Strength of dry and wet quartz in the low-temperature plasticity regime: insights from nanoindentation

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Aim

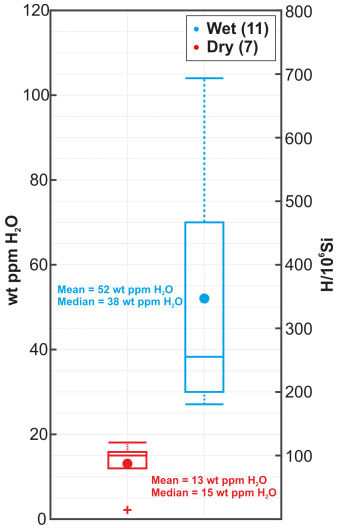
Characterise the effects of intracrystalline **water content** on the **strength of quartz** in the **Low-Temperature Plasticity** Regime

Research question: does hydrolytic weakening occur in the Low-Temperature Plasticity regime?

Methods

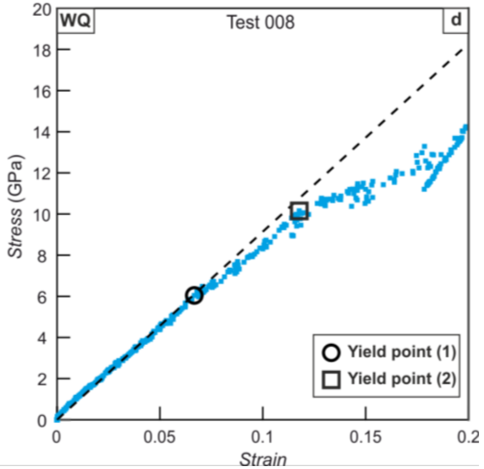
Secondary Ion Mass Spectrometry
On optically clear (no fluid inclusions) natural quartz grains

Quantification of intracrystalline H_2O content



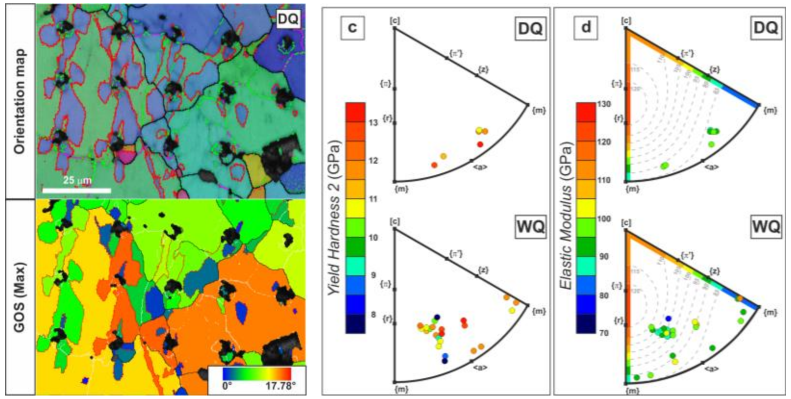
Nanoindentation experiments
On optically clear (no fluid inclusions) natural quartz grains

Quantification of yield hardness and elastic modulus



Electron Backscatter Diffraction
on nanoindented natural quartz aggregates

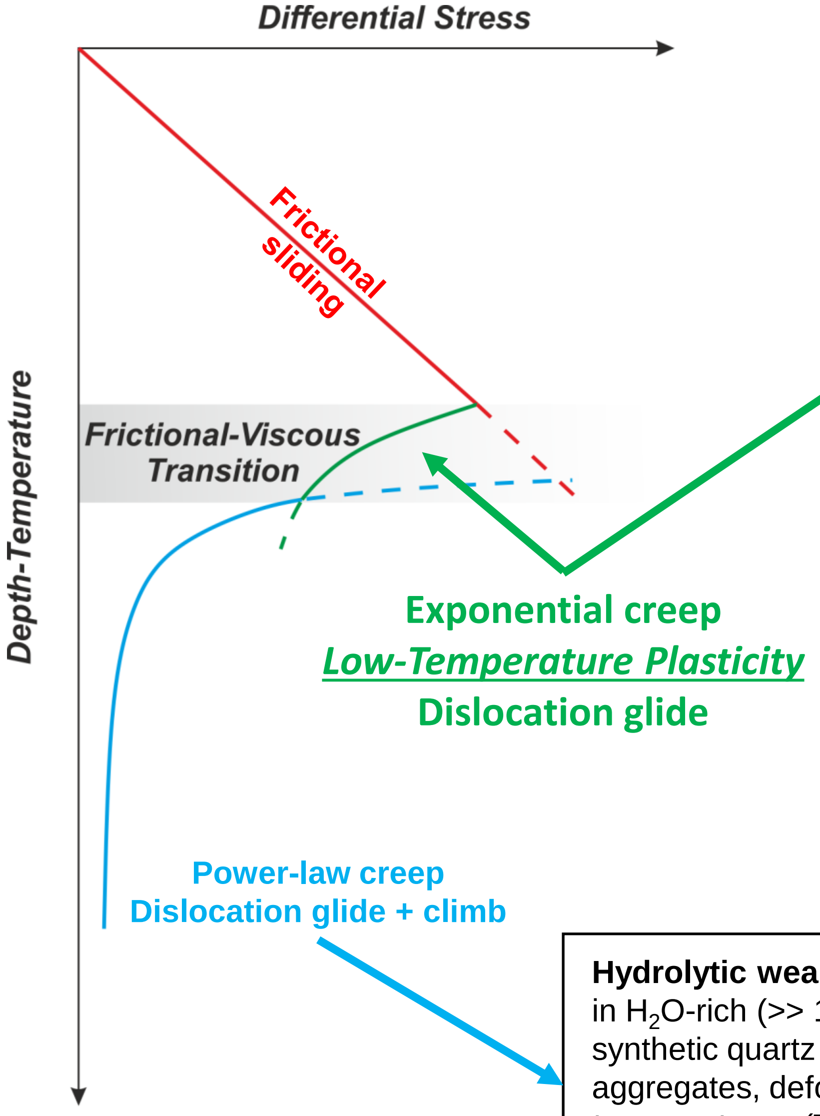
Identification of intracrystalline deformation mechanisms and crystallographic directions



Low-Temperature Plasticity

is the dominant deformation mechanisms at ***low temperature*** (T_h<<$0.5T_m$) and ***high stress*** conditions characteristics of the <u>frictional-viscous transition</u>

LTP involves **<u>glide</u>**-accommodated intracrystalline deformation



Constitutive law for Low Temperature Plasticity

$$\dot{\varepsilon} = A \cdot \rho \cdot exp^{\left(\frac{Q}{RT}\right)} \sinh\left(\frac{Q}{RT} \cdot \frac{\sigma - \sigma_b}{\epsilon}\right)$$

Hansen et al. (2019) for LTP in Olivine

BackStress: stress related to long-range elastic interactions between dislocations – proportional to dislocation density

Dislocation density

enhanced by microfractures and water clusters (micro-fluid inclusions) [Stünitz et al., 2017]

<u>Peierls Stress</u>

Hydrolytic Weakening *by* **H_2O-related** ***intracrystalline defects is expected to decrease the resistance to glide (Peierls stress) of dislocations*** *through the hydrolisis of Si-O-Si bonds and the formation of Si-OH:OH-Si bonds*

Hydrolytic weakening is usually observed in H_2O-rich (>> 150 H/10^6Si), mainly synthetic quartz single crystals and aggregates, deformed at **high homologous temperatures** (T_h>$0.5T_m$), where diffusion of H_2O-related intracrystalline defects is promoted, triggering **dislocation climb.**

"So far, all observed effects of H_2O weakening in synthetic crystals can be explained by the H_2O-cluster induced dislocation nucleation and multiplication without a necessary reduction of Peierls stress for dislocation glide [McLaren et al., 1989], although it does not exclude that H_2O or OH may have an effect on the resistance to glide." – Stünitz et al., (2017).

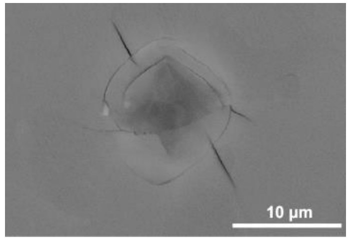
Nanoindentation

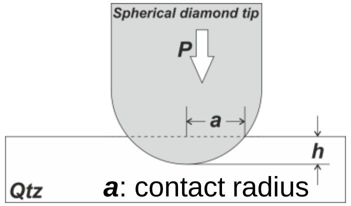
Simple experimental set-up: a diamond tip of variable geometry is pushed at constant rate into the sample. Load (*P*) and displacement into the sample (*h*) are continuously measured (CSM method) and mechanical parameters computed considering the geometrical proportions of the indenter tip.
Nanoindentation can produce high stress conditions, given that the indented volume is confined by the surrounding specimen itself, allowing to **suppress brittle deformation** at room conditions (25°C).

→ *The resulting plasticity is related to dislocation glide only*

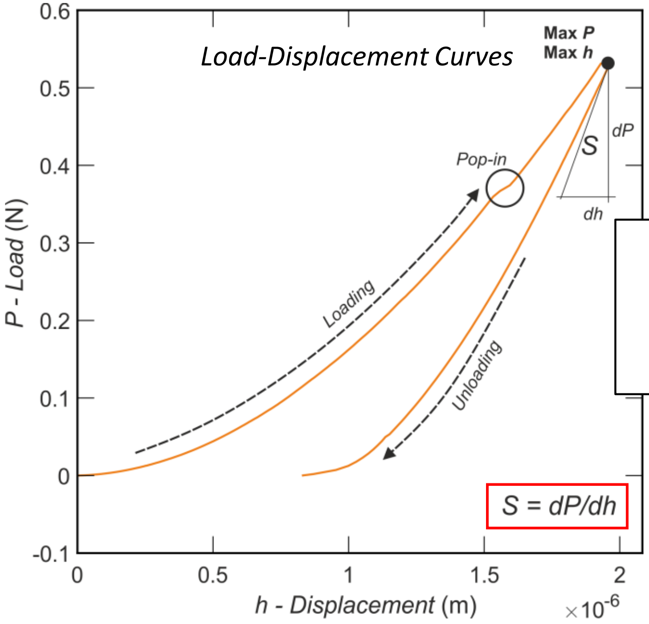
Spherical Nanoindenter

BSE image of spherical nanoindentation mark on quartz





Maximum Depth = 2 µm
Maximum Load = 530 mN
Constant strain rate = 0.05 s^{-1}
Radius spherical tip = 7 µm
Pyramidal angle Berkovich = 65.27°



Continuous Stiffness Measurement
S

$$a = \frac{S}{2E_{ind}}$$

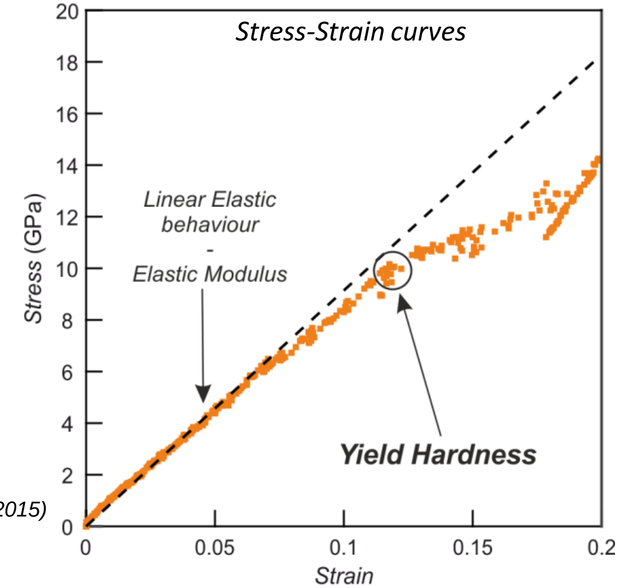
Stress

$$\sigma = \frac{P}{\pi}\frac{1}{a^2}$$

Strain

$$\varepsilon = \frac{4h}{3\pi\, a}$$

Pathak and Kalidindi (2015)



Elasto-plastic behaviour

What we can retrieve:
Yield Hardness
(proportional to yield stress)
and
Elastic Modulus

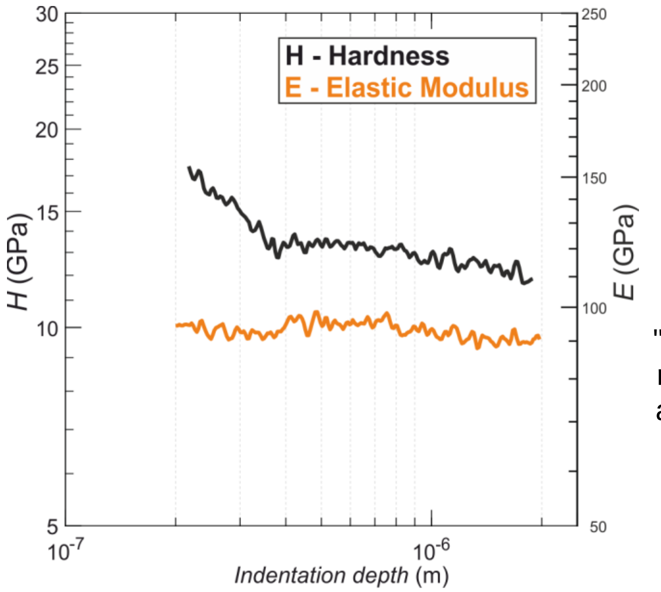
Elastic Modulus

$$E = \frac{\sqrt{\pi}}{2}\frac{S}{\sqrt{A}}$$

Hardness

$$H = \frac{P}{A}$$

Oliver and Pharr (1992)

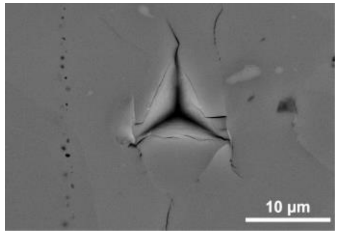


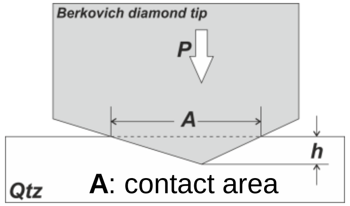
Rigid-plastic behaviour (negligible elastic strain)

What we can retrieve:
Variation of **Hardness**
and
Elastic Modulus during indentation

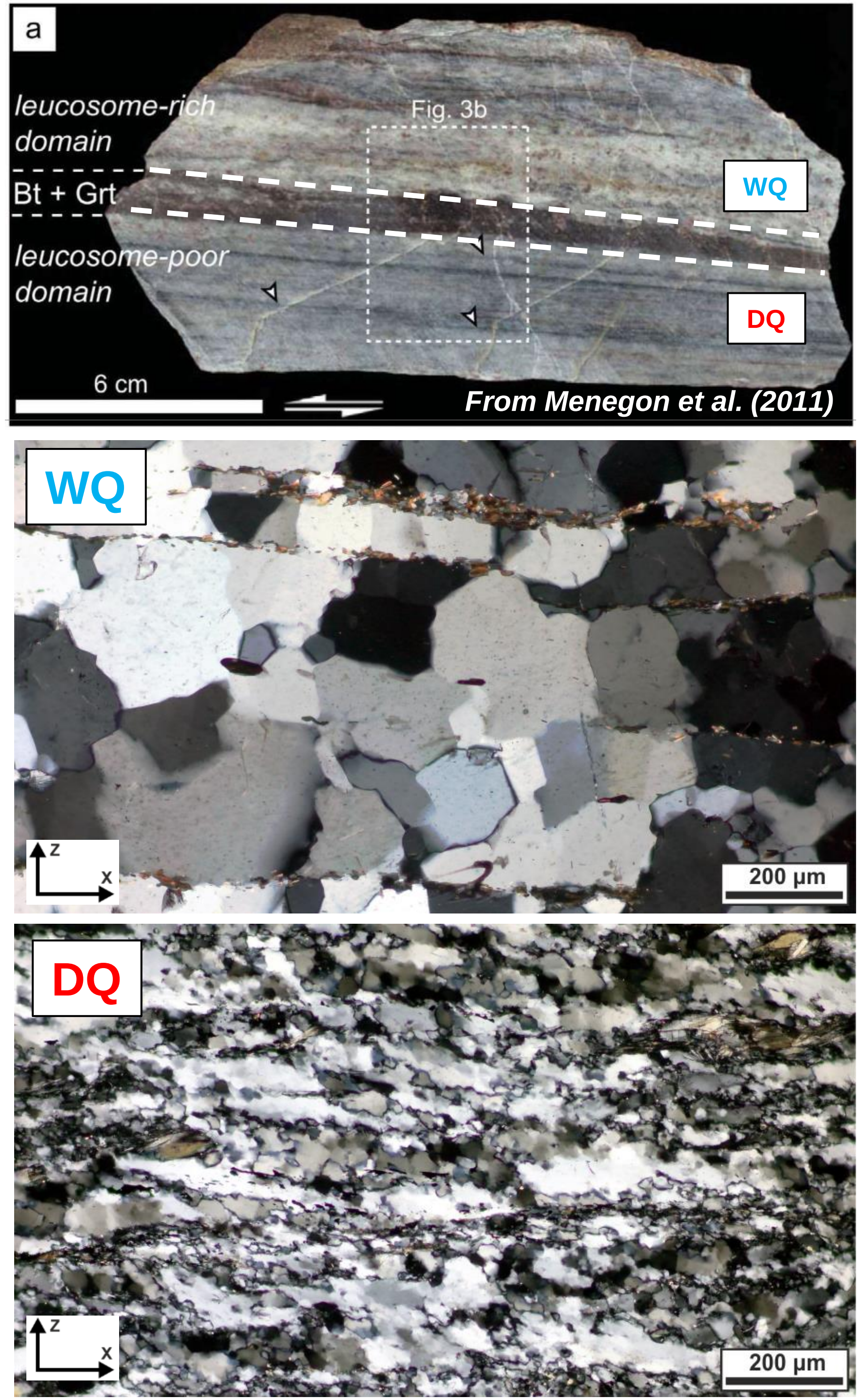
"The indentation hardness represents the flow stress at 7% strain" = strength of quartz after the yield point.

Berkovich Pyramidal Nanoindenter





BSE image of Berkovich nanoindentation mark on quartz



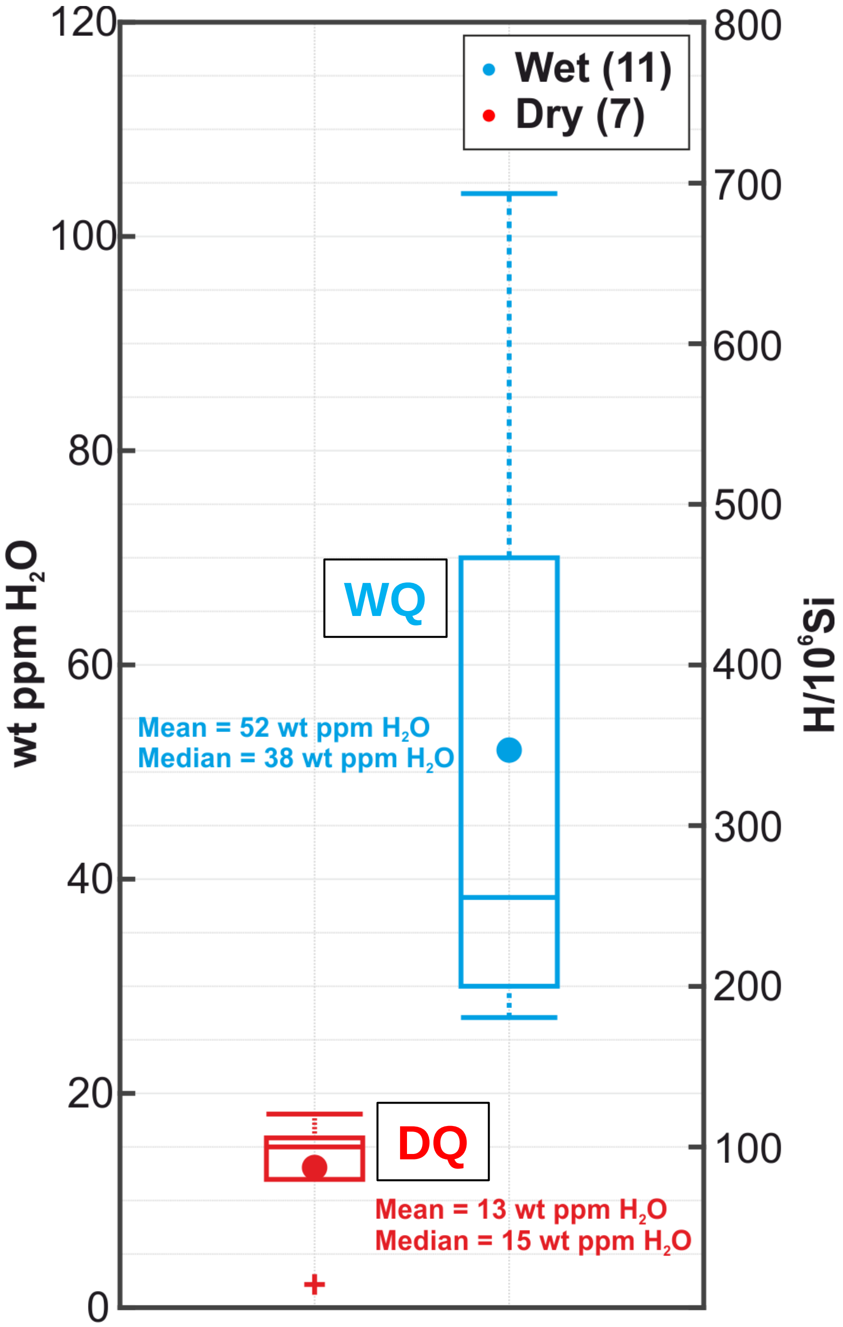
Natural quartz samples from sheared leucosome-rich and leucosome-poor layers of a granulite-facies **migmatitic gneiss** from the Seiland Igneous Province (Norway)

Deformed @
P = 0.75-0.95 GPa; T = 760-820°C
Under high-differential stresses by dislocation creep processes (Menegon et al., 2011)

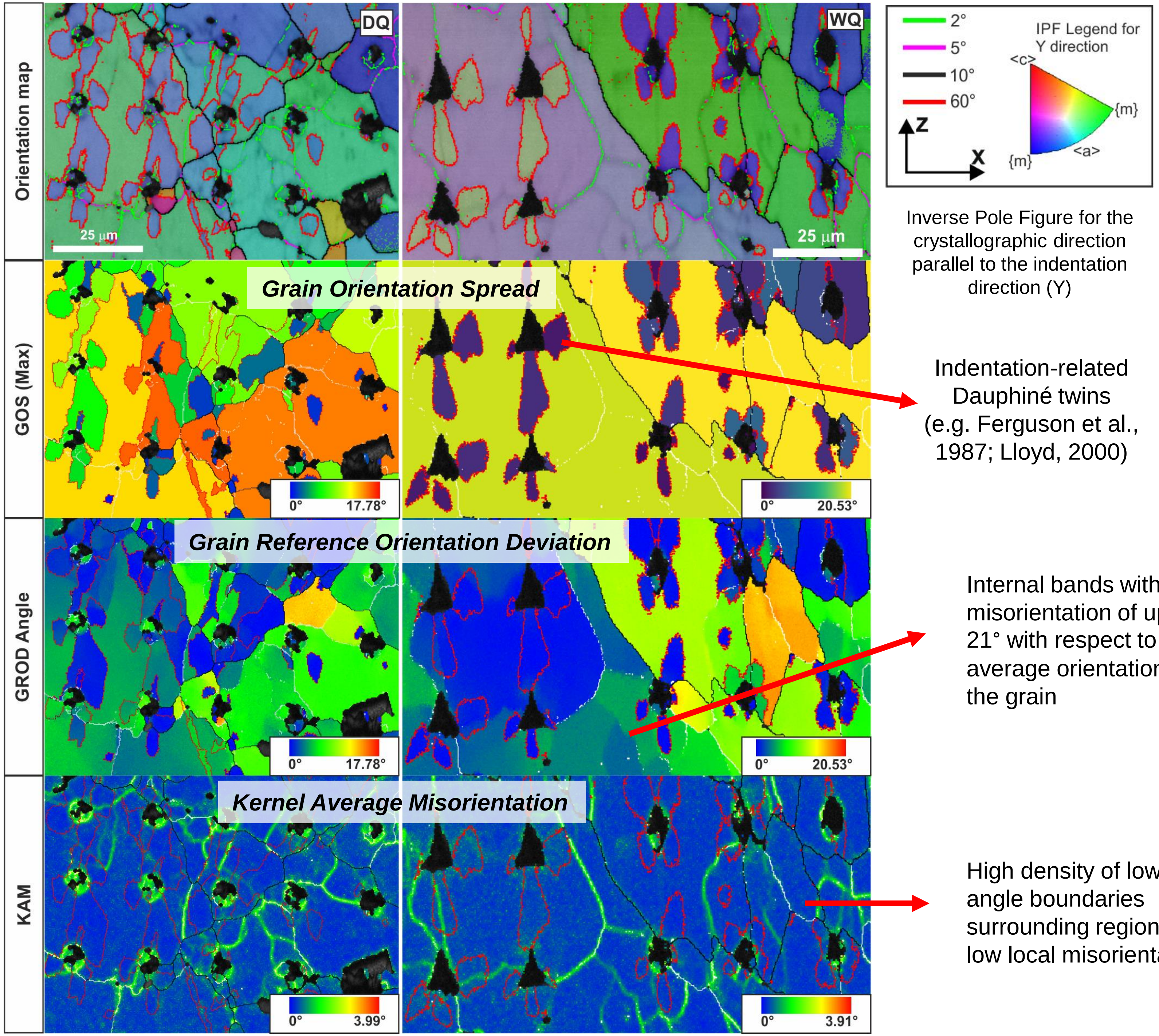
Leucosome-rich = Water present:
WQ – H_2O content > 20 wt ppm H_2O

Leucosome-poor = Water deficient:
DQ – H_2O content < 20 wt ppm H_2O

Grain sizes >> 10 µm, thus each nanoindentation test is performed on a single crystal of natural quartz



Quantification of intracrystalline water content by **Secondary Ion Mass Spectrometry**



Inverse Pole Figure for the crystallographic direction parallel to the indentation direction (Y)

Indentation-related Dauphiné twins (e.g. Ferguson et al., 1987; Lloyd, 2000)

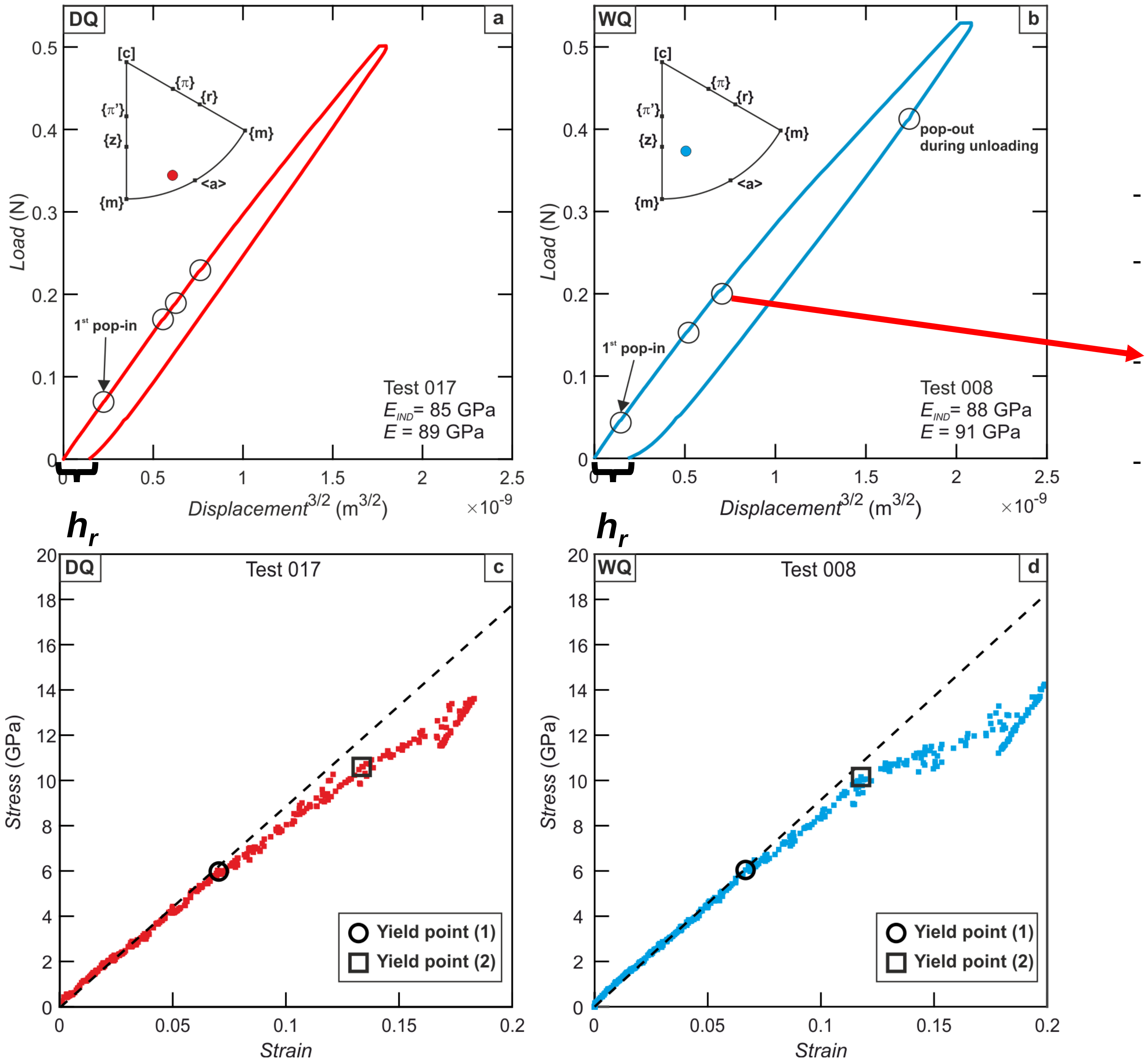
Internal bands with misorientation of up to 21° with respect to the average orientation of the grain

High density of low-angle boundaries surrounding regions of low local misorientation

Electron Backscatter Diffraction orientation and misorientation maps

- Strong intracrystalline (pre-indentation) strain suggested by sub-structures (subgrain boundaries and misorientation bands) resulting from dislocation glide and climb at granulite-facies conditions

High density of dislocations related to pre-indentation strain



Spherical nanoindentation

Load – Displacement curves

- A linear relationship between Load and Displacement$^{(3/2)}$ would suggest purely elastic deformation
- The occurrence of a **residual displacement h_r** suggests non-recoverable plastic deformation

- "Pop-in", small bumps on the load-displacement curves occurring when dislocations sources are activated during loading
- We observe very small pop-ins = **large density of dislocation sources** within the indentation volume (e.g. Kumamoto et al., 2017)

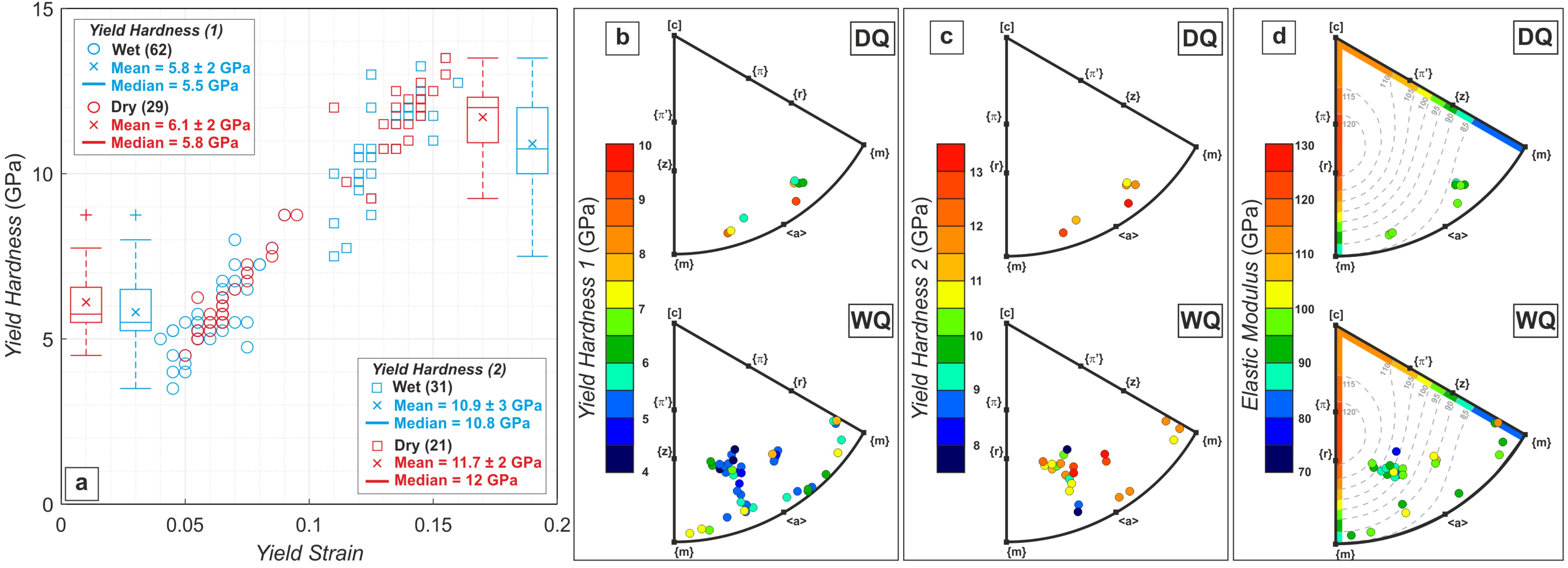
Stress – Strain curves

The identification of the yield point is rather subjective… thus, we have analysed the position of the two breakpoints along the data curve which possibly represent the yield point.

Yield Point (1): *first departure of the data curve from linear-elastic stress-strain curve (dashed line)*
Yield Point (2): *breakpoint on the slope of the data curve, abrupt change of the slope.*

Spherical nanoindentation *- Yield hardness: no statistically significant differences between WQ and DQ*

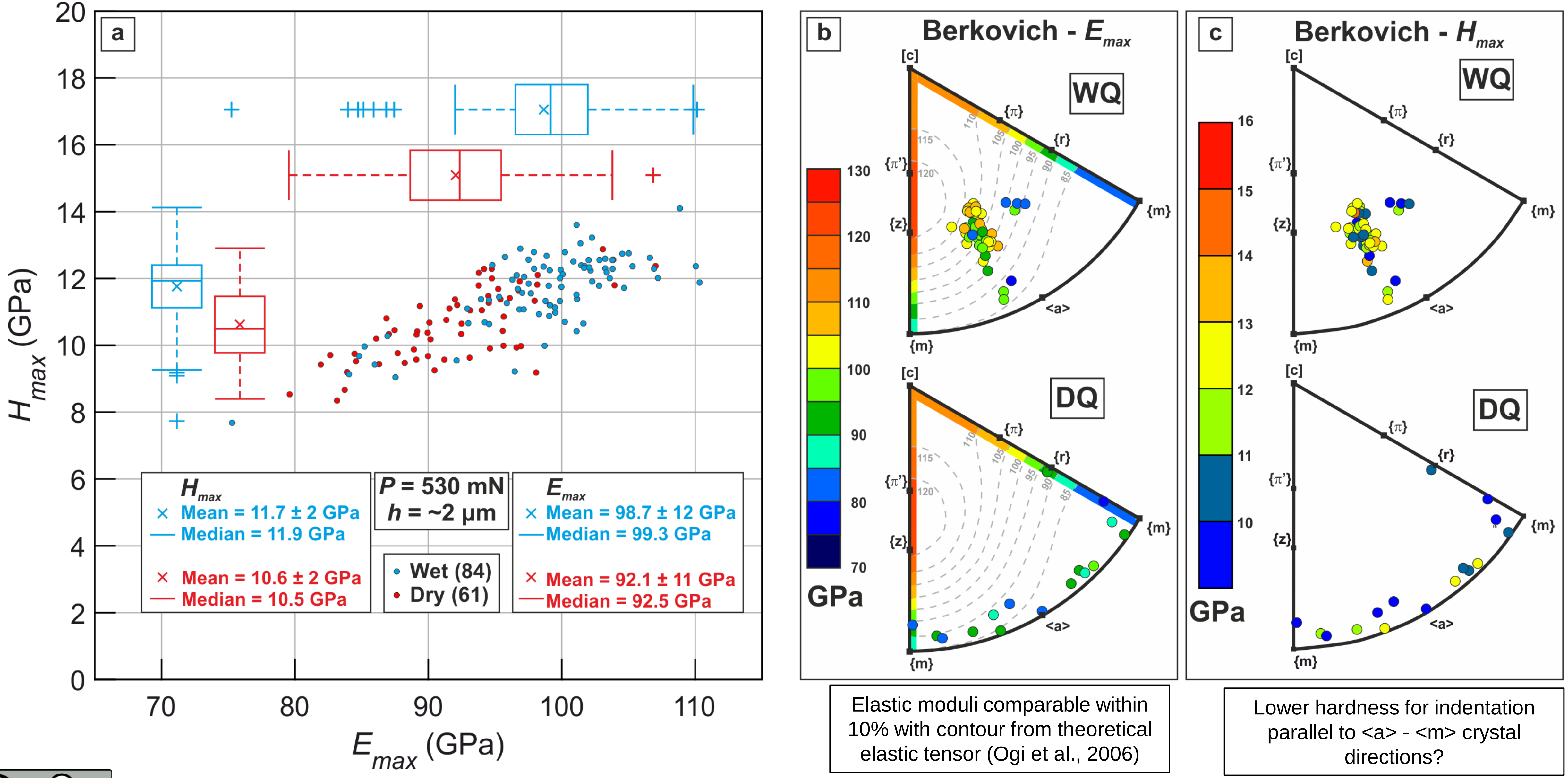
The small differences between WQ and DQ and the large spread in yield hardness values are probably related to the inherent crystallographic anisotropy of quartz (e.g. elastic modulus).



Larger Yield Hardness (1) values for indentation // to <a> or <m>

Elastic moduli comparable within 10% with contour from theoretical elastic tensor (Ogi et al., 2006)

***Berkovich nanoindentation** – Hardness and Elastic Modulus: no statistically significant differences between WQ and DQ*



Elastic moduli comparable within 10% with contour from theoretical elastic tensor (Ogi et al., 2006)

Lower hardness for indentation parallel to <a> - <m> crystal directions?

Discussion

- No statistically significant difference between yield hardness of DQ (<20 wt ppm H_2O) and WQ (>20 wt ppm H_2O) = **No hydrolytic weakening**

- Small and frequent pop-ins = **high density of dislocation sources**

- Natural crystals showing well developed network of intracrystalline substructures related to dislocation motion and recovery processes (subgrain boundaries and misorientation bands) = **high dislocation density related to pre-indentation strain**

- The observed differences in hardness seem to be affected by the anisotropic elastic properties of quartz

Conclusions

Intracrystalline H_2O content does not affect yield hardness (stregnth) of quartz in the Low-Temperature Plasticity regime, at least for the analysed range of H_2O intracrystalline content (2-100 wt ppm H_2O)

The pre-indentation strain history of the natural sample might have masked the potential effect of H_2O content, by generating a consistently high dislocation density in all the tested grains.

1) Indentation parallel to specific crystallographic directions may activate specific slip systems (those having the highest CRSS), thus Hardness should show some dependence on crystal direction
2) Long-range elastic interactions (back-stress), controlled by the anisotropic elastic properties of quartz, might control indentation hardness

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