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Evolution in H₂O contents during deformation of polycrystalline quartz: An experimental study

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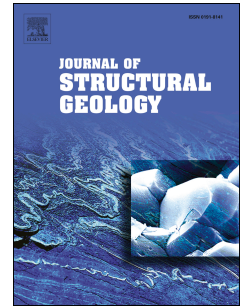
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1 EVOLUTION IN H₂O CONTENTS DURING DEFORMATION OF POLYCRYSTALLINE
2 QUARTZ: AN EXPERIMENTAL STUDY

3 **ABSTRACT**

4 Shear experiments were performed in a Griggs-type apparatus at 800°C and 1.5GPa, at a
5 strain rate of $2.1 \times 10^{-5} \text{ s}^{-1}$ using different starting materials: (i) Powder (grain size 6-10 μm) of
6 dry Brazil quartz with 0.15wt% added H₂O, (ii) “dry” Brazil quartz porphyroclasts (grain size
7 ~100-200 μm), devoid of fluid inclusions embedded in the same fine grained powder, and (iii)
8 “wet” porphyroclasts (grain size ~100-200 μm), containing initially a high density of μm -scale
9 fluid inclusions embedded in the same powder. After hot pressing, samples were deformed to
10 large shear strains ($\gamma \sim 3$ to 4.5), in order for the microstructures and H₂O distribution to
11 approach some state of “equilibrium”. The H₂O content and speciation in quartz were
12 analyzed by Fourier Transform Infra-Red (FTIR) spectroscopy before and after the
13 experiments. Mechanical peak strength is generally lower in experiments with 100% hydrated
14 matrix, intermediate in experiments incorporating wet porphyroclasts (with a proportion of 30
15 or 70%) and highest in those with dry porphyroclasts. All experiments with porphyroclasts
16 show pronounced strain weakening, and the strengths of most samples converge to similar
17 values at large strain. Wet porphyroclasts are pervasively recrystallized during deformation,
18 while dry porphyroclasts recrystallize only at their rims and remain weakly deformed.
19 Recrystallization of the initially fluid-inclusion-rich porphyroclasts results in a decrease in
20 inclusion abundance and total H₂O content, while H₂O content of initially dry clasts increases
21 during deformation. H₂O contents of all high strain samples converge to similar values for
22 matrix and recrystallized grains. In samples with wet porphyroclasts, shear bands with high
23 porosity and fluid contents develop and they host the precipitation of euhedral quartz crystals
24 surrounded by a free-fluid phase. These high porosity sites are sinks for collecting H₂O in
25 excess of the storage capacity of the grain boundary network of the recrystallized aggregate.
26 The H₂O storage capacity of the grain boundary network is determined as a H₂O-boundary-
27 film of ~0.7 nm thickness.

28 **1. INTRODUCTION**

29 Quartz weakening by H₂O is well known since the seminal papers by Griggs and Blacic
30 (1965) and Griggs (1967). In natural rocks, it is tacitly assumed that quartz is sufficiently
31 “wet”, because quartz usually is one of the weakest components in plastically deformed rocks.
32 However, some recent observations have described potentially drier natural rocks, which are

33 deformed (Fitzgerald et al., 2006, Menegon et al., 2011, Kilian et al., 2016). On the other
34 hand, there is clear evidence for shear zones involving material initially rich in H₂O
35 (principally in the form of fluid inclusions), such as metasediments along the subduction plate
36 interface (Palazzin et al., 2016; Raimbourg et al., 2018; Raimbourg et al., 2015, Saffer and
37 Tobin, 2011), and the final deformed rocks do not necessarily indicate high H₂O contents.
38 Thus, the introduction or reduction of H₂O in quartz in natural rock deformation remains one
39 of the great unknown parameters.

40 As pointed out by Griggs (1967), the H₂O weakening effect in quartz may combine different
41 elementary processes, which all contribute to enhance plastic deformation. One process is
42 related to the enhanced intra-crystalline plasticity of quartz. It has been extensively studied in
43 single crystals, most of them synthetic (Griggs, 1967, 1974; Griggs and Blacic, 1965;
44 Kekulawala et al., 1978, 1981; McLaren et al., 1983; McLaren et al., 1989). The microscopic
45 weakening phenomenon may eventually depend on the hydrolysis of Si-O bonds in the cores
46 of dislocations (Griggs, 1974), on enhanced climb of dislocations (Cordier and Doukhan,
47 1989; Mainprice and Jaoul, 2009; Tullis and Yund, 1989), or involve the increased dislocation
48 nucleation at nano-scale H₂O clusters acting as dislocation sources (Fitz Gerald et al., 1991;
49 McLaren et al., 1989). H₂O, in the form of molecular H₂O is most efficient to weaken quartz
50 single crystals (e.g., Paterson, 1989, Kekulawala et al., 1978, 1981). However, the growth of
51 nano-scale clusters of H₂O to form larger fluid inclusions, resulting from heat treatment,
52 increases quartz strength (Kekulawala et al., 1978): milky quartz containing a large
53 concentration of H₂O confined in μm -scale fluid inclusions is stronger than synthetic crystal
54 with a much lower H₂O concentration. The effect of OH structural defects on deformation is
55 unclear but appears limited (Doukhan and Trépiéd, 1985; Paterson, 1989; Kronenberg, 1994;
56 Cordier et al., 1994). However, in a given quartz material, the weakening effect increases with
57 the H₂O content (Griggs, 1967, Blacic and Christie, 1984, Kronenberg and Tullis, 1984,
58 Cordier and Doukhan 1989, Hirth and Tullis 1992, Den Brok et al., 1994, Stunitz et al., 2017).

59 Another elementary process, proposed by Griggs (1967) as a cause of quartz hydrolytic
60 weakening, is recrystallization, which operates in polycrystals (Jaoul et al., 1984; Tullis and
61 Yund, 1989; Hirth and Tullis, 1992). Similar to single crystals, in quartz aggregates, there is
62 an inverse correlation between the amount of added H₂O and the assemblage strength (Jaoul
63 et al., 1984; Kronenberg and Tullis, 1984). In particular, in H₂O-rich experiments, the small
64 grain sizes decrease strength, suggesting some contribution of grain-boundary mediated
65 process to weakening (Kronenberg and Tullis, 1984).

66 The case of deformation of polycrystalline material is of prime interest to nature, as it directly
67 applies to the strength of mylonites and ultramylonites. It involves the combination of
68 intracrystalline and grain boundary processes, so that identifying the H₂O-weakening effect is
69 difficult. In addition, natural material may contain H₂O concentrations varying over several
70 orders of magnitude (Ito and Nakashima, 2002): microcrystalline cherts, non-metamorphic or
71 of diagenetic grade, contain up to ~40,000 H/10⁶Si. In contrast, the threshold for the onset of
72 weakening, in other words the boundary between wet and dry quartz in experiments on
73 synthetic quartz, is ~100 H/10⁶ Si (Griggs and Blacic, 1965; Cordier and Doukhan, 1991, Den
74 Brock, 1994; Christie et al., 1964, Kilian et al., 2016). Not all of the H₂O content of natural
75 quartz (primarily in μm-scale fluid inclusions) has a weakening effect (Kekulawala et al.,
76 1978), but the mechanical role of large H₂O concentrations is still to be determined.
77 In particular, considering natural quartz as a two-phase-system of crystal and fluid inclusions,
78 the transfer of H₂O from the inclusions into the crystal (and the associated weakening) is
79 difficult because of the very low solubility and diffusive flux of H₂O in quartz (Kronenberg et
80 al., 1986, Paterson 1986, Gerretsen et al., 1989). As a consequence, micro-fracturing
81 (Kronenberg et al., 1986, 1990, Gerretsen et al., 1989, FitzGerald et al., 1991, Stunitz et al.,
82 2017) and diffusion (along subgrain boundaries or dislocation cores; Post and Tullis, 1998)),
83 as well as grain boundary migration (Gleason and DeSisto, 2008), have been proposed as
84 mechanisms responsible for H₂O uptake, because oxygen diffusion may be increased along
85 dislocations or grain boundaries.
86 Finally, H₂O concentration is not a fixed quantity and depends itself on deformation, as
87 recrystallization redistributes H₂O within the material. For example, in rock of low
88 metamorphic grade from Japanese accretionary complexes, the H₂O concentration decreases
89 with increasing grade, reflecting the progress of recrystallization (Ito and Nakashima, 2002).
90 In grains with a large initial H₂O content stored in fluid inclusions, the migration of grain
91 boundaries that accompanies recrystallization leads to the loss of most fluid inclusions and the
92 decrease H₂O concentration (Bakker and Jansen, 1994; Kilian et al., 2016; Palazzin et al.,
93 2016). Therefore, the “steady-state” H₂O concentration (and the associated strength) in a
94 deforming and recrystallizing aggregate is poorly known. FTIR measurements in natural
95 mylonites formed at mid-greenschist and amphibolite facies conditions show low H₂O
96 contents, <100 to ~320 H/10⁶ Si at grain boundary regions (Gleason and DeSisto, 2008) and
97 in individual single grains (Kilian et al., 2016).
98 Given the wealth of existing experimental and natural studies on H₂O weakening of quartz,
99 this study specifically focuses on the strength of quartz as a function of H₂O-content. Another

100 aspect of this study is the evolution of H₂O-content (i.e. increasing and decreasing H₂O
101 contents in deforming polycrystals). "Wet" initial conditions (e.g., applicable to examples to
102 sediments in subduction settings) and dry initial crystals are compared and their H₂O-
103 evolution studied. We have carried out high strain experiments in order to simulate natural
104 shear zones but also to be as close as possible to steady-state conditions, both in terms of
105 microstructures and H₂O distribution. We focused on the role of H₂O on recrystallization and
106 the effect of H₂O content and speciation.

107 **2. METHODS**

108 **2.1 Experimental procedure**

109 All experiments were performed in a Griggs-apparatus at 800°C, ~1500 MPa and a constant
110 strain rate of $\sim 2 \times 10^{-5} \text{ s}^{-1}$. These conditions were chosen in order to activate dislocation creep
111 in the samples (cf. Hirth and Tullis, 1992). Pre-cut (at 45°) Al₂O₃ pistons were inserted into a
112 pre-annealed platinum jacket. A ~1mm thick layer of fine quartz matrix powder was placed
113 between pistons, which contained a fixed proportion of larger grains ("porphyroclasts"). The
114 matrix material (Brazil quartz) was the same in all experiments while two distinct types of
115 porphyroclasts were used.

116 The quartz matrix comes from a dry Brazil single-crystal crushed in a stainless steel mortar.
117 After crushing, we applied repeated cycles of sedimentation in a H₂O column to sort grains
118 of a specific size. The powder we obtained consisted of grains with a diameter in the range of
119 ~6-20µm, although a small fraction of the grains (~15% in volume), had larger, up to 110µm,
120 diameter.

121 The first material chosen for the porphyroclast was dry Brazil quartz. A single euhedral
122 crystal of ~4 cm long was cut, trying to avoid optically visible secondary fluid inclusions
123 planes. Porphyroclasts were obtained by crushing the selected part of the crystal in a stainless
124 steel mortar and separating a size in the range of 200-250 µm by sieving.

125 The second porphyroclast material was milky vein quartz from the Hyuga mélange, a low-
126 grade metamorphic unit from the Shimanto Belt in Japan (Raimbourg et al., 2014; Palazzin et
127 al., 2016 for detailed description). Fragments from mm-wide veins were crushed in an agate
128 mortar and quartz was separated from the remaining matrix by a Frantz magnetic separator
129 and density (Sodium Polytungstate) techniques. The material was sieved to separate the 200-
130 250 µm size fraction. A final hand-picking was carried out to avoid possible clay mineral
131 contamination.

132 The matrix and porphyroclasts were dried at 110°C for 48 hours before preparing the mixture.
133 Four experimental samples were prepared by mixing 30% and 70% porphyroclasts of either
134 Hyuga or Brazil quartz with the pure Brazil quartz matrix. In addition, one sample with 100%
135 pure Brazil matrix was deformed.

136 To ensure an homogenous distribution of clasts in the matrix, we added acetone to the
137 clasts+matrix mixture in a glass beaker and stirred the slurry obtained in an ultrasonic bath,
138 until complete acetone evaporation (cf. de Ronde et al. (2005)). The porphyroclasts and matrix
139 quartz mixtures were dried at 110°C and then placed on the lower Al₂O₃-piston surface after
140 adding distilled water with a micropipette. The material was wrapped in Ni-foil inside the Pt-
141 jacket. The amount of water was adjusted to the proportion of the matrix (100, 70 or 30%),
142 corresponding to an H₂O-content of 0.15 wt.% for matrix (**Table 1**). The second pre-cut
143 piston was placed on top of the sample, and the Pt jacket was welded with a Lambert
144 precision point welder. The sample was then placed in the center of a graphite furnace inside
145 the solid confining medium (NaCl). The sample-piston assembly is illustrated in **Figure 1a**.

146 Pumping and heating were performed slowly to reach the desired temperature and pressure
147 conditions (normally over ~9 hours). Confining pressure was initially increased to 150 MPa
148 before heating. Temperature was increased in steps of 100°C at a rate of 25°C per minute at
149 pressure intervals of several hundreds of MPa. When pressure and temperature were at 1.5
150 GPa and 800°C, axial piston movement was started at a constant displacement rate. The
151 typical time to reach the hit point was ~20 to 24 hrs. During this stage, the sample was
152 effectively subjected to hot isostatic pressing, leading to a denser aggregate.

153 The hit point, marked by a sharp increase in axial force, corresponds to the onset of sample
154 loading and deformation. Axial force then rises rapidly to a maximum value (“peak stress”).
155 The subsequent deformation of the sample, up to $\gamma \sim 4-6$, is achieved for near constant, or
156 slowly decreasing axial force.

157 At the end of each experiment, the sample was quenched to a temperature of 200°C within 3
158 minutes. Subsequently, the confining pressure was lowered to room pressure over a period of
159 several hours, keeping a differential stress of (initially) 100-200 MPa on the sample in order
160 to minimize unloading cracks.

161 Some samples were kept under hydrostatic conditions without deformation to obtain
162 information of the microstructures during the initial steps of the experiments. All samples

163 were cut along their long axis normal to the shear zone in order to provide thin and thick
164 sections for microscopy and FTIR analysis, respectively.

165 **2.2 FTIR measurements**

166 To enable analysis of the H₂O-content, slices of the single Brazil quartz crystal (cut in the
167 direction normal to the [c]-axis) and isolated porphyroclasts of Hyuga quartz (both
168 corresponding to the starting material) were firstly embedded in orthodontic acrylic resin
169 (Vertex Orthoplast) and then manually doubly polished (thickness 120-140 μm). Deformed
170 samples were cutted and directly polished to 120-140 μm thick sections. All samples were
171 then accurately cleaned in ultrasonic bath with acetone to remove remaining resin. The H₂O-
172 content was determined by Fourier Transform Infrared (FTIR) spectroscopy with a
173 microscopic FTIR continuum spectrometer (Nicolet-6700, Thermo Scientific) at the Institut
174 des Sciences de la Terre d'Orléans (France). All the measurements were carried out at
175 atmospheric temperature, after purging the optical path of the IR beam with dry air in order to
176 avoid measurement of atmospheric water. A sodium chloride window was used to collect and
177 subtract the background for each measurement. A 50×50 μm aperture window was used for
178 all the analyses. 256 scans per spectrum were collected with 4 cm⁻¹ resolution. We estimated
179 the concentration of “molecular” H₂O, using the Paterson (1982) calibration of the integral
180 absorption band between ~2800 and 3780 cm⁻¹ using the Beer-Lambert law,

$$181 \quad A = C * t * e$$

182 where C is the concentration, t the thickness, and e the integrated molar absorption coefficient
183 (0,8120 L cm⁻² mol⁻¹). Sample thicknesses t was obtained from the height of the peak at 1790
184 cm⁻¹ corresponding to the Si–O band, again making use of the Beer-Lambert law (e.g., Ito and
185 Nakashima, 2002). H₂O concentration (wt. ppm H₂O/SiO₂) was obtained (**Table 1**) by
186 dividing the H/10⁶Si-value of the Paterson (1982) calibration by a factor 6.67 given in Kilian
187 et al. (2016).

188 **2.3 EBSD - CIP - Grain Size determinations**

189 Crystallographic preferred orientation (CPO) of quartz was measured by electron backscatter
190 diffraction (EBSD) (Lloyd and Freeman, 1994; Prior et al., 1999) and by computer integrated
191 polarized (CIP) microscopy (Heilbronner and Barrett, 2014). EBSD patterns were acquired
192 with an Oxford AZTEC system and a Nordlys detector on a FE- Zeiss Merlin compact SEM
193 at the University of Tromsø. We used thin sections with a thin carbon coat at 70° tilt angle, 20

194 kV acceleration voltage, \square 10 nA beam current, and 11 to 14 mm working distances at a step
195 size of 0.1 μm . Initial noise reduction was performed with CHANNEL 5 software by
196 removing isolated points and replacing non-indexed points with the orientation of their
197 neighbors (interactively filled starting with eight similar neighbors down to six or five similar
198 neighbors). Thin sections were rotated 45° counterclockwise in order to align shear zone
199 boundaries (forcing block interface) to reference frame direction. Data were analyzed with
200 MTEX toolbox (Hielscher and Schaeben, 2008). Analysis of the grain boundary fraction was
201 carried out using EBSD maps. Grains were segmented based on c-axis misorientation after
202 converting EBSD images to CIP images using a procedure described in Heilbronner and
203 Kilian (2017).

204 3. RESULTS

205 3.1 Characterization of the starting material

206 Hyuga quartz has a milky appearance due to the great abundance of many tiny fluid
207 inclusions (Palazzin et al., 2016). These inclusions range from a few to $10\mu\text{m}$ in diameter
208 (Raimbourg et al., 2015) and are heterogeneously distributed in the porphyroclasts which look
209 dark in thin section and grain mounts (**Figure 1b-1**). As shown by FTIR spectra, OH content
210 is variable as a consequence of the distribution of fluid inclusions (**Figure 1b-1**). Mean
211 measured values (listed in **Table 1**) are of the order of $\sim 23,000 \text{ H}/10^6\text{Si}$, or $\sim 0.34\text{wt}\%$ H_2O ,
212 which is about twice the amount of H_2O added to the sample matrix. After the rise in T and P
213 up to 800°C

214 and 1.5GPa , Hyuga porphyroclasts show a lower abundance of fluid inclusions than the
215 starting material, so that they appear clearer (**Figure 1b-2**). The measured amount of OH is
216 lowered to about half of the initial quantity ($\sim 12,000 \text{ H}/10^6\text{Si}$), corresponding to $\sim 0.18\text{wt}\%$,
217 similar to the added H_2O content of $0.15\text{wt}\%$ (**Table 1, Figure 1b-2**).

218 Porphyroclasts of dry Brazil quartz are optically strain free and contain no fluid inclusions
219 (**Figure 1b-3**). The mean measured H content in Brazil quartz is about $260 \text{ H}/10^6\text{Si}$ and
220 confirms that this material can be considered as "dry" quartz for deformation (**Table 1; Post**
221 **and Tullis, 1998; Paterson, 1989**).

222 3.2 Mechanical data

223 Moderate peak shear stress and lower flow strength values (**Figure 2, Table 2**) indicate
224 dominant plastic deformation in most samples at the applied strain rate of $\sim 2.1 \times 10^{-5} \text{ s}^{-1}$. Only
225 the 70% Brazil clasts sample reaches peak stress above the Goetze criterion ($\Delta\sigma = 1600 \text{ MPa}$

226 at gamma ~ 2 ; **Figure 2**) for plastic deformation ($\Delta\sigma \approx P_{\text{conf}}$; Kohlstedt et al., 1995), all other
227 samples are in the fully plastic regime. All curves are characterized by a first stage of a rapid
228 increase in stress up to peak values ($\gamma = 0$ to $\sim 0.5/1.5$), followed by a weakening stage that
229 may or may not reach steady state stress values.

230 Two samples with 100% matrix show a $\sim 50\%$ difference in peak stress (at $\gamma \sim 0.8$) and a
231 smaller difference at $\gamma \sim 3.5$ (**Figure 2**). The sample with 30% Hyuga porphyroclasts shows a
232 peak shear stress between that of the two matrix samples (**Figure 2**) and a final stress value
233 that is almost identical to that of the matrix sample (~ 260 MPa) at $\gamma \sim 3.2$. The sample with
234 70% Hyuga porphyroclasts shows a considerably higher peak stress but weakens to a similar
235 finite strength as the 30% Hyuga and matrix samples.

236 Samples with Brazil porphyroclasts reach higher peak shear stresses than their Hyuga
237 porphyroclasts counterparts: up to ~ 650 MPa for 70% clasts and ~ 420 MPa for 30% Brazil
238 clasts. After the peak stress, all matrix + clasts assemblages display significant weakening
239 with a similar slope, irrespective of the nature of the clasts. It is remarkable that the flow
240 stresses of three assemblages, containing 70% and 30% of Hyuga porphyroclasts and 30% of
241 Brazil porphyroclasts, converge towards a common flow stress of ~ 250 - 280 MPa at $\gamma \sim 3.3$
242 (**Figure 2**), similar to the 100% matrix, regardless of their peak stress values.

243 **3.3 Microstructural observations**

244 **3.3.1 Hot pressed material**

245 After hot-pressing, only little porosity is observed, typically at triple junctions of grains
246 (**Figure 3**). Pores rarely exceed 1μ diameter, and total porosity is estimated to be ~ 2 to 4%
247 of the sample volume. Very few open grain boundaries are present, but these are
248 approximately normal to the piston axis, so that they probably result from quenching and
249 unloading (**Figure 3**).

250 **3.3.2 Pure matrix deformation**

251 The deformed samples with pure 100% matrix are characterized by pervasive recrystallization
252 of the deformed parts of the samples. Strain is partitioned into narrow regions at the piston
253 ends, extending into a broader region, which occupies almost the full width of the shear zone
254 in the center (**Figure 1a**). The quartz grains in the regions of strain localization show a strong
255 shape fabric, and individual grain boundaries are difficult to detect in the high strain regions
256 in the light microscope because of their strong CPO (see paragraph 3.5.1).

257

258 3.3.3 Matrix + Brazil porphyroclasts

259 In these samples, a foliation results from the elongation of matrix domains and recrystallized
260 regions extending from porphyroclasts at an angle of about 18° to the shear zone boundaries
261 (piston interfaces; **Figure 4a,b**). In the sample with 70% clasts, tails of recrystallized quartz
262 (**Figure 4b,d**) extending from porphyroclasts define σ -type clasts (Hanmer, 1984b; Passchier
263 and Simpson, 1986). Porphyroclasts in the assembly with 30% clasts show a variable shape:
264 some are elongated, while others have an equant shape, both of which are mainly inherited
265 from their pre-deformation state (**Figure 4a,c**). Porphyroclasts contain few or no subgrains.
266 Their rims are commonly sutured and their cores are surrounded by small recrystallized grains
267 (**Figure 4c,d**). Some undulatory extinction and deformation lamellae are common (**Figure**
268 **5a,b**). These microstructures are characteristic of dislocation creep regime 1 described by
269 Hirth and Tullis (1992). In both Brazil clast samples the extent of recrystallization of
270 porphyroclasts is limited, and relict clasts and recrystallized rims are easy to distinguish
271 (**Figure 4-5a,b**).

272 3.3.4 Matrix + Hyuga porphyroclasts

273 Hyuga porphyroclasts (**6a,b**) invariably are strongly elongated, up to an aspect ratio of ~ 10 .
274 Their shape fabric defines a foliation at about 10° to the shear zone boundaries. They are
275 extensively recrystallized into elongated grain aggregates, with serrated boundaries, and
276 subgrains, forming a microstructure of dislocation creep regime 2 of Hirth and Tullis (1992).
277 Because of the penetrative recrystallization, former porphyroclasts are difficult to distinguish
278 from the surrounding matrix (**Figs 5c,d and 6c**), except for the fact that porphyroclasts
279 recrystallized and grown into larger grains and subgrains than the matrix (**Figs 5c,d and**
280 **6c,d**). The clasts in the 70% Hyuga porphyroclasts sample are more pervasively recrystallized
281 than in the 30% clasts sample, possibly due to higher strain.

282 3.3.5 Shear Bands

283 In both samples containing Hyuga porphyroclasts, shear bands develop oblique to the shear
284 zone boundaries in a synthetic orientation (c' -orientation) with the imposed shear sense (**Figs**
285 **6c,d and 7**). The angle between these planes and the shear zone boundary varies between ~ 25
286 and $\sim 35^\circ$. The stretched porphyroclasts define the S-planes of a SC' fabric (C-planes are
287 absent). Plane polarized light images show the shear bands as trails of small fluid inclusions
288 (**Figure 7a**). The shear bands are most ubiquitous in the sample containing 70% of Hyuga
289 porphyroclasts, where the bands cut across the matrix and the stretched porphyroclasts,
290 making an average angle of 27 degrees with porphyroclast long axes. SEM images (**Figure**

291 **7c)** show that the C' bands are zones of high porosity, composed of cube-shaped, idiomorphic
292 grains, of size ~2-5 μm , surrounded by voids.

293 **3.4 H₂O content/distribution**

294 **3.4.1 Matrix**

295 The original Brazil quartz crystal, from which the matrix was produced, contains a very low
296 proportion of H₂O, of the order of ~250 H/10⁶Si (**Table 1 and Figure 1b-3**). In each
297 experiment, H₂O had been initially added to the dry Brazil quartz matrix, with a proportion of
298 0.15wt%, or equivalently 10 000 H/10⁶Si.

299 After the experiments, the matrix displays a broad absorption band in the region between
300 3000 and 3800 cm^{-1} (**Figure 8a**), representing the molecular H₂O in quartz and in the grain
301 boundaries. From this broad absorption band, the H₂O content after experiments can be
302 estimated as ~900 to 2900 H/10⁶Si in deformed samples and ~4200 H/10⁶Si in an undeformed
303 sample (464GP, **Table 1**). The water initially added has been retained to variable extent in the
304 matrix during the application of pressure and temperature and later deformation.

305 The same initial material (Brazil quartz matrix + 30% Hyuga porphyroclasts) was brought to
306 high P and T in one experiment and then retrieved (464GP). In another experiment it was
307 deformed to high strain (428GP). The Brazil matrix in the deformed sample contains ~1500
308 H/10⁶Si, i.e. 2 to 3 times less than the corresponding experiment without deformation (~4200
309 H/10⁶Si; **Table 1**).

310 Comparing the different experimental materials, the H₂O content of the matrix is
311 significantly higher for experiments containing initially “wet” Hyuga porphyroclasts (~1500
312 for 30% and ~2900 H/10⁶Si for 70% porphyroclasts) than in experiments containing initially
313 “dry” Brazil porphyroclasts (~950 and ~1300 H/10⁶Si for 30% and 70% of porphyroclasts) or
314 experiments with 100% matrix (~800 H/10⁶Si) (**Figure 8a, Table 1**). Additionally, in
315 experiments containing Hyuga porphyroclasts, the H₂O -content of the quartz matrix and that
316 of the recrystallized Hyuga clasts are similar after deformation, considering the large standard
317 deviation: with 30% of clasts, the matrix contains ~1500 H/10⁶Si and porphyroclasts ~2300
318 H/10⁶Si, while for 70% clasts, the matrix contains ~2900 H/10⁶Si and porphyroclasts ~2350
319 H/10⁶Si (**Table 1**).

320 All spectra show discrete absorption bands at 3363, 3382, and 3595 cm^{-1} , which were not
321 present in the original Brazil quartz spectra (cf. **Figures 1D and 8**). The most prominent
322 discrete absorption band in the deformed matrix measurements is at 3595 cm^{-1} .

323 3.4.2 Porphyroclasts

324 Hyuga porphyroclasts display a broad absorption band in the region between 3000 and 3800
325 cm^{-1} (**Figures 1b,c,d and 10a**), which is related to molecular H_2O contained in the large
326 number of fluid inclusions initially present. During hot pressing the broad band of molecular
327 H_2O shows a general decrease with respect to the as-is material. This reduction in water
328 content is enhanced with deformation, as Hyuga porphyroclasts in deformed samples contain
329 $\sim 1/10$ of their initial water content (**Table 1, Figure 9a**).

330 In addition to this evolution of the H_2O content, the shape of the H_2O spectrum is also
331 modified by the application of P-T conditions and deformation from a broad triangular
332 absorption centered around around 3400cm^{-1} that is characteristic of fluid H_2O to a very broad
333 flat flat shape absorption (**Figure 9a**) that is unlike absorption spectra of liquid H_2O . The
334 position of discrete absorption bands, related to structurally-bound H_2O , are also modified.
335 The initial spectrum displays only a discrete absorption band at 3382 cm^{-1} . Application of P-T
336 condition results in the development of a band at 3585cm^{-1} , while after deformation a discrete
337 band around 3595cm^{-1} appears as well. As a result of this evolution in shape and integrated
338 area, recrystallized Hyuga porphyroclasts and the fine grained matrix converge towards a
339 similar IR spectrum (**Figure 9b**).

340 Initially, Brazil porphyroclasts contain virtually no H_2O ($\sim 250\text{ H}/10^6\text{Si}$), resulting in a flat
341 absorption spectrum (**Figure 8b**), where only one secondary absorption band at 3485 cm^{-1} is
342 visible. The application of P-T conditions and deformation (**Figure 10, Table 1**) results first
343 in the increase in H_2O content in the cores of the porphyroclasts ($\sim 650\text{ H}/10^6\text{Si}$) and in their
344 recrystallized rims (~ 1500 for 30% and $\sim 900\text{ H}/10^6\text{Si}$ for 70% of porphyroclasts). The very
345 weakly deformed cores, showing only undulatory extinction, contain a smaller amount of H_2O
346 (**Figure 10b,c,f**) than observed for the recrystallized regions with their grain boundaries
347 (**Figure 10d,e,f**). Furthermore, new discrete absorption bands appear at 3595 cm^{-1} and at 3363
348 cm^{-1} in the recrystallized region, whereas the core shows a discrete band at 3585 cm^{-1} , which
349 is absent in the recrystallized region (**Figure 10a,f**).

350 3.4.3 Shear bands

351 In the experimental sample containing 30% of Hyuga porphyroclasts, the shear bands that cut
352 across porphyroclasts and matrix contain a high H_2O concentration of $\sim 3700\text{ H}/10^6\text{Si}$ (**Table**
353 **1**). This H_2O content is significantly higher than either porphyroclasts ($\sim 2300\text{ H}/10^6\text{Si}$) or the
354 matrix ($\sim 1500\text{ H}/10^6\text{Si}$) that hosts these bands. It corresponds to trails of fluid inclusions

355 (optical observations) and the presence of abundant voids (SEM observations) along the shear
356 bands (**Figure 7a,c**).

357 **3.5 Crystallographic fabrics**

358 Grain boundary maps, orientation images and pole figures are derived from EBSD maps and
359 shown for a pure matrix sample and for one sample containing 70% Hyuga and one with 70%
360 Brazil clasts. For easier interpretation, the orientation images are recalculated as c-axis
361 orientation images (see color look-up table on the right of **Figs 11b-12b and 13b**).

362 **3.5.1 100% Matrix**

363 In the 100% matrix experiment, the central region of pervasive recrystallization of the sample
364 shows elongated grains, whose long axes are oriented at ~25 degrees (on average) from the
365 shear plane (**Figure 11a,b**). Their CPO shows a well-defined maximum rotated synthetically
366 with the sense of shear, and all crystallographic axes are concentrated in or near the X-Z plane
367 (**Figure 11c**).

368 **3.5.2 Recrystallized Hyuga porphyroclasts CPO**

369 EBSD map shows that a large proportion of initial Hyuga porphyroclasts, strongly elongated
370 after deformation, consists of recrystallized grains with small grain size (light blue domain,
371 **Figure 12a,b**).

372 The CPO shows a similar asymmetry with respect to the shear plane as the 100% matrix.
373 Parts of the recrystallized regions show many subgrain boundaries in a rather uniform CPO
374 domain (**Figure 12b**).

375

376 **3.5.3 Recrystallized tail of a Brazil porphyroclast**

377 In the experiment with 70% Brazil quartz, the crystallographic fabric of the recrystallized tail
378 is qualitatively similar as that of the 100% matrix, but the grain size distribution is broader
379 (**Figure 13a,b**). The c-axis maxima are slightly weaker (**Figure 13c**). The recrystallized tail
380 appears to have a better developed CPO than the matrix (orange domain, **Figure 13b**).

381 **3.5.3 Shear bands and strain shadows**

382 Shear bands are developed only in Hyuga clast samples. CIP analysis of these samples reveals
383 that shear bands inside larger porphyroclasts have a completely different c-axis orientation
384 from that of the surrounding material, as seen in light microscope images with the
385 compensation plate inserted (**Figure 7b**). Strain shadows around Brazil porphyroclasts

386 constitute other high-porosity domains where small idiomorphic grains are surrounded by
387 voids, and the crystallographic orientation of these small grains, similar to that of shear bands,
388 is very different from surrounding quartz. The strong contrast in orientation between the
389 grains in shear bands and pressure shadows and the surrounding material, the high-porosity,
390 and the grain shapes suggest that these grains formed as a result of precipitation in a fluid
391 filled porosity.

392 **4. DISCUSSION**

393 **4.1 Mechanical Data**

394 After exhibiting an initial peak stress, all samples deform at flow stresses well below the
395 values of the confining pressure (**Figure 2**; Goetze Criterion: Kohlstedt et al., 1995). The
396 inference of the Goetze Criterion that fractures opening and extension are suppressed when P_c
397 $>$ differential stress is consistent with the fact that none of our samples contained
398 thoroughgoing fractures. The 100% Brazil quartz matrix samples show a higher flow stress
399 than that of wet polycrystalline quartz of Hirth and Tullis (1992) in coaxial experiments at the
400 same temperature and confining pressure. The shear strain rate of our experiments is faster
401 than the coaxial strain rate of Hirth and Tullis (1992), which may explain the differences.
402 From the mechanical data it is clear that the originally dry Brazil quartz matrix material has
403 become fully "wet" during pressurization and heating, as it has been achieved in experiments
404 previously by Post and Tullis (1998) and Rutter and Brodie (2004a).

405 All samples with porphyroclasts show a pronounced peak stress and subsequent weakening
406 behavior, consistent with a higher initial strength of the large porphyroclasts, which
407 subsequently weaken during recrystallization. Even the Hyuga quartz, which contains a lot of
408 H₂O in the form of aqueous fluid inclusions and thus may be expected to be weaker than the
409 pure Brazil quartz matrix, shows this behavior. The mechanical evolution of the sample raises
410 two points: (1) Porphyroclast material shows pronounced strain weakening, probably caused
411 by recrystallization (2) Fine grained quartz material tends to be weaker than that with coarse
412 grained porphyroclasts. The former point has already been addressed by Hirth and Tullis
413 (1992), who have observed strain weakening behavior for dislocation creep regime 1. The
414 weakening is attributed to local grain boundary migration (bulging recrystallization) of more
415 or less undeformed porphyroclasts. In our examples here, dynamic recrystallization takes
416 place by progressive subgrain rotation (see below), so that the recrystallization mechanism
417 does not seem to be the only controlling factor for the weakening.

418 Steady state is reached by the 30% Hyuga material (428GP) after $\gamma \approx 1.5$ (**Figure 2**). The 70%
419 Hyuga sample (456GP) reaches similar stresses as the 30% sample, but at higher gamma
420 values and after higher peak stress. The grain sizes of the 70% Hyuga sample are smaller,
421 even though the finite stress values of the samples are identical. The findings are consistent
422 with the results by Kidder et al. (2016), who find that the recrystallized grain size is
423 dependent on stress history.

424 Samples with dry Brazil porphyroclasts do not reach steady state after $\gamma = 3.5$ or 4 is
425 consistent with Brazil clasts behaving as more rigid particles, and their recrystallization takes
426 more strain than does recrystallization of the Hyuga clasts. The high peak strength of the 70%
427 Brazil clast sample can be attributed to the high strength of the Brazil clasts themselves with
428 low H₂O content. The fact that they survive deformation as more or less rigid particles implies
429 that they have not become sufficiently hydrated. Only limited recrystallization takes place at
430 their margins, where tails of recrystallized quartz grains develop (**Figs. 5-6a,b and 14**). The
431 CPO of their recrystallized grains is oriented synthetically with respect to the imposed shear
432 sense (dextral; **Figure 14**), i.e. similar to that of weaker material of other samples.

433 Applying the empirical quartz flow law by Hirth et al. (2001), and the Paterson & Luan
434 (1990) flow law (for silicic acid), we estimated the differential stress of our quartz matrix for
435 strain rate values of $2 \times 10^{-5} \text{ s}^{-1}$. Both flow laws predict lower shear stresses ($\Delta\sigma/2$) than our
436 experimental values for pure matrix (111 MPa and 178 MPa versus observed ~200 MPa) but
437 the values are not far off (yellow star and red dot in **Figure 2**).

438 **4.2 Effect of H₂O on deformation**

439 Our samples are deformed by crystal-plastic processes, so that they can be compared with the
440 different deformation regime defined in Hirth and Tullis (1992). Even though Brazil and
441 Hyuga porphyroclasts were deformed at the same P and T, the degree and mechanism of
442 recrystallization was quite different in the two materials.

443 Dry Brazil porphyroclasts show undulatory extinction and abundant deformation lamellae as
444 typical features for dislocation glide with limited recovery or recrystallization in quartz. These
445 features usually occur together with small scale fractures, kinks or short wavelength
446 misorientation bands, and dislocation tangles (Hirth and Tullis, 1992, Trepmann and
447 Stoeckhert, 2013, Stunitz et al., 2017) and can be compared to microstructures observed in the
448 dislocation creep regime 1 of Hirth and Tullis (1992). The presence of small recrystallized
449 grains limited to porphyroclasts rims suggests the onset of subgrain rotation recrystallization.
450 Recrystallized tails at porphyroclasts form a CPO similar to the matrix CPO (**Figure 13**),

451 consistent with activation of slip on the basal <a> system (Schmidt and Casey, 1986; Law,
452 1990).

453 Deformed milky Hyuga quartz shows very different microstructures. The shape of highly
454 elongated Hyuga porphyroclasts can be compared with natural quartz aggregates deformed at
455 mid-greenschist conditions (Law, 1984) or with experimentally deformed Black Hill Quartzite
456 (BHQ) described in regime 2 by Hirth and Tullis (1992) or by Hirth et al., (2001). These
457 elongated grain aggregates are recrystallized to a great extent (**Figs. 6 and 12**). Similar
458 microstructures, and corresponding activated slip systems, are reported also for BHQ
459 (Heilbronner and Tullis, 2006) deformed at higher temperatures and higher strain rates.
460 According to our microstructural observations and CPO, recrystallization took place by
461 subgrain rotation. The development of a common CPO for recrystallized porphyroclasts and
462 matrix indicates that deformation is rather homogeneously accommodated within the whole
463 system and dominated by basal <a> slip.

464 The difference between Brazil porphyroclasts, deforming with limited recrystallization, and
465 Hyuga porphyroclasts, pervasively recrystallized by subgrain rotation, can only be explained
466 by their original difference in H₂O content. Our observations further support the effect of H₂O
467 on enhancing microstructural development and recrystallization proposed by Jaoul et al.
468 (1984), Tullis and Yund (1989) and Hirth and Tullis (1992).

469 Most samples converge to a similar strength after a shear strain of ~3 and recrystallization of
470 large volume fractions of the samples (**Figure 2**), even though the initial concentrations of
471 H₂O differed (**Figs. 9 and 11, Table 1**). Some of the main parameters controlling strength are
472 therefore grain size and H₂O distribution, and we can deduce that weakening in experiments
473 with Hyuga porphyroclasts is due to grain size reduction and fluid redistribution as a
474 consequence of dynamic recrystallization.

475 **4.3 Evolution of H₂O with deformation**

476 **4.3.1 H₂O speciation**

477 In addition to the “broad” band of molecular H₂O in the range 2800-3800 cm⁻¹, our samples
478 show a large set of secondary, discrete absorption bands distributed between 3660 and 3300
479 cm⁻¹ (**Figs 8-9 and 10 and Table 3**). Most of these bands were not present in the original
480 material and appear after deformation.

481 **4.3.1.1 – Absorption band at 3595 cm⁻¹.**

482 The band 3595 cm^{-1} has been detected in different kinds of natural clear quartz and
483 natural/synthetic amethyst (e.g. (Kats, 1962; Aines and Rossman, 1984; Rovetta, 1989;
484 Kronenberg, 1994), and in natural deformed and then annealed quartzite (Niimi et al., 1999).
485 The common interpretation is that H^+ charge compensates for Al^{3+} substituting for Si^{4+} .
486 Gleason and DeSisto (2008) described this band in pegmatitic quartz and quartz ribbons,
487 giving the same interpretation.

488 In our experiments, the band at 3595 cm^{-1} is not detected in all samples but it is strictly
489 correlated with attaining P and T and most importantly with deformation. This band is first
490 identified in all matrix analyses (**Figure 8a**), while it is absent in the IR spectra of
491 undeformed Brazil quartz (**Figure 8b**). In Hyuga porphyroclasts, it is not observed at hot-
492 pressed conditions, but it develops after deformation, when porphyroclasts are pervasively
493 recrystallized (**Figure 9**). The band is also observed in Brazil porphyroclasts, but exclusively
494 in their recrystallized tail (**Figure 10b,f**). The 3595 cm^{-1} band is therefore closely associated
495 with recrystallized aggregates of grains, suggesting that the OH species of this band are
496 associated with grain or perhaps subgrain boundaries.

497 Several studies on quartz IR spectra in naturally-deformed rocks further substantiate the
498 connection between a discrete absorption band near 3600 cm^{-1} and recrystallization
499 microstructures. Quartz in mylonites from Sambagawa metamorphic rocks in Japan
500 (Nakashima et al., 1995) and the western Adirondack in the USA (Gleason and DeSisto,
501 2008) show a discrete absorption band around 3600 cm^{-1} . Such a peak is absent in other
502 mylonites, such as granite mylonite in the vicinity of the Median Tectonic Line in Japan
503 (Nakashima et al., 1995; Niimi et al., 1999). However, in these samples it is not clear whether
504 grain boundaries were analyzed by FTIR in addition to grain interiors. The speciation of OH
505 in quartz at subgrain/grain boundaries may be related to silanols at the quartz surface,
506 although the corresponding absorption bands are reported at slightly higher wavenumbers
507 (e.g. 3627 and 3649 cm^{-1} , see the review in (Kronenberg, 1994)) than the $\sim 3595\text{ cm}^{-1}$ peak
508 observed in our study. In summary, a strong connection between increased surface area by
509 recrystallization microstructure and 3595 cm^{-1} absorption band is clear from this study, but
510 the nature of this OH absorption band requires further work.

511 **4.3.1.2 – Absorption band at 3585 cm^{-1}**

512 The absorption band at 3585 cm^{-1} exists in both, Hyuga and Brazil porphyroclasts after
513 deformation (**Figs. 9a,b and 10**). This band has been observed in different materials as

514 amethyst (Kronenberg, 1994, Chakraborty and Lehmann 1976), metamorphic cherts (Ito and
515 Nakashima, 2002), chalcedony (Frondel, 1982; Graetsch, 1985,1987), flint (Graetsch, 1987),
516 agate (Yamagishii et al., 1997) and synthetic quartz (Stalder and Konzett, 2012) Wood, 1960,
517 Kats, 1962; Aines and Rossman, 1984; Cordier and Doukhan, 1989; Chakraborty and
518 Lehmann, 1976; Paterson, 1986; Rovetta, 1989). In experiments of hydrothermal growth of
519 quartz, the intensity of the band increases with pressure and H₂O activity in the surrounding
520 fluid phase (Stalder and Konzett, 2012). A connection of this 3585 cm⁻¹ absorption band to
521 deformation was established in deformation experiments (Stünitz et al., 2017), where the
522 development of 3585 cm⁻¹ band is confined to deformed parts of single quartz crystals. In
523 addition, a band at 3580 cm⁻¹ was observed to develop after annealing of quartz at high
524 temperature (Cordier and Doukhan, 1991; Rovetta et al., 1986). In the latter set of
525 experiments, it was correlated with the formation and healing of cracks during annealing,
526 while no cracks were reported in the former study. Stünitz et al. (2017) suggest that the 3585
527 cm⁻¹ band may record OH-defects associated with dislocations. The systematic association
528 between this band and deformation microstructures is also apparent in our samples. This
529 band, absent in “as-is” Hyuga milky quartz samples, appears after both, hot-pressing and
530 deformation (**Figure 10a**), while in Brazil quartz it is observed only in unrecrystallized but
531 deformed (e.g. lamellae) porphyroclasts cores (**Figure 10f**). This close connection to
532 microstructures supports the conclusion by (Stünitz et al., 2017) that the band 3585 cm⁻¹ is
533 caused by structurally bond OH at dislocations.

534 **4.3.1.3 – Absorption bands at 3382 cm⁻¹ and at 3363 cm⁻¹:**

535 The sharp absorption bands at 3382 cm⁻¹ and at 3363 cm⁻¹ are specific to the nature of the
536 experimental material, either Hyuga or Brazil quartz.

537 The absorption band at ~3380 cm⁻¹ is systematically observed in Hyuga milky quartz before
538 and after deformation. It has been detected in quartz grains of gneiss (Gleason and DeSisto,
539 2008) and in cherts (Ito and Nakashima, 2002) and is attributed by several authors to OH
540 groups bonded with Al⁺³ substituting for Si (Pankrath, 1991; Stalder and Konzett, 2012)
541 Kronenberg, 1994; Suzuki and Nakashima, 1999; Gleason and DeSisto, 2008). This
542 interpretation is supported in our case by the high content of aluminum in Hyuga quartz
543 (Raimbourg et al., 2015).

544 The band at 3363 cm⁻¹ is observed only in deformed and recrystallized Brazil quartz, either in
545 the matrix (**Figure 9a**) or at recrystallized tails of porphyroclasts (e.g. **Figure 11**). While it is

546 generally assigned to surface Si-OH groups (Yamagishi et al., 1997), our study does not yield
547 further clues to this attribution.

548 To summarize, we infer that three different species of H₂O are observed after deformation.
549 The first one is molecular H₂O incorporated in porphyroclasts on the form of fluid inclusions,
550 represented by the broad absorption band between 2800 and 3800 cm⁻¹. The second type of
551 H₂O is stored in grain boundaries as a result of recrystallization processes. It is represented by
552 the discrete band at 3595 cm⁻¹ corresponding to structurally bond OH-defects. The third type
553 of H₂O is characterized by the discrete band at 3585 cm⁻¹ and is probably due to OH-defects
554 on dislocations.

555 **4.3.2 Mechanisms of H₂O incorporation and expulsion**

556 H₂O content in “as-is” Hyuga clasts is estimated at ~22,900 H/10⁶Si. It decreases first with
557 the application of temperature and pressure to ~12,000 H/10⁶Si (hot-pressed conditions), and
558 then further decrease to ~2,300 H/10⁶Si after deformation of $\gamma \sim 4$ (**Table 1 and figs. 1b,c,d**
559 **and 10**). The expulsion of H₂O during the application of pressure and temperature does not
560 proceed through recrystallization, as the corresponding new grains were not observed (**Figure**
561 **1c**). In the absence of significant deformation and formation of grain boundaries through
562 recrystallization, the expulsion of H₂O is probably caused by micro-fractures draining fluids
563 from inclusions. One driving force for fracturing during the rise in P and T conditions is the
564 ΔP between the fluid pressure in the inclusions initially present (imposed by the fluid
565 isochoric line) and the confining pressure (experimentally imposed). Decrepitation of fluid
566 inclusions is observed for relatively low ΔP of less than a couple of 100 MPa in experiments
567 (Hall and Sterner, 1993; Vityk and Bodnar, 1995). Furthermore, the initial assembly has a
568 relatively large porosity and heterogeneous grain size distribution (clast + matrix). The
569 application of P and T results in compaction, hence in local stress concentration, which may
570 result in fracturing that may drain fluid inclusions. These fractures are not easily observable
571 because they are systematically healed at high pressure and temperature (Tarantola et al.,
572 2010).

573 During subsequent plastic deformation, dynamic recrystallization (**Figs. 6-7-13**) involving
574 formation and mobility of grain boundaries, provides an efficient process to further decrease
575 the H₂O concentration in the quartz porphyroclasts (**Figure 14a**). Grain boundary mobility
576 has an important effect on modification of volume and distribution of fluid inclusions in
577 experiments (Olgaard et FitzGerald, 1993; Schmatz et Urai, 2010). Observations in natural

578 samples (e.g. Kilian et al., 2016) are consistent with experimental ones. In domains where the
579 Hyuga quartz recrystallized in nature as a result of deformation, the number of fluid
580 inclusions, hence the H₂O content, is strongly decreased (Palazzin et al., 2016). Similarly, Ito
581 and Nakashima (2002) show a strong decrease in the total H₂O content with increasing
582 recrystallization. This implies that extensively recrystallized “dry” porphyroclasts in natural
583 shear zones might have been initially wet.

584 In contrast to Hyuga porphyroclasts, “as-is” Brazil porphyroclasts have a very low initial H₂O
585 content (~260 H/10⁶Si). After deformation, both, slightly deformed cores and strongly
586 recrystallized domains, show a significant increase in H₂O: up to 640 and 950-1530 H/10⁶Si,
587 respectively (**Table 1, Figures 11-14a**). Their final content is similar to the hydrated matrix,
588 which indicates a transfer of H₂O from the matrix to the porphyroclasts during deformation.

589 The process responsible for the increased H₂O content of recrystallized tails of Brazil
590 porphyroclasts is probably identical to that of Hyuga clasts inferred above. The transfer of
591 H₂O to the unrecrystallized cores of Brazil porphyroclasts is probably caused by
592 microcracking as inferred by Kronenberg et al., (1986); Rovetta et al., (1986); Gerretsen et al.,
593 (1989) and Cordier and Doukhan (1989, 1991). The H₂O uptake by non-recrystallized cores
594 of Brazil porphyroclasts, has a limited weakening effect, as attested by the higher strength of
595 samples with a high content of Brazil porphyroclasts (**Figure 2**). Their final H₂O content,
596 ~640H/10⁶ Si, is nevertheless higher than the minimum amount of H₂O in wet synthetic
597 quartz (~200 H/10⁶ Si) necessary for weakening of these crystals (Kekulawala et al., 1978,
598 1981).

599 **4.3.3 H₂O budget**

600 **4.3.3.1 Concentration and distribution of H₂O**

601 We measured relatively large and variable (from ~810 to ~3710 H/10⁶Si) concentrations of
602 H₂O in the deformed quartz assemblies (**Table 1**). The large variability reflects first the
603 difference in initial H₂O content: in deformation experiments with Hyuga porphyroclasts, the
604 final H₂O content is between ~1470 and 3710 H/10⁶Si, while in experiments with Brazil
605 porphyroclasts, or pure matrix, the final H₂O content is between ~640 and 1530 H/10⁶Si.
606 Hyuga porphyroclasts, with their stored high H₂O content in fluid inclusions, act as an
607 additional source of H₂O.

608 The experiments were carried out to large shear strain in an attempt to reach some steady-state
609 of the microstructure and H₂O concentration. The flat portions of σ - ϵ curves do not reach

610 perfect steady-state, but the convergence of strengths of most samples indicates that some
611 final stage of the microstructural development has been reached. In order to find a physical
612 meaning of the H₂O concentration in experiments with Hyuga porphyroclasts, we need to
613 consider where the H₂O is stored, as the IR analysis window size (50x50µm) is larger than the
614 grain size, so that the analyses include grain interiors and grain boundaries.

615 In experiments in quartzite of a large grain size, carried out at the same P-T conditions as
616 ours, a strain rate of 10⁻⁶s⁻¹ and with 0.3 wt% H₂O (Post and Tullis, 1998), the H₂O content in
617 quartz interiors is ~800 H/10⁶Si, i.e. considerably lower than that in the finely recrystallized
618 Hyuga material, in spite of the very large amount of initially added H₂O (0.3 wt% H₂O ≈
619 20,000H/10⁶Si). In natural mylonite deformed at 800°C and 800MPa, the intracrystalline H₂O
620 content is ~320 H/10⁶Si (Gleason and DeSisto, 2008). A compilation of data of natural
621 quartz deformed in nature and in experiments, shows that intragranular H₂O is significantly
622 lower than bulk measurements, which include the contribution of H₂O at grain boundaries
623 (Kilian et al., 2016). This hypothesis is supported by direct FTIR transects across grains and
624 their boundaries (Post and Tullis, 1998), or by the inverse relationship, in various
625 metamorphic rocks, between the grain size of a rock and the H₂O volume that can be stored in
626 the grain aggregate (Ito and Nakashima, 2002).

627 The concentration of H₂O stored in the grain boundaries of the recrystallized material varies
628 systematically; in experiments with 30% or 70% of Hyuga porphyroclasts, the recrystallized
629 porphyroclasts yield an approximately uniform content of ~2300 H/10⁶Si. The matrix
630 contains similar amounts of H₂O (~1500 and 2900 H/10⁶Si). These matrix H₂O contents are
631 systematically larger than in the 100% matrix experiment (~800 H/10⁶Si), despite the same
632 amount of initially matrix-added water. Thus, H₂O is redistributed from Hyuga porphyroclasts
633 to the matrix producing a uniform range of H₂O contents in Hyuga porphyroclasts and matrix.
634 The H₂O concentration tends to some “equilibrium” concentration, similar to the
635 microstructural evolution which tends to some final “equilibrium” state (**Figure 14a**).

636 **4.3.3.2 Shear bands: evidence for excess H₂O**

637 Shear bands are primarily observed in experiments with Hyuga porphyroclasts and are
638 composed of small faceted quartz grains surrounded by void space (**Figure 7c**). IR
639 measurements show that they contain a significantly larger amount of H₂O than the
640 surrounding matrix (**Table 1**). Their CPO is also different from the surrounding quartz matrix
641 (**Figure 12**). The grain shapes, presence of voids between crystals, and the different crystal
642 orientations from host quartz suggest growth of these quartz grains in a pore space filled with

643 fluid during deformation at high P and T. These shear bands appear to be the locations where
644 excess free fluid phase is stored.

645 **4.3.4 H₂O stored in the grain boundary region**

646 We observed that the deformed quartz aggregates develop towards a common microstructure
647 (**Figs. 11-12 and 13**), strength (**Figure 2**), and H₂O content of the matrix, clasts, and
648 recrystallized material regardless of the initial starting material and relative clast contents
649 (**Figure 14a**). The redistribution of H₂O mainly takes place by recrystallization and formation
650 of new grain boundary area. If it is assumed that the largest part of the H₂O is distributed
651 along the grain boundary regions (the grain interiors cannot store a large amount of H₂O as
652 fluid inclusions because the grain size is below 10 μm), then the volume fraction of H₂O in
653 the quartz aggregate can be plotted against the grain boundary area per analyzed volume
654 (**Figure 14b**). The volume fraction of H₂O is measured by FTIR (**Table 1**), and the grain
655 boundary density (length per surface) is determined by EBSD in the deformed microstructures
656 (**Figs. 11-12 and 13, Table 4**). A similar approach was taken by (Ito and Nakashima, 2002),
657 who used modeled average grain sizes instead of measured boundary fractions. As a result,
658 the pure matrix and the matrix with Brazil clasts have the same nominal grain boundary
659 widths of ~0.7 nm, whereas the matrix with Hyuga clasts has a grain boundary width which is
660 more than twice this width (~1.7 nm; **Figure 14b**). Realistic grain boundary widths have been
661 determined to be ~0.5 nm for feldspar (Hiraga et al., 2004) and ~1 nm for pyroxene
662 (Raimbourg et al., 2011), of similar magnitude to those determined here for quartz. The
663 physical state of H₂O stored at grain boundaries is not established, nor the precise nature of
664 the grain boundary itself (Raimbourg et al., 2011). Two types of models are usually proposed
665 for H₂O along the grain boundary: (1) A thin molecular film or (2) A “channel-island”
666 structure, where domains of thin film (“islands”) are separated by channels where the
667 thickness of H₂O is larger (e.g. (Den Brok, 1998; Nakashima, 1995)). Our results cannot
668 resolve the details of H₂O distribution along grain boundary, and the method employed here is
669 neither appropriate nor intended for an exact determination of a grain boundary width. The
670 “nominal boundary width” obtained here is merely a measure of the H₂O storage in the grain
671 boundary region under the assumption that the H₂O is evenly distributed along the grain
672 boundaries with a common grain boundary width (**Figure 14a**).

673 The thicker nominal grain boundary width of the sample with Hyuga clasts and higher H₂O
674 content coincides with the occurrence of shear bands (absent in other samples), which are
675 sites of porosity and thus H₂O storage. It is likely that the nominal boundary width of ~1.7 nm
676 corresponds to the H₂O storage capacity of the grain boundary region. If this storage capacity

677 is exceeded, shear bands may develop. This process accounts for the fact that shear bands
678 develop principally in the material with the highest initial H₂O content (i.e. in the samples
679 with Hyuga porphyroclasts). Riedel shear bands, formed during deformation and acting as
680 drains to collect the H₂O from the surrounding matrix, have been similarly described in wet
681 (1.3 wt% H₂O) Dover flint experiments (Schmocker et al., 2003).

682 The shear bands do not have a weakening effect on the bulk sample: The sample with 70%
683 Hyuga clasts and the highest H₂O content is not weaker than others (**Figure 2**). The lack of
684 weakening by shear bands can be explained by a lack of simple connectivity of these bands on
685 the sample scale (Pec et al., 2016; Marti et al., 2017).

686 If H₂O is principally stored at grain boundaries, the storage capacity of the grain aggregate is
687 controlled by the grain size distribution and evolution. The process of redistribution of H₂O
688 takes place by different processes of microcracking (including fluid inclusion decrepitation)
689 and formation of grain boundaries by recrystallization. These processes can be observed in
690 natural samples and the H₂O storage capacity will be an important parameter to be determined
691 for deformation in natural samples, too.

692 **5. Conclusions**

693 In this experimental study the mechanical behavior, microstructural evolution, and H₂O
694 content of different starting materials of “wet” quartz converge at higher shear strain at
695 T=800°C, strain rate=5*10⁻⁵ s⁻¹ and Pc=1.5GPa. From these results we draw several
696 conclusions:

- 697 • The high crystalline H₂O content, initially present in the form of fluid inclusions in
698 wet quartz, is responsible for enhancing the recrystallization rate, in contrast to
699 initially dry crystals that do not recrystallize extensively.
- 700 • Sharp absorption bands at 3585 cm⁻¹ and 3595 cm⁻¹ develop during deformation. The
701 occurrence of the 3585 cm⁻¹ band is consistent with dislocation-bound OH, whereas
702 the 3595 cm⁻¹ band most likely indicates OH adsorbed at grain boundaries.
- 703 • Recrystallization results in a clear decrease in H₂O concentration in quartz crystals
704 initially rich in fluid inclusions, whereas H₂O uptake in initially dry crystals takes
705 place by microcracking.
- 706 • In the deformed and recrystallized assemblies, most H₂O is stored in the grain
707 boundary region. The amount that can be stored in the grain boundary (i.e. the storage
708 capacity) is limited and corresponds to a nominally □1.7 nm thick grain boundary

709 region. H₂O in excess of this nominal thickness is drained into micro-veins, formed as
710 dilatant synthetic shear bands.

- 711 • These dilatant shear bands do not control the strength of samples as they are not
712 simply connected.

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Table 1 - Water content

Sample number	Composition of sample	Condition of sample	Measured material	Thickness (cm)	Abs (cm ²)	SD	wt. ppm H ₂ O	SD	wt. ppm H/10 ⁶ Si	SD	Number of analyses
457GP	100% matrix	deformed	Matrix	0.0120	11.1	2.90	121	28	807	189	31
starting material	Hyuga porphyroclasts	as-is	Porphyroclast	0.0140	383.5	164.4	3446	1234	22973	8224	16
464GP	Hyuga porphyroclasts	attained P-T conditions	Core of porphyroclast	0.0133	191.2	56.2	1809	516	12058	3448	16
464GP	Matrix with Hyuga porphyroclasts	attained P-T conditions	Matrix	0.0127	63.9	34.7	633	344	4219	2296	10
428GP	Hyuga porphyroclasts	deformed	Porphyroclast	0.005	13.6	5.61	342	141	2278	941	8
428GP	Matrix with Hyuga porphyroclasts	deformed	Matrix	0.005	8.76	1.31	220	33	1469	220	9
428GP	Matrix with Hyuga porphyroclasts	deformed	Shear Bands	0.005	22.1	5.66	556	142	3710	949	12
456GP	Hyuga porphyroclasts	deformed	Recrystallized porphyroclast	0.0141	39.6	7.77	353	76	2355	509	15
456GP	Matrix with Hyuga porphyroclasts	deformed	Matrix	0.013	44.8	14.8	430	129	2868	863	9
starting material	Brazil porphyroclasts	as-is	Porphyroclast	0.0136	4.19	0.9	39	10	258	68	7
426GP	Brazil porphyroclasts	deformed	Core of porphyroclast	0.0123	9.36	6.18	96	68	638	455	13
426GP	Brazil porphyroclasts	deformed	Recrystallized porphyroclast	0.0118	21.5	14.9	229	131	1526	873	11
426GP	Matrix in Brazil sample	deformed	Matrix	0.0131	14.8	5.03	142	45	947	299	12
465GP	Brazil porphyroclasts	deformed	Recrystallized porphyroclast	0.0201	21.5	8.35	135	52	898	348	16
465GP	Matrix in Brazil sample	deformed	Matrix	0.0201	31.9	9.39	200	59	1332	391	24

Table 2-Mechanical Data

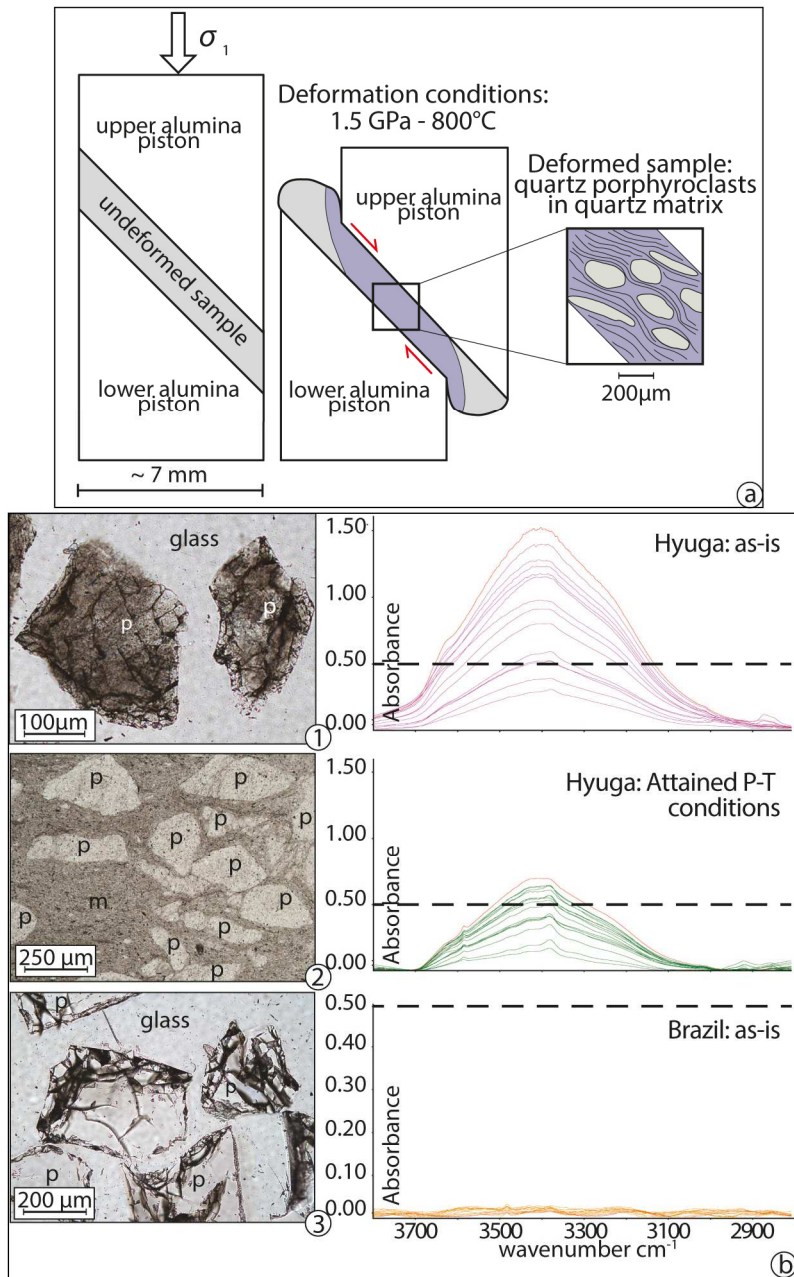
Sample number	Composition of sample	% water added	$\dot{\gamma}$ [s^{-1}]	Peak τ [MPa]	γ at peak shear stress	τ at $\gamma = 3$ [MPa]	τ at end [MPa]	γ_{final}
457GP	100% matrix	0.15	2.21×10^{-5}	192	0.61	164	201	4.59
462GP	"	"	2.19×10^{-5}	307	0.78	247	256	3.54
426GP	30% Brazil p.	0.10	2.12×10^{-5}	421	0.81	286	271	3.30
428GP	30% Hyuga p.	0.10	2.08×10^{-5}	245	0.80	247	256	3.14
465GP	70% Brazil p.	0.045	2.17×10^{-5}	645	1.55	553	445	4.31
456GP	70% Hyuga p.	0.045	2.07×10^{-5}	398	0.69	277	292	3.87
464GP	30% Hyuga p.	0.10	0.5	-	-	-	-	-
459GP	100% matrix	0.15	18	-	-	-	-	-

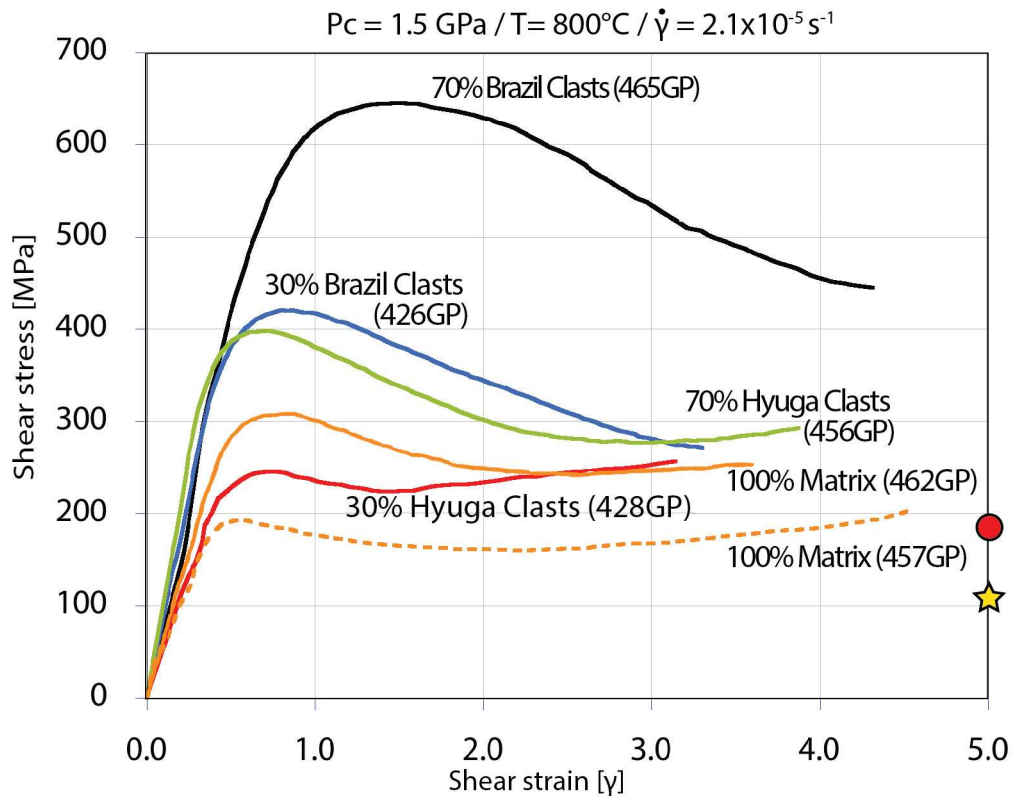
Table 3 - Absorption bands

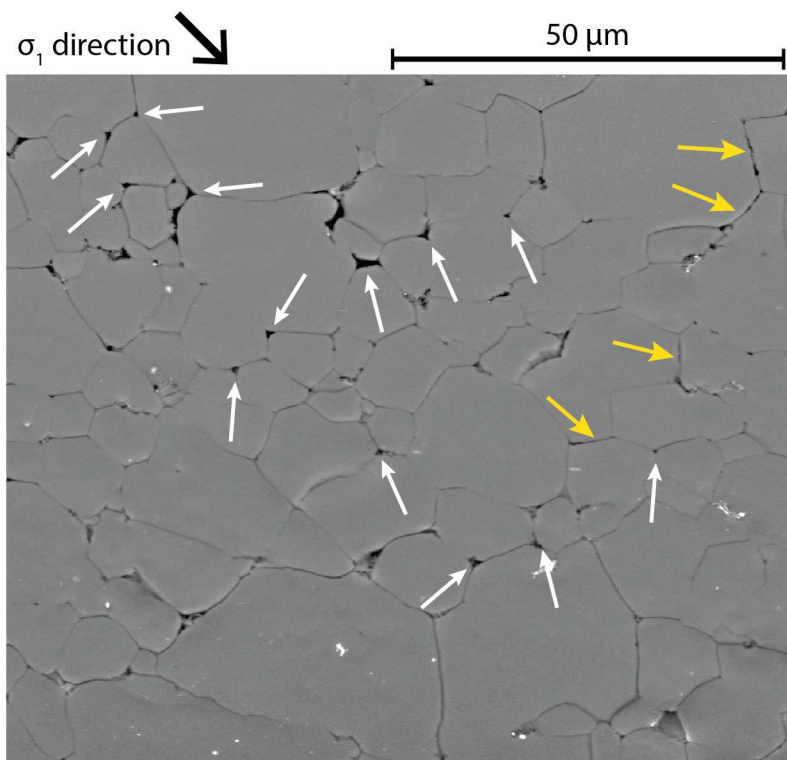
Experiment	Material	Conditions	Absorption [cm^{-1}]							
			3363	3385	3430	3485	3585	3595	3625	
-	Hyuga porphyroclasts	as-is		x	x	x				x
464GP	Hyuga porphyroclasts	attained P-T cond.		x	x	x		x		x
456GP	Hyuga porphyroclasts	deformed		x				x	x	
-	Brazil porphyroclasts	as-is				x				
426GP	Brazil porphyroclasts	deformed	x					x	x	
464GP	Matrix in Hyuga assembly	attained P-T cond.		x						x
456GP	Matrix in Hyuga assembly	deformed		x						x
426GP	Matrix in Brazil assembly	deformed	x							x

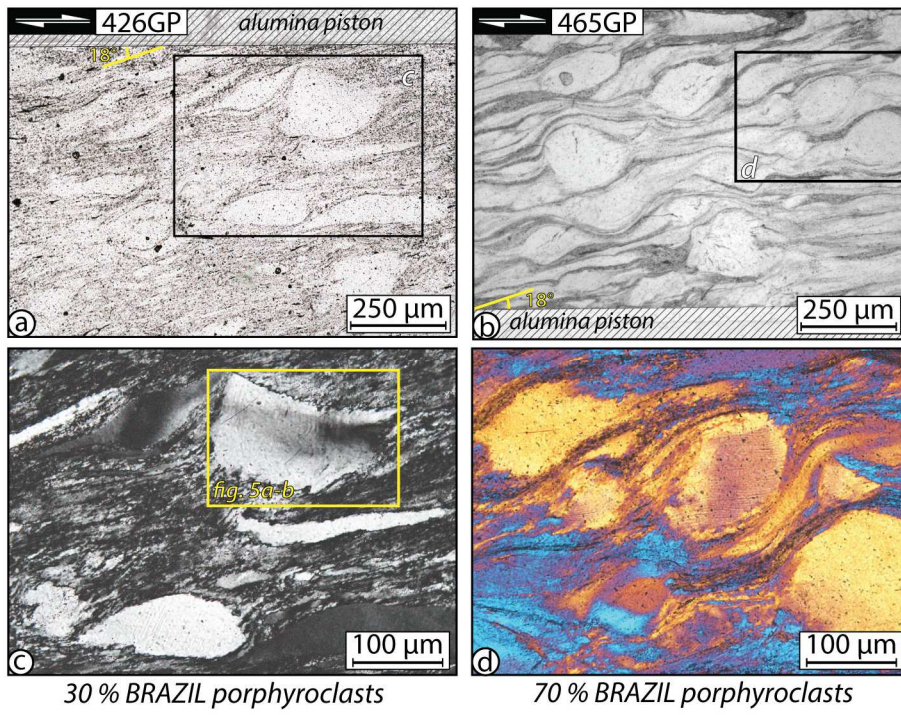
Table 4- Grain boundary density

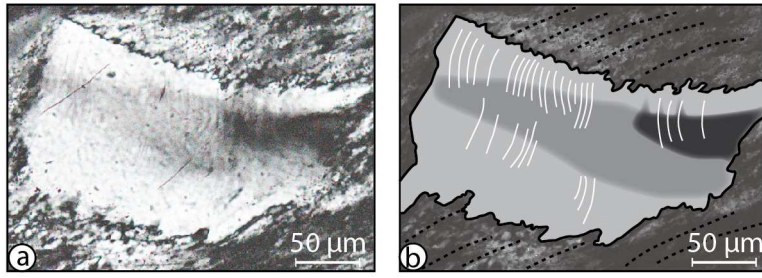
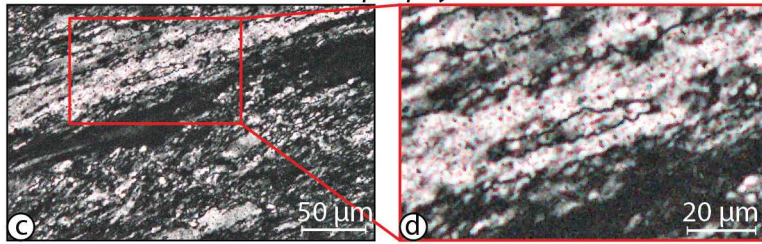
Experiment	Composition of sample	Grain boundary density (1/m)
457GP	100% matrix	$4.7 \cdot 10^5$
456GP	70% Hyuga porphyroclasts	$6.7 \cdot 10^5$
426GP	30% Brazil porphyroclasts	$6.09 \cdot 10^5$
465GP	70% Brazil porphyroclasts	$7.75 \cdot 10^5$

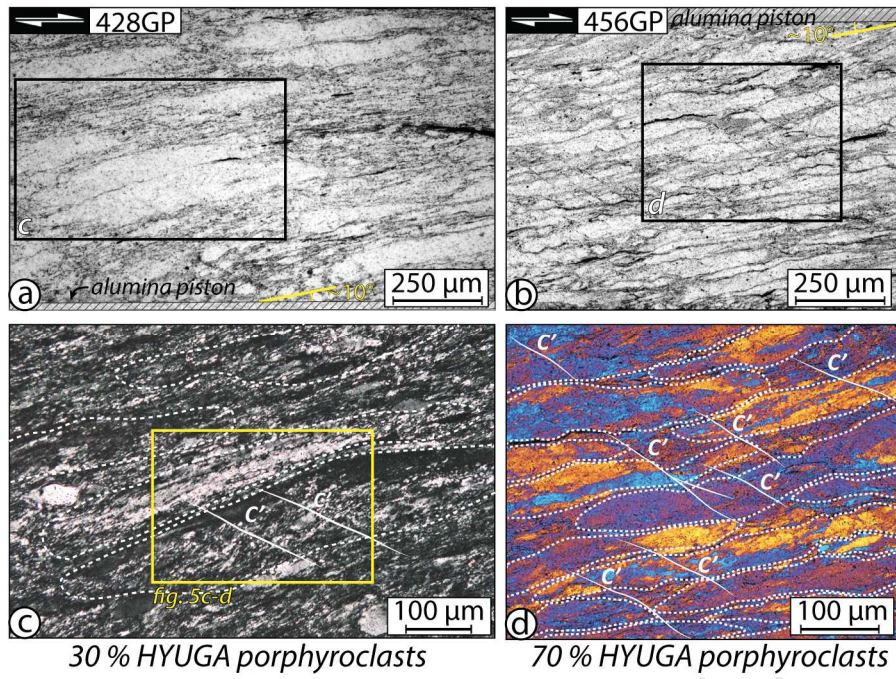


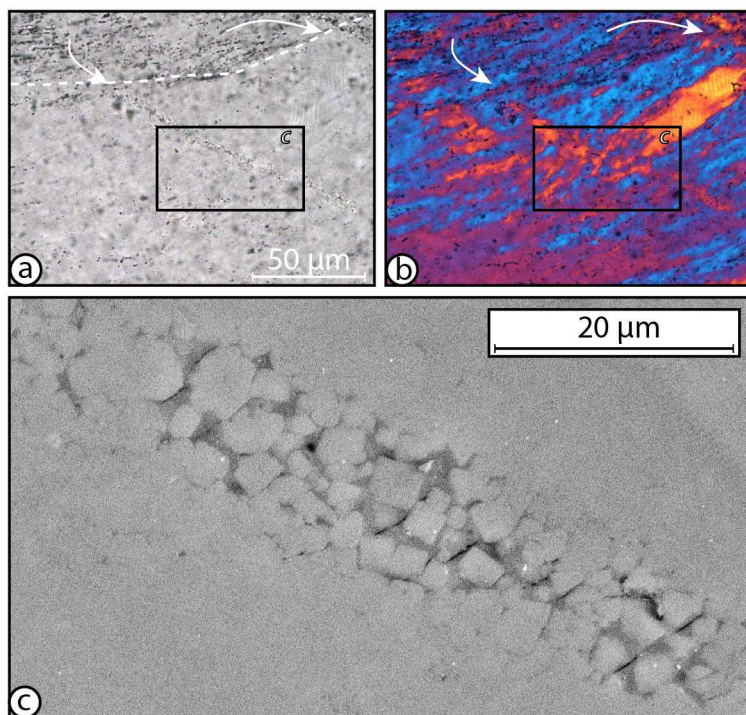


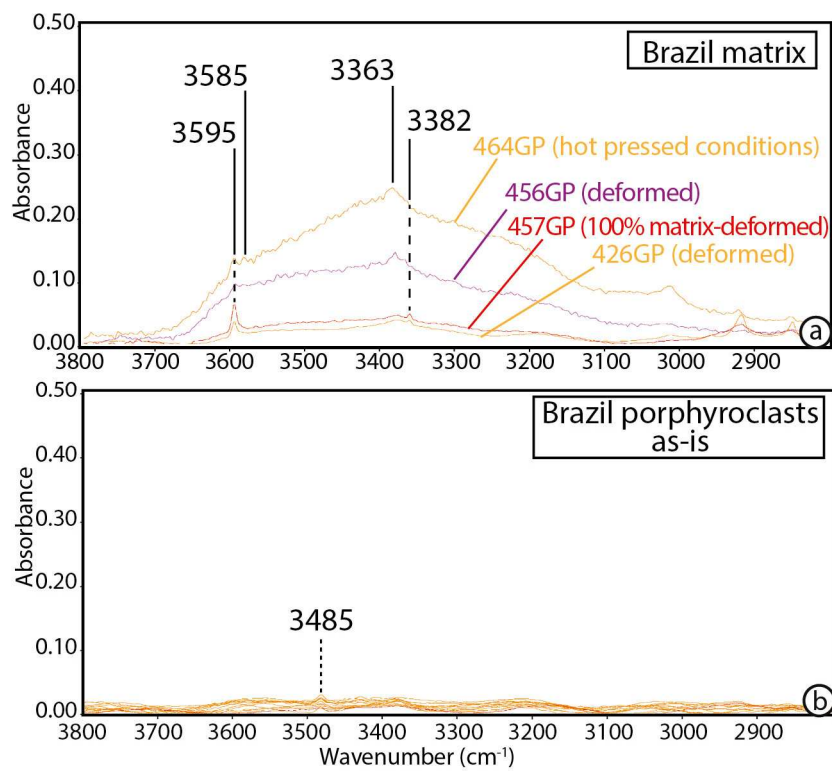


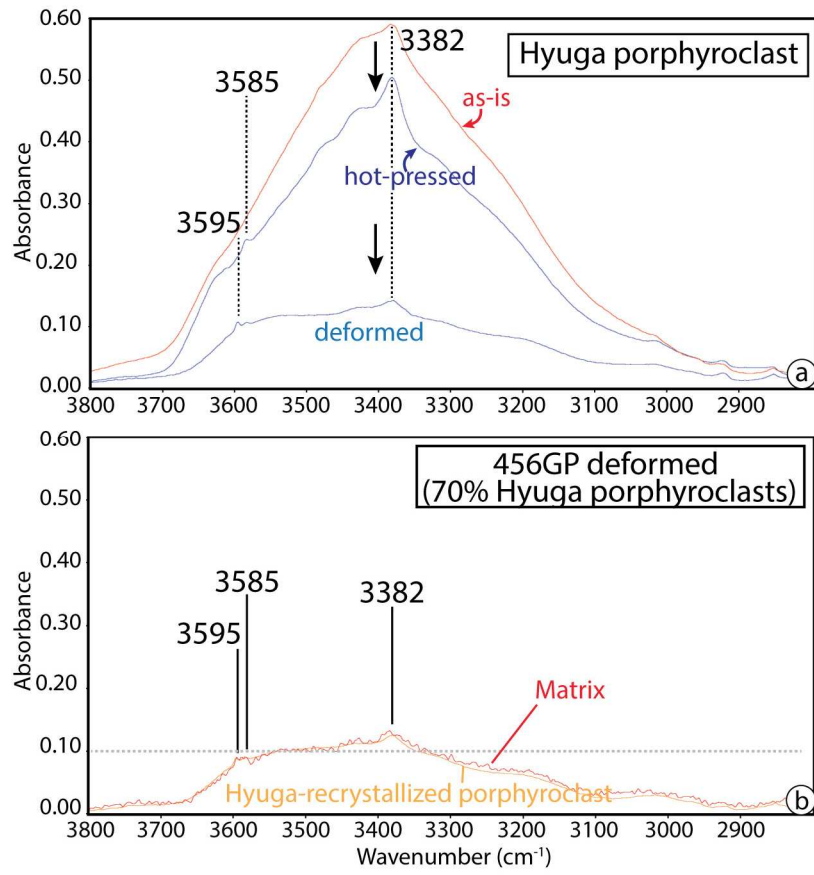


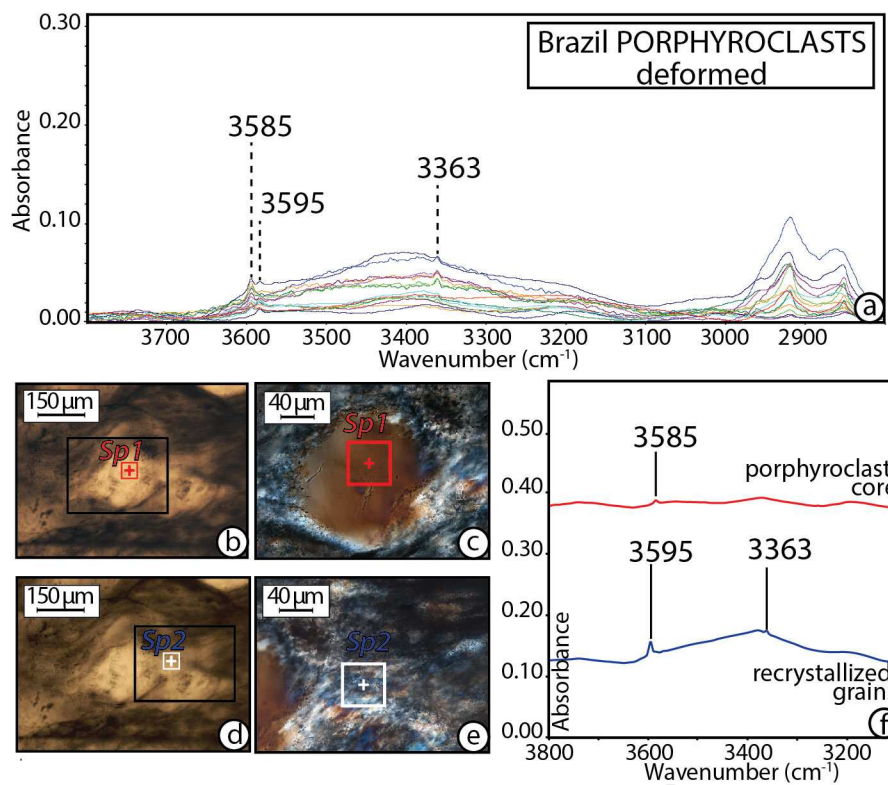
BRAZIL porphyroblast*HYUGA porphyroblast*

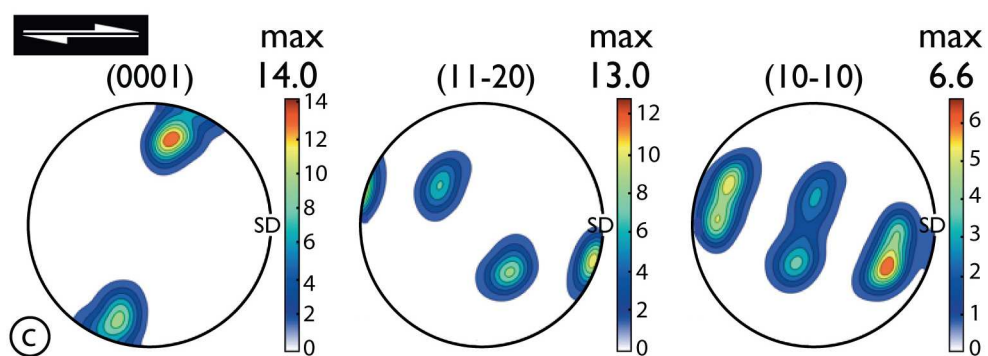
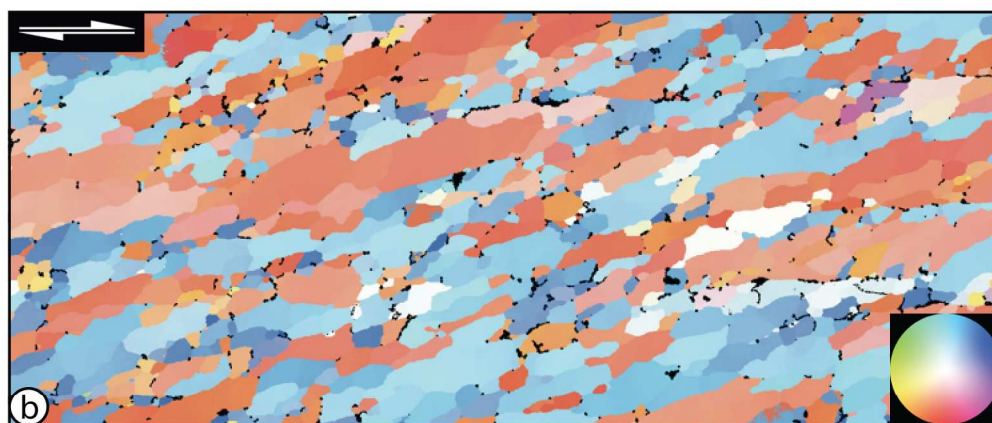
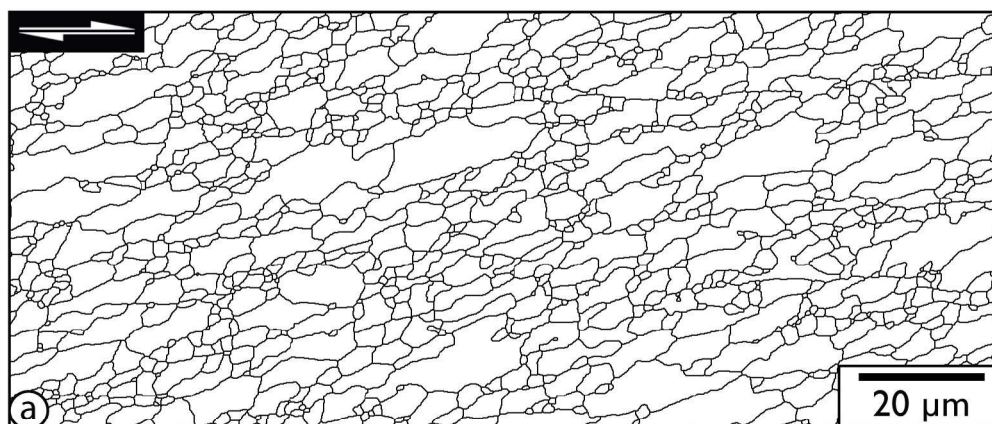


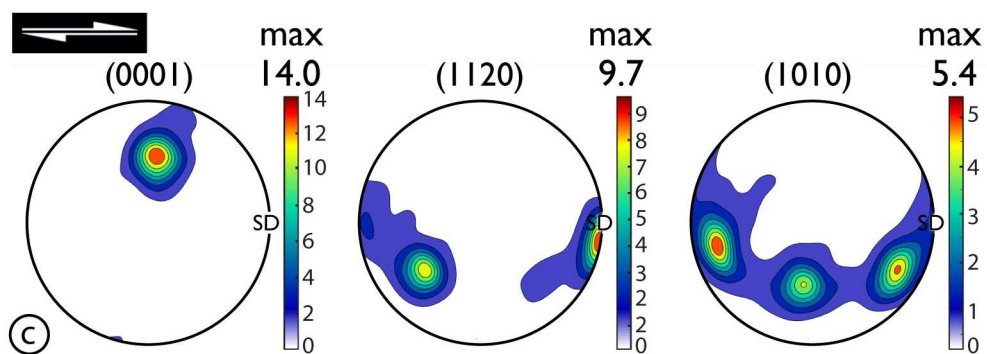
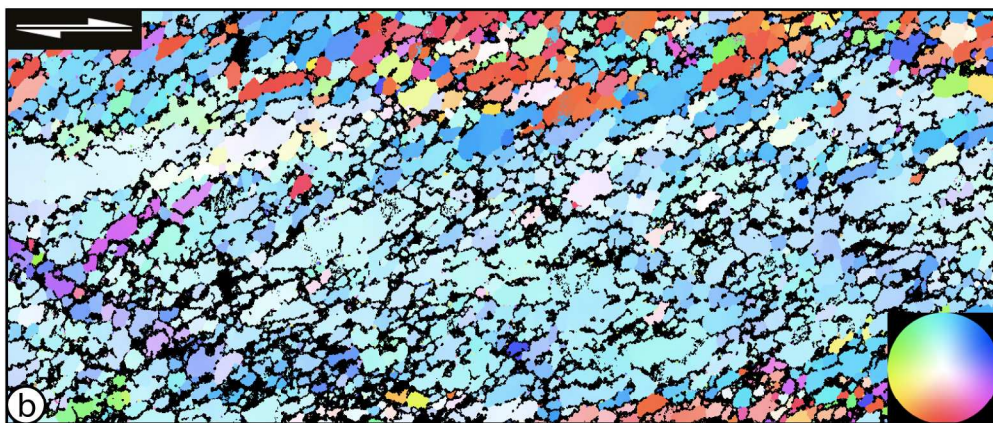
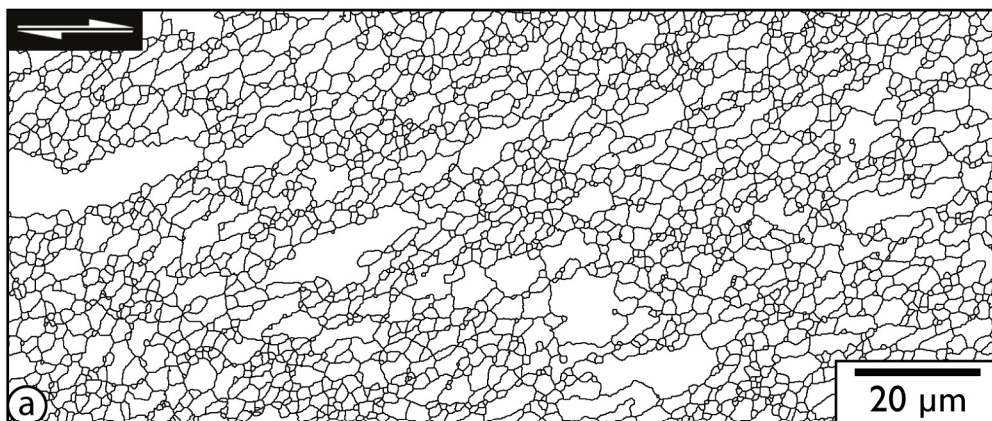


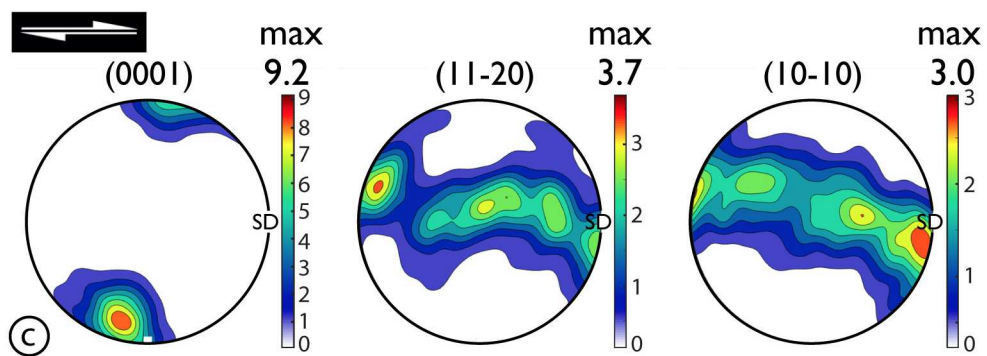
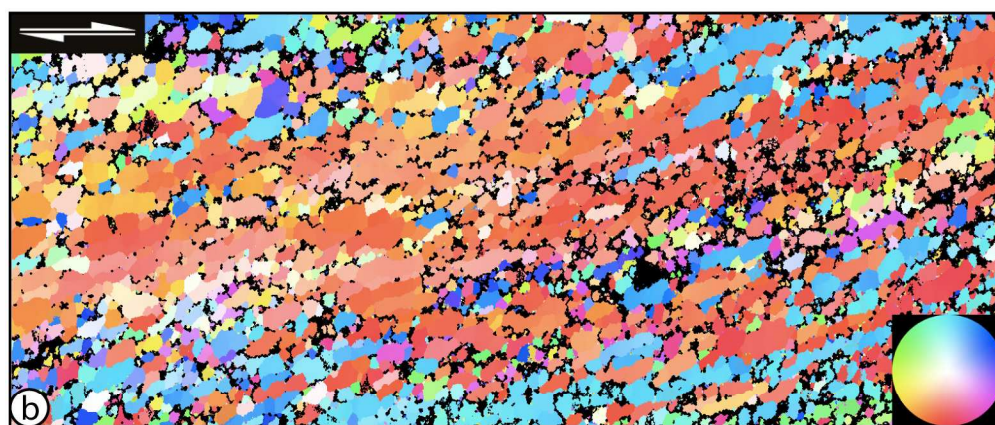
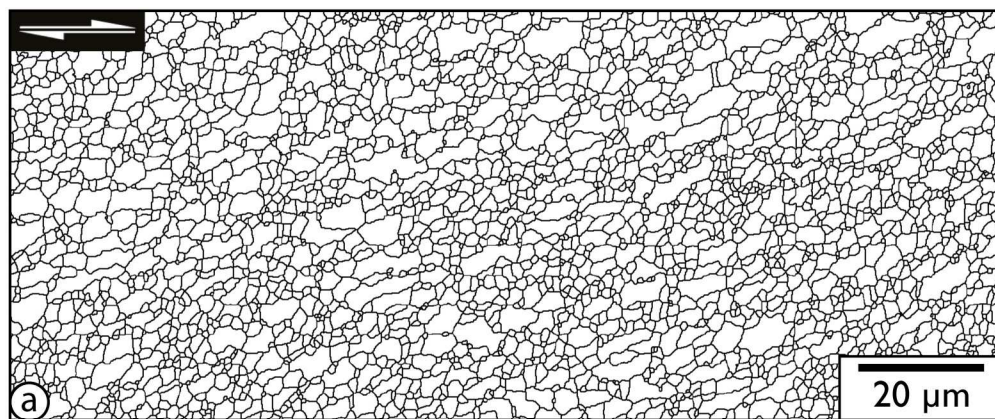


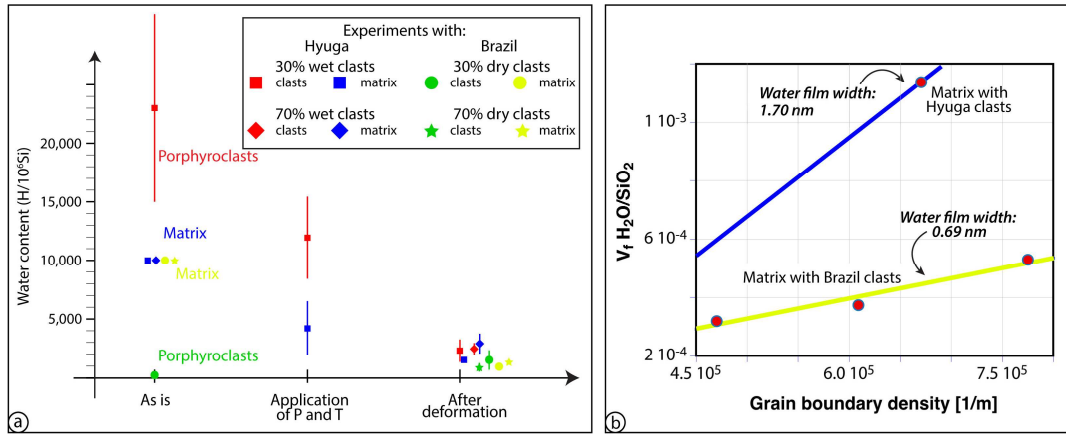












- Long-term creep of crustal shear zones is governed by H₂O changes
- H₂O content is not a static value during deformation and metamorphism
- H₂O absorption bands correspond to specific structural positions in quartz

ACCEPTED MANUSCRIPT