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# The use of $\mu$ XRF to resolve textural and mineral arrangements

**Michel Cathelineau**, Marie-Christine Boiron

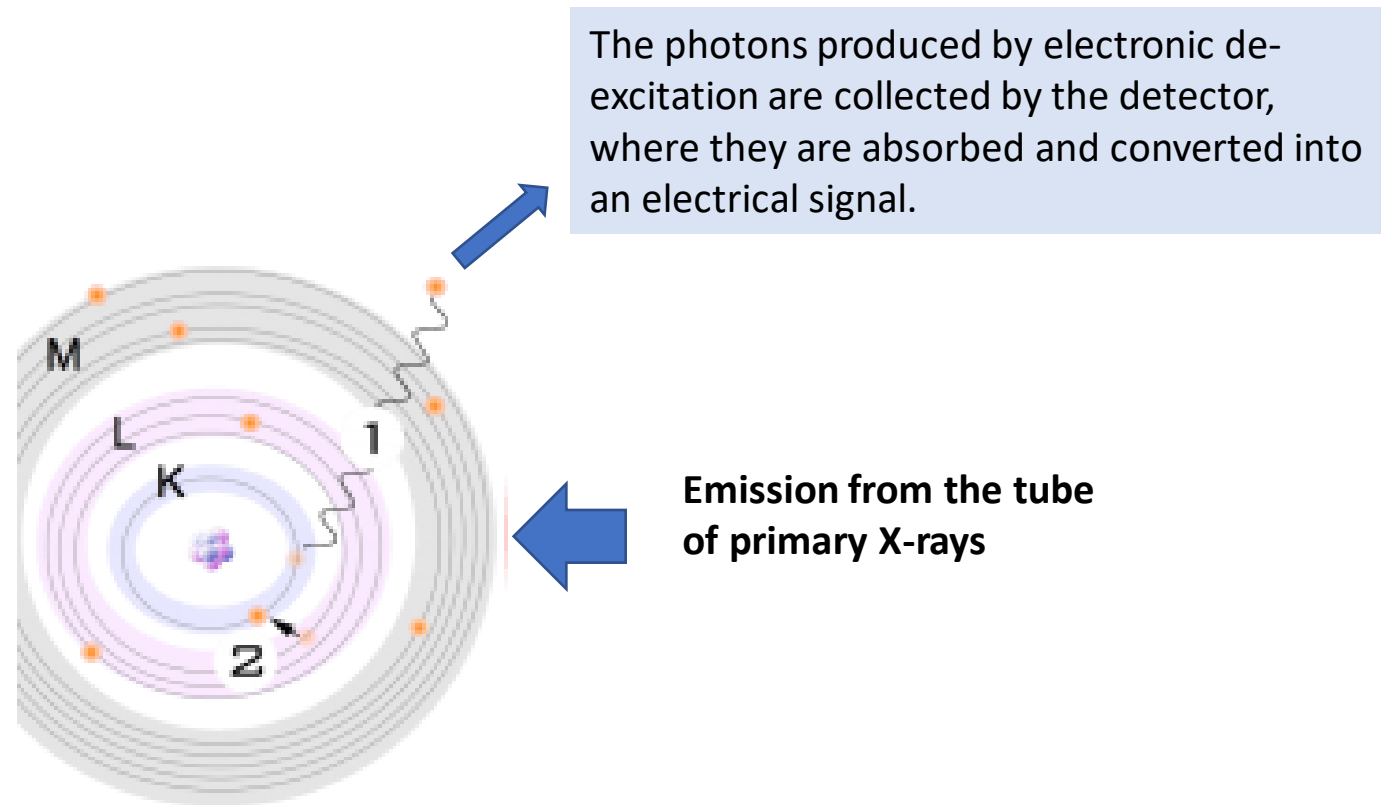
in coll.

Ivo Martins, Antonio Mateus

## Principles behind X-ray fluorescence

In X-ray fluorescence, **irradiation by a beam of primary X-rays from an X-ray tube causes the emission of fluorescent X-rays with discrete energies characteristic of the elements present in the sample.**

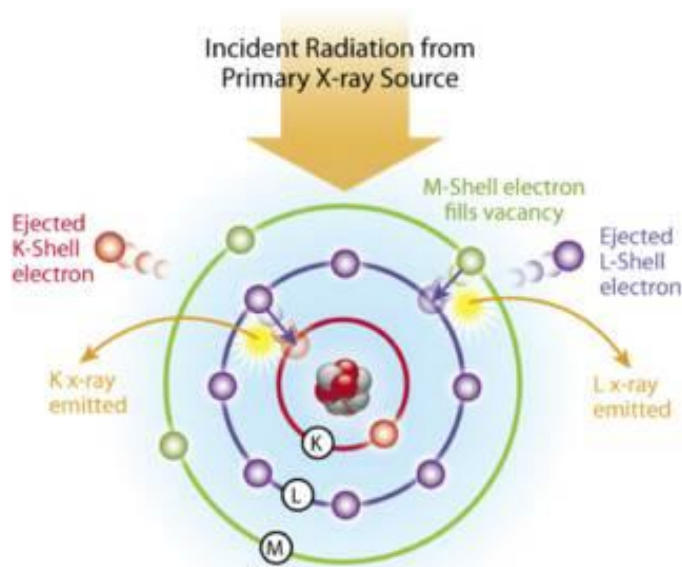
>>> measurement of the wavelength and intensity of the 'light' (X-rays in this case) emitted by the energised atoms in the sample.



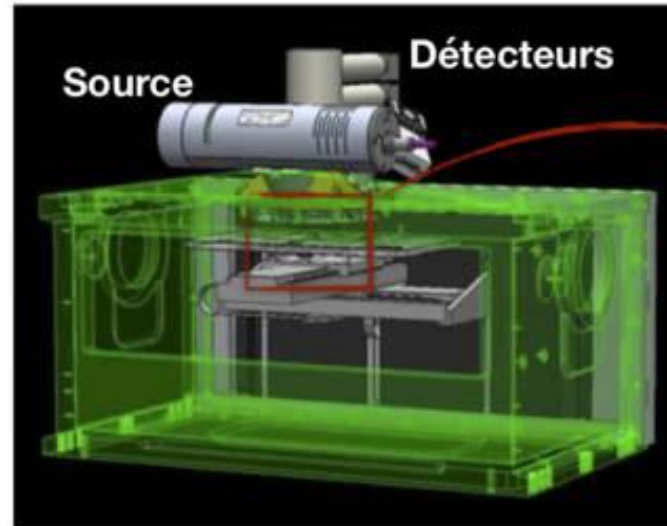
the incident photons are able to eject electrons from the K, L or M layer orbitals of the atoms making up the sample, creating a vacancy (1) and therefore an unstable excited state.

An electron located in a more external orbital can then fill this gap, and the atom tends towards a 'less unstable' state (2) releasing energy in the form of a secondary X-ray photon (fluorescence).

Each photon generated by the electronic reorganisation can be collected by the detector's semiconductor crystal. It generates a current, which is amplified, converted to voltage and digitised in an ADC (analogue-to-digital converter). It is then assigned a channel number (in the multi-channel analyser).



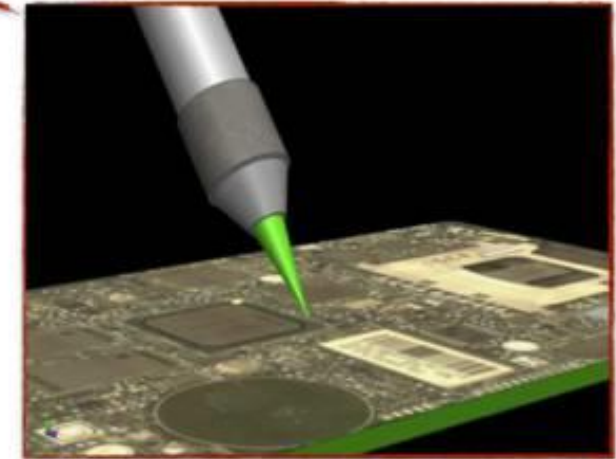
X-ray fluorescence emission and electronic transitions



### Determining elemental composition

The technology used to separate (disperse), identify and measure the intensity of the X-ray fluorescence spectrum of a sample gives rise to two main types of spectrometer: wavelength-dispersive (WDXRF) and energy-dispersive (EDXRF) systems.

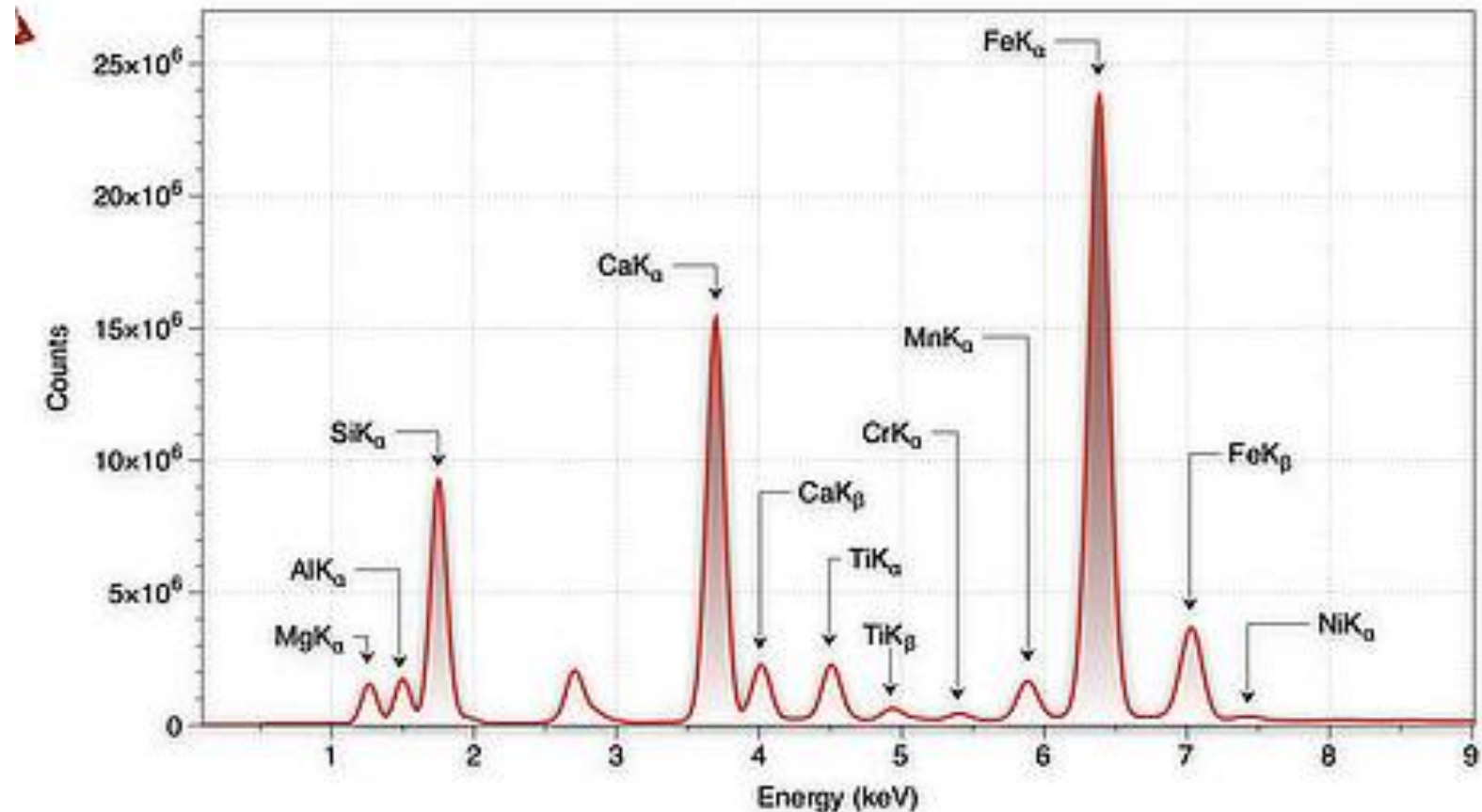
*Poly-capillary optics focusing X-ray tube radiation*



Signal intensity is added to a discrete graph called « spectrum », the X axis of which is the channel number (energy of the photon analysed) and the Y axis is the intensity (number of photons collected at each energy). The area under each line in the spectrum is representative of the concentration of the chemical element it represents.

## For each pixel of 20 microns in diameter, a spectrum is obtained

It is possible to detect elements from **sodium to uranium with variable detection limits:** from a few percent for the lightest elements (sodium) to less than **ten ppm for the elements most sensitive to this technique (e.g. zirconium).**



The M4 Tornado (Bruker) enables semi-quantitative and quantitative analysis (calibration required) as well as large-scale 2D chemical mapping (up to 550 cm<sup>2</sup>).  
non-destructive approach  
solids, particles, biological samples, multi-layer systems and liquids.



Microfluorescence X at GeoRessources- Nancy

**Micro X-ray fluorescence ( $\mu$ -XRF or micro-XRF) is an analysis technique based on the principles of X-ray fluorescence (XRF). The difference is that  $\mu$ -XRF has a spatial resolution level at the  $\mu$ m scale, whereas XRF operates at the mm level.**

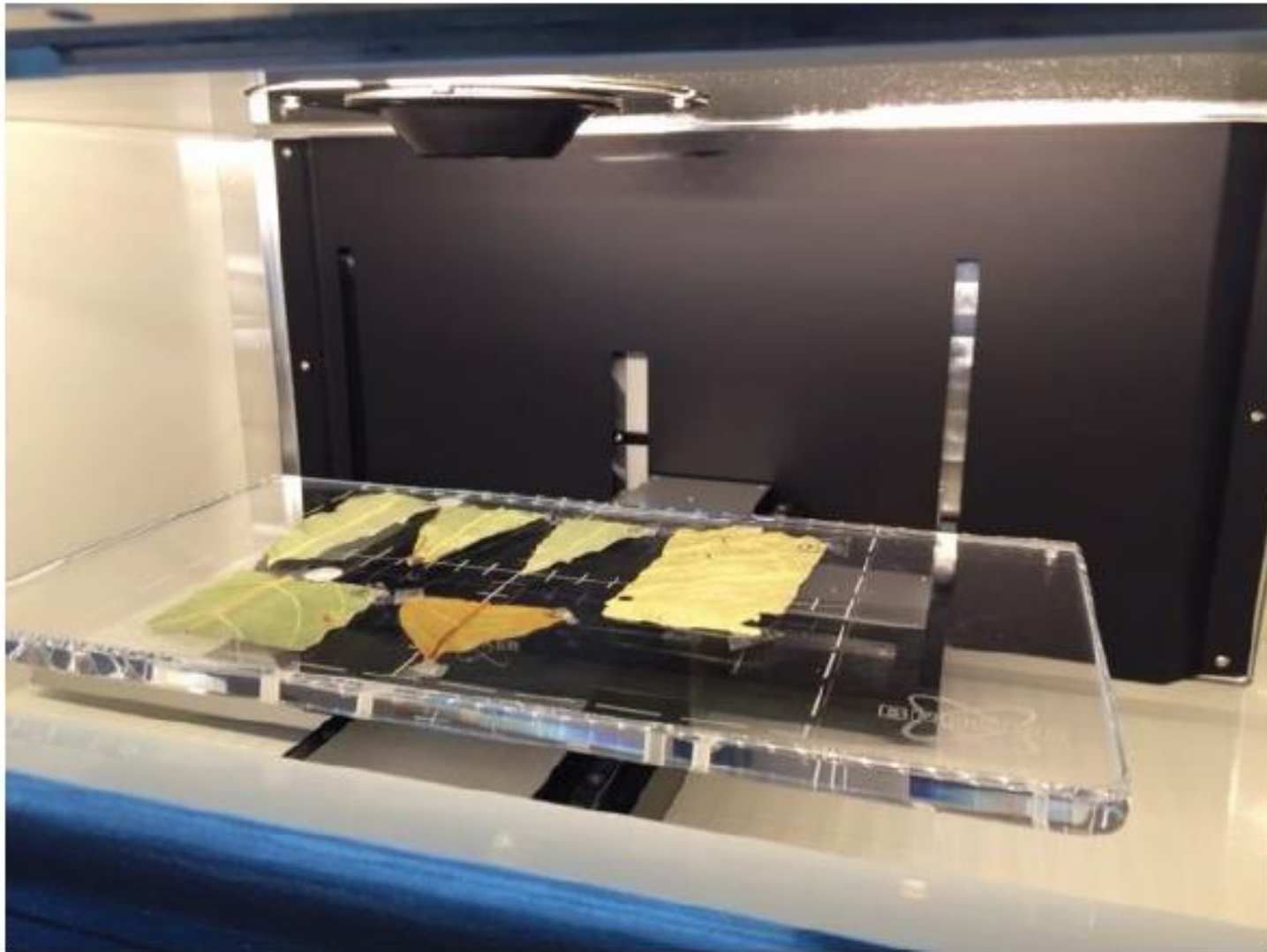
spatial resolution : 20 $\mu$ m

**Specialised polycapillary optics are used to reduce the size of the X-ray beam spot to the  $\mu$ m range.**

It is also possible to rapidly map multi-centimetre samples without any prior preparation (flat sample but no polishing or metallisation).

max. 330 x 170 mm<sup>2</sup>, max. high 120 mm , weight < 5 kg





## Making the image

- scanning the area to be analysed with an adjustable speed (generally from  $10 \mu\text{s}/\text{mm}$  to  $80 \mu\text{s}/\text{mm}$ )
- Distance between pixel from 10 to 120 microns
- Voltage from 200 to 600 mV

## Duration

6 thin sections : around 4-6h

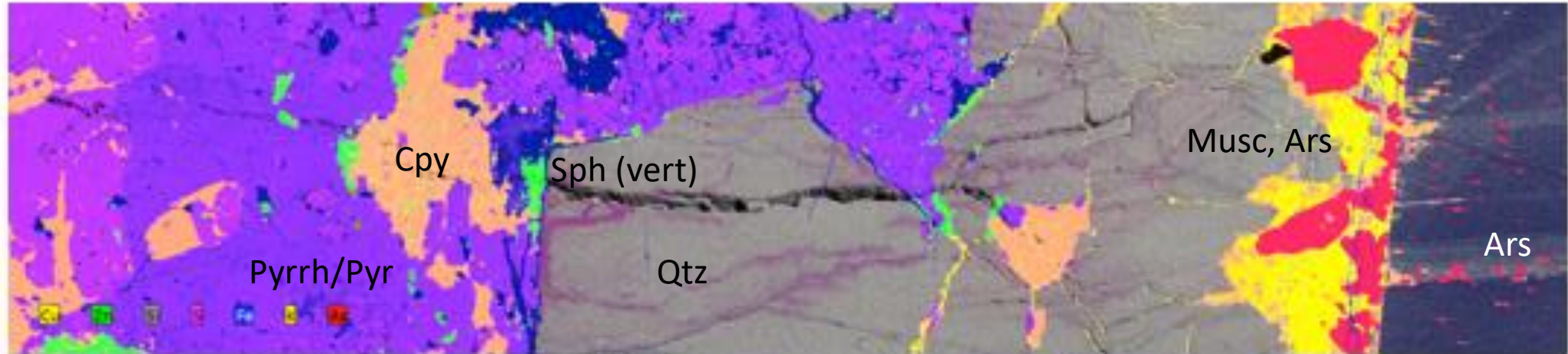
1 core sample 25x 8 cm : 3 to 7h depending of the wished resolution

# Rock sample petrography :

## *A vein from Panasqueira (15 cm long)*

With complex mineral assemblage, combined elemental maps

One element can be converted into only one mineral phase: Si (quartz), K, Al (muscovite), Cu, (Chalcopyrite) , Zn (sphalerite), As (arsenopyrite), P (apatite)





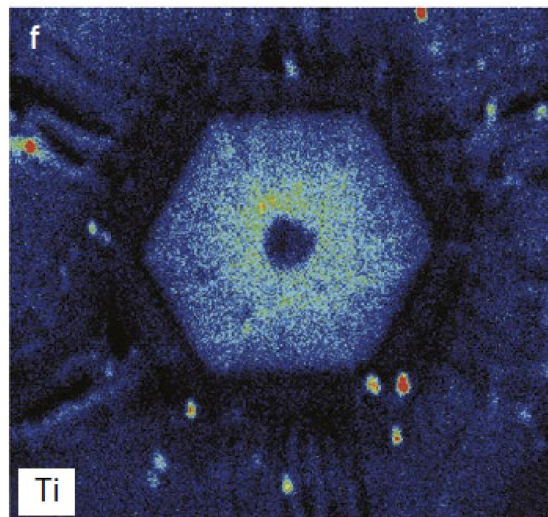
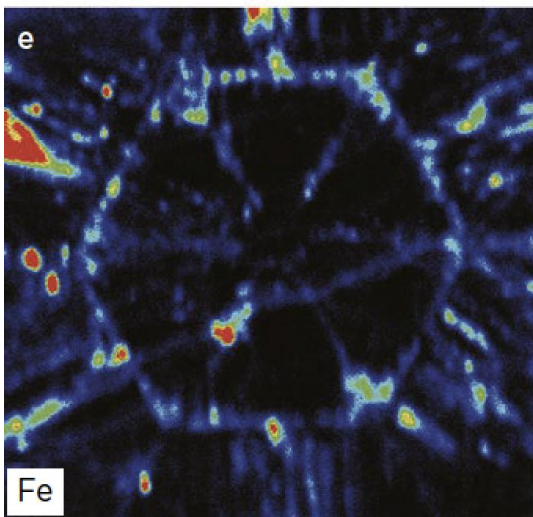
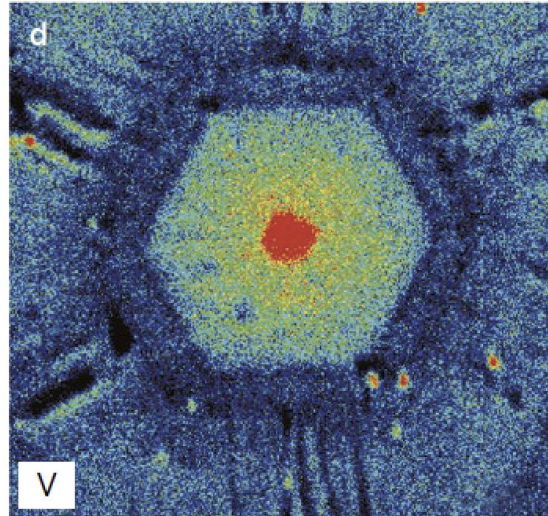
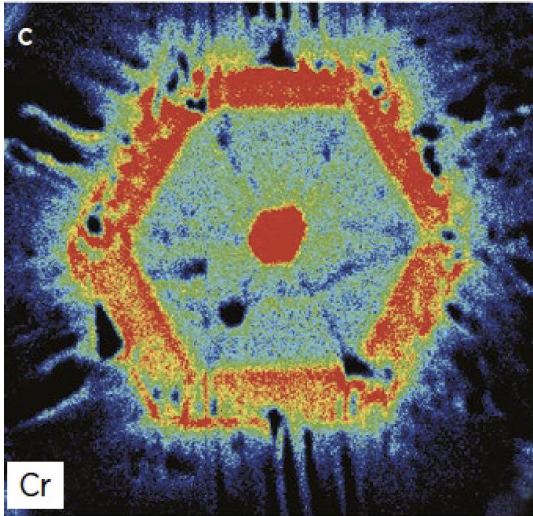
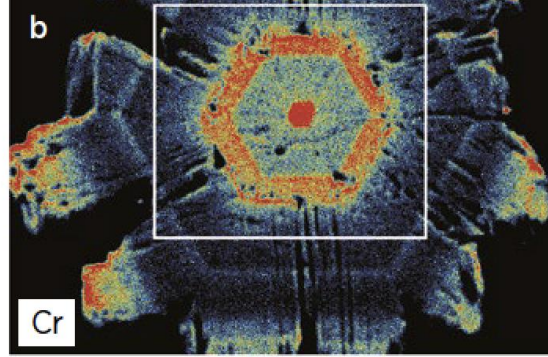
Mapping of a given mineral: growth bands, healing, inclusions

# Flower-Shaped Trapiche Ruby from Mong Hsu, Myanmar: A Revised Growth Mechanism

Isabella Pignatelli, Gaston Giuliani, Christophe Morlot, Michel Cathelineau and Shang I (Edward) Liu

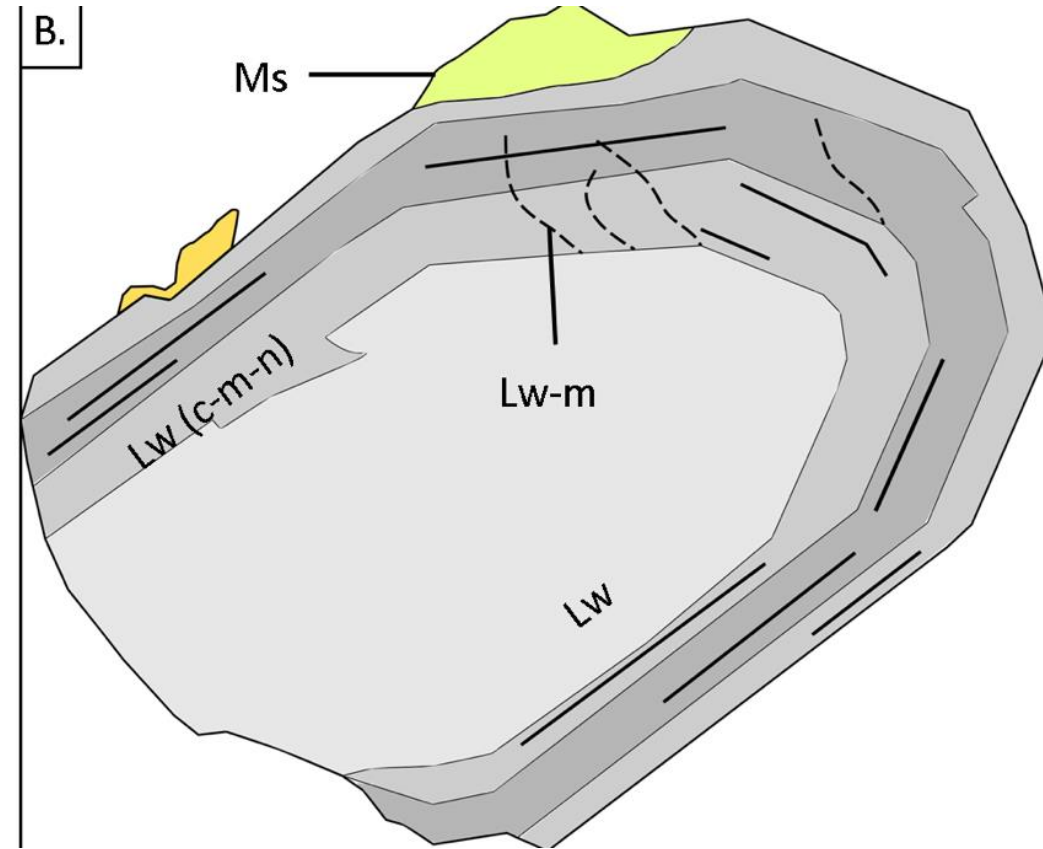
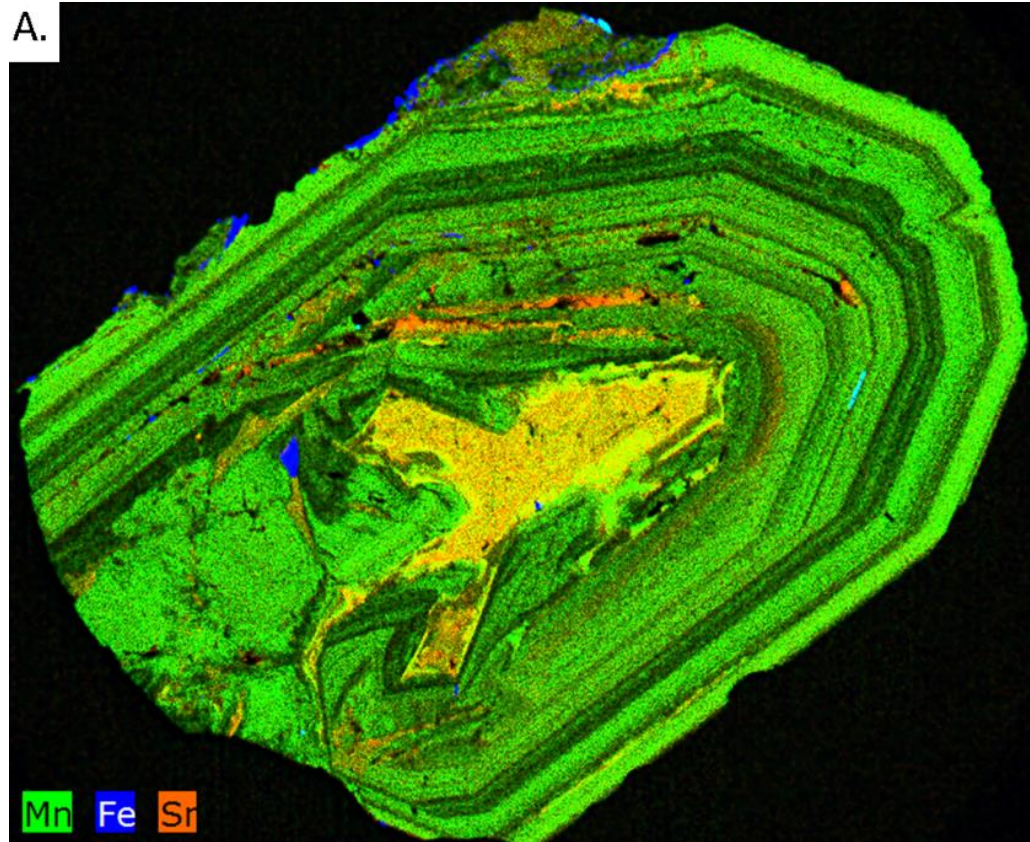
**ABSTRACT:** Two polished slices of flower-shaped trapiche ruby from Mong Hsu were analysed by X-ray computed tomography and X-ray micro-fluorescence. They are characterised by the presence of a core overgrown by two layers of ruby (with the outer one forming the 'petal' shape), and these three domains were previously attributed by Liu (2015) to a multi-stage growth mechanism. The present research indicates that these specimens show textural sector zoning associated with chemical sector zoning. In agreement with literature data, three different growth sectors are identified: a pinacoidal growth sector (corresponding to the core) and two sets of dipyrnidal growth sectors with different inclinations with respect to the *c*-axis. The core, middle and outer layers are thus growth sectors of the same crystal, and no successive stages are needed to explain their formation. Therefore, the growth model proposed for other trapiche rubies from Myanmar also applies to the formation of these flower-shaped specimens. The distinctive shape of these rubies is due to weathering of the growth sectors and the sector boundaries.

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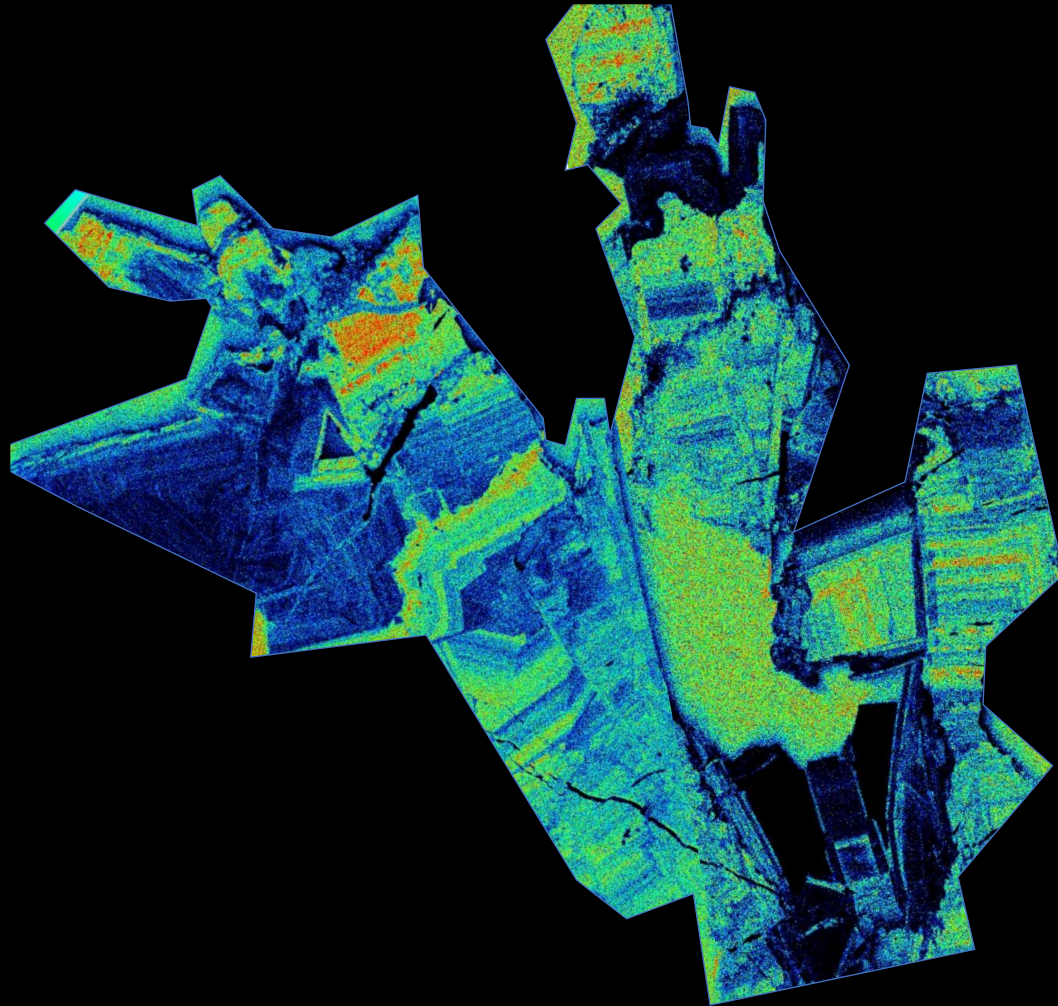
# Relationships between mineral growth bands and location of fluid inclusions in wafers



Example of Mn mapping in an apatite crystal (dimension 3 cm) revealing growth bands, and making it possible to link certain types of fluid inclusions to stages of crystal growth or cracking.

## Distribution of niobium in wolframite

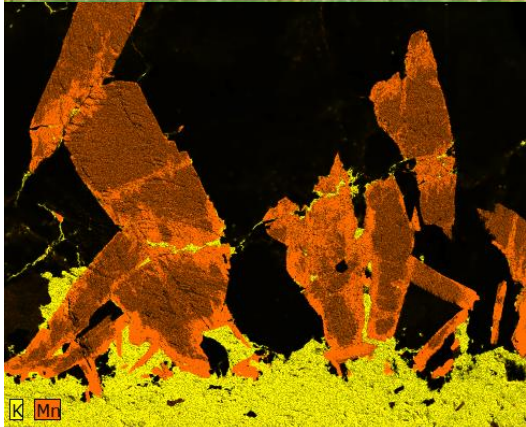
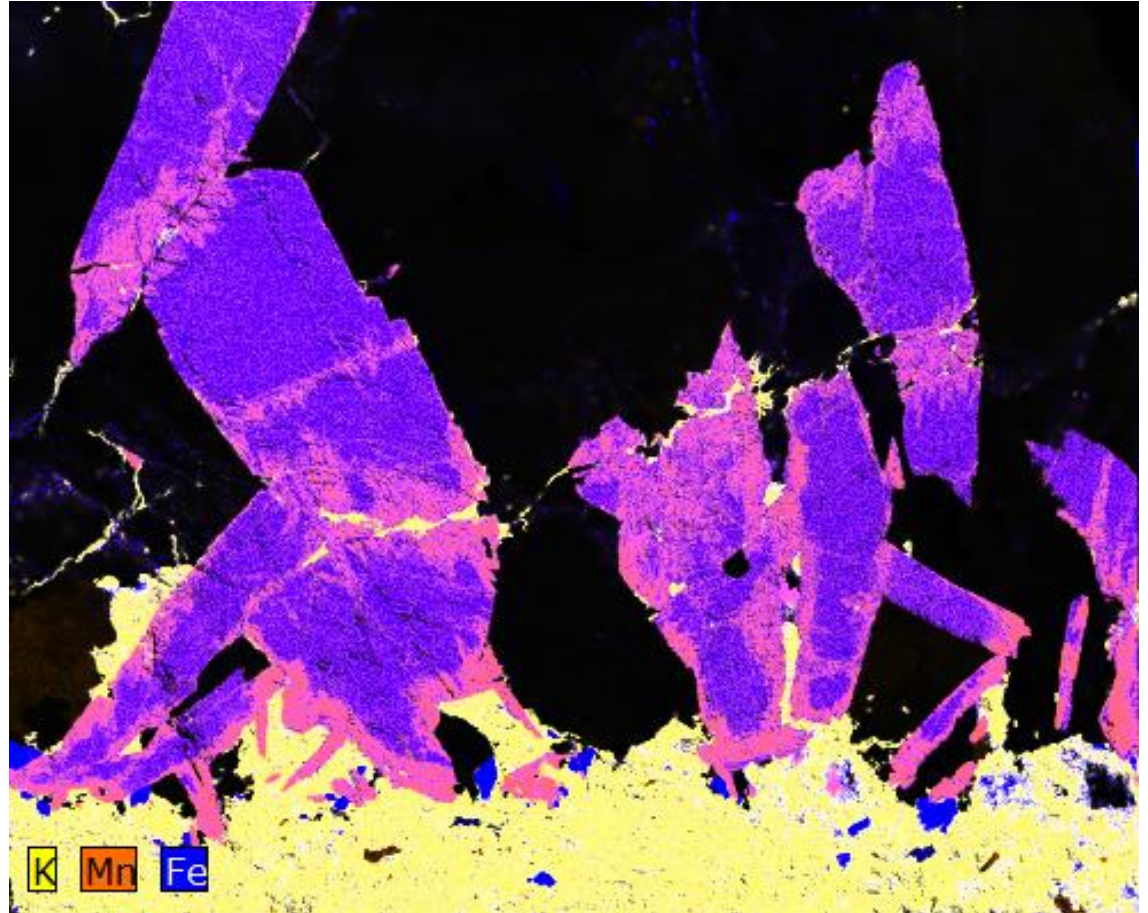
- reveals growth bands
- but also dissolution –recrystallization processes



Panasqueira , PAN-181-2  
L1-D5-R7-AW-15 (pt 181)

(Result NewOres)





**Mn Increase in Wolframite  
when affected by the muscovite stage**

PAN-V-16d  
Bank  
L0-D15-R15-I2  
Pillar 2-1-W-face C

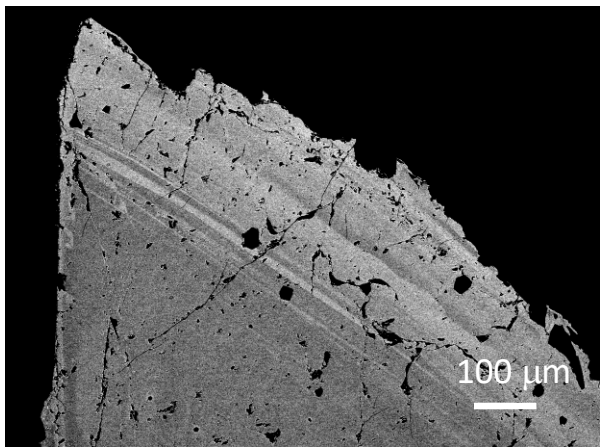
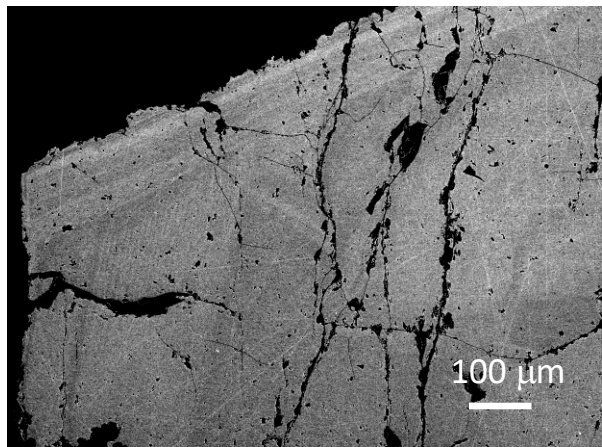
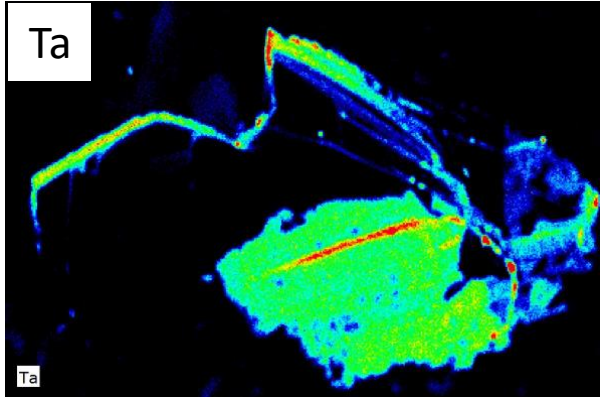
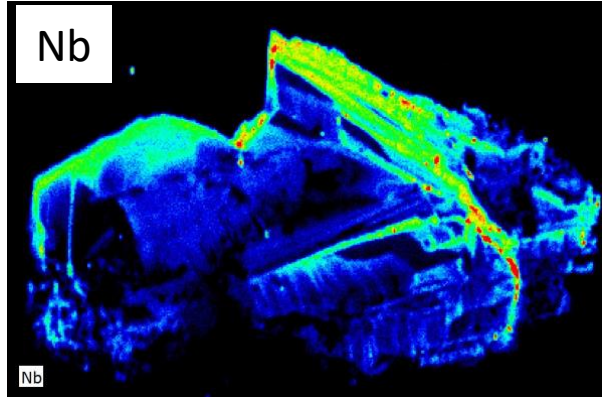
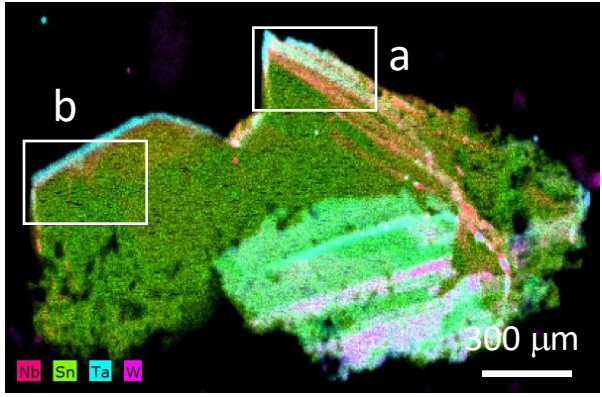
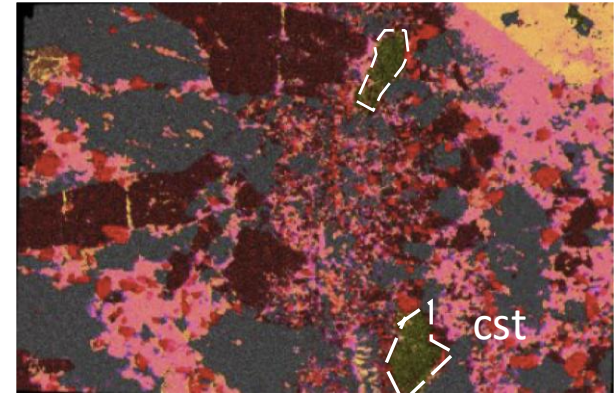
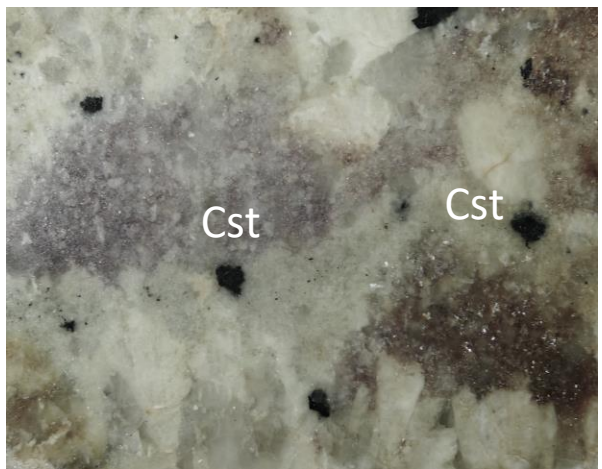
(Result NewOres)



# Cassiterite - second stage in the dykes

Second stage of cassiterite formation :  
large euhedral crystals in lepidolite-rich altered dykes

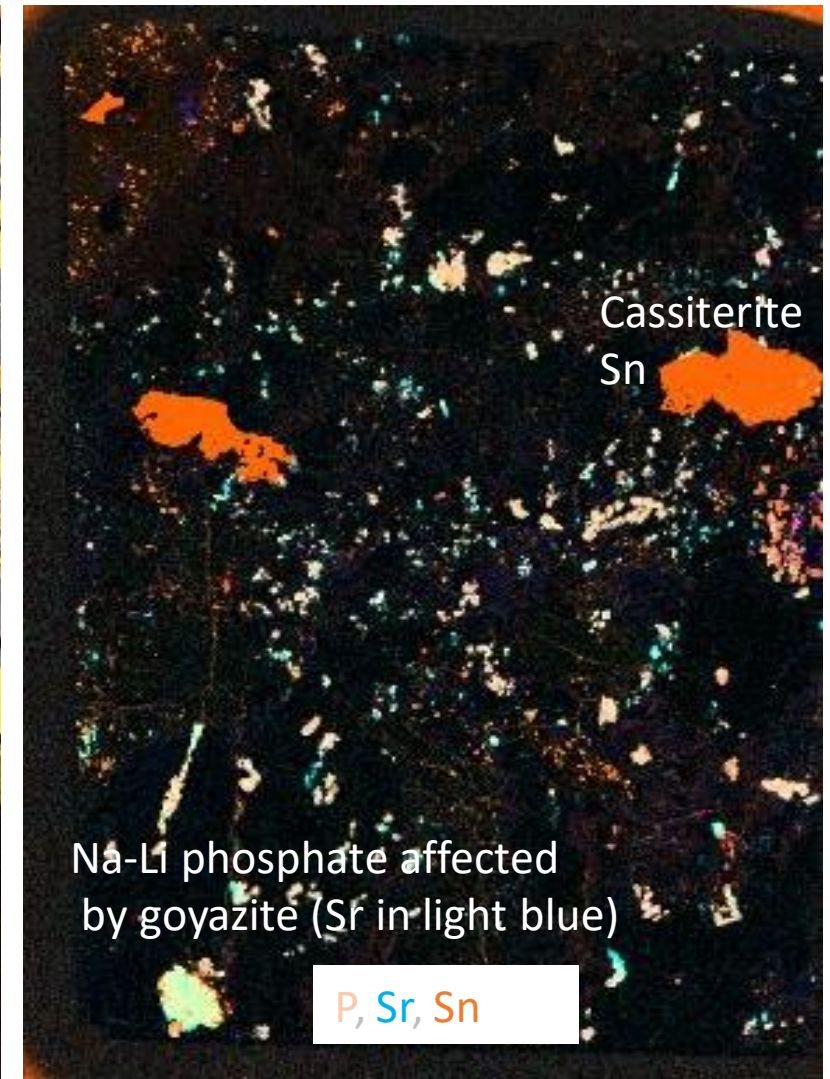
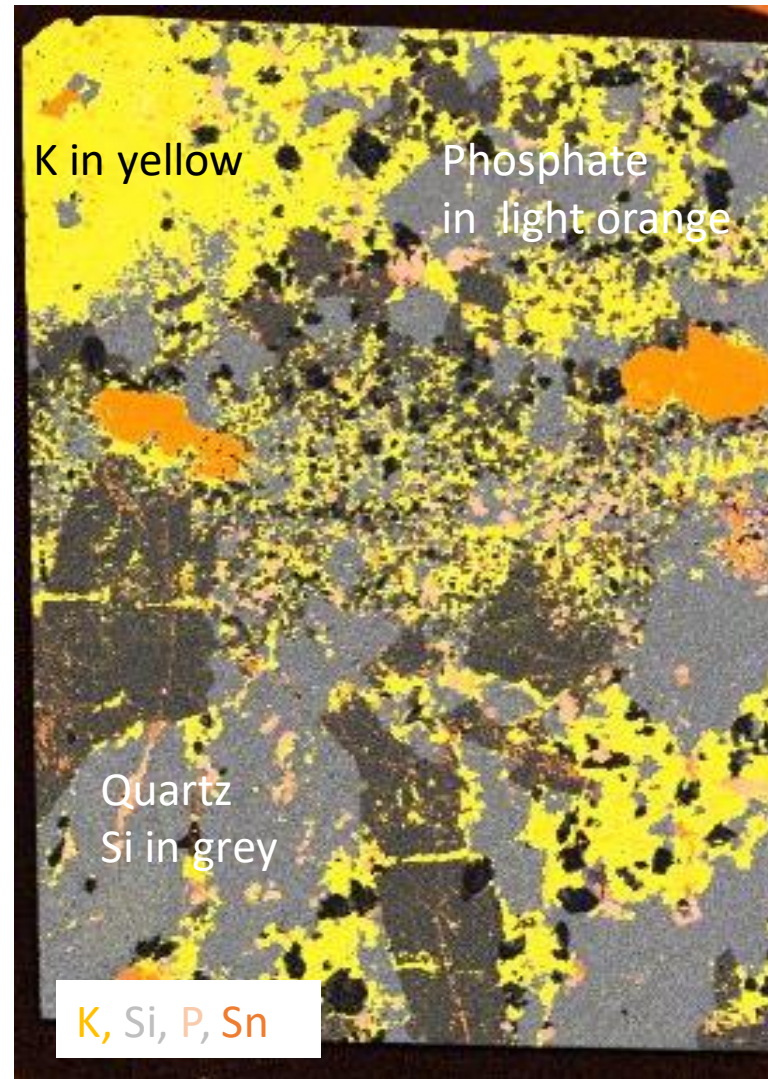
## Cerro Queimado



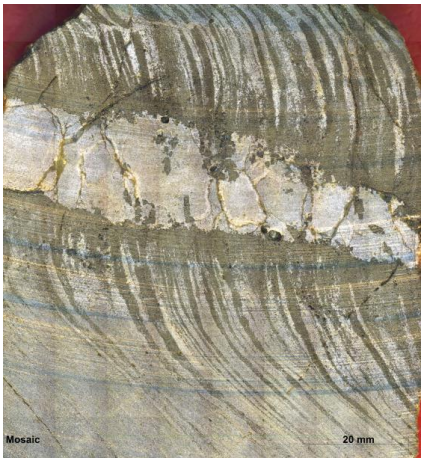


# Mineral relationships at the thin section scale

Search for small mineral phases : phosphates, Nb-Tantalates, zircon, monazite, ...

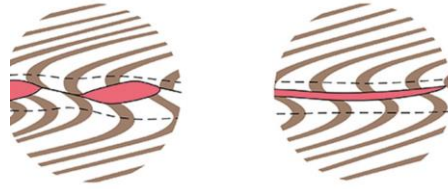




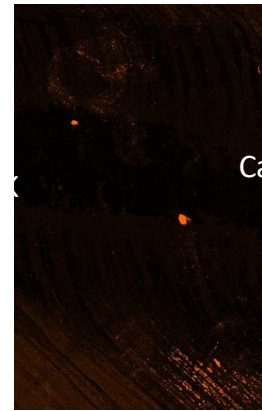


Mata Rainha- tourmalinisation of the schists  
 Raw block MRT-Tur  
 Schist minerals (muscovite) are replaced  
 entirely by tourmaline except quartz

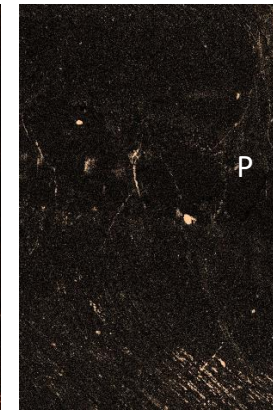
ASYMMETRIC FOLD-RELATED VEINS



K-micas

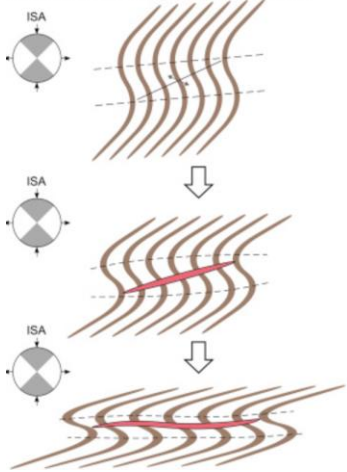


Ca



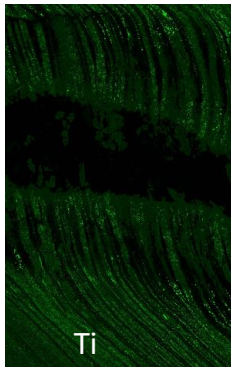
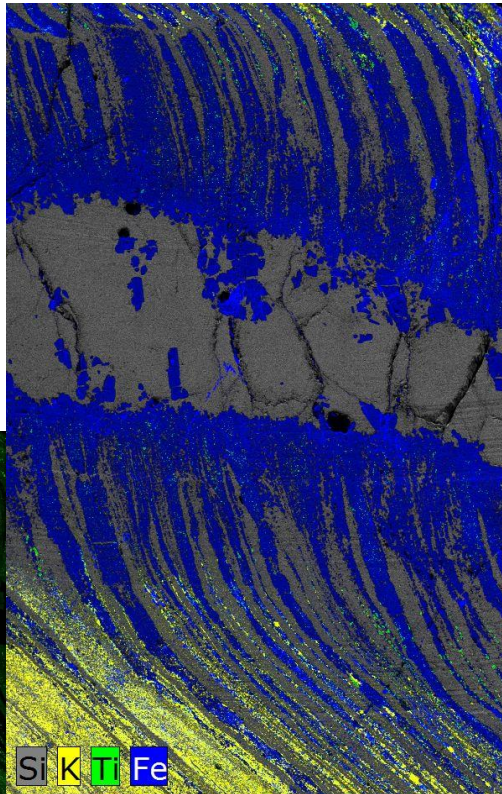
apatite

(b) dilatant Riedel shears along folds short limb



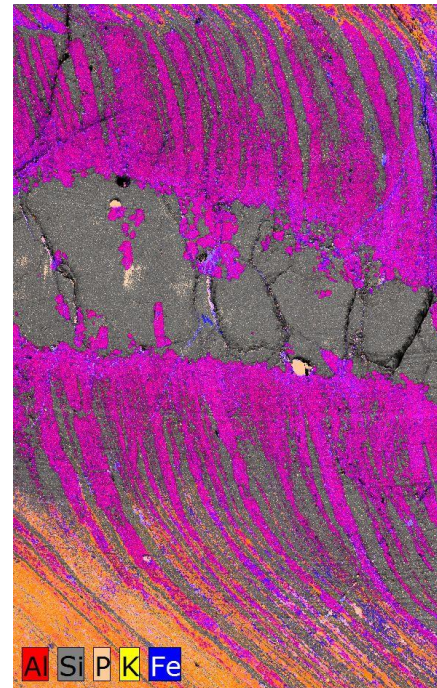
Druguet (2019)  
 Geoscience frontiers  
 2101-2115  
 Deciphering the presence  
 of axial-planar veins in tectonites

Tourmaline in blue  
 Quartz in grey  
 Micas in yellow

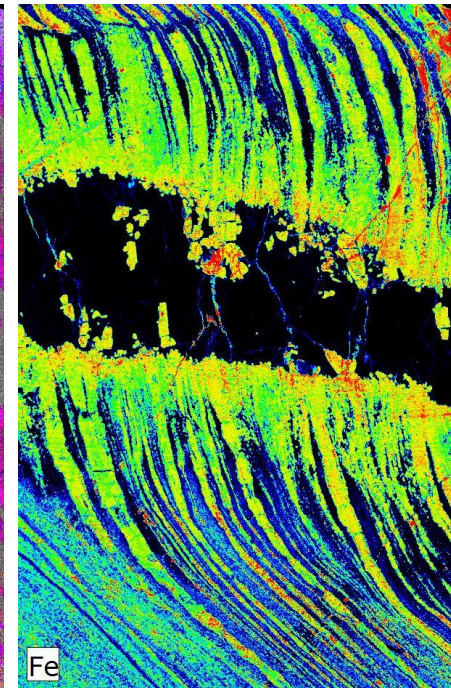


Ti

Si K Ti Fe



Al Si P K Fe

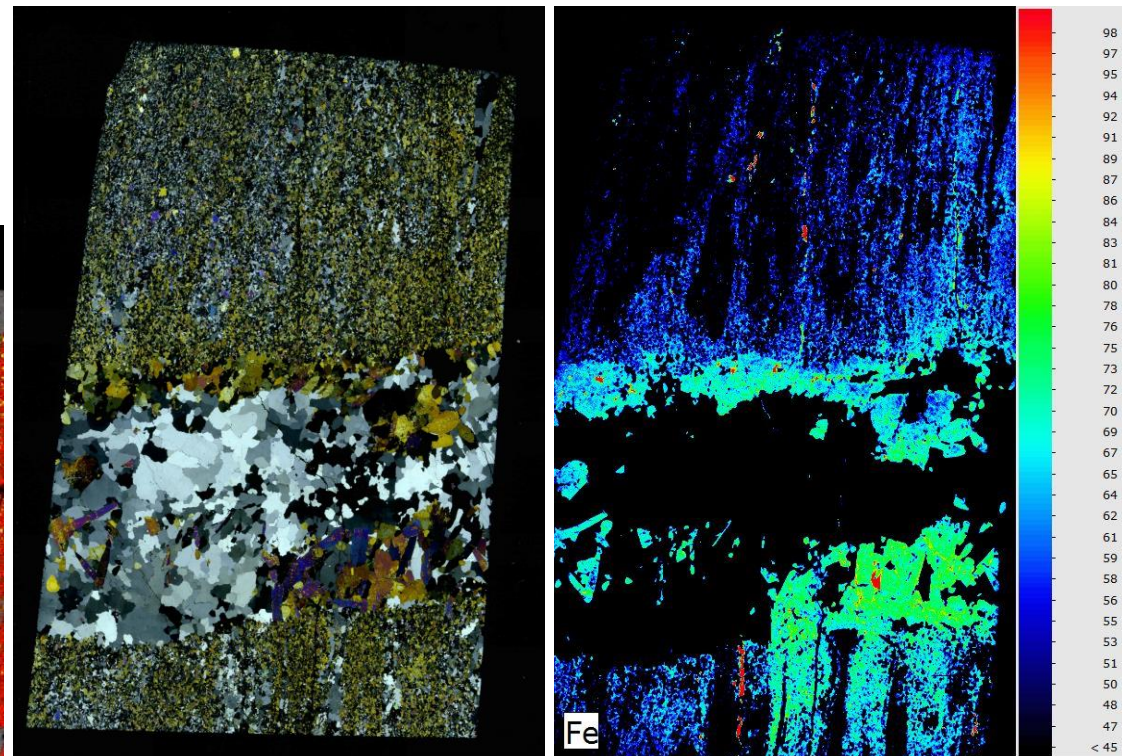
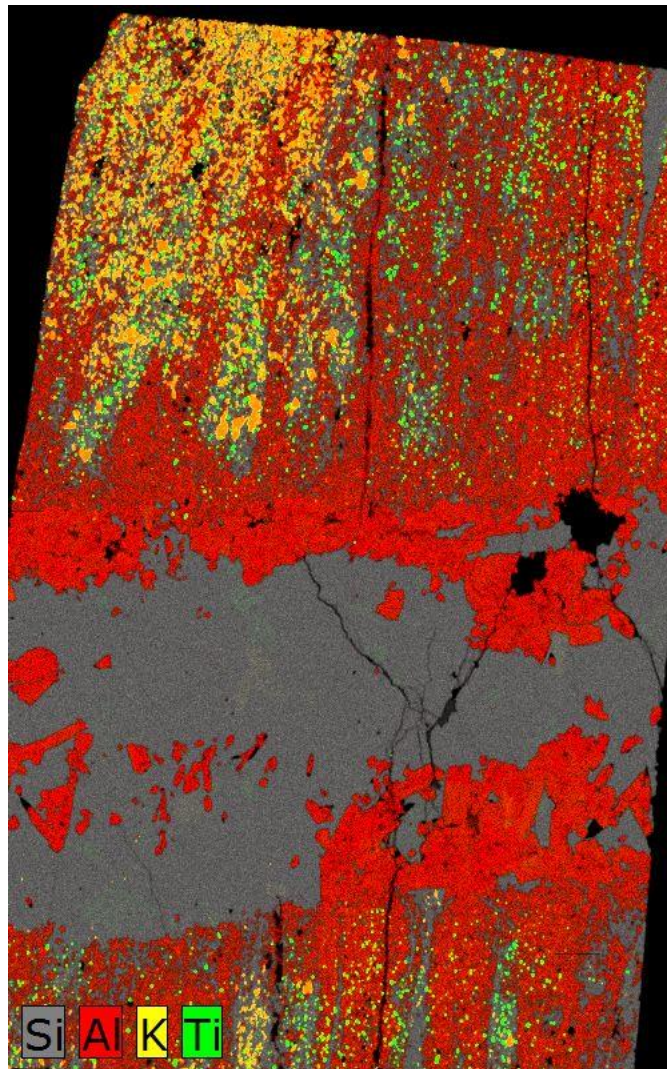
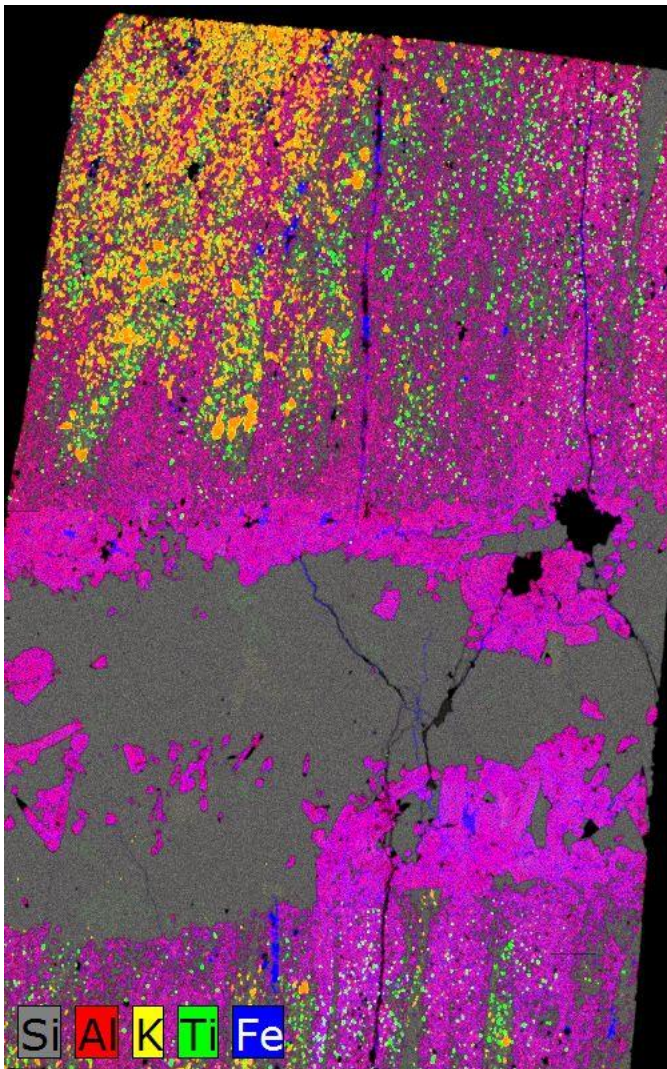


Fe

Schist is deformed but not the quartz vein where tourmalines  
 are euhedral and unbroken (free quartz-Tur infilling), not curved : not an antiaxial vein ?



# Chemical gradients, replacements, chemical alterations



LOMDR 1: vein with tourmalinisation



# Segura-schist

Identification of the spot locations

Evidence of S0, lithology

Effects of deformation

Mosaic 10 mm

