1	Fluid assisted strain localization in quartz at the brittle/ductile transition
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9	Key Points:
10	• Strain partitioning between recrystallized grains and 'stiff' quartz porphyroclasts;
11	• Fracturing and fluid ingress assist propagation of shear bands;
12	• Authigenesis of new quartz and phyllosilicate grains from circulating fluids promotes strain
13	localization on shear bands;

14 Abstract

A mylonitic quartzite with conjugate and synthetic shear bands was investigated by Electron 15 BackScatter Diffraction (EBSD) and optical microscopy to obtain insights on recrystallization 16 mechanisms and strain localization in quartz at plastic to semibrittle conditions close to the brittle-17 ductile transition. The mylonitic quartzite deformed during Late Miocene thrusting coeval with 18 19 contact metamorphism in the high-strain domains of the Calamita Schists (Elba Island, Italy). Mylonitic deformation occurred from amphibolite to lower greenschist facies conditions during 20 21 cooling of the aureole. Dynamic recrystallization, dominated by the activity of dislocation creep 22 by prism <a> slip, produced recrystallized quartz layers mantling relic large quartz porphyroclasts. Under decreasing temperature and fluid-rich conditions, quartz porphyroclasts acted as relatively 23 rigid bodies and fractured along synthetic and conjugate C' shear bands. Shear bands developed 24 along kinematically favored orientations, just locally assisted by weak crystallographic planes in 25 quartz. Fracturing along shear bands was assisted by cataclasis and fluid infiltration enhancing 26 27 fracture propagation and healing by recrystallization and authigenesis of new quartz and phyllosilicate grains. The process likely operated in a cyclical fashion enhancing propagation of 28 and strain localization in shear bands, with the development of bands of 'weak' phyllosilicates. 29 30 Furthermore, we observed the development of a CPO related to dissolution and precipitation of new grains parallel to shear bands. This study highlights the importance of the interplay between 31 32 brittle and crystal-plastic processes and fluid ingress in the semibrittle regime to understand 33 deformation partitioning and strain localization.

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35 Plain Language Summary

Quartz is one of the main constitutive minerals of the Earth's rocks and largely controls how rock 36 deform. We used the optical microscope to investigate quartz and a special technique called EBSD, 37 38 that is based on the interaction between a beam of electrons and a crystalline material, to generate maps of how quartz crystals are oriented in space, in order to investigate quartz deformation. We 39 studied rocks that were heated up to 650 °C six million years ago by a chamber of molten magma 40 41 and at the same time were squeezed by tectonic forces in the Calamita peninsula (Elba Island, Italy). During cooling from such high temperatures, deformation in quartz was first accommodated 42 43 by plastic mechanisms, like metal warped by a blacksmith, producing large quartz crystals wrapped by newly formed smaller quartz crystals. Subsequently, at lower temperatures ($\sim 300 -$ 44 400 °C), deformation in cool large quartz crystals started to produce cracks and fractures. As 45 fractures opened, high temperature water-rich fluids flooded the fractures, encrusting them with 46 tiny quartz and platy mica crystals. This process likely operated multiple times, progressively 47 leading to the development of bands of 'weak' platy micas in 'hard' quartz crystals. 48

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50 **1. Introduction**

Deformation in shear zones is accommodated by brittle, frictional mechanisms in the upper crust 51 52 and by plastic mechanisms at higher temperature in the lower crust. The transition between purely brittle to purely crystal-plastic deformation in natural shear zones occurs over a wide range of 53 54 temperature conditions at which deformation is controlled by a combination of brittle and plastic 55 mechanisms (semibrittle deformation; Evans & Kohlstedt, 1995; Kohlstedt et al., 1995). A classic 56 example is represented by sheared quartz-feldspar aggregates at mid-crustal conditions, where quartz typically recrystallizes and feldspar forms fractured porphyroclasts (Vernon & Flood, 1988; 57 58 Tullis et al., 1990, 2000). Quartz at mid-crustal conditions (300 - 450 °C) is typically thought to

deform by dislocation creep (Hirth & Tullis, 1994; Gleason & Tullis, 1995; Stipp et al., 2002; Behr 59 & Platt, 2011, 2014). However, many studies focused on quartz monomineralic aggregates 60 highlighted the complex role played by grain scale strain partitioning causing semibrittle 61 deformation in quartz (van Daalen et al., 1999; Vernooij et al., 2006a, b; Muto et al., 2011). Intra-62 grain bands of deformation in quartz, typically constituted by trails of small grains hosted by larger 63 64 grains, have been classically described as the result of the interplay between brittle and crystalplastic processes. Their development has been alternatively explained as the result of failure along 65 the rhomb planes of quartz (van Daalen et al., 1999; Vernooij et al., 2006a,b), coalescence of 66 microfractures developed along specific crystallographic planes (Trepmann & Stöckhert, 2003; 67 Trepmann et al., 2007) or localized coaxial deformation in 'stiff' domains (Menegon et al., 2008). 68 Several contrasting mechanisms have been proposed to explain the growth of new grains in such 69 bands: (1) subgrain rotation followed by rigid-body rotation of grains (Bestmann & Prior, 2003; 70 71 Ceccato et al., 2017; Trepmann et al., 2017), (2) cataclasis and healing by recrystallization (den 72 Brok, 1992; van Daalen et al., 1999; Vernooij et al., 2006a,b), (3) dissolution-precipitation creep, with solution of material which is precipitated as new grains (Hippertt & Egydio-Silva, 1996; 73 Takeshita & Hara, 1998; Takeshita & El-Fakharani, 2013; Kjøll et al., 2015) and (4) 74 75 recrystallization along mechanically formed Dauphiné twins (Stipp & Kunze, 2008; Menegon et al., 2011). These structures have also been shown to form during the earthquake cycle immediately 76 77 below the brittle-ductile transition (Trepmann & Stöckhert, 2003; Trepmann et al., 2007, 2017). 78 In this study, we present an EBSD based investigation of the development and evolution of intra-79 grain shear bands in quartz in the semibrittle regime, investigated in a natural study case represented by a cooling contact aureole (Papeschi et al., 2017, 2018). The research presented here 80 81 highlights how grain-scale contrasts drive strain partitioning from the early stages of dynamic

recrystallization to the brittle regime and how the interplay between brittle and crystal-plastic
processes with intergranular fluids may assist softening and strain localization in shear bands that
may efficiently act as precursory structures for discrete faults.

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86 **2. Geological Outline**

87 Elba Island, located in the northern Thyrrhenian Sea, exposes a complete cross section through the hinterland sector of the northern Apennines belt. The nappe pile is characterized by east-verging 88 89 structures stacked over W-dipping top-to-the-E thrust sheets during the Early Miocene (Keller & Coward, 1996; Massa et al., 2017). The nappe stack comprises an Upper Complex, characterized 90 by ophiolite-bearing oceanic and continental units with anchizone to lower greenschist facies 91 metamorphism, and a Lower Complex, consisting of the upper greenschist to amphibolite facies 92 Ortano and Calamita Units (Fig. 1a). Blueschist facies metamorphism related to Early Miocene 93 underthrusting and nappe stacking is locally preserved in the Ortano Unit (Bianco et al., 2015). 94 95 However, the dominant metamorphic imprint is the Late Miocene LP/HT metamorphism related to the emplacement of granitic bodies, coeval with the late phase of east-verging thrusting (Duranti 96 et al., 1992; Musumeci & Vaselli, 2012; Musumeci et al., 2015; Viola et al., 2018). 97

The Calamita Schists, part of the Calamita Unit (Fig. 1a), are an amphibolite facies metapsammitic complex that crop out in SE Elba Island (Barberi et al., 1967). These rocks experienced Miocene deformation and LP/HT metamorphism triggered by the intrusion of the buried Porto Azzurro pluton (Papeschi et al., 2017) with peak temperatures around 625 °C (Caggianelli et al., 2018) or exceeding 650 °C (Musumeci & Vaselli, 2012) at pressure lower than 0.2 GPa (Duranti et al., 1992). Deformation, related to the activity of thrust sheets coeval with pluton emplacement, affected the Calamita Schists at upper crustal conditions during post-magmatic cooling. Geochronological data constraint ductile shearing between 6.8 – 6.3 Ma (Musumeci et al., 2015) and the subsequent brittle deformation between 6.1 and 4.9 Ma (Viola et al., 2018), indicating that the equilibration to upper crustal temperature occurred in less than 1 Ma. Deformation was heterogeneously distributed in top to the east ductile shear zones that recorded the transition from an upper amphibolite facies foliation to a greenschist facies mylonitic foliation, overprinted at the brittle/ductile transition by brittle fault zones and shear fractures. These latter cross cut the mylonitic foliation exploiting precursory ductile shear bands (Papeschi et al., 2017, 2018).

112 The Praticciolo Cape (Fig. 1b; see details in Papeschi et al., 2018) offers a natural cross sections through mylonitic quartities and micaschists belonging to the Calamita Schists, tectonically 113 overlain by metacarbonate rocks over the flat segment of a large-scale east-verging thrust (Fig. 114 1b). Here, the Calamita Schists are characterized by a well-developed W-dipping foliation (mean 115 dip-direction/dip: N261°/33°), a stretching lineation defined by quartz and phyllosilicate 116 aggregates (trend/plunge: N255°/32°) and synthetic and conjugate sets of C' shear bands (synthetic 117 set: N250°/03°; antithetic set: N227°/72°) (Fig. 1c). Shear fractures and brittle fault zones 118 (N156°/01°), parallel to C' shear bands (Fig. 1d), cross cut the foliation and represents the last 119 deformation structures developed. For the present study, a mylonitic quartile sample (sample 120 121 IESP3SP78 highlighted in Fig. 1b) have been selected for fabric analysis.

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123 **3. Analytical Method**

Standard oriented thin sections (i.e. cut orthogonal to the foliation and parallel to the stretching
lineation) were investigated using the optical microscope and the Scanning Electron Microscope
(SEM), and for Electron Back Scatter Diffraction (EBSD) analysis of the quartz microfabric (see
Prior et al., 1999).

Thin sections were polished using an alkaloid colloidal suspension (SYTON) with a Buehler 128 Vibromet 2 for at least 3 hours and then carbon coated to about 3.5 nm thickness. EBSD maps 129 were acquired at the Electron Microscope Centre of Plymouth University with a (1) JEOL 6610 130 LV SEM equipped with a NordLys Nano EBSD detector and a (2) JEOL 7001 FEG SEM equipped 131 with a NordLys Max EBSD detector, using a 20-25 mm working distance, 70° of sample tilt with 132 133 respect to the horizontal and accelerating voltage set at 20 keV. The sample symmetry used was monoclinic and quartz was the only phase indexed, using trigonal crystal system (Laue group 3/m). 134 135 EBSD patterns were automatically detected and indexed with the software AZTec (Oxford 136 Instruments). The step size used and the size of the EBSD map frame are provided for each map in the corresponding figure (Fig. 4a, 6a and 8a). Noise reduction, following Bestmann & Prior 137 (2003), was performed using the HKL CHANNEL 5 software (Oxford Instruments). The critical 138 misorientation for the definition of high angle boundaries (shown in black in orientation maps) 139 was set at 10°, allowing grain boundary completion down to 0°, and at 2-10° for low-angle 140 141 boundaries (in white). Dauphiné twin boundaries (in red; Frondel et al., 1962) were recognized as grain boundaries with $60^{\circ} \pm 2^{\circ}$ of misorientation and $\langle c \rangle$ as misorientation axis and disregarded 142 from the grain detection procedure. Grain size was obtained using the grain detection routine of 143 144 Channel 5 (Tango software) that recalculates grain diameters (μm) from equivalent area circles (μm^2) (as in Berger & Herwegh, 2004). As a rule, grains measuring less than 3 times the step size 145 146 (i.e. containing less than 4-9 pixels) were nullified.

Pole figures and misorientation axis orientations in sample coordinates (MOSC) are equal angle,
lower hemisphere projections oriented with respect to the finite strain ellipsoid reference frame (X
= lineation; Z = pole to the foliation). Inverse pole figures and misorientation axis orientations in
crystal coordinates (MOCC) are equal area, upper hemisphere projections. Contoured pole figures

(one-point-per-grain) were performed using 10° half width and 10° cluster size with density shown 151 as multiples of a uniform distribution (MUD). The misorientation axis distribution in crystal 152 coordinates (or MOCC) is a powerful tool to guess the active slip system(s) in a crystal lattice. 153 Following Lloyd and Freeman (1994) and Neumann (2000), if we assume the ideal activity of edge 154 dislocations associated with a slip system the misorientation axis (i.e. axis of rotation with the 155 156 smallest rotation angle among equivalent rotation relating two given orientations of an object; Moriawiec, 2004) is (1) contained in the slip plane and (2) oriented perpendicular to the Burgers 157 vector. A scheme showing the misorientation axes and related slip systems for quartz (after 158 159 Neumann, 2000) is reported in Fig. 2.

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161 4. Microstructural and EBSD Analysis

162 **4.1 Sample Description**

The investigated mylonitic quartzite sample (IESP3SP78; Fig. 1b) shows a well-developed foliation (oriented N220°/24°) defined by the subparallel disposition of quartz and phyllosilicate layers (Fig. 3a). The kinematics is top-to-the-E, defined by asymmetric objects at the meso- and microscale and by S-C' structures. The foliation is cut and offset by two sets of C' shear bands: a dominant top-to-the-E set (C'1), subhorizontal and synthetic with respect to the sample kinematics, and a less-developed top-to-the-W antithetic set, which is steeply dipping at the mesoscale (N227°/72°).

At the microscale, phyllosilicate layers are very fine-grained ($<< 5 \mu m$) and almost exclusively constituted by sericite and chlorite mixed with tiny ($< 5 \mu m$) quartz grains and accessory ilmenite and magnetite that surround fractured and sericitized andalusite and cordierite porphyroclasts (50173 200 μ m). Large chlorite stacks (up to 200 μ m), biotite relics and white mica grains (grain size: 10 174 - 100 μ m) are locally preserved in coarse-grained quartz lenses.

Quartz shows a strongly heterogeneous microstructure, consisting of a variable percentage of relic 175 quartz porphyroclasts, either organized in lenses (e.g. Fig. 3b) or present as isolated grains lacking 176 a clear preferred orientation (e.g. Fig. 3c), surrounded by aggregates (e.g. Fig. 3c) and well-defined 177 178 subparallel layers of recrystallized quartz grains (e.g. Fig. 3a). Because of the marked microstructural differences observed within the quartz layers, we have studied in detail several 179 180 domains, each characterized by internally homogeneous microstructures. Three different domains 181 have been identified, described individually and mapped by EBSD: Subparallel quartz layers (Domain 1; Fig. 3a), (2) quartz porphyroclasts with conjugate shear bands (Domain 2; Fig. 3b) and 182 (3) quartz layers with synthetic shear bands (Domain 3; Fig. 3c). 183

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185 4.2 Subparallel Quartz Layers

Subparallel quartz layers (Domain 1), ranging in thickness between 50 and 500 μ m, are continuous and stretched parallel to the mylonitic foliation (Fig. 3a). Thin sericite bands (<< 5 μ m grain size) and ellipsoidal phyllosilicate aggregates, the latter representing pseudomorphs over cordierite, occur interlayered with quartz (Fig. 3a). C' shear bands are uncommon and, when present, are localized in the phyllosilicate rich interlayers.

The quartz layer microstructure is dominated by small $(10 - 100 \ \mu m)$ recrystallized grains with serrated grain boundaries enveloping sparse quartz porphyroclasts (up to 500 μm) with lobate boundaries and amoeboid shape variably stretched parallel to the foliation (Fig. 3a). Undulose to patchy extinction patterns are common in quartz porphyroclasts. Small white mica inclusions display evidence for pinning of quartz grain boundaries. Large areas of recrystallized grains appear extinct at the same polarizer orientation, indicating the presence of a CPO (see gypsum plate insertin Fig. 3a).

The EBSD analysis, carried out in an area representative of Domain 1 (Map 1 in Fig. 3a), image larger grains (100-300 μ m grain size), interpreted as relic grains and showing amoeboid shape and relatively high aspect ratio (2-4), , defining a shape preferred orientation parallel to the foliation (Fig. 4a). Such grains are surrounded by smaller new grains (10-50 μ m) with equidimensional shape and serrated grain boundaries (Fig. 4a). Discontinuous low-angle boundaries with lobate shape are contained in old grains and, to a lesser extent, in some of the new grains. Irregular Dauphiné twin boundaries are present in all grains.

The bulk c-axis distribution defines a Y-max with limited tails on the XY-plane, associated with <a> axes on the periphery, distributed along 6 regular maxima every 60 $^{\circ}$ (Fig. 4b). The correlated distribution in the misorientation angle distribution (MAD) shows two strong maxima, one at low angle misorientations (2-10 $^{\circ}$; Fig. 9a) and the other for 55-60 $^{\circ}$ (Fig. 9a). In crystal coordinates the misorientation axes for low misorientation angles (2 up to 30 $^{\circ}$) are clustered in correspondence of the c- axis and are partially spread over the acute rhombs (Fig. 4c). In sample coordinates, the maximum for low misorientation angles is localized defines a strong Y-max (Fig. 4d).

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213 4.3 Conjugate Shear Bands

This domain (Domain 2) is represented by quartz lenses (grain size: 100-1000 µm; thickness: 100-200 µm up to some mm) constituted by large quartz porphyroclasts, surrounded by recrystallized
quartz grains belonging to Domain 1 (Fig. 3b). Such lenses represent boudins of competent
material (i.e. coarse-grained quartz) laterally bound by swells where the foliation is necked (Fig.
3b). Porphyroclast quartz grains feature extensive patchy to undulose extinction and host conjugate

and roughly orthogonal C' shear bands associated with irregular patterns of fractures (Fig. 3b). 219 Conjugate shear bands are strictly localized in coarse-grained quartz porphyroclast and do not 220 221 affect the neighboring fine-grained quartz layers and phyllosilicate domains, as shown in Fig. 3b. As shown in Fig. 5a, conjugate shear bands are defined by very fine-grained ($<10-20 \mu m$) trails of 222 quartz. The host porphyroclast grains are fractured and feature fragments that have slightly 223 224 different orientation (Fig. 5a). The contact between host grains and shear bands is marked by 225 slightly misoriented areas and by small quartz trails with different orientation with respect to the 226 host and often displaying a c-axis preferred orientation (Fig. 5a). At the SEM, the shear bands are 227 characterized by fluid inclusion planes enclosing grains and cracks (Fig. 5b). Pitted grain boundaries, indicative of fluid-present conditions during deformation (e.g. Mancktelow et al., 228 229 1998) are widespread (Fig. 5b). Small chlorite and white mica inclusions are locally present.

A representative EBSD area was selected at the intersection of two conjugate C' shear bands 230 hosted by quartz porphyroclasts (Map 2 in Fig. 3b). The misorientation angle distribution shows 231 232 high values of relative frequency for the correlated distribution, corresponding to 2-15° and 55- 60° of misorientation respectively (Fig. 9b). The EBSD map images large (>500 μ m) grains (i.e. 233 host grains) that contains two nearly orthogonal shear bands (dextral and sinistral as shown in Fig. 234 235 6a) defined by grains smaller than 50 µm (i.e. shear band grains) and characterized by variable along-strike thickness from 150 to $10 \,\mu m$ (Fig. 6a). Minor shear bands decorated by few tiny grains 236 237 and oriented parallel to the larger ones are also present, like the small dextral band marked by a 238 yellow arrow in Fig. 6a.

Host grains display wavy grain boundaries, locally associated with tiny grains and bulges (5-20 µm), and irregular Dauphiné twin boundaries that are cross cut by conchoidal fractures (Fig. 6a).
In the pole figures, they display 'single crystal' orientations, with c-axes randomly clustered and

 $\langle a \rangle$ axes and rhombs drawing small (20-40°) rotations, highlighting the internal distortion of the 242 crystal lattice (Fig. 6b). Shear band grains range in size between 3 and 30 µm, forming 243 244 heterogeneous aggregates that envelope larger grains with variable shape and size up to 100 μ m. In pole figures, shear band grains are broadly characterized by host control, as they mimic the host 245 grains orientation, and display a c-axis maximum in the upper-right quadrangle of the pole figure 246 247 (Fig. 6c). As shown by misorientation profiles, large areas of shear band grains are slightly misoriented with respect to the host grains (less than 20-30°; Fig. 6d, e) and just some grains are 248 249 characterized by high misorientation with respect to the host (Fig. 6e).

In crystal coordinates, host grains display a moderate clustering on the c-axis associated with minor scattering towards the rhomb, corresponding to a weak maxima developed in the lower-left quadrangle of the pole figure in sample coordinates (Fig. 6f). Shear band grains show clustering of the misorientation axis in sample coordinates close to <c> with a wider spreading towards the rhombs and the prism (Fig. 6g). In sample coordinates a weak maximum is present, close to Y in the upper-right quadrangle of the pole figure (Fig. 6g).

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4.3.1 Relationships between shear bands and host grains

The attitude of the shear bands in Map 2 was compared with the orientation of the major lattice planes within selected host grains adjacent to shear bands (subsets numbered from 1 to 4 in Fig. 7a). The crystallographic orientation of the selected host grains was also compared with the crystallographic orientation of the grains associated with the dextral and sinistral shear bands (subsets highlighted in Fig. 7d). The dextral shear band separates the adjacent grains 1, 2 and 3, whereas the sinistral is localized between grains 3 and 4. Two grains with identical crystallographic orientation are present on the opposite sides of the sinistral shear band and interpreted to beoriginally part of the same grain (grain 4; Fig. 7a).

Host grains display c-axes oriented halfway between the periphery and the center of the pole figure 266 (Fig. 7b). The trace of the shear bands does not evidently match most of the crystallographic planes 267 of the selected host grains. A slight parallelism exists only between the trace of the sinistral shear 268 269 band and the positive and negative rhomb planes of grain 3 and the basal plane of grain 4 (Fig. 7b). Other major crystallographic planes are oblique to shear bands. In crystal coordinates, the 270 271 misorientation axis clusters in correspondence of the c-axis and the acute rhombs, with minor 272 spreading close to {m} and (c), as in grain 1 and 4 (Fig. 7c). In sample coordinates, host grains display clustering away from Y with faint girdles (grain 1) and secondary maxima (grains 3 and 273 4; Fig. 7c). 274

The comparison of the c-axes of the sinistral and dextral shear band subsets (Fig. 7d) with that of 275 their respective host grains shows that the c-axes of shear band grains cluster in the same 276 277 orientation of those of their hosts (Fig. 7e). The distribution of the c-axes of shear band grains with respect to the host suggests a clockwise rotation consistent with the, local, dextral (Fig. 7e, above) 278 and sinistral (Fig. 7e, below) sense of shear. Considering the sinistral shear band, a third cluster is 279 280 located in the upper right quadrant of the pole figure, parallel to the sinistral shear band (Fig. 7e). This latter does is not related to any orientation observed in the neighboring host grains and is 281 related to grains characterized by relative misorientation up to 70-90° with respect to the hosts i.e. 282 283 as the grains intercepted by misorientation profile B (Fig. 6e).

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285 **4.4 Synthetic Shear Bands**

Large areas of the sample are characterized by a single set of synthetic top-to-the-E C' shear bands 286 (Domain 3), oriented ~30-35° with respect to the foliation that, differently from conjugate shear 287 288 bands, does not appear restricted to coarse-grained quartz lenses but invariably affects quartz and phyllosilicate-rich layers (Fig. 3c). With respect to the subparallel quartz layers (Domain 1), the 289 quartz layers where C' shear bands are more developed appear richer in large quartz porphyroclasts 290 291 (grain size: $100 - 500 \,\mu$ m) with lensoidal shape and lobate grain boundaries that are surrounded by mantles of equigranular, recrystallized grains $(5 - 50 \,\mu\text{m})$ with serrated boundaries (Fig. 3c). 292 293 Quartz porphyroclasts feature undulose extinction and serrated contacts with the recrystallized 294 grains surrounding them and are often wrapped by strain caps rich in phyllosilicates or opaque mineral grains (Fig. 5c). Sometimes irregular intra-granular cracks are well developed in quartz 295 porphyroclasts, dissecting angular sub-areas (Fig. 5c). Lens-shaped quartz aggregates are 296 commonly dragged synthetically with the shear bands, defining an S-C' fabric (Fig. 3c). Synthetic 297 298 shear bands are often developed within or at the contact with quartz porphyroclasts with spacing 299 lower than the millimeter and offsets that may reach several hundreds of micrometers (Fig. 5d). Sometimes they are partially reactivated as small-scale shear fractures that are continuous for 300 several millimeters through multiple mica and quartz layers characterized by millimetric offsets 301 302 (Fig. 5d) and bridged by en-echelon subsidiary sets of fractures (Fig. 5d, see insert). The shear band architecture is characterized by a $50 - 100 \,\mu\text{m}$ thick core zone containing very fine-grained 303 304 quartz grains (i.e. shear band grains), locally with a shape preferred orientation parallel to the band 305 and a preferred orientation of the c-axis, associated with bands of tiny, platy white mica and chlorite grains oriented parallel to the shear band (Fig. 5e). As shown by the SEM image the core 306 307 of the shear band displays cracks and fractures associated with fluid inclusion planes and pitted 308 quartz grain boundary surfaces (Fig. 5f). Chlorite and white mica are locally associated with oxides

309 (i.e. limonite; Fig. 5f) and found as single grains included in quartz (Fig. 5f). These features are
310 indicative of fluid-rock interaction during deformation (e.g. Mancktelow et al., 1998).

The area to map by EBSD (Map 3 in Fig. 3c) has been positioned within two paired, synthetic, dextral shear bands cross cutting quartz and characterized by a total offset of ~500 μ m. Since quartz is the only phase indexed, phyllosilicate-rich cores appear black (Fig. 8a). The large porphyroclast grains hosting the shear band (grain size > 100 μ m; host grains in Fig. 8; appearing grey in Fig. 8d) are surrounded by small grains displaying grain size in the range 3 – 65 μ m. The MAD shows high correlated frequencies for low angles of misorientation (<10°) and for 55-60° of misorientation (Fig. 9c).

Host grains display lobate to serrated boundaries with small bulges and are characterized by wriggly Dauphiné twin boundaries and relatively straight low-angle boundaries that separate subgrains of about $10 - 50 \mu m$ grain size (Fig. 8a). The c-axis of the host grains subset displays several 'single grain' orientations scattered on the pole figure and slightly clustered close to Y (Fig. 8b). Host grains are in first order mantled by new grains with equigranular shape, serrated boundaries, grain size ranging between 20 and 60 μm and aspect ratio between 1 and 1.5-1.6 (Fig. 8d).

The smaller grains of the dataset ($< 5 - 20 \mu$ m; shear band grains in Fig. 8) occur localized on shear bands, largely associated with bands of phyllosilicates and characterized by an equigranular shape (Fig. 8d). In the pole figure two trends are recognizable in shear band grains: (1) a contouring generally inherited from the crystal orientation of the host grains (Fig. 8c; compare with Fig. 8d) and (2) a strong maximum developed in the upper-left quadrangle of the pole figure parallel to the shear band, in an orientation where no corresponding maximum associated with the host grains subset exists (Fig. 8c). In crystal coordinates host grains display a strong clustering for $2-15^{\circ}$ of misorientation angles around <c> which corresponds in sample coordinates to a misorientation axis maximum clustered on Y (Fig. 8e). Shear band grains are characterized in crystal coordinates by a weaker maximum with respect to the host grains clustered on <c> and a wider scattering towards the rhombs and the acute rhombs for $2-15^{\circ}$ of misorientation angles (Fig. 8f). In sample coordinates they display clustering loosely centered on Y (Fig. 8f).

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339 **5. Discussion**

5.1 Grain-scale strain partitioning in the different domains

Our data set documents an example of strain partitioning at the thin section scale in a quartz-341 dominated sample that was sheared during retrograde metamorphism from upper amphibolite to 342 lower greenschist facies conditions. Close to peak metamorphic conditions deformation was likely 343 344 accommodated by grain boundary migration recrystallization, as indicated by relic amoeboid 345 grains and dissection microstructures (see in detail Papeschi et al., 2017). During cooling, dynamic recrystallization by subgrain rotation and bulging led to the development of a heterogeneous 346 microfabric generally characterized by large quartz porphyroclasts and lenses embedded in a 347 348 relatively fine-grained recrystallized quartz-rich matrix (Fig. 3). The high frequencies shown by the correlated MAD curve for low-angle misorientations is consistent with fabric development 349 350 under conditions dominated by dislocation creep (Fig. 9a, b, c). The 55-60° peak, observed in all 351 investigated maps, is related to Dauphiné twinning (Fig. 9). The c-axis clustering with limited spreading towards the rhombs of the misorientation axis in crystal coordinates observed for both 352 353 host grains and recrystallized grains in the investigated EBSD areas (Fig. 4c, 6f, g, 8e, f) is 354 consistent with the dominant activity of the prism $\langle a \rangle$ slip system, associated with secondary

rhomb $\langle a \rangle$ slip (see Fig. 2 for reference). Though the dominant activity of prism $\langle a \rangle$ slip is 355 witnessed in all the investigated maps, very different microstructures evolved in the different 356 357 domains investigated. In Domain 1, deformation produced straight and parallel recrystallized quartz layers (Fig. 3a), whereas in Domains 2-3 large quartz porphyroclasts survived (Fig. 3b, c), 358 leading to the development of sets of shear bands. Two major mechanisms are believed to have 359 360 controlled the development of such diverse microstructures: (1) grain scale strain partitioning leading to a completely different microfabric evolution within the different domains and (2) fluid 361 ingress and fluid-rock interaction, as documented by the abundant pitted grain boundaries, trails 362 363 of fluid inclusions and secondary phases trapped in quartz (Fig. 5; e.g. Drury & Urai, 1990; Mancktelow et al., 1998; Mancktelow & Pennacchioni, 2004). 364

Domain 1 is characterized by large areas that are extinct at the same time (Fig. 3a) corresponding 365 to portions where relic and recrystallized grains contributing to define a typical Y-max texture 366 (Schmidt & Casey, 1986; Fig. 4b). In this domain large relic grains were compliant during 367 368 deformation developing a high aspect ratio and a preferred orientation parallel to the foliation, as it is expected for grains with c-axis parallel to Y under conditions of dominant prism <a> slip (e.g. 369 Muto et al., 2011; Ceccato et al., 2017). The favorable orientation of the recrystallizing material 370 371 assisted recrystallization at low stresses favoring the development of a strong CPO (Fig. 3a). On the other hand, in Domain 2 and 3, the presence of large grains with c-axis orthogonal or oblique 372 373 to Y (Fig. 6b, 8b) disadvantaged dislocation creep by dominant prism <a> slip. Secondary slip 374 systems, such as rhomb <a> (e.g. grain 2-3 in Fig. 7c) or basal <a> slip (e.g. grain 1 in Fig. 7c) 375 might have locally activated as their misorientation axis was lying closer to the vorticity axis Y for 376 those grains (e.g. Michels et al., 2015). Nevertheless, the activation of slip systems differing from 377 prism <a> slip was energetically unfavored and grains with c-axis oriented far from Y were less

stress compliant during dynamic recrystallization compared to the Y-grains of Domain 1. 378 Therefore, deformation likely localized in recrystallized portions surrounding the 'hardened' 379 380 porphyroclast grains that acted as the main strain-supporting framework leaving behind coarsegrained pods and lenses (Fig. 3b, c). Large quartz porphyroclasts behaved as relatively hard 381 domains, fracturing and concentrating strain in conjugate and synthetic shear bands. The 382 383 development of conjugate sets of shear bands in quartz has been described by several authors as a result of fracturing along planes of weakness such as the rhombs (van Daalen et al., 1999; Vernooij 384 385 et al., 2006a, b; Kjøll et al., 2015). The analysis of the shear band attitude performed by Papeschi 386 et al. (2018) indicate a nearly constant orientation through the sample which is not compatible with the local orientation of quartz rhomb planes. Moreover, the investigate conjugate shear bands are 387 just locally parallel to planes of weakness in quartz such as the rhombs (Fig. 7a, b), indicating little 388 to no host control during their development. Conjugate shear bands in coarse-grained quartz 389 domains may develop after deformation partitioning, as a result of coaxial deformation localizing 390 391 in 'hard' domains surrounded by a non-coaxially deforming matrix, as suggested by Menegon et al. (2008) in the Arolla Unit; on the other hand, they might be developed during general shear close 392 to the direction of maximum shear stress or to the eigenvectors of the flow (e.g. Bobyarchick, 393 394 1986; Simpson & de Paor, 1993; Kurz & Northrup, 2008; Gillam et al., 2014), as suggested for the Calamita Schists by Papeschi et al. (2018). In this sense, the conjugate sets may be 395 396 preferentially developed in large and relatively isotropic quartz lenses, as the presence of a strong 397 mechanical anisotropy (i.e. the mylonitic foliation) outside inhibits the development of the steeper 398 set, as shown by Cobbold et al. (1971), Cobbold (1976) and Platt and Vissers (1980).

399

400 5.2 Role of fluids and dynamic recrystallization in shear band development

Formation of shear bands at greenschist to amphibolite facies conditions has classically been 401 associated with a combination of brittle and crystal-plastic processes (Berthé et al., 1979; Gapais 402 403 & White, 1982; Passchier, 1984; Gapais, 1989; van Daalen et al., 1999; Vernooij et al., 2006a,b). In the present study case, evidence for intra-granular microcracking is invariably found as fractures 404 and fluid inclusion planes (Fig. 3b, 5b, c, f) in quartz porphyroclasts that occur in strict association 405 406 with conjugate and synthetic shear bands. Cataclasis, accompanied by rigid-body rotation of host quartz grains fragments may explain the weak misorientation of shear band grains with respect to 407 408 the host, highlighted by pole figures (Fig. 6c, 8c) and by misorientation profiles (Fig. 6d, e), and 409 the inhomogeneous grain size of shear band grains (Fig. 6a, 8d). Rigid-body rotation is also consistent with the local clockwise and anticlockwise rotation of shear band grains with respect to 410 the host in sinistral and dextral shear band respectively (Fig. 7e). Host grains are characterized by 411 a distorted lattice with clustering on $\langle c \rangle$ in crystal coordinates, indicative of dominant prism $\langle a \rangle$ 412 slip, centered on Y in sample coordinates (Fig. 6f, 8e). These patterns are largely inherited as 413 414 intracrystalline features by shear band grains, although there is evidence of an increased activity of rhomb <a> slip (Fig. 6g, 8f; see Fig. 2 for reference). After microcracking and rigid-body 415 rotation, fluid ingress might have favored dynamic recrystallization and healing of microcracks, 416 417 sealing deformation in the shear band. Evidence for fluid-accompanied fracturing is supported by the presence of pitted grain boundaries and trails of fluid inclusions (Fig. 5b), as well as many 418 419 secondary phases trapped in quartz (Fig. 5e, f); see e.g. Drury & Urai, 1990; Mancktelow et al., 420 1998; Mancktelow & Pennacchioni, 2004). Shear bands might have deformed cyclically accommodated by multiple cycles of cracking and sealing assisted by fluid ingress in a similar 421 422 fashion as the example described by Kjøll et al. (2015) and rapidly followed by dynamic

recrystallization as described by van Daalen et al. (1999) in the Glarus Nappe and experimentally
by Vernooij et al. (2006a, b).

425 Nevertheless, this process cannot fully explain the development of CPOs oriented parallel to shear bands associated with the smaller grains (Fig. 6c, 8c) that would require the activity of prism <c> 426 slip and should be discouraged under conditions favoring prism and rhomb $\langle a \rangle$ slip. Furthermore, 427 428 this CPO is related to grains strongly misoriented with respect to the host (up to 70° in 429 misorientation profiles; Fig. 6d, e) and is developed in an orientation which cannot be inherited from the host grains population (Fig. 7e). Bons and den Brok (2000) showed numerically how 430 431 CPOs in rocks may develop as a result of dissolution-precipitation creep or pressure solution with the growth of new grains controlled by specific crystallographic directions. We suggest that the 432 CPO in our investigated sample was controlled by the preferred growth of quartz grains with c-433 axes parallel to shear bands, which followed the opening of small dilatant sites during deformation. 434 435 The process might have also been associated with pressure solution of quartz, as in strain caps 436 surrounding larger porphyroclasts (e.g. Fig. 5c), readily redeposited in fractures sealing shear bands. This interpretation extends previous data gathered by Takeshita and Hara (1998) and 437 Takeshita and El-Fakharani (2013), who observed the development of random textures by 438 439 dissolution-precipitation, showing that precipitation of new grains from fluids may also cause the development of a CPO. 440

The precipitation of very fine-grained quartz and, in particular, 'weak' phyllosilicates may have assisted progressive strain softening of shear bands, enhancing grain size reduction (e.g. White et al., 1980; Behrmann & Mainprice, 1987; Fliervoet et al., 1997) and reaction softening (e.g. White et al., 1980; Stünitz & Tullis, 2001; Bukovskà et al., 2016). In particular, inclusions of phyllosilicates organized in bands (Fig. 5e) are widespread along synthetic C' shear bands that

occur indeed not restricted to large quartz porphyroclasts (Fig. 3c) and show larger eastward
displacements with respect to the conjugate set. The feedback between deformation, fluid-rock
interaction and chemical processes controlled the progressive organization of phyllosilicate grains
in bands on the synthetic set, promoting slip.

To summarize, the observed quartz microstructure of C' shear bands can be explained as resulting from the combination of two mechanisms: (1) microfracturing and rigid-body rotation of fragments separated from the parent grain, (2) dynamic recrystallization and healing associated with (3) authigenesis of quartz and phyllosilicate grains from circulating intergranular fluids with the development of a CPO in quartz parallel to the shear bands.

455

456 **5.3 From dynamic recrystallization to strain localization in the semibrittle regime**

457 The data set presented here documents the progressive development of deformation structures in a quartz-rich system at the transition from purely plastic to purely brittle deformation under fluid-458 459 rich conditions (see also Papeschi et al., 2017, 2018). The structural evolution, controlled in first order by the decreasing temperature during deformation, is conceptually summarized in Fig. 10. 460 At relatively high metamorphic grade conditions (amphibolite facies; Musumeci & Vaselli, 2012; 461 462 Caggianelli et al., 2018) quartz recrystallized producing stretched mylonitic ribbons (Fig. 10). Deformation concentrated in first order in recrystallized portions, leaving behind large quartz 463 464 porphyroclasts, where dislocation creep was recorded as intracrystalline deformation (Fig. 10). As 465 temperature progressively decreased, large quartz relics underwent hardening with respect to the 466 surrounding 'soft' quartz + phyllosilicate matrix, fracturing along conjugate shear bands (Fig. 10). 467 Opening of intra-granular cracks allowed fluid infiltration and the consequent authigenesis of new 468 quartz and phyllosilicate grains. This occurred under greenschist facies conditions, as indicated by

the white mica + chlorite + opaque assemblage that is invariably found on shear bands (Fig. 5), 469 although early precursory cracking might have opened even earlier. Fluid ingress may also have 470 471 aided fracture propagation by mechanisms such as stress corrosion cracking or microplasticity (Atkinson, 1984; Kerrich, 1986; Stünitz & Fitz Gerald, 1993). Transient surges in pore fluid 472 pressure or strain rate may have also promoted fracturing and fluid ingress in a cyclical fashion, 473 474 followed by recrystallization and precipitation of new grains, as shown e.g. by Kjøll et al. (2015). Slip on antithetic shear bands was hindered by their steeper orientation with respect to the 475 mylonitic foliation, promoting strain localization on the synthetic set (Fig. 10). As slip 476 477 accumulated on synthetic C' shear bands, more fluids were called in, activating a positive feedback mechanisms that enhanced lubrication by continuous authigenesis of 'soft' phyllosilicates 478 479 organized in subparallel bands (Fig. 3c, d). A similar process was documented in quartzfeldspathic rocks of the South Armorican Shear Zone by Bukovskà et al. (2016), who documented 480 481 shear band propagation by fluid infiltration promoting reaction softening at lower greenschist 482 facies conditions. Propagation of shear bands outside of the coarse and 'stiff' quart porphyroclasts might have likely promoted by temperature decrease, as basal <a> slip is energetically favored at 483 low temperature conditions but no evidence for it was found in the analyzed domains, suggesting 484 485 that the presence of strong Y-max textures possibly hindered dislocation creep by basal <a> slip (geometric hardening; Poirier, 1980; Toy et al., 2008), forcing early strain localization in 486 487 phyllosilicate-rich layers and shear bands. Finally, following the embrittlement of the system 488 below the brittle-ductile transition for quartz (i.e. 310 ± 30 °C; Stöckhert et al., 1999; 280 ± 30 °C; Stipp et al., 2002), the presence of bands of phyllosilicates in shear bands oriented obliquely to the 489 490 mylonitic foliation formed a 'weak' network acting as ductile precursors (Fig. 1c) for faults and 491 shear fractures (Fig. 1d), as documented by Papeschi et al. (2018) and, in the studied sample, by

shear fractures locally connecting and reactivating shear bands (Fig. 5d). At this stage, slip on the
mylonitic foliation is halted and top-to-the-E deformation starts to be accommodated by nonAndersonian faults, discordant over the foliation.

495

496 **6.** Conclusions

The microstructures presented in this paper contribute to the understanding of the switch from purely crystal-plastic to semibrittle deformation in quartz, showing how shear bands may develop and act as precursors for brittle structures. The data shown here supports previous studies on the subject and adds further constraints by showing the following:

- At high grade metamorphic conditions, the dominant activity of a slip system, in this case
 prism <a> slip, promotes deformation in grains that are efficiently oriented for slip, leaving
 behind porphyroclasts that remain relatively undeformed, wrapped by the soft mylonitic
 matrix.
- In the semibrittle regime, deformation partitioning promotes fracturing and cataclasis along
 conjugate and synthetic shear bands in 'hard' quartz porphyroclasts, while deformation in
 the mylonitic foliation is still controlled by dislocation creep. The direction exploited for
 fracturing is not necessarily coincident with crystallographic planes of weakness but is predetermined by the vorticity of the flow.

Under fluid rich conditions, fluid ingress assists propagation, healing of fractures by
recrystallization and authigenesis of new quartz and phyllosilicate grains in microfractures.
The process may operate cyclically, assisting slip on shear bands and enhancing strain
softening with the formation of bands of 'soft' tiny quartz and phyllosilicates. The opening

of dilatant sites during slip promoted fluid infiltration and authigenesis of quartz grainswith a CPO parallel to shear bands.

4. Progressive strain localization on shear bands was likely favored by the geometric
hardening of mylonitic ribbons and the progressive interconnection of shear band
segments. In the brittle regime, faulting reactivates shear bands, concentrating slip on
structures discordant to the foliation.

520

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- 796 Figures



Figure 1 – (a) Simplified geological map of the Elba Island (modified after Massa et al., 2017)
showing the location of the study area. (b) Sketch structural-geological map of the study area
(Praticciolo Cape). Insert stereographic projections are in equal angle, lower hemisphere. The

yellow star marks the location of sample IESP3SP78. Mesoscale structures of the Calamita Schists
at the Praticciolo: (c) well foliated top-to-the-E mylonitic micaschists with S-C' fabric and (d) topto-the-E shear fractures cross cutting the mylonitic fabric and developed subparallel to C' shear
bands. Yellow arrows: C' shear bands; white arrows: shear fractures.



Figure 2 – Sketch illustrating the relationships between position of misorientation axis clustering
in crystal coordinates and rotation axis of uncommon (light grey), common (grey) and most
common (dark grey) slip systems in quartz. Modified after Neumann (2000).



Figure 3 – Microstructures of the investigated sample collected at crossed polarizers. The yellowcyan boxes highlight the location of EBSD maps. And: andalusite; Chl: chlorite; Q: quartz; Ser:
sericite; (a) Domain 1: recrystallized subparallel quartz layers interlayered with mica domains and
containing large quartz porphyroclasts. The gypsum plate insert highlights the c-axis orientation.
(b) Domain 2: relic lens of quartz porphyroclasts surrounded by smaller recrystallized grains and
cross cut by conjugate shear bands (C'1 and C'2). (c) Domain 3: large quartz porphyroclasts
surrounded by recrystallized grains, eastwardly dragged along numerous synthetic C' shear bands.



Figure 4 – EBSD analysis of Domain 1. (a) Grain size map colored in respect to the legend shown in the lower-right corner. (b) Contoured one-point-per-grain pole figures showing the distribution of <c> and <a> axes and poles to $\{m\}$, $\{r\}$ and $\{z\}$ planes for the complete dataset. (c-d) Contoured misorientation axis distribution (c) in crystal (MOCC) and (d) sample (MOSC) coordinates for 2- 10° , $10-20^{\circ}$ and $20-30^{\circ}$ of misorientation angle for the complete dataset.



Figure 5 – Microstructures of shear bands. Chl: chlorite; Lim: limonite; Q: quartz; Wm: white
mica (a) Conjugate shear bands hosted in large quartz porphyroclasts with small grains with
similar c-axis orientation (white arrow) and slightly misoriented damaged areas of the host grains
(crossed polarizers, gypsum plate). (b) SEM BSE-image of grains localized on conjugate shear

828 bands showing trails of fluid inclusions (yellow arrows) and pitted grain boundaries (red arrow). 829 (c) Quartz porphyroclast in Domain 3 mantled by recrystallized grains and phyllosilicate-rich strain caps (purple arrows) showing evident internal microfracturing (crossed polarizers). (d) 830 Shear band reactivated as a shear fracture (marked by yellow arrows) with 0.5 mm offset cross 831 cutting the main foliation through several quartz and mica domain. The insert highlights a portion 832 of the same shear fracture where different segments are bridged by en-echelon fractures (parallel 833 polarizers). (e) Architecture of a synthetic shear band (C'1; yellow dashed line) characterized by 834 an inner core defined by small quartz grains and a well-defined band of chlorite + white mica 835 836 (crossed polarizers). The red dashed line traces the foliation. (f) SEM BSE-image of a shear band core showing mica inclusions, a straight mica + chlorite + limonite band and pitted grain 837 boundaries (red arrows). 838



840 Figure 6 – EBSD analysis of Domain 2. (a) Orientation map with color-coding according to the inverse pole figure in the upper-left corner and grain boundaries colored according to the key on 841 842 top. A and B white lines correspond to misorientation profiles Fig. 6d, e. The yellow arrow flags 843 a small trail of recrystallized grains. White arrows mark the shear sense of conjugate shear bands. 844 The area bound by a yellow line marks the 'shear band grains' subset. (b-c) Pole figures showing the orientation of $\langle c \rangle$ and $\langle a \rangle$ axes and poles to $\{r\}$ for (b) host grains and (c) shear band grains 845 846 (contoured, one-point-per-grain). (d-e) Misorientation profiles for (d) profile A and (e) profile B (location in Fig. 6a). Relative misorientation with respect to the starting point plotted against 847 distance (µm). (f-g) Contoured misorientation axis distribution in crystal (MOCC, above) and 848

sample (MOSC, below) coordinates for $2-15^{\circ}$ of misorientation angle for (f) host grains and (g)



shear band grains subsets.

Figure 7 – Relationships between host grains and shear band grains. IPF and grain boundary
coloring after Fig. 6a. (a) Orientation map indicating four host grains subsets, numbered from 1 to

4. (b) Pole figures showing the orientation of $\langle c \rangle$ and $\langle a \rangle$ axes and poles to $\{r\}$ for the host grains 854 subsets. The trace of shear bands is shown with red dashed lines. Crystallographic planes that are 855 subparallel or closely oriented to shear bands are highlighted with black dashed lines. (c) 856 Contoured misorientation axis distribution in crystal (MOCC, above) and sample (MOSC, below) 857 coordinates for 2-15° of misorientation angles related to the host grains subsets. (d) Orientation 858 859 map highlighting the dextral and sinistral shear band subsets. (e) Comparison between <c> axis pole figures of host grains (left) and contoured one point per grain pole figures for shear band 860 861 grains (right) relative to the dextral shear band (above) and the sinistral shear band (below). Red 862 dashed lines mark the trace of C' shear bands.



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Figure 8 – EBSD analysis of Domain 3. (a) Orientation map with IPF and grain boundary coloring
as in Fig. 4a. The yellow lines delimitate the shear band grains subset (in the center). (b-c) Pole

figures showing the orientation of $\langle c \rangle$, $\langle a \rangle$ axes and poles to {r} for (b) host grains and (c) shear band grains (contoured, one-point-per-grain). Red dashed lines outline the trace of the shear bands. (d) Grain size distribution map showing grains with equivalent circle diameter between 0 and 100 µm, colored as in the lower-left corner key. (e-f) Contoured misorientation axis distribution in crystal (MOCC, above) and sample (MOSC, below) coordinates for 2-15° of misorientation angle for (e) host grains and (f) shear band grains subsets.



Figure 9 – Misorientation angle distribution (MAD) for correlated (light blue curve), uncorrelated
(red curve) and theoretically random (black curve) distributions for EBSD maps: (a) Domain 1;
(b) Domain 2; (c) Domain 3.



Figure 10 – Sketch diagram showing the reconstructed evolution of the investigated sample in
function of time and temperature decrease (dark grey to light grey arrow). BDT: brittle/ductile

transition. BPT: brittle/plastic transition (definitions after Kohlstedt et al., 1995) Steps are: (a)
Dynamic recrystallization on mylonitic ribbons leaving behind quartz porphyroclasts, (b)
development of conjugate shear bands in quartz porphyroclasts, (c) strain localization on synthetic
C' shear bands and (d) reactivation of C' shear bands in the brittle regime. See text for a detailed
comment.