressive stress (positive) lies within the equatorial
598 plane around the cavity (red color). This can be explained by
599 the flattening of the spheroid, like what occurred with the
600 remote stress above. The simulation indicates that the principal
601 stresses are aligned with the geometrical axes, that is, the radial,
602 tangent, and axial directions of the ellipsoid (see the r , t , and z
603 directions, respectively, in the inset top-right in Figure 12). In
604 the equatorial plane, the compressive axial stress σ_z is the
605 largest contribution to the total pressure while the magnitudes
606 of the tangent and radial stresses σ_t and σ_r are much smaller.
607 The tangent stress σ_t is compressive as well and contributes to
608 a lesser extent to the total pressure. On the other hand, radial
609 stress σ_r does not have a monotonous change. It has a negative
610 value in the very vicinity of the edge, quickly inhibited by the
611 global flattening of the inclusion yielding a compressive stress. 612

3.4.2. Real Inclusion Shape and the Stress Concentration 613
in the CsCl Inclusion. The Raman shift can be evaluated from
614 either from Grüneisen’s constant as shown above or from the
615 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.⁶² 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 Ramdas⁶³ determined the deformation potential constants of
625 the zone-center optical phonons of α -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 Ramdas⁶³ were used to calculate the
635 464 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 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 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 cm^{-1} .

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

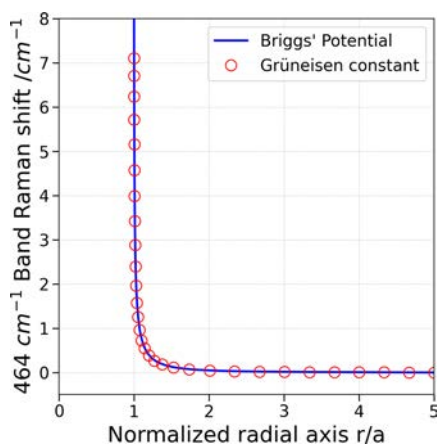


Figure 13. Raman shift evaluation along the radial axis.

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 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

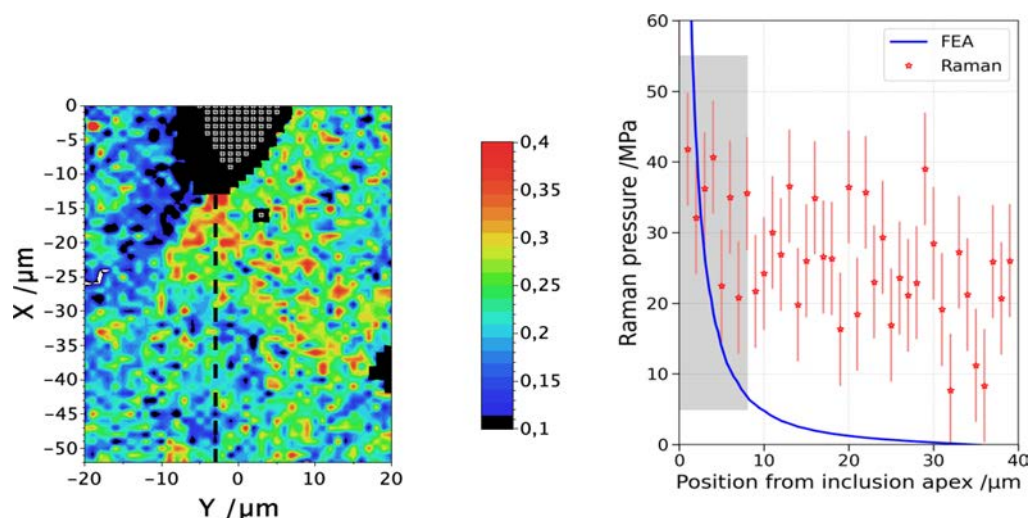


Figure 14. Left, Zooming in the southern area having the larger average wavenumber Raman shift (i.e., Figure 9). Right, Raman pressure (red stars) vs simulation (blue curve). The behavior close to the interface is highlighted as a gray area.

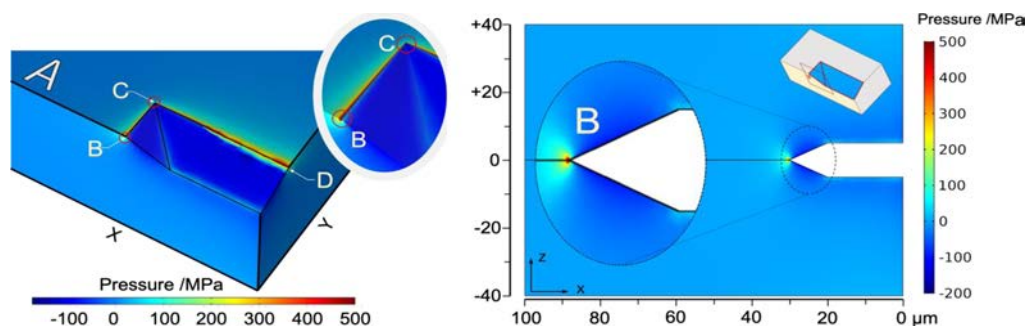


Figure 15. Pressure field showing (left) stress concentration along the longest edge lying in the symmetry plane XY (see Figure 5) near inclusion wall angles and (right) domains of negative/positive stress in the XZ symmetry plane.

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 polyminerals 755
assemblages containing various solid inclusions in minerals 756
(e.g., refs^{64–70}). The dominant compression mechanism is 757
considered to be the reduction of (Si-O-Si) (e.g., ref.⁷¹). 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.^{72,73}). 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.⁷⁴ 767
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

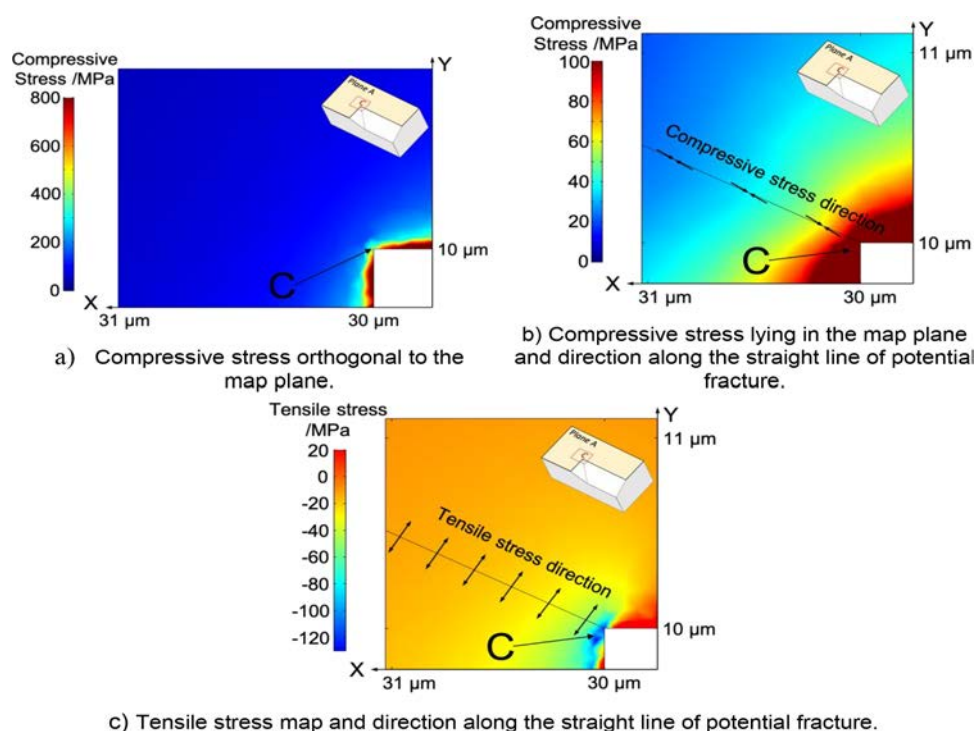


Figure 16. Principal stress magnitude map near the corner of the symmetry plane XY (see Figure 5, plane noted A). (a) Principal compressive stress (σ_{\perp}) perpendicular to the plane. (b) Second principal compressive stress (σ_{\parallel}) field near the corner of the symmetry plane XY (Figure 5, plane noted A). The double black arrows indicate the direction of σ_{\parallel} along the line corresponding to the potential crack direction. (c) Principal tensile stress (σ_{\perp}) field near the corner of the symmetry plane XY (see Figure 9, plane noted A). The double black arrows indicate the direction of σ_{\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.^{75–78}).

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
803 certainly increased by the pre-existence, before installing any
804 new constraints, of a certain degree of heterogeneity that is
805 visible in the Raman maps at RT (Figure 7 left). 806

4.3. Stress Accumulation and Fracturing Threshold. It
807 is difficult to be quantitative here; however, the stress
808 generated around the water-bearing cavity appears moderate,
809 especially compared to the observations of the damage (T_{H}
810 variations, apex fractures) in the host quartz. One proposition
811 for reconciling low stress and evidence of cracking is the role
812 played by fatigue effects in the resistance of materials. Stresses
813 that vary with time and in intensity are able to cause the rock
814 failure while below the yield strength, and even in the linear
815 elastic domain (e.g., refs.^{5,79–81}). The best illustration is what is
816 known as “reequilibrium” in fluid inclusions studies, which is
817 a modification of the inclusion shape and/or a fluid leakage
818 because of the effective stress, namely, the pressure difference
819 between host mineral stress and cavity-filling fluid pressure
820 (e.g., refs.^{82–86}). One strong hypothesis, often claimed to infer
821 various deep fluid conditions from fluid inclusions, is their
822 isochoric behavior along the rock pathway throughout the
823 Earth’s crust (burial and/or uplift). To validate it, the
824 resistance of quartz to differential stresses was measured on
825 SFIs for internal under- or overpressure (respectively $P_{\text{solid}} >$
826 P_{fluid} or $P_{\text{solid}} < P_{\text{fluid}}$). Overpressure causes reequilibration from
827 reaching 100 MPa.^{82,85} Underpressure caused visible cracks
828 from around 200 MPa, while reequilibration proceeded by
829 dissolution–precipitation in the range of 100–200 MPa (e.g.,
830 ref.⁸³). In a later study, cracking was observed when internal
831 underpressure only exceeded 270 MPa.⁸⁵ 832

In our case, the amplitude of tensile stress in the inclusion,
833 analogous to an underpressure stress, is either ~ 200 MPa 834

(CsCl sample) or ~ 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.⁸⁵ 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 theory⁴ 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_{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.^{87,88}), 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 (CO₂, 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 CO₂ storage is a crucial property that prevents any leakage from occurring. However, the injection of supercritical CO₂ severely dries out the formation, especially at the highest part where the CO₂ 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.^{89–91} 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.^{92,93} 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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Notes

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