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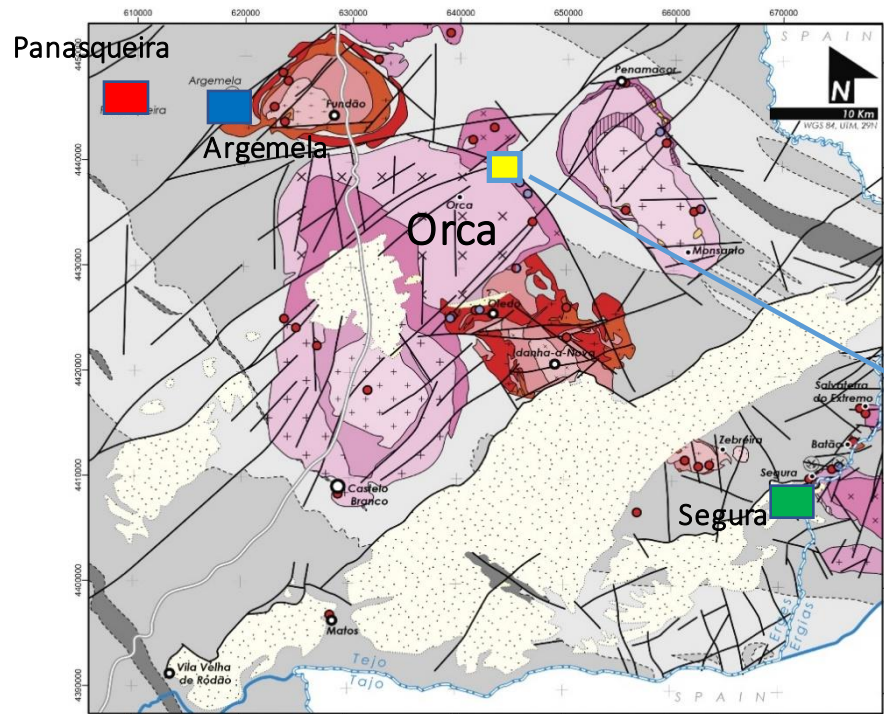
ERA-MIN Joint Call 2019 (EU Horizon 2020 ERA-NET Co-fund Project ERA-MIN2, Grant agreement N° 730238)



The W-Sn quartz lodes of Mata da Rainha and related anomalous tourmalization; insights from integrated fluid inclusion analysis and boron isotopes

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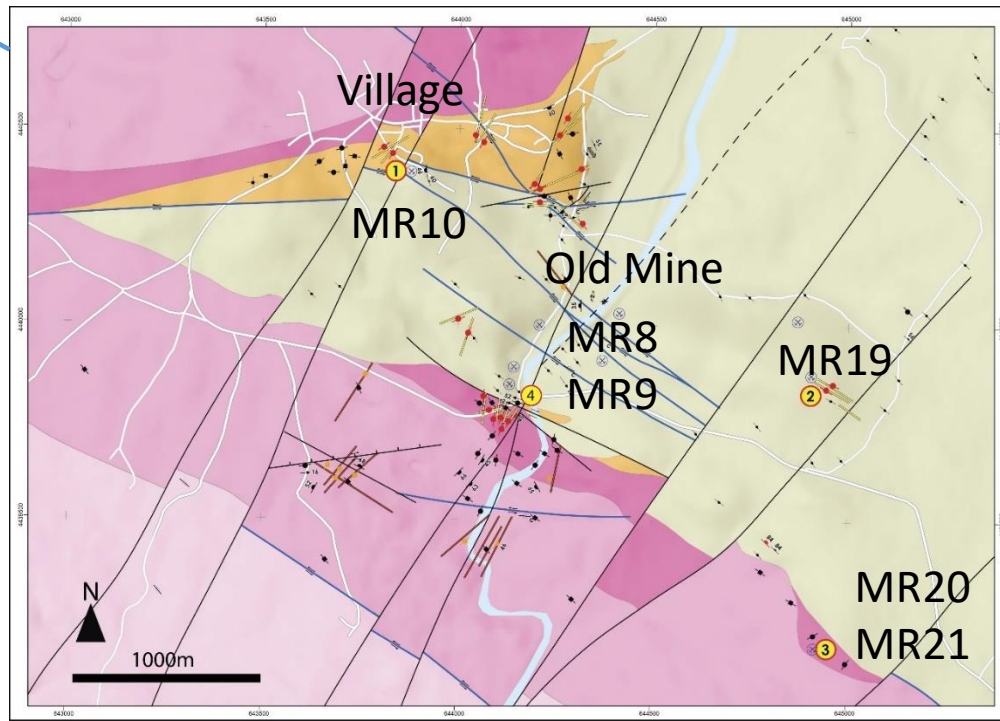
Mata da Rainha



Romão et al., 2010

Granite type S : 310 - 295 Ma (Villaseca et al., 2011; Roda-Robles et al., 2018)

- W deposit exploited by Germans during the second World War
 - extended zones of tourmalinisation at the contact between schists and the Orca granite
 - tourmaline also associated to greisens
 - tourmaline in W quartz veins from the deposit
- objectives: tourmaline crystal-(geo)-chemistry and comparisons
 → Nature of the fluids



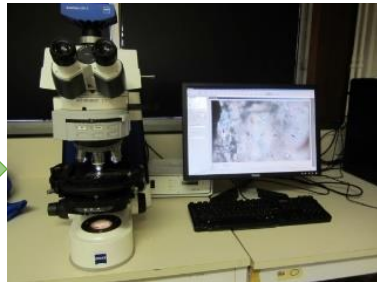
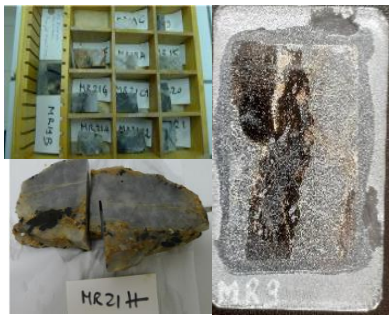
Sample location in the Mata da Rainha area

Materials and Methods

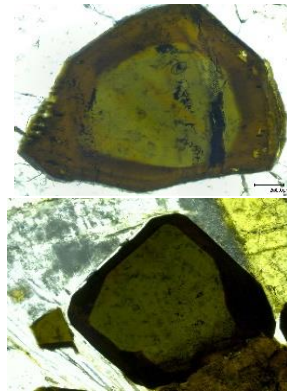
Field work



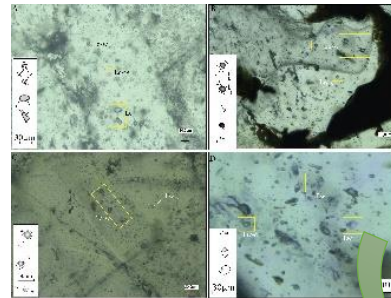
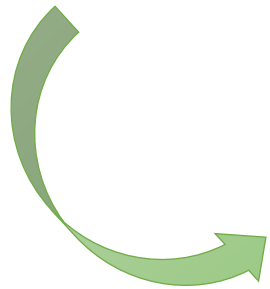
Rock preparation



Tourmaline



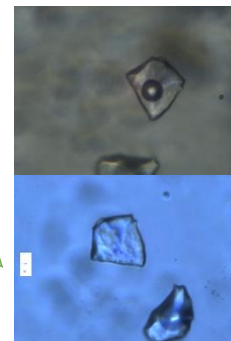
Petrography



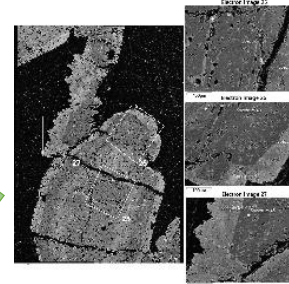
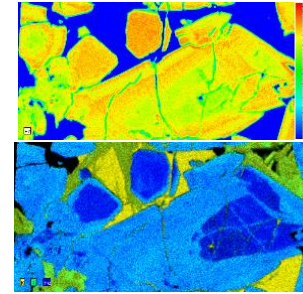
Fluid inclusions



Microthermometry

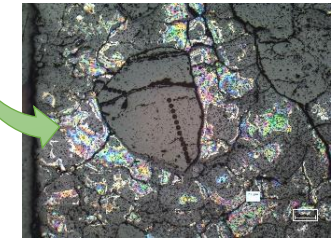
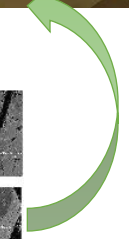


microXRF



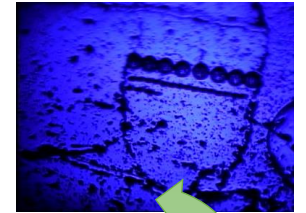
SEM

EPMA



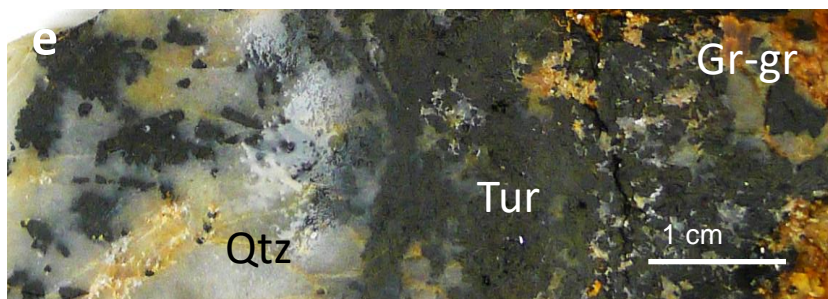
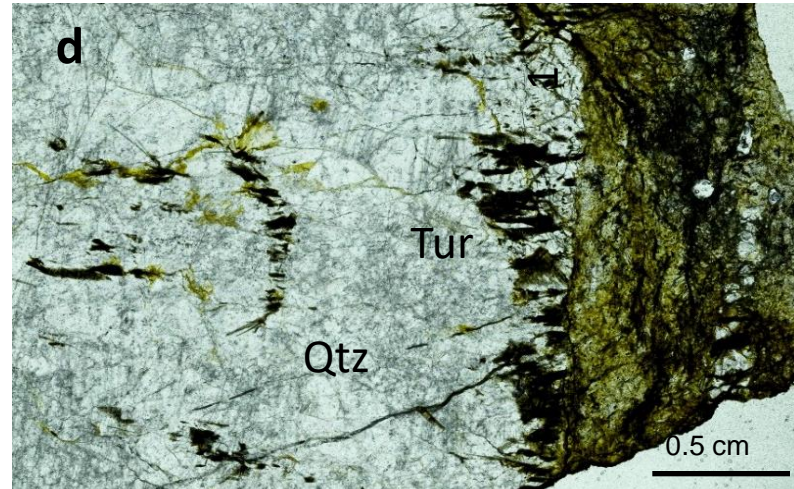
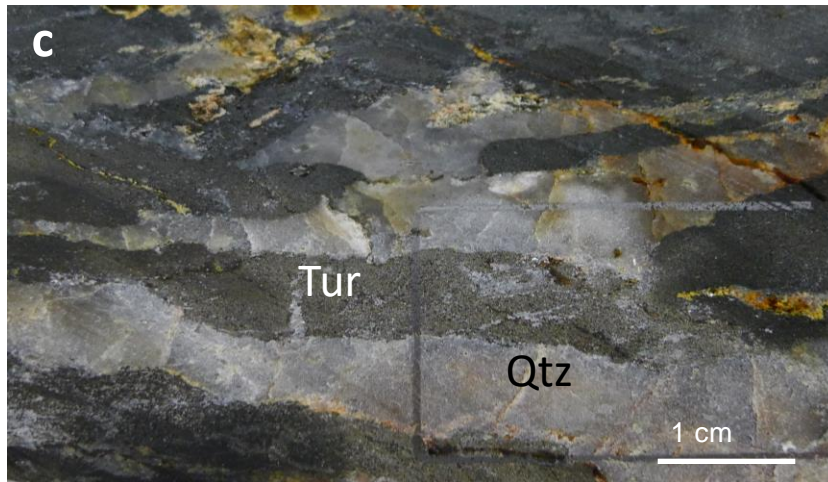
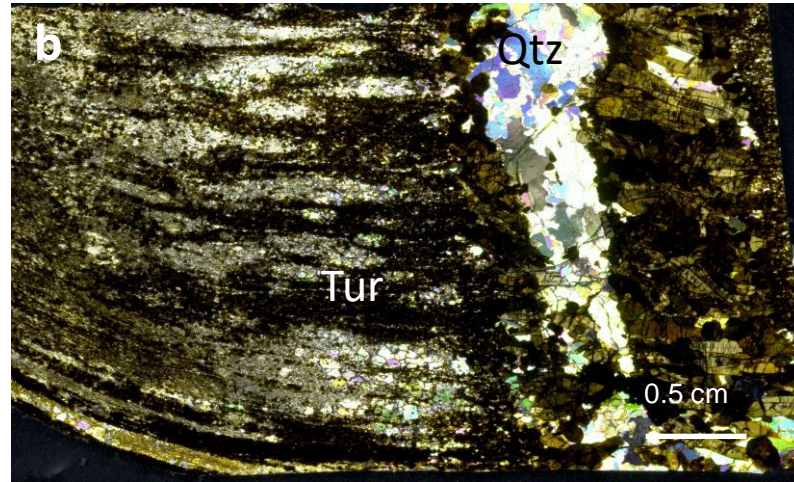
LA-ICPMS

SIMS ($\delta^{11}\text{B}$)



Raman

Tourmalinites, quartz-tourmaline veins, greisen with tourmaline

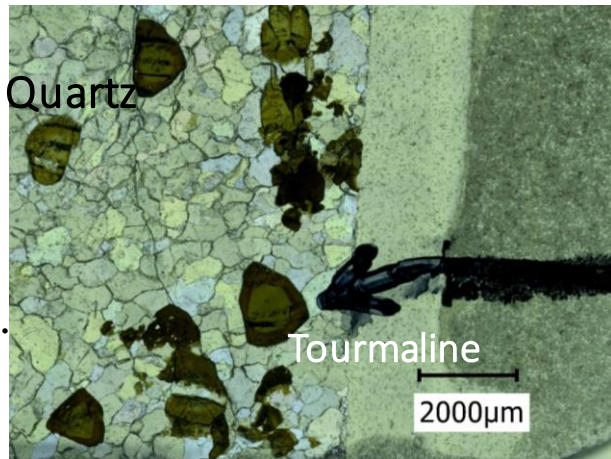


Expression of Tourmaline at Mata da Rainha

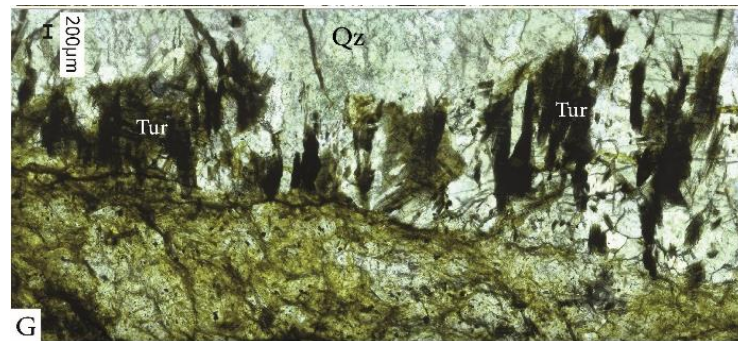
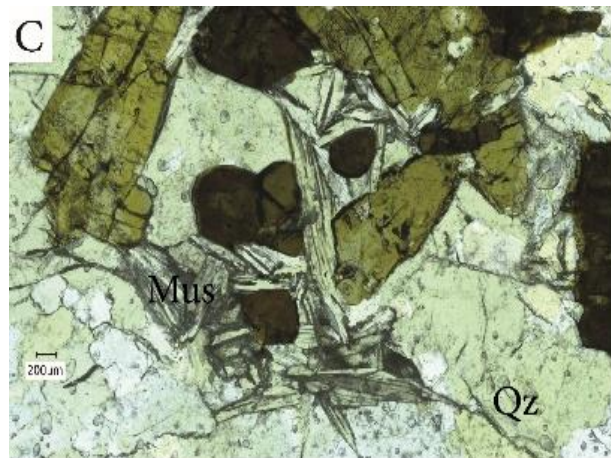
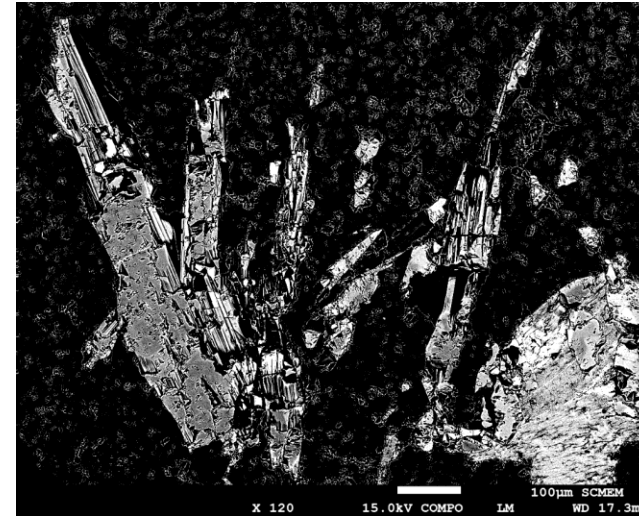
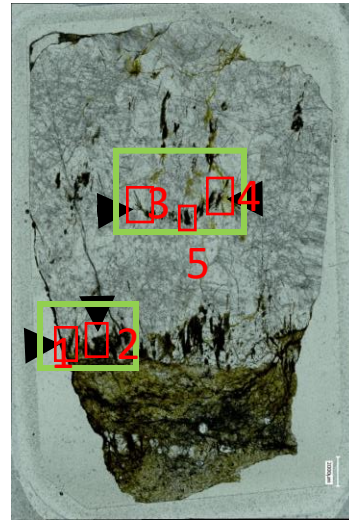
- schist tourmalinisation around syn-deformational quartz veins
- tourmaline in mineralized quartz veins from the deposit
- tourmalinized schists cemented by quartz
- tourmaline in and at the contact with greisens

Tourmalinites, quartz-tourmaline veins, greisen with tourmaline

Euhedral tourmalines in thick quartz veins

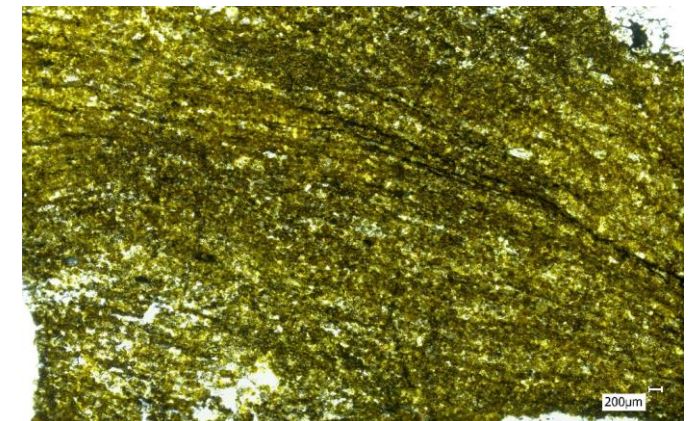


Tourmalines in needles in quartz veins.



Tourmaline as first vein infilling
 Growing perpendicular to fracture edge
 And then in between quartz generations
 Poorly zoned, probably synchronous
 of muscovite selvage

Tourmalines in micaschists

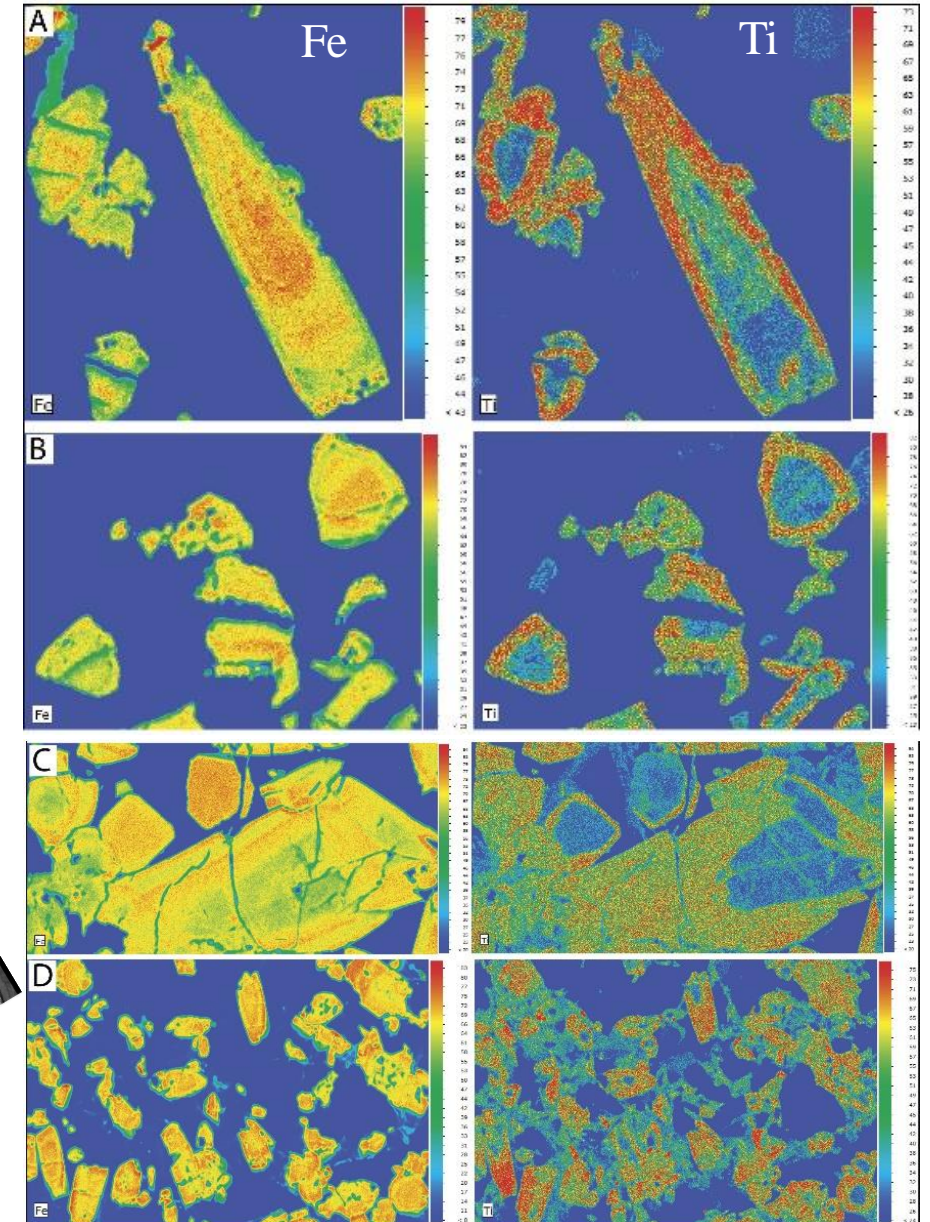
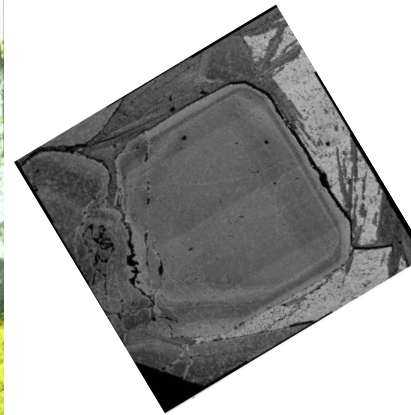
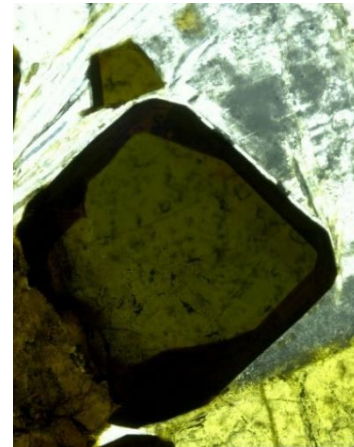
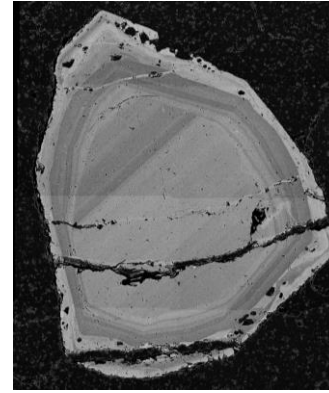
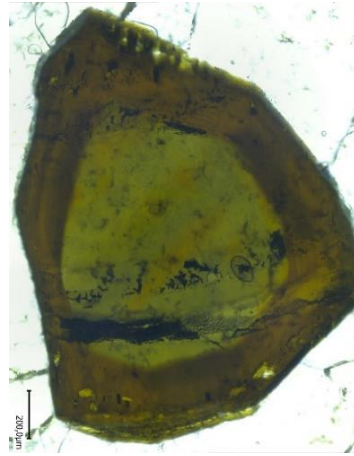


Tourmaline zoning - Mapping with micro-XRF

Variations mostly for Fe, Ti
(Mg, Mn and sometime Ca).

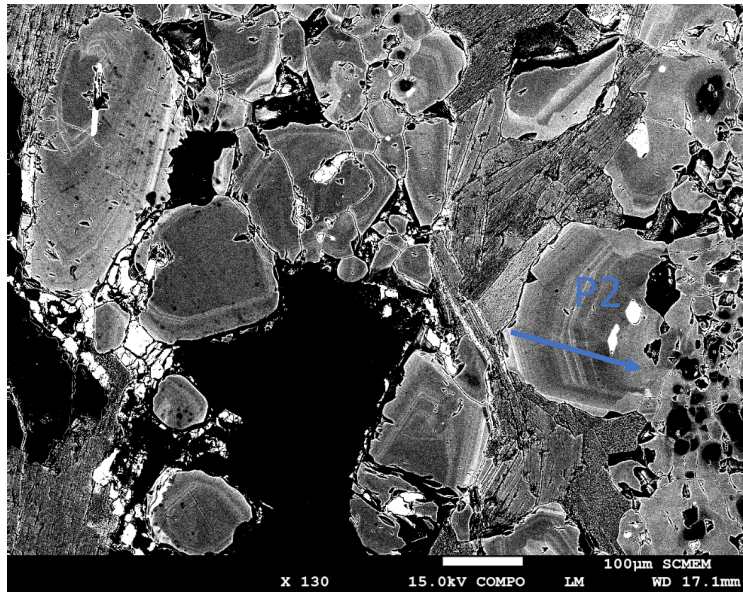
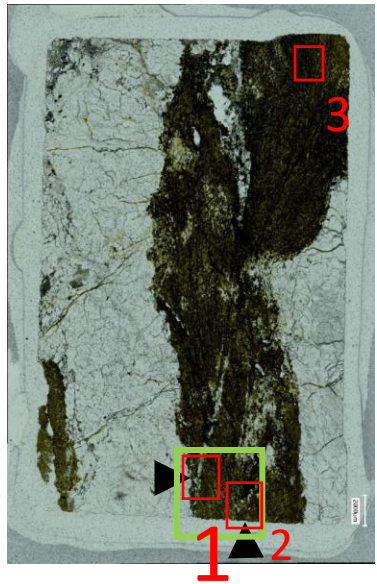
Ti, Fe and Ca are more
concentrated in the outer dark
bands.

Mg is more concentrated in the
core of zoned tourmalines.

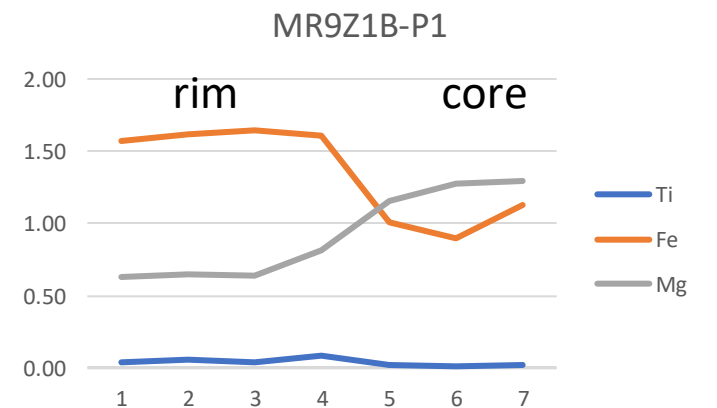
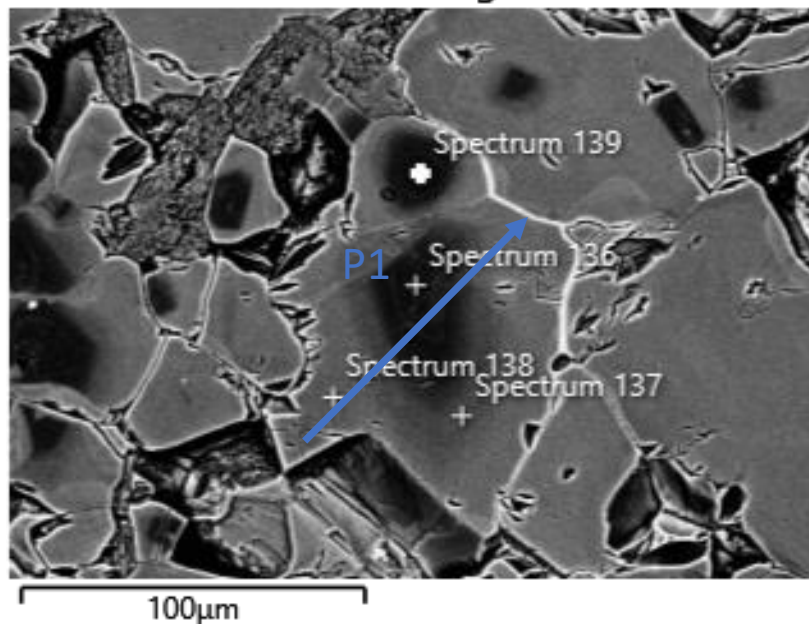
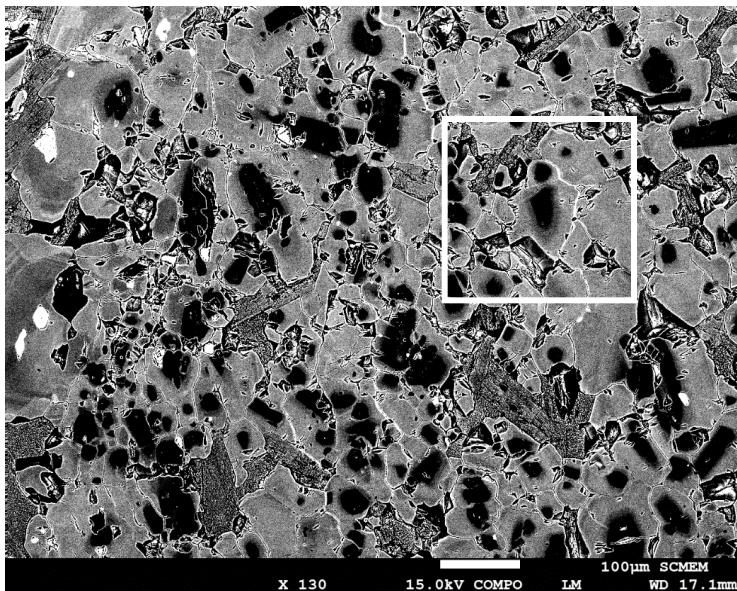
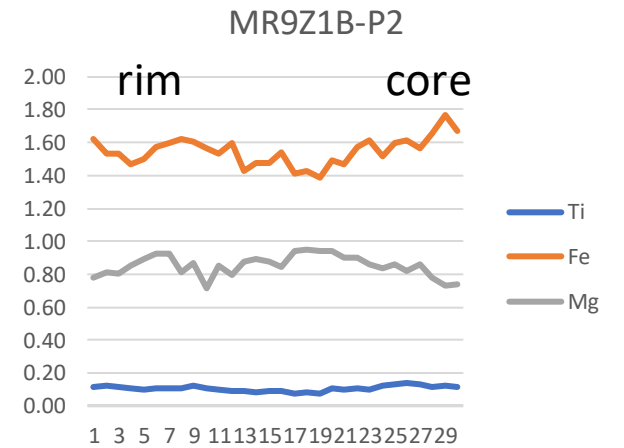


MR 9 Old mine

Quartz-tourmaline vein



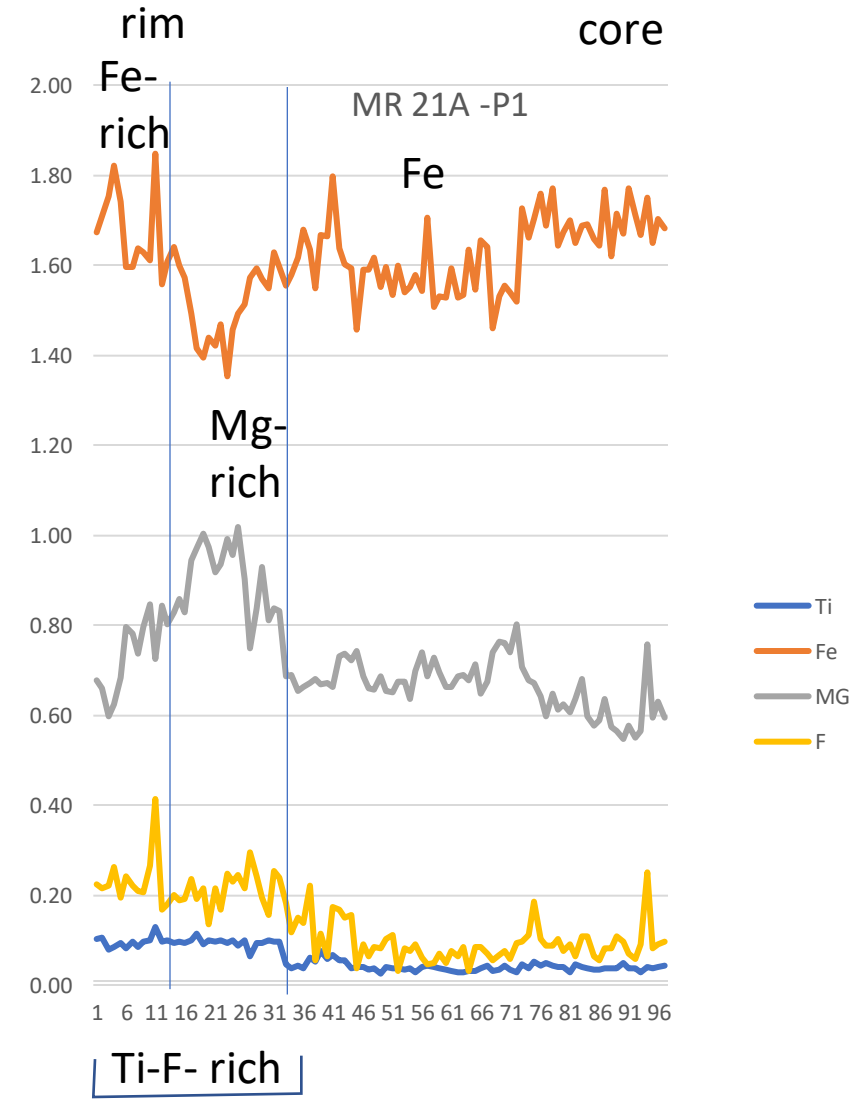
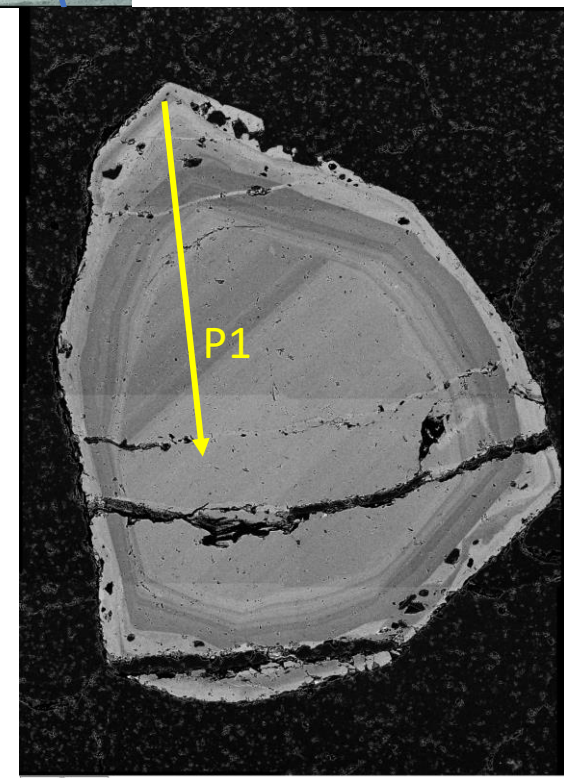
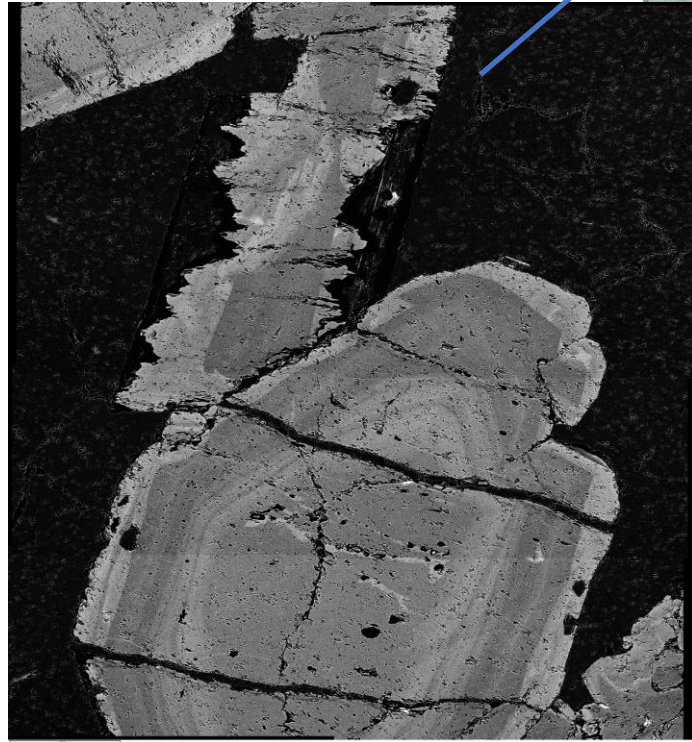
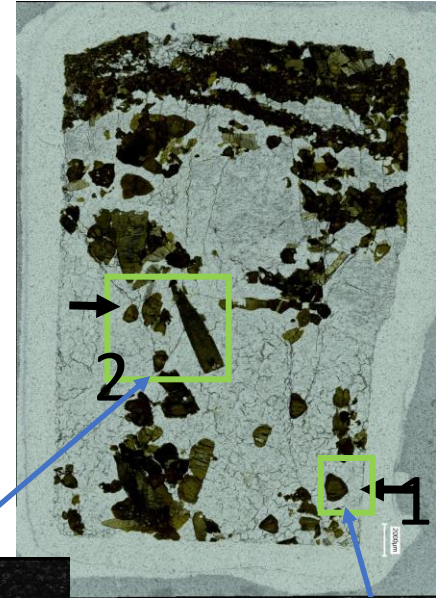
Schist tourmalinization- fine grained zoned tourmalines,
 « Classic » Fe-Mg zoning
 Later microveinlets with quartz and coarser tourmalines



Pervasive tourmalinization

MR 21 A

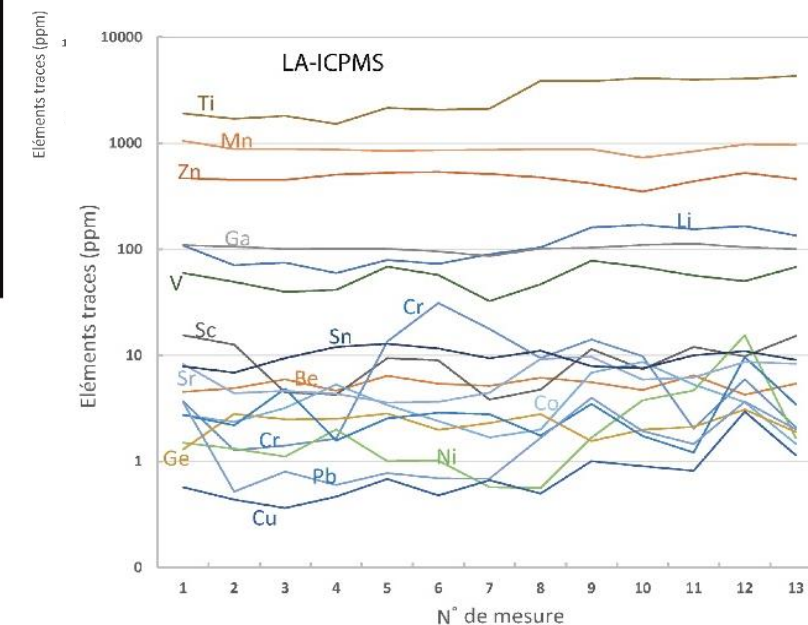
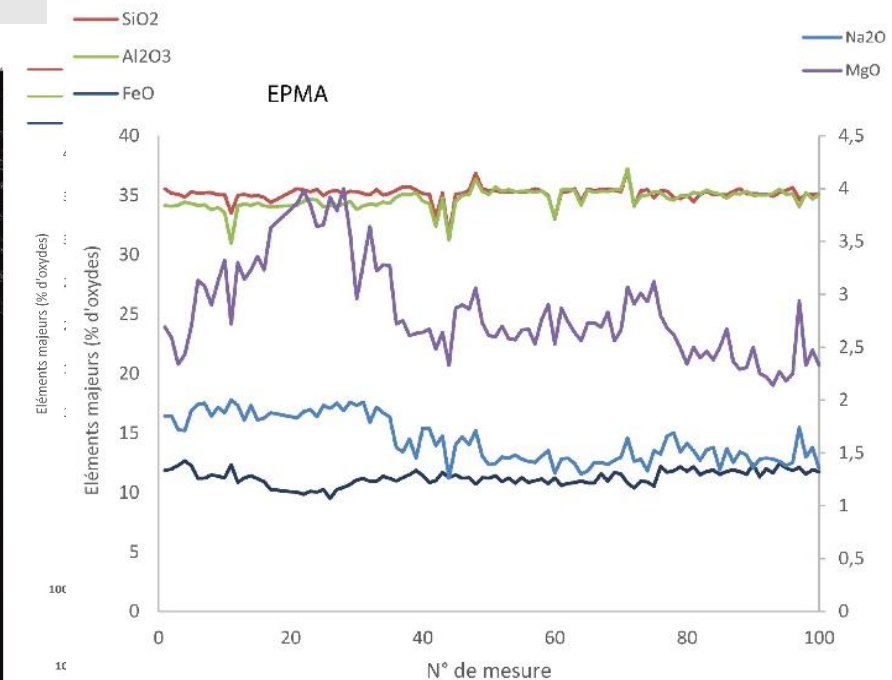
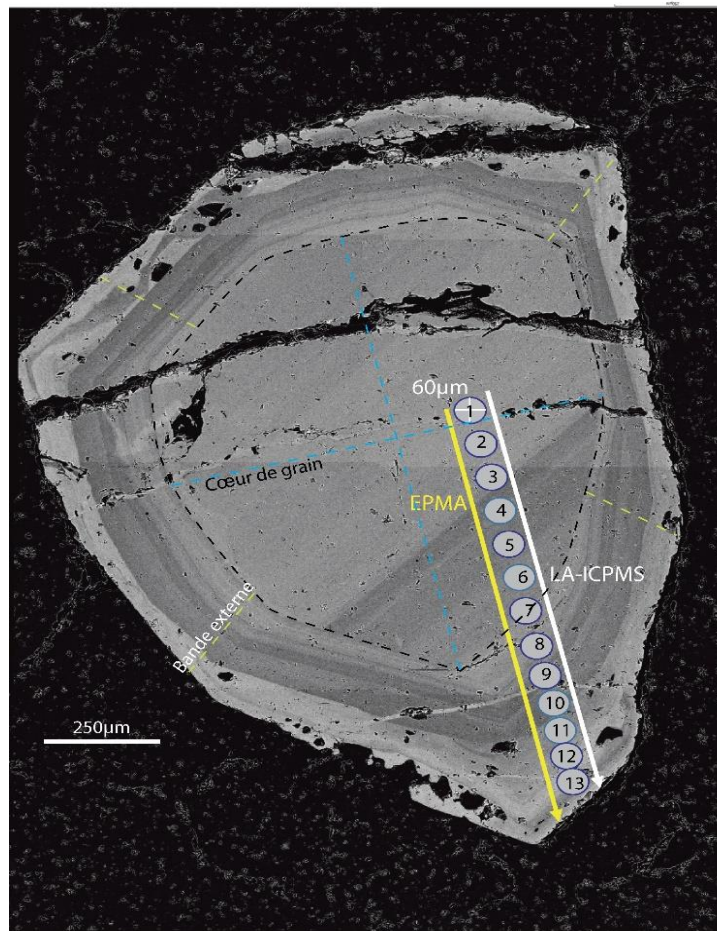
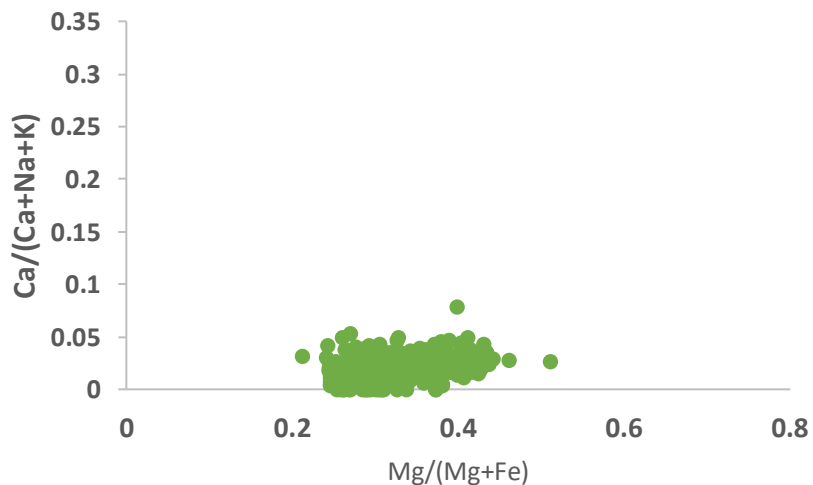
Quartz –tourmaline vein



Trace elements in tourmalines

The dark growth bands are enriched in MgO (and Na₂O).

The light bands are enriched in FeO and TiO



Zn and Mn remain constant at 800 and 1000 ppm along the profiles.

Li shows the same trend as Ti.

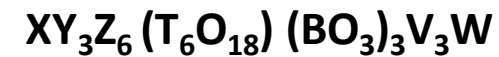
Other elements show concentrations of 100 ppm and less.

Chemical composition of Tourmalines

X (Na⁺, K⁺, Ca²⁺, □ = vacancy),

Y (Fe²⁺, Mg²⁺, Al³⁺, Li⁺)

et le site W (OH⁻, O²⁻, F⁻, Cl⁻) ([Henry et al., 2011](#)).



with :

X = Na, Ca, K

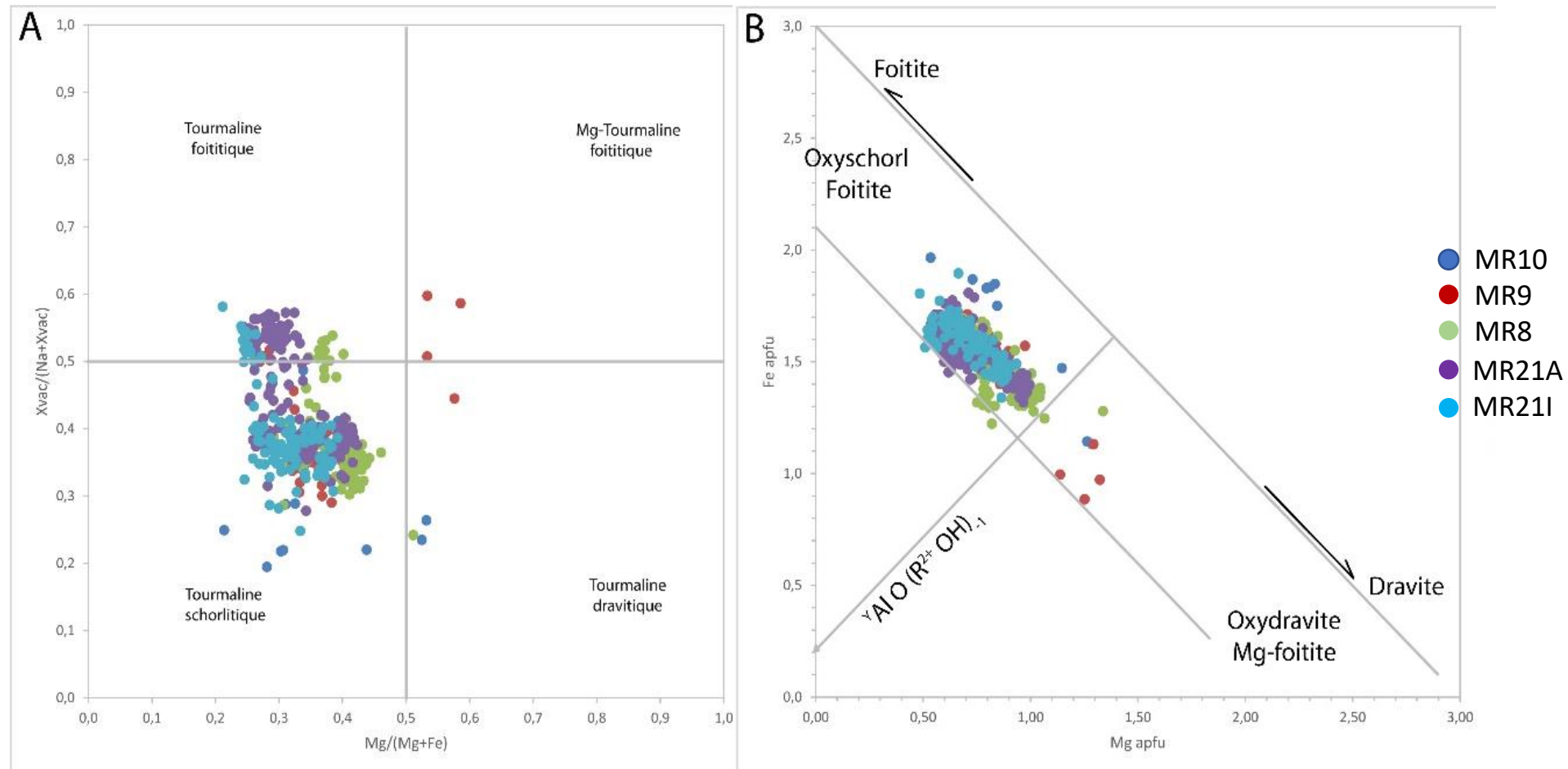
Y = Li, Mg, Fe²⁺, Mn, Al, Cr,
V, Fe³⁺, Ti ;

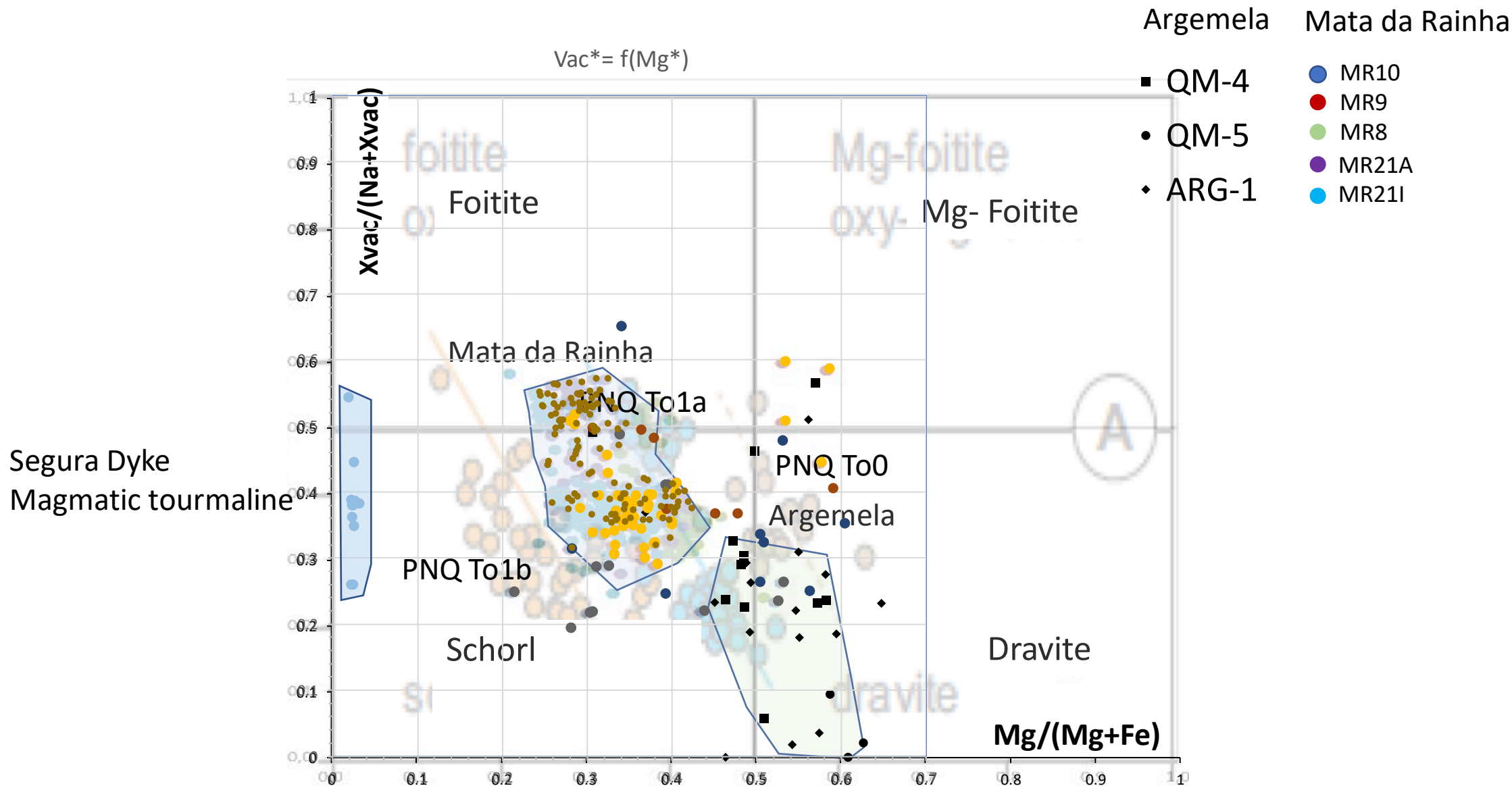
Z = Al, Mg, Fe³⁺, V, Cr

T = Si, Al, B; X = Na, Ca, K

V = OH, O

W = OH, F, O





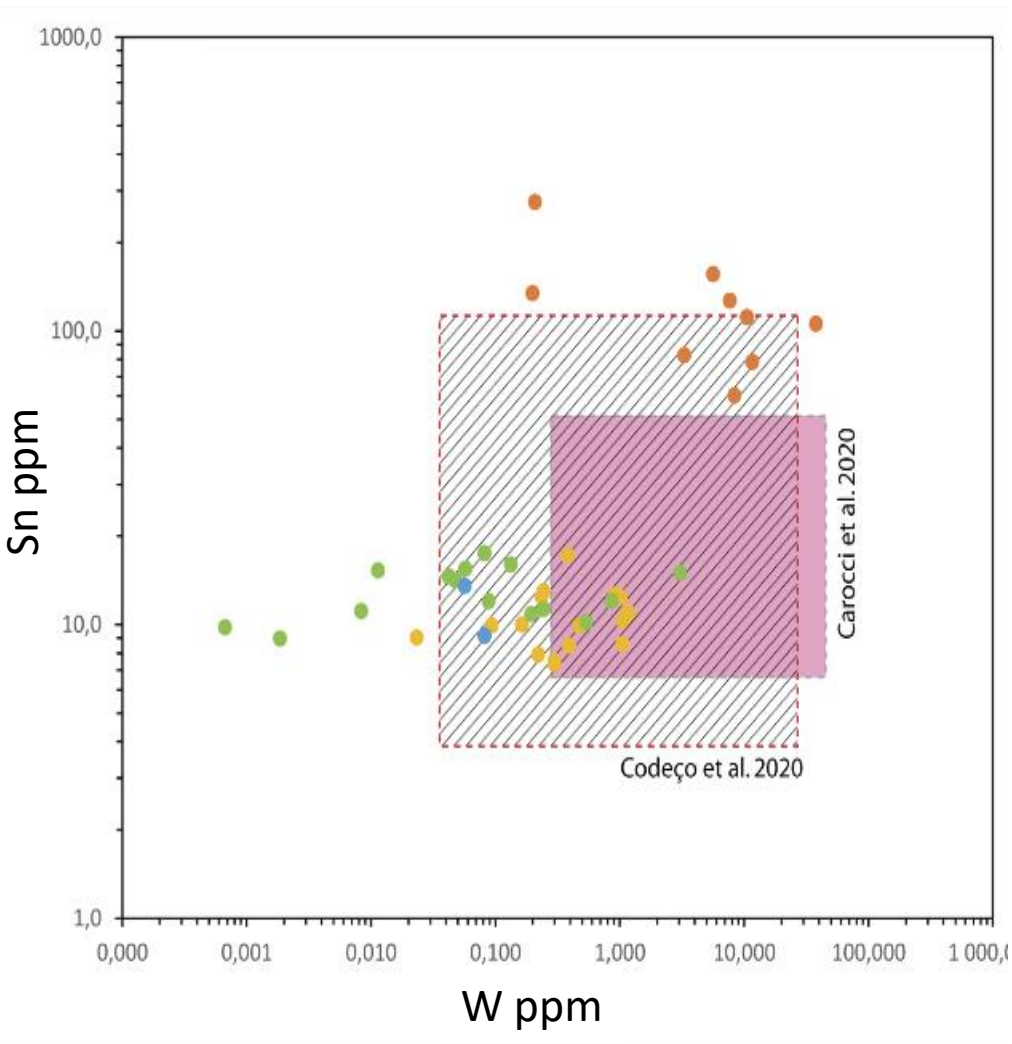
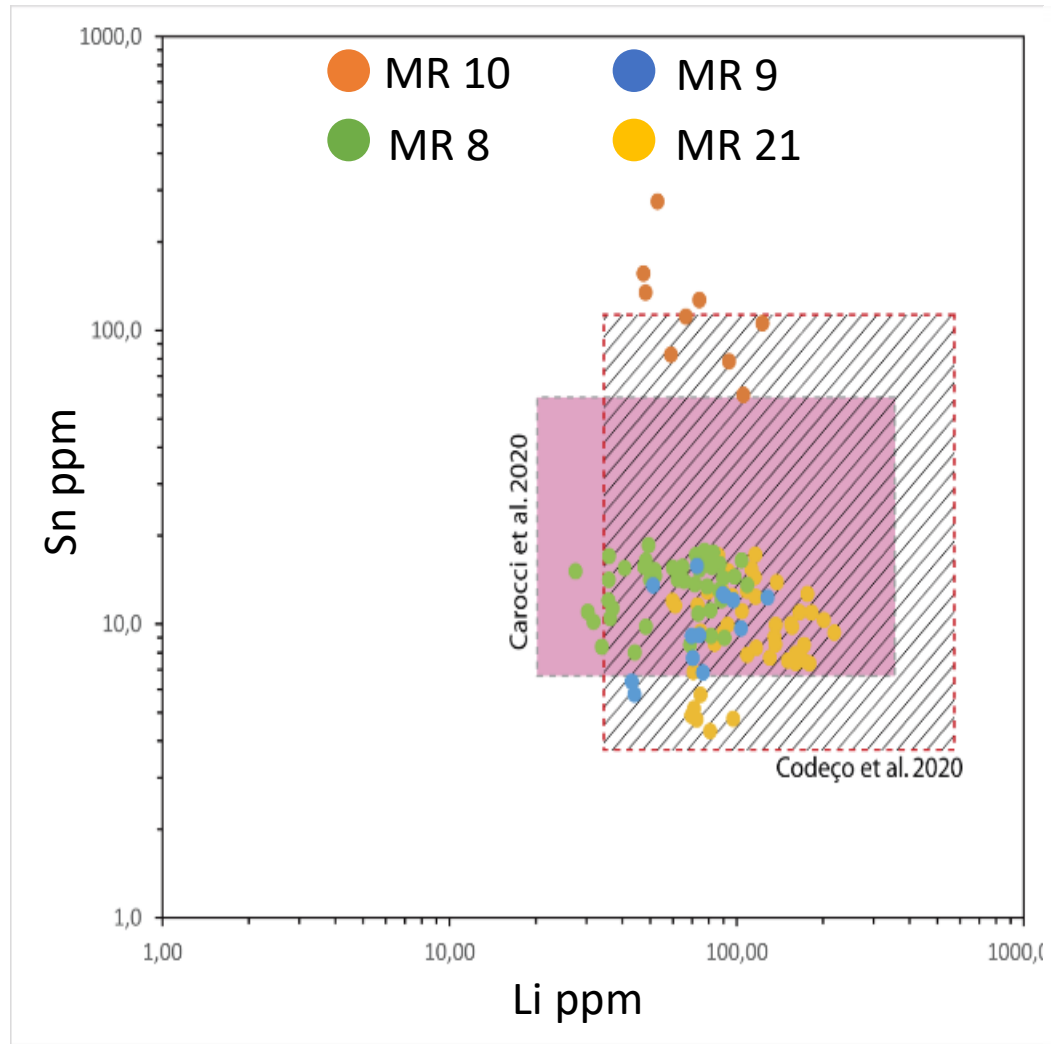
Trace elements in tourmalines

Comparison Mata Da Rainha and Panasqueira

No simple relationships could be defined between the various trace elements analysed. Values similar to those for Panasqueira tourmalines.

Overlay between the data in the diagrams indicates that the same processes are involved in both zones.

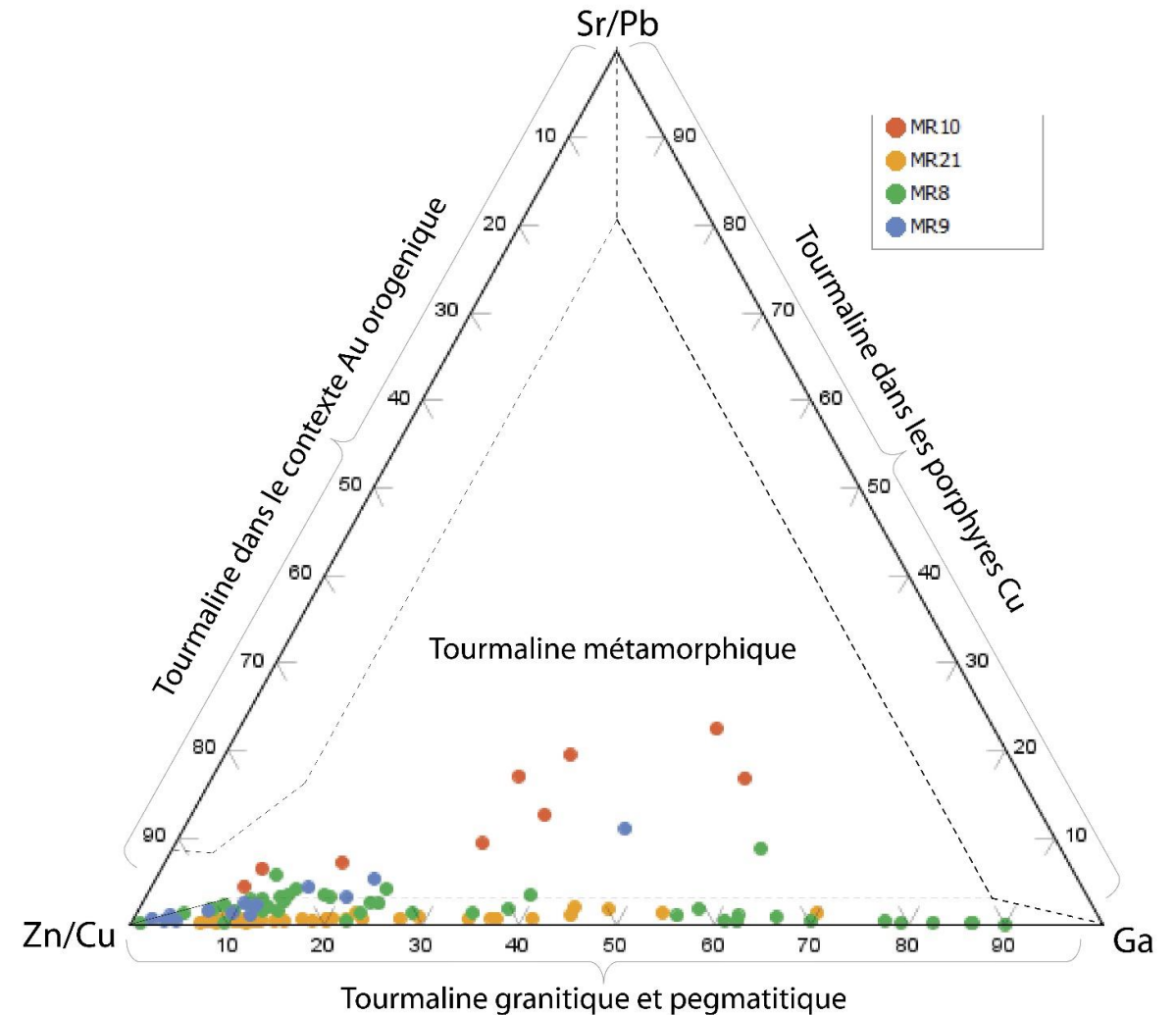
Influence of the host schists on the quantities of trace elements incorporated into tourmaline.



Origin of trace elements in tourmalines



- The composition of tourmalines is partly controlled by the nature of the altered rocks and the physico-chemical conditions of formation.
- Systematic zonation of major element concentrations (Mg, Fe, Ti, Ca)
The succession of dark and light bands on a micrometric scale, linked to the availability of elements in the percolating fluids. (Norton and Dutrow, 2001 ; Dutrow and Henry, 2011).
- Enrichment of fluids with Fe and Ti as in the case of magmatic tourmalines (Marks et al., 2013 ; Da Costa et al., 2014 ; Fischer et al., 2023).

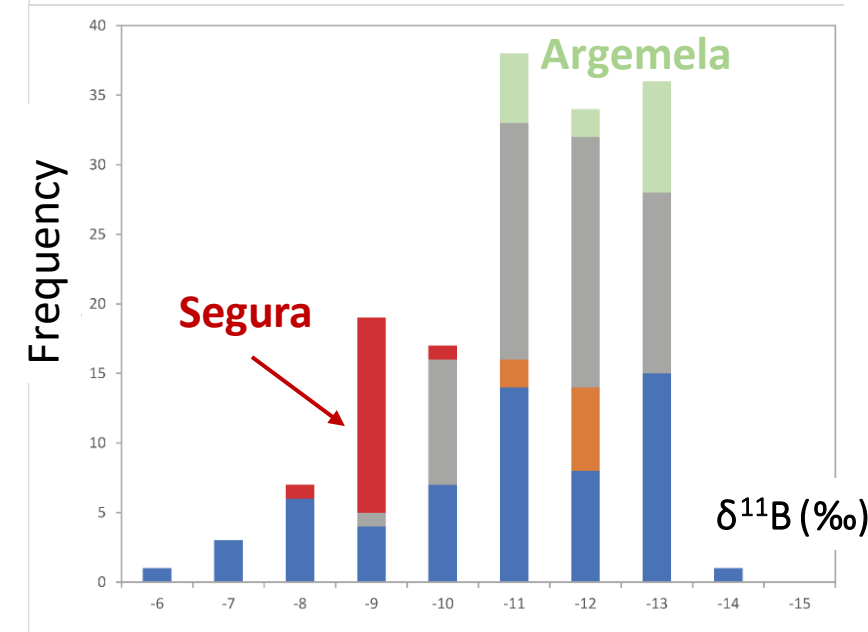
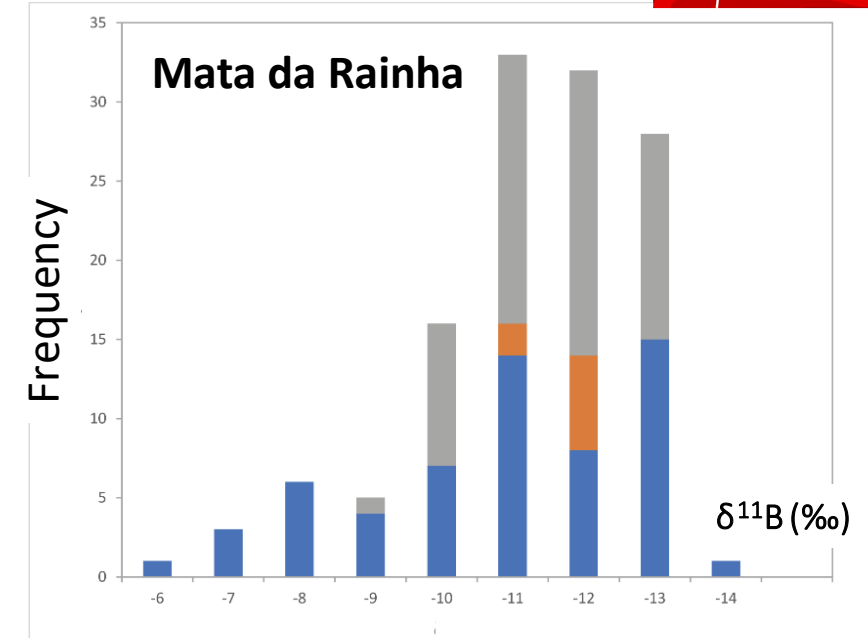
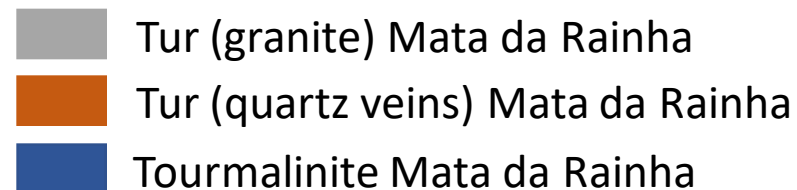


The low Sb/Pb ratio would also suggest a magmatic origin.

Boron isotopic composition of tourmalines

- MR21 (quartz-tourmaline and greisen) and MR10 (quartz vein) $\delta^{11}\text{B}$ between -10 and -13 ‰).
- MR8 (schists) $\delta^{11}\text{B}$: -7 to -13 ‰ similar to the tourmaline-bearing rocks of Argemela, but larger range
- Magmatic Fe-rich tourmaline from Segura dykes are the only ones showing distinct values

Echantillon	Faciès	Nombre mesures	$\delta^{11}\text{B}$ (‰) Minimum	$\delta^{11}\text{B}$ (‰) Maximum	Moyenne	Mode
MR21I	granite	58	-13,56	-10,35	-12,10	-11, 34
MR10	vein	8	-12,91	-11,69	-12,50	-
MR8	Host rock	59	-14,00	-6,76	-11,22	-8,84
ARGEMELA 32	Host rock	7	-11,23	-8,68	-10,41	-
ARGEMELA 1	Host rock	9	-12,89	-10,40	-11,18	-
SEGURA 2-1	Host rock	8	-10,01	-8,81	-9,50	-



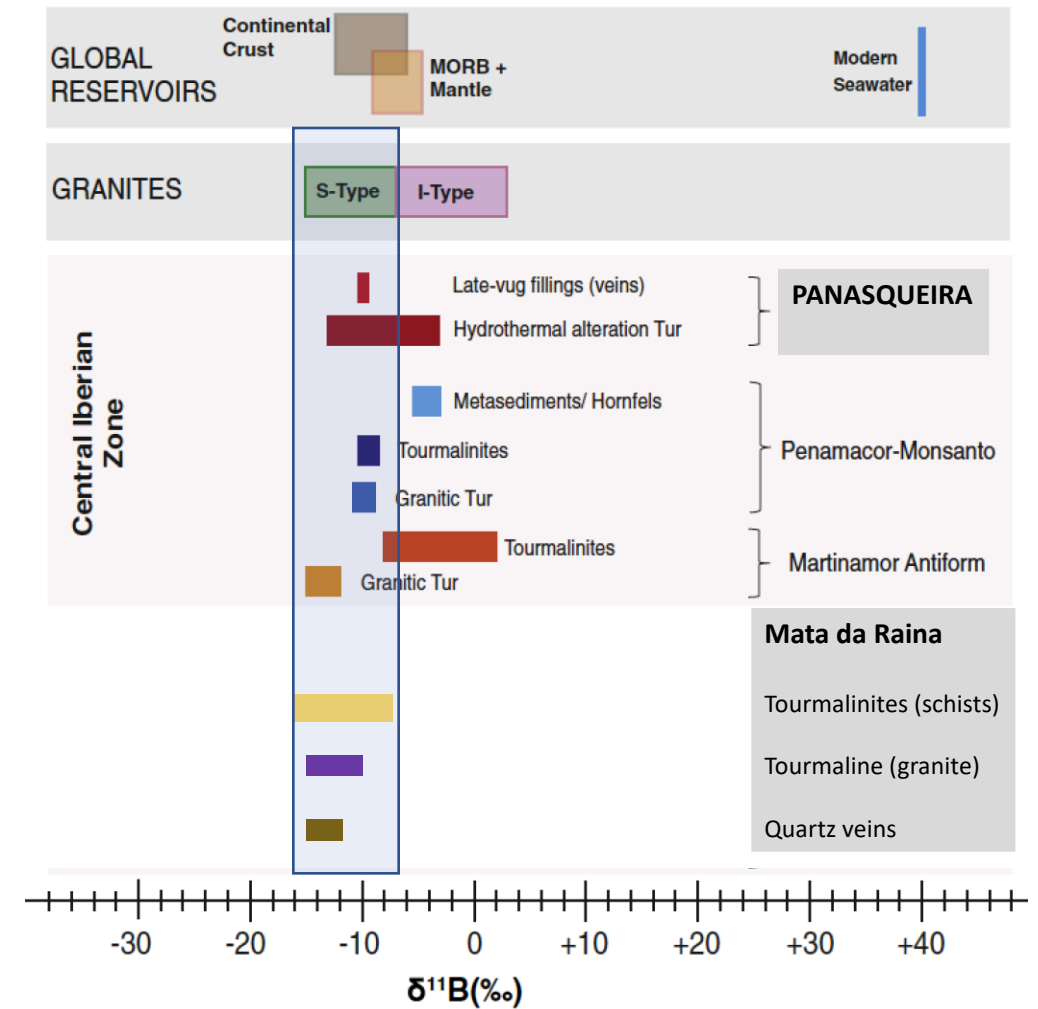
Boron isotopic composition of tourmalines

The tourmalines (quartz-tourmaline and greisen veins) were developed on a hydrothermal edge of the magmatic-hydrothermal system associated with the Orca granite.

The very strong tourmalinisation of the schists produces tourmalines whose isotopic characteristics are slightly more extended but centered on the same values.

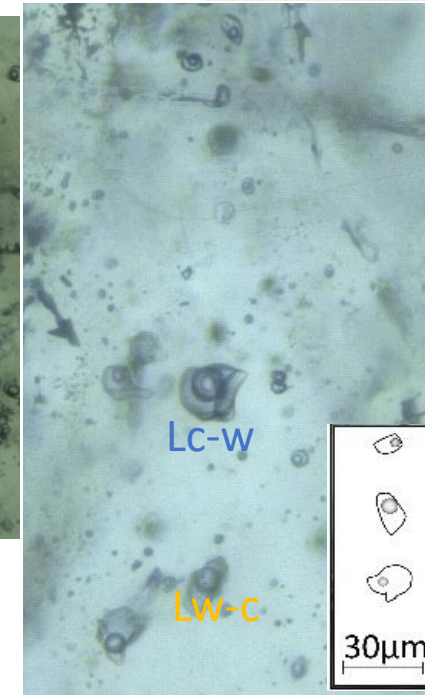
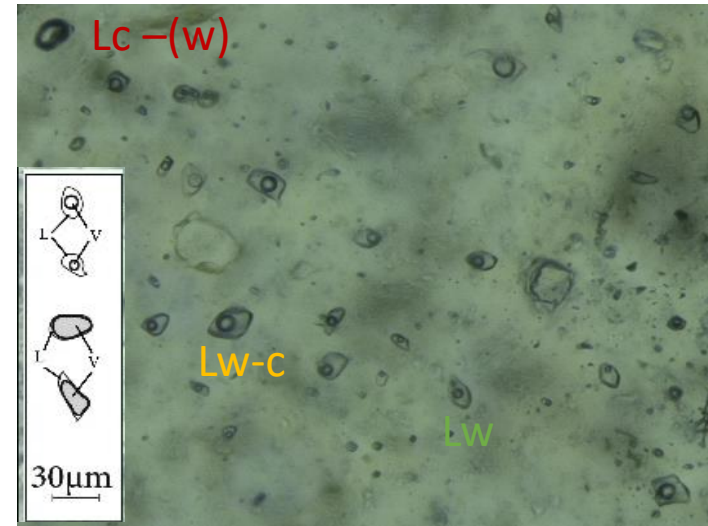
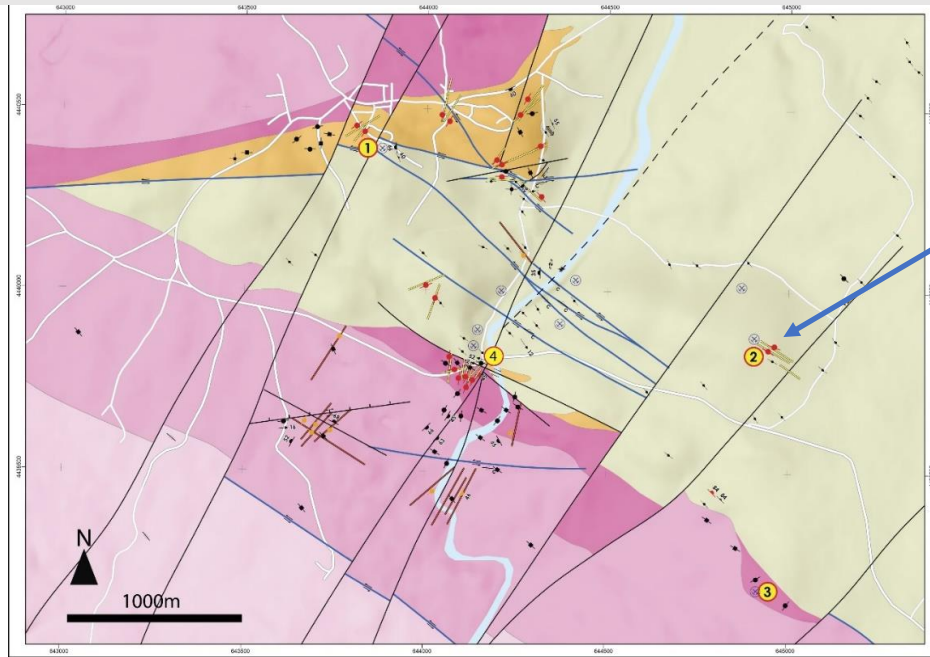
At Panasqueira according to Codeço et al., (2017), a significant amount of boron is required. For Codeço, this implies a magmatic source. But remains to be demonstrated.

Values of $\delta^{11}\text{B}$ around -10/ -11 ‰ are effectively close to those of magmatic tourmalines and S-type granites.



Ribeiro da Costa et al 2013 ; Codeço et al., 2017

Fluids in quartz lodes



Aqueous carbonic fluids

Lc-w : abundant, size < 30µm, 3-phases (LH₂O, LCO₂ et VCO₂, vapor phase 20 to 40 %).

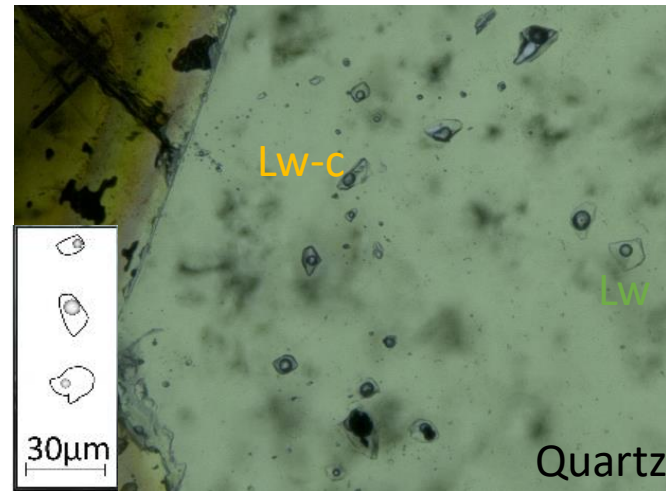
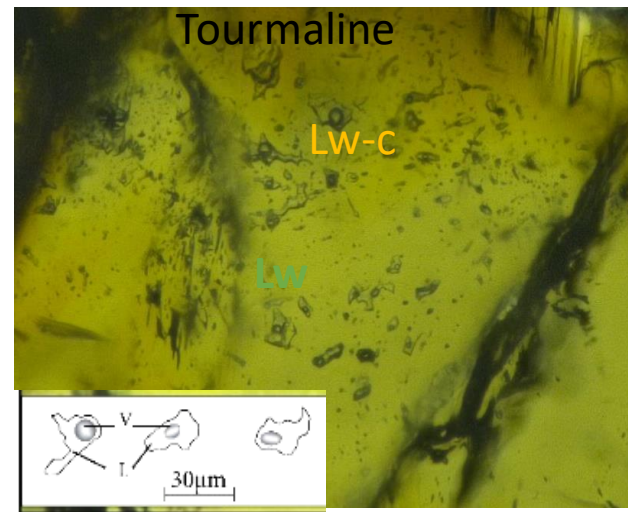
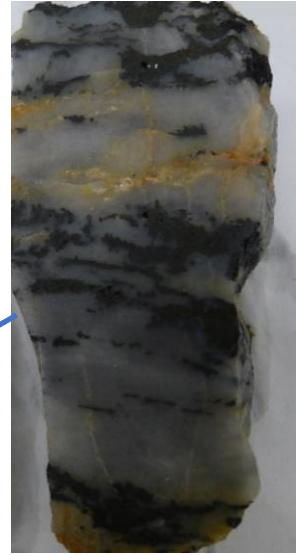
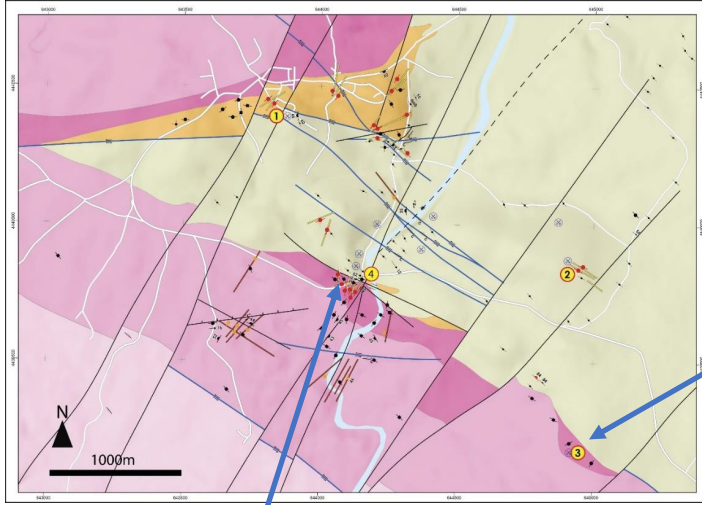
Lc and Lc-(w) : few, size < 30µm, vapor phase (90 to 95%) ± water coating

Lw-c : abundant, size < 30µm, lfs 2 phases (LH₂O VCO₂, vapor phase de 10 to 40 %).

Aqueous fluids

Lw less abundant size :10-30µm. 2 phases, vapor phase 15 to 40 %.

Fluids in quartz and tourmaline



Aqueous carbonic fluids

Lc-(w) and Lc-w : very few, size < 30µm, 3-phases (LH₂O, LCO₂ et VCO₂) vapor phase 20 to 45%.

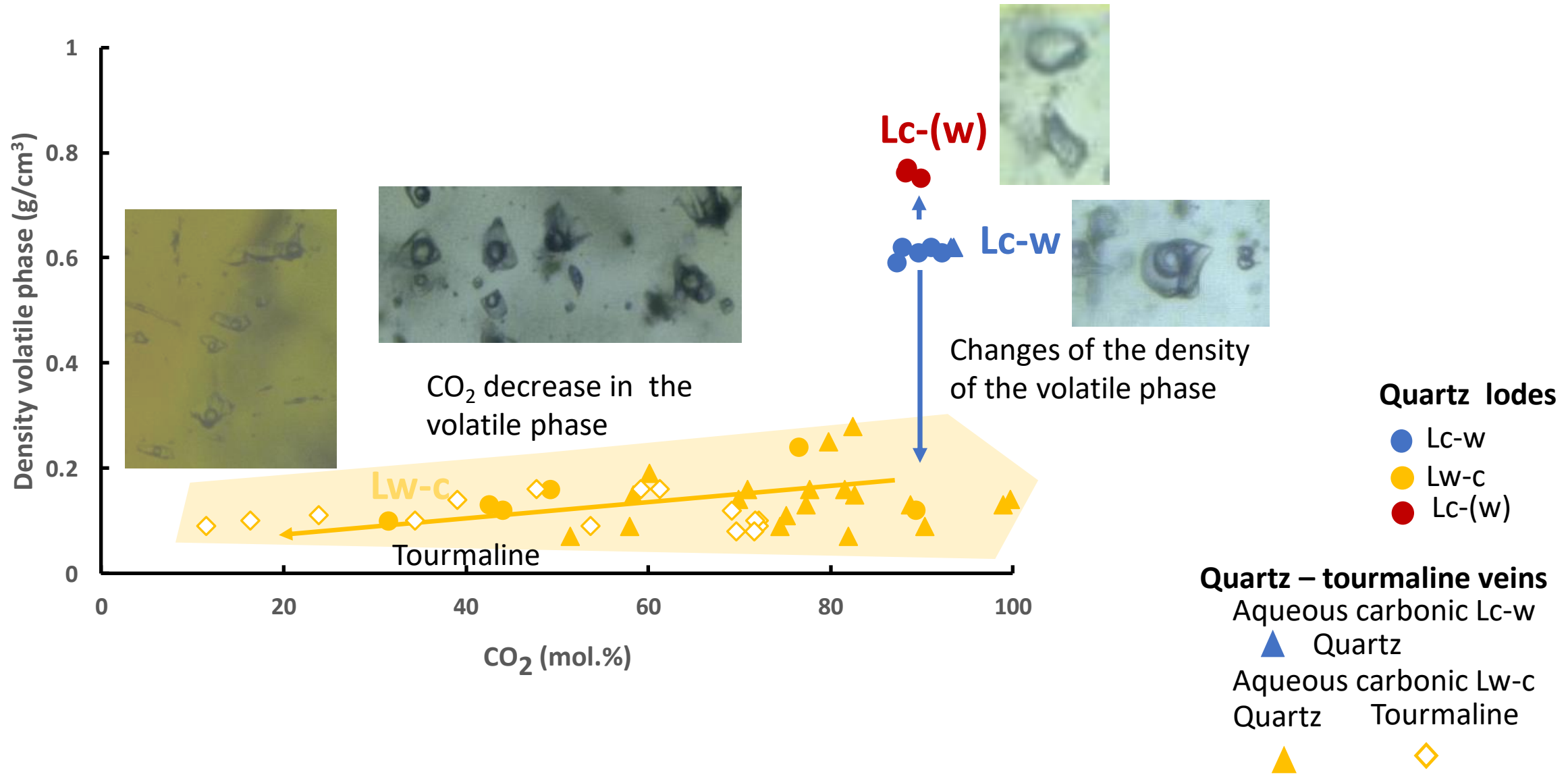
Lw-c : **abundant**, size < 30µm. 2 phases (LH₂O VCO₂) vapor phase 15 to 45%.

Aqueous fluids

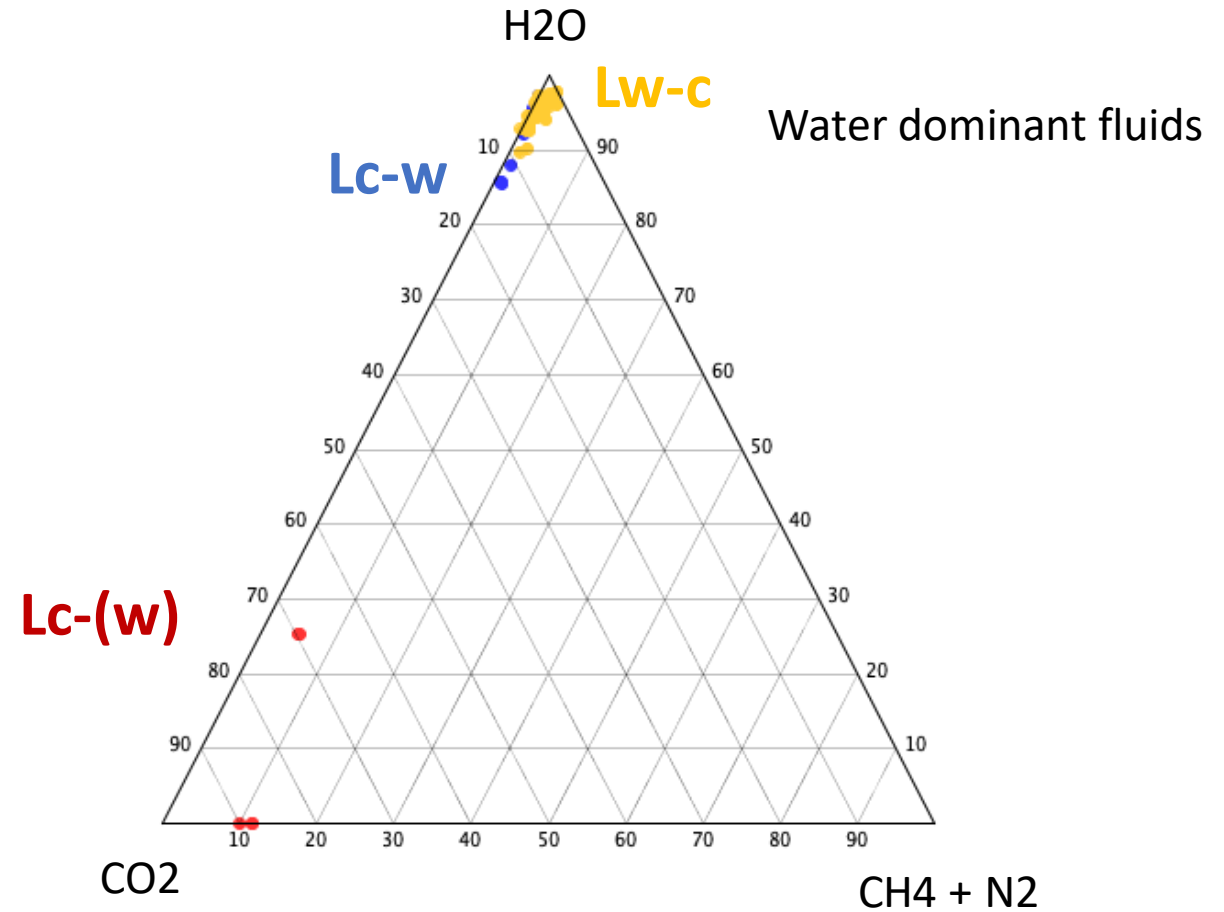
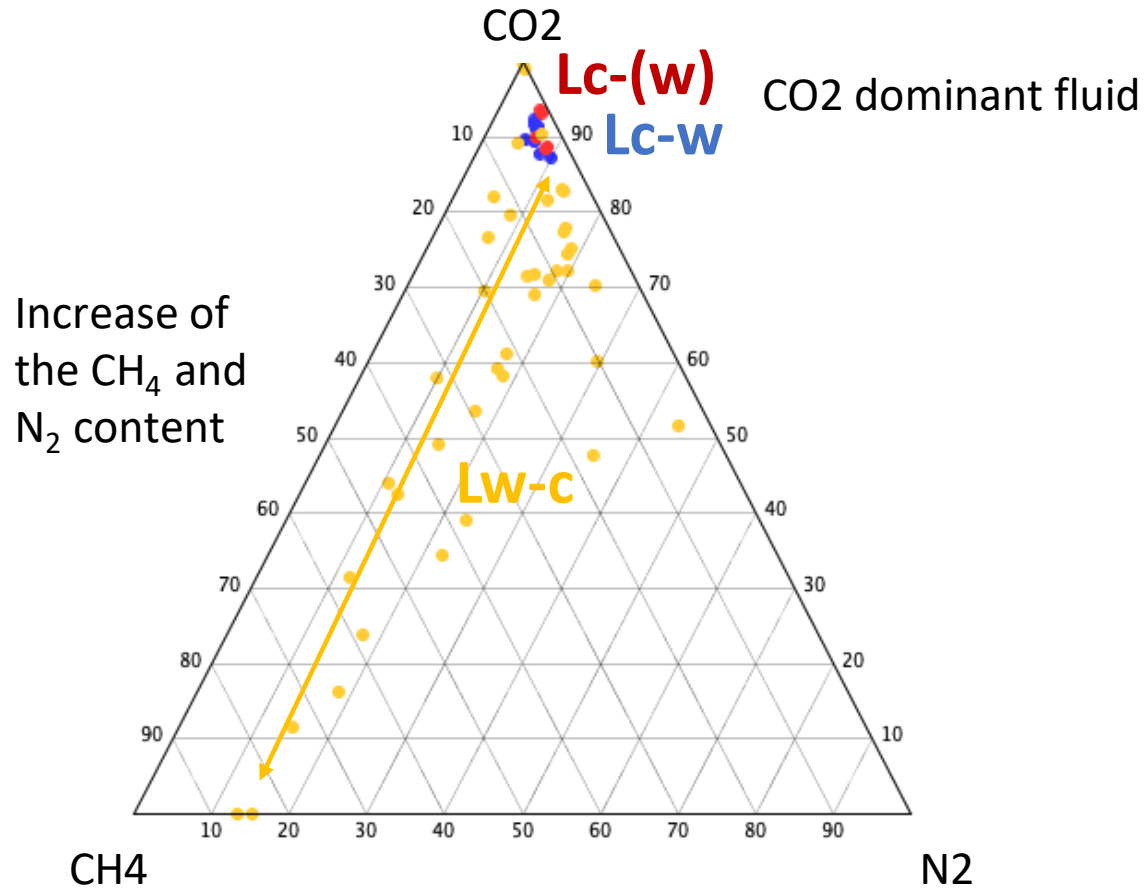
Lw : **abundant**, size 10-30µm. 2 phases, vapor phase 15 to 30%.

Fluids in quartz and tourmaline

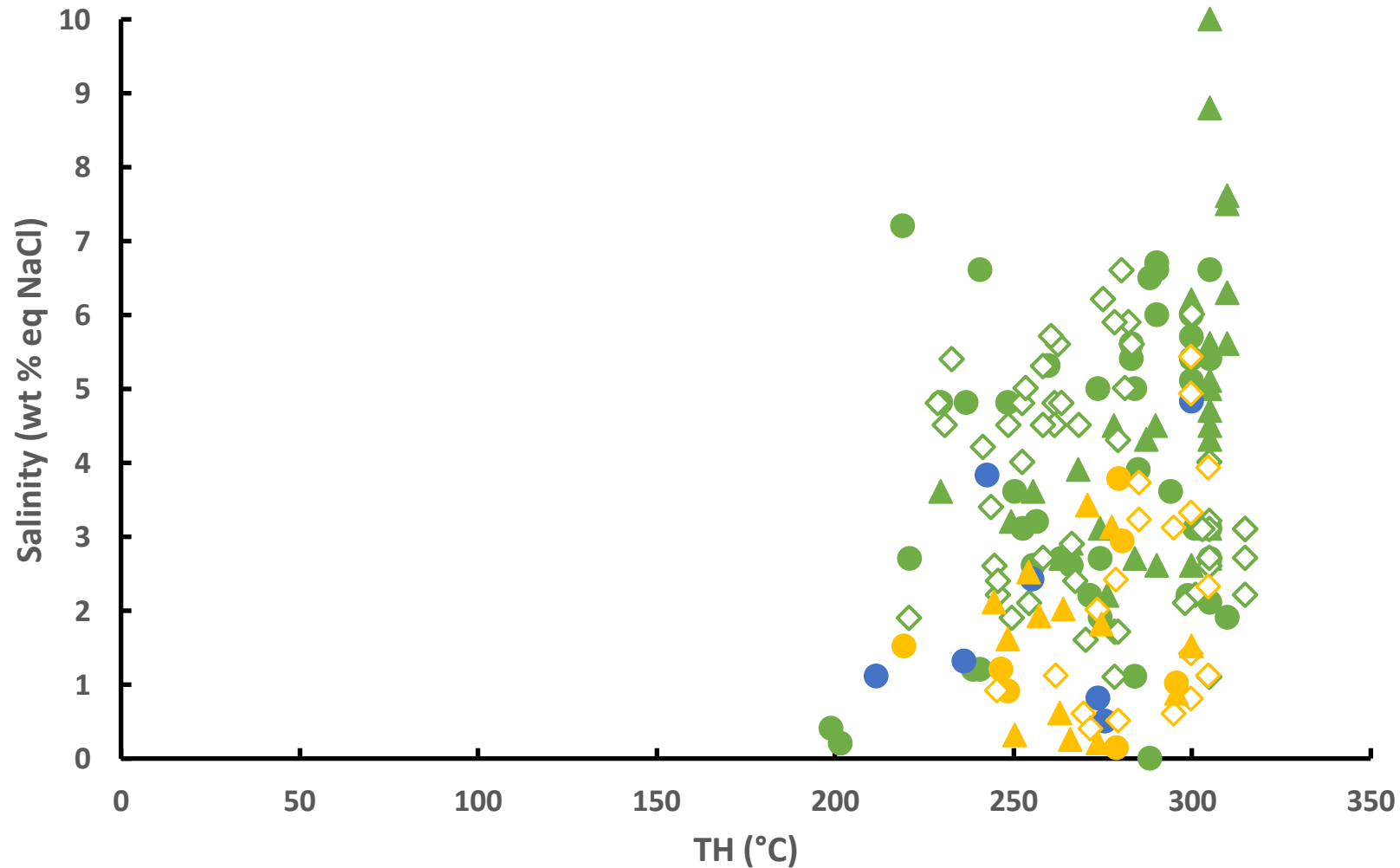
Aqueous-carbonic fluids



Fluids in quartz and tourmaline



Salinity and minimal trapping temperature of the fluids



Quartz lodes

- Aqueous carbonic Lc-w
- Aqueous carbonic Lw-c
- Aqueous Lw

Quartz-tourmaline veins

Quartz

- ▲ Aqueous carbonic Lw-c
- ▲ Aqueous Lw

Tourmaline

- ◇ Aqueous carbonic Lw-c
- ◇ Aqueous Lw

P-T Conditions and origin of fluids

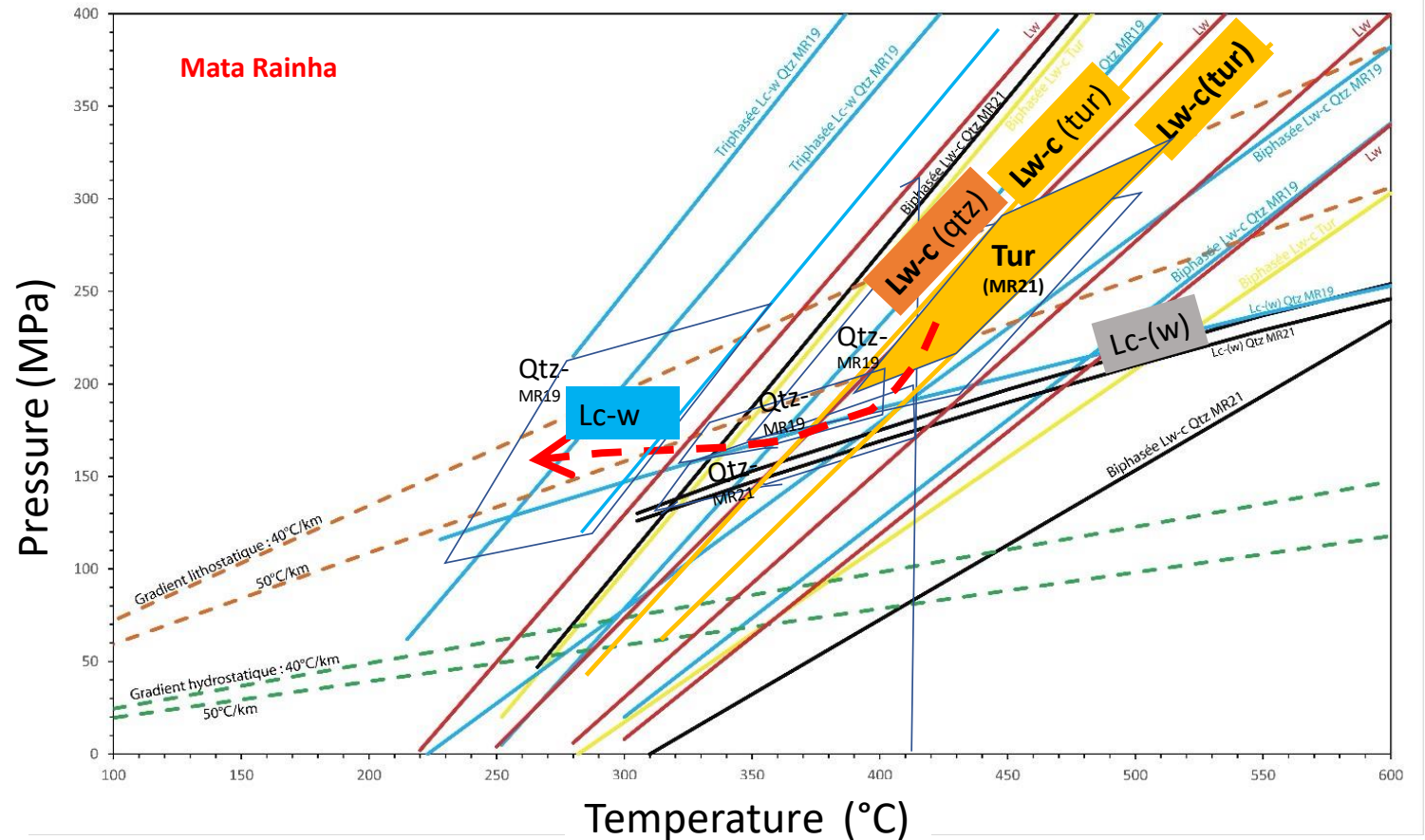
Evolution in three stages

- 1) Crystallization of tourmalines (MR21) and first quartz stage: Aqueous fluids (Lw) trapped at temperatures of 320-470°C and lithostatic pressures (180-280 MPa), gradients of 40-50°C/km
- 2) Pressure drop >> trapping of Lc and Lc-(w) inclusions
- 3) Lc-w water-carbonic fluid inclusions from MR19 (quartz lodes) and Lc-w, Lw-c from MR21 (tur quartz) = 240 to 290°C under lithostatic pressures.

Most fluids are predominantly aqueous, with moderate to low salt content and a minor volatile phase of decreasing density

>> composition of the fluids are not representative of demixed fluids from granitic magmas.

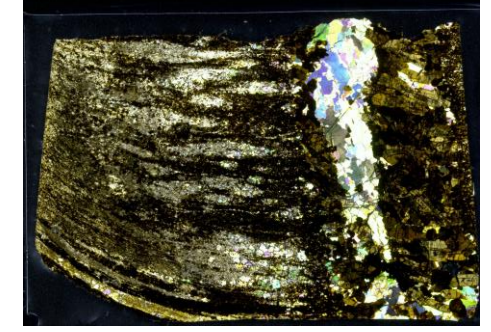
>>> fluids linked to migmatization at depth, interaction with the metamorphic host rocks.



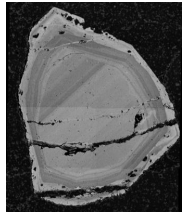
Main Conclusions

Expression of Tourmaline at Mata da Rainha

- Tourmalinisation around syn-deformational quartz veins
- Tourmaline in mineralized quartz veins from the deposit
- Tourmaline in and at the contact with greisens
- Tourmalinized schists cemented by quartz



Chemistry of Tourmaline.



- Variations mostly for Fe, Ti, (Mg, Mn and sometime Ca).
- Ti, Fe and Ca more concentrated in the outer dark bands, Mg enriched in the core of zoned tourmalines
- Zn and Mn remain constant (800 to 1000 ppm). Other elements show concentrations of 100 ppm or less

Boron isotopic composition of tourmalines

- $\delta^{11}\text{B}$ around -10/ -11 ‰ are close to those of magmatic tourmalines and S-type granites.
- Very strong tourmalinisation of the schists produces tourmalines whose isotopic characteristics are slightly more extended ($\delta^{11}\text{B}$: -7 to -13 ‰) but centered on the same values.

P-T Conditions and origin of fluids

- Evolution in three stages, from 320-470°C and lithostatic pressures, 180-280 MPa, gradients of 40-50°C/km to 240 and 100-150 MPa
- Interaction of fluids with the metamorphic host rocks.
- Composition of the fluids are not representative of demixed fluids from granitic magmas

Significant mobility of boron by hydrothermal fluids in this area