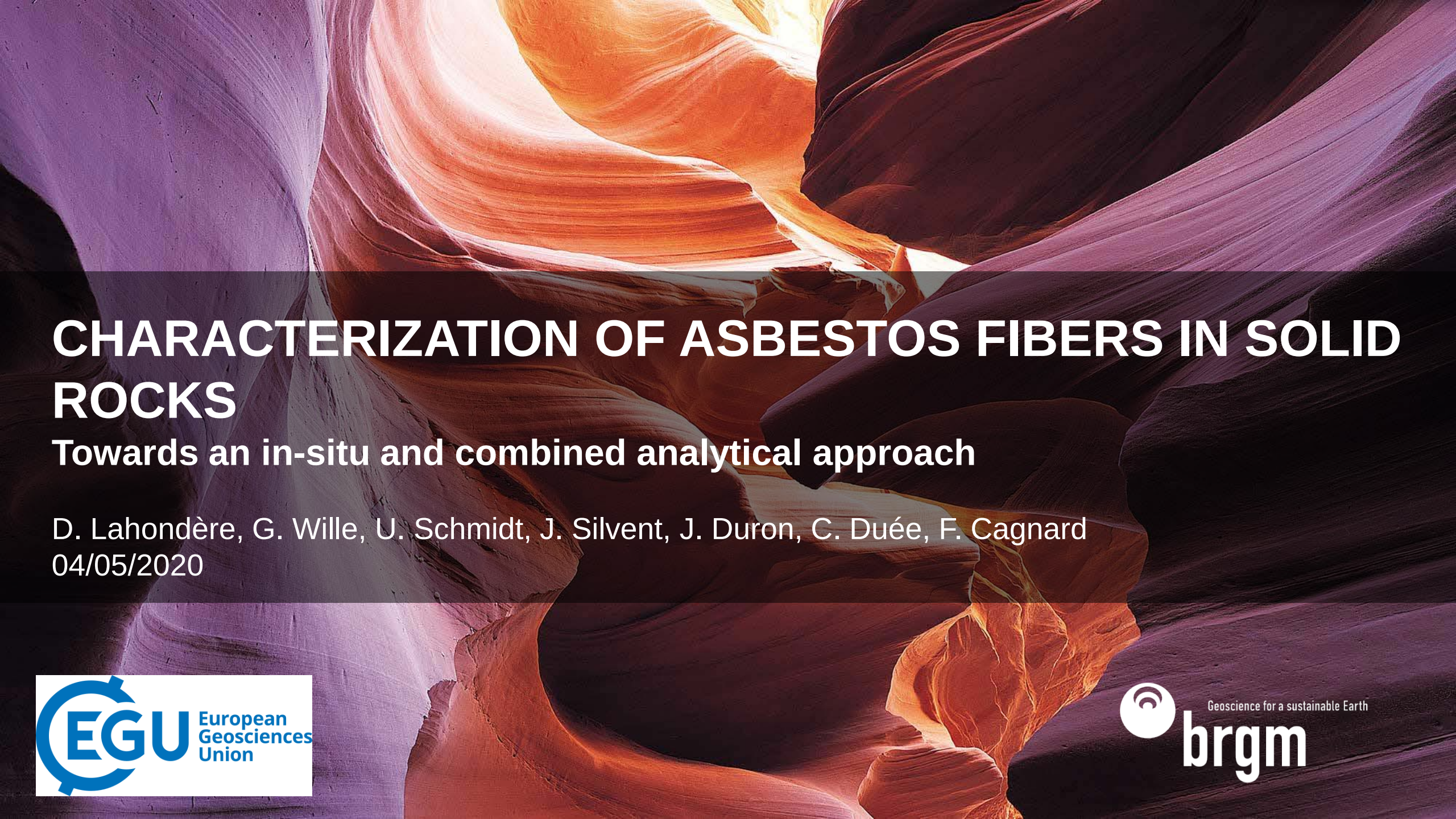

CHARACTERIZATION OF ASBESTOS FIBERS IN SOLID ROCKS

Towards an in-situ and combined analytical approach

D. Lahondère, G. Wille, U. Schmidt, J. Silvent, J. Duron, C. Duée, F. Cagnard

04/05/2020

EGU European Geosciences Union

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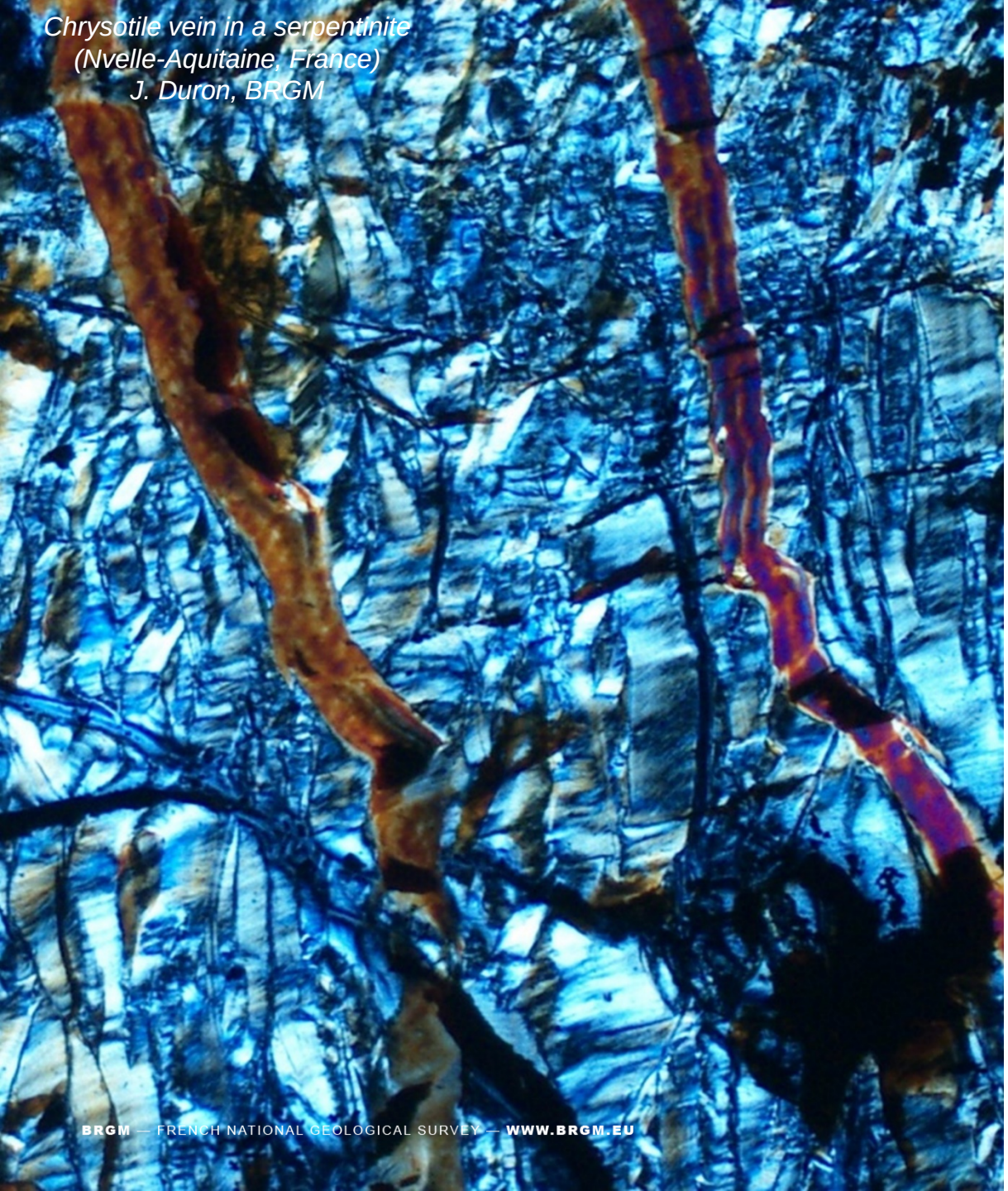

Chrysotile vein in a serpentinite (Nvelle-Aquitaine, France) J. Duron, BRGM

Morphological and chemical characterization of asbestos fibers in solid rocks: Towards an in-situ and combined analytical approach

- Introduction: Context and objectives
- Part I: Robust methods for mineralogical characterization and innovative techniques for improved characterization
- Part II: Towards a new 5-steps analytical protocol for an in-situ diagnosis
- Conclusion and perspectives

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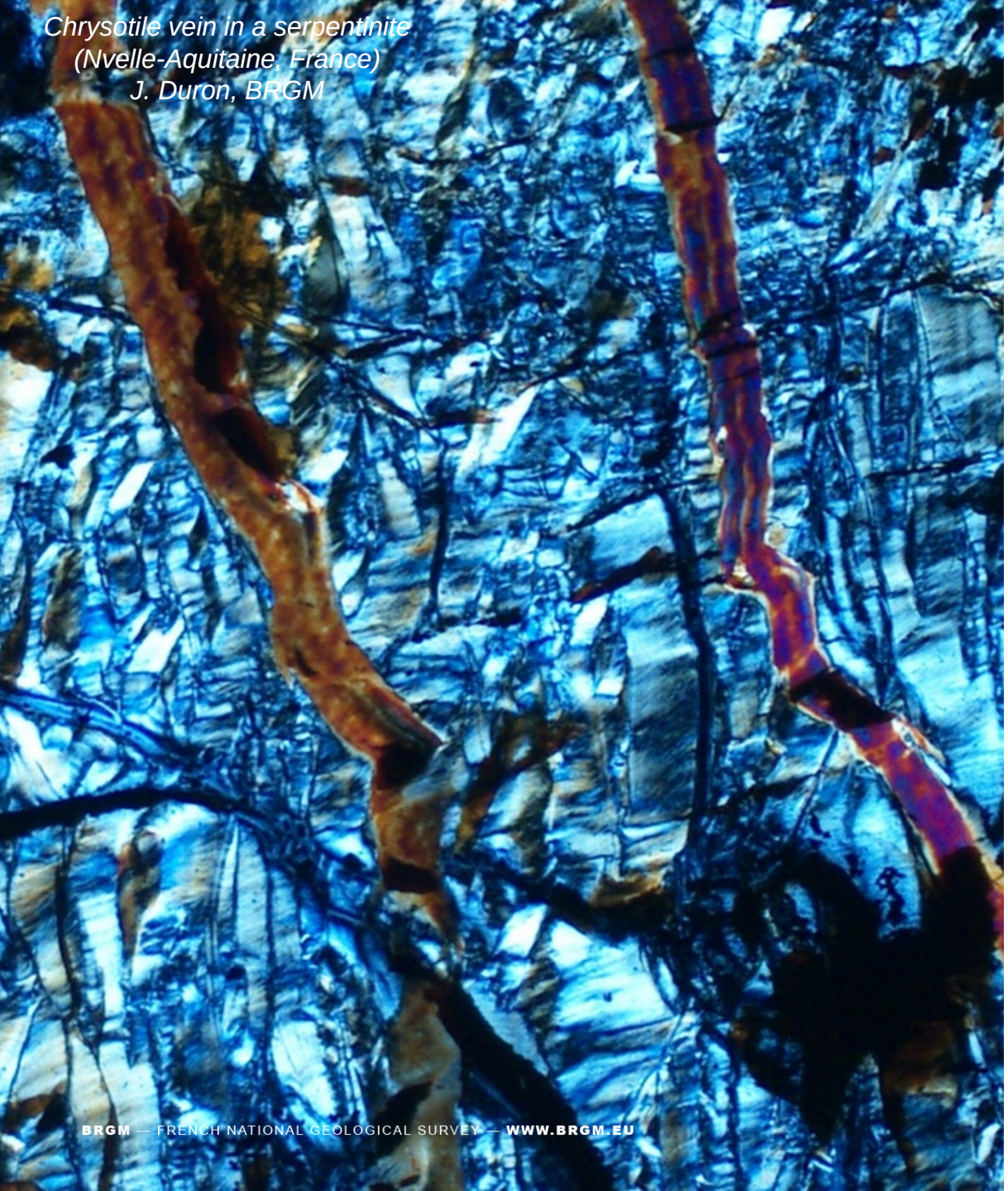


Chrysotile vein in a serpentinite
(Nvelle-Aquitaine, France)
J. Duron, BRGM

Introduction

Context and objectives

Asbestos

Asbestos

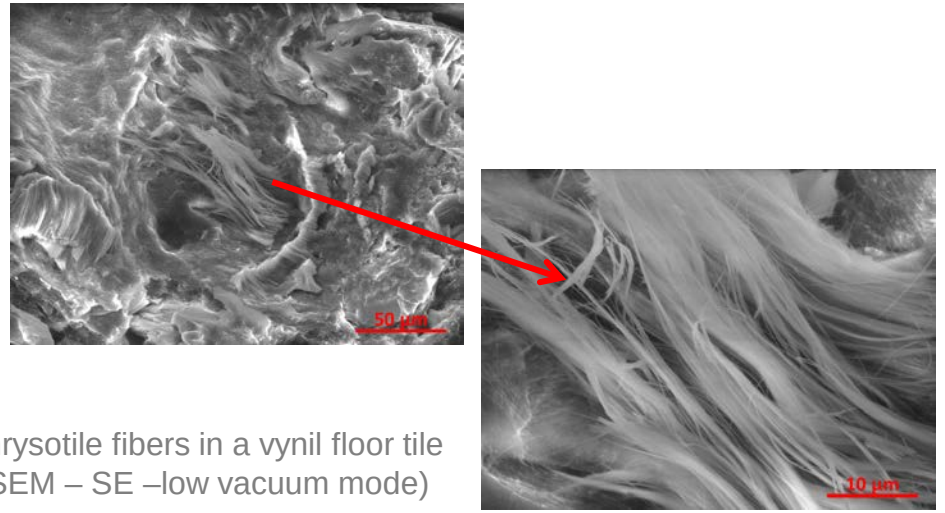
From the greek word *Asbestos* (incombustible) - Refers to a group of 6 natural fibrous silicates (as well as any mixture of these fibers)

Known and used since the greek and roman antiquity, for their physical and chemical properties (Halleux, 2010 – *in French*)

commercial definition → limited to the varieties exploited industrially

legal and regulatory definition →
Asbestos Ban in European union: Amphiboles (1991) / Chrysotile (1999)
Definition: In the european union directive 2009/148/EC (protection of workers from the risk related to exposure to asbestos at work)

Serpentines	
Chrysotile	$Mg_3Si_2O_5(OH)_4$
Amphiboles	
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
Anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$
Amosite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$
Crocidolite	$NaFe_5Si_8O_{22}(OH)_2$



Chrysotile fibers in a vynil floor tile
(SEM – SE –low vacuum mode)

Breathable Fiber (WHO 1998) = L > 5 µm ; D < 3 µm ; L/D > 5

Asbestiform fiber (EPA) = L/D > 20, fine fibers (< µm)

Context

Characterization of the morphology and the chemistry of asbestos fibers in solid rocks.

- Characterization of Asbestos in manufactured products and Asbestos fibers in suspension in air: existence of suitable analytical standards and protocols

- For natural materials (rocks): no specific analytical protocol is currently defined in France. In general, the sub-sample is grinded, calcinated and submitted to an acid attack. Then, the final sample is examined with a transmission electron microprobe (TEM).

⇒ The grinding of the sub-sample is a critical step which affect the quality of the final diagnosis.

- Grinding can create artificial cleavage fragments quite similar to asbestos fibers

- Is the sub-sample observed by SEM / TEM representative of the sample ?

Objectives

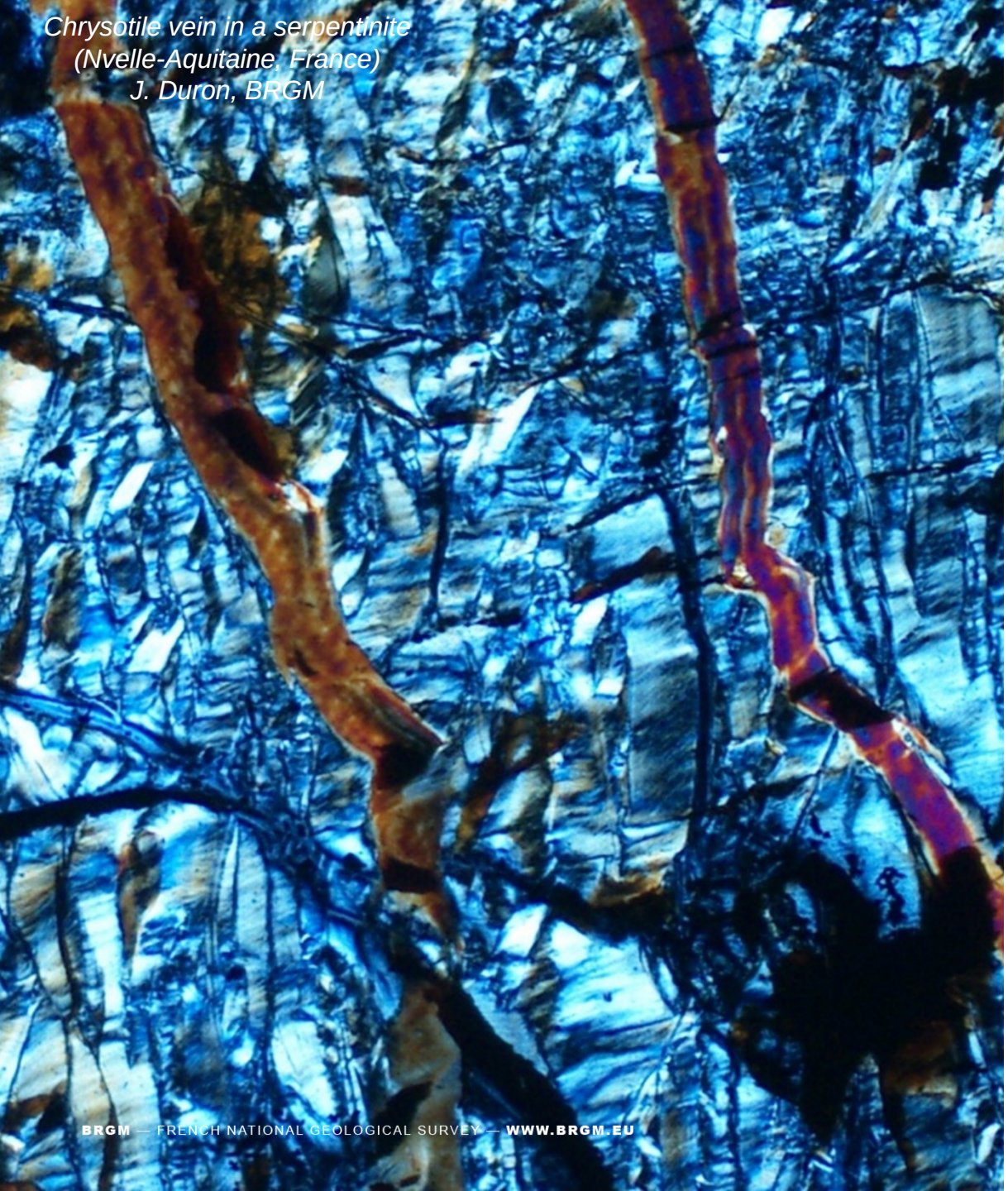
Development of a new analytical, multi-steps protocol for the asbestos diagnosis in natural rocks in their native state

- No artefact (cleavage fragments) created during the sample preparation
- No quartering / subsampling / sample alteration : the sample is kept in its natural state

New protocol

- Combination of robust analytical techniques from **a single support (thin section)**
- No grinding and no subsampling steps
- In-situ characterization

⇒ Development of a new protocol for a representative and reliable in-situ diagnosis of the initial state of the fibers in solid rocks



Chrysotile vein in a serpentinite (Nvelle-Aquitaine, France) J. Duron, BRGM

Part I

Robust methods for mineralogical characterization and innovative techniques for improved characterization

Analytical techniques of the new protocol

This protocol consists of a maximum of 5 steps on a unique sample support.
***Key point*: it can be interrupted at the end of each step, depending of the complexity of the sample.**

Are asbestiform fibers present in a solid natural material (rock sample) ?
Are these fibers affected by asbestos regulations ?

⇒ Acquisition of precise data about:

- the chemical composition
- the 2D and 3D dimensional characteristics.

1) Macroscopic observations

2) Microscopy / petrographic observation (Polarized Light Microscopy)

3) 2D morphological characteristics and « routine » mineral identification (Scanning Electron Microscopy)

4) Precise mineral identification (EPMA, Raman in SEM)

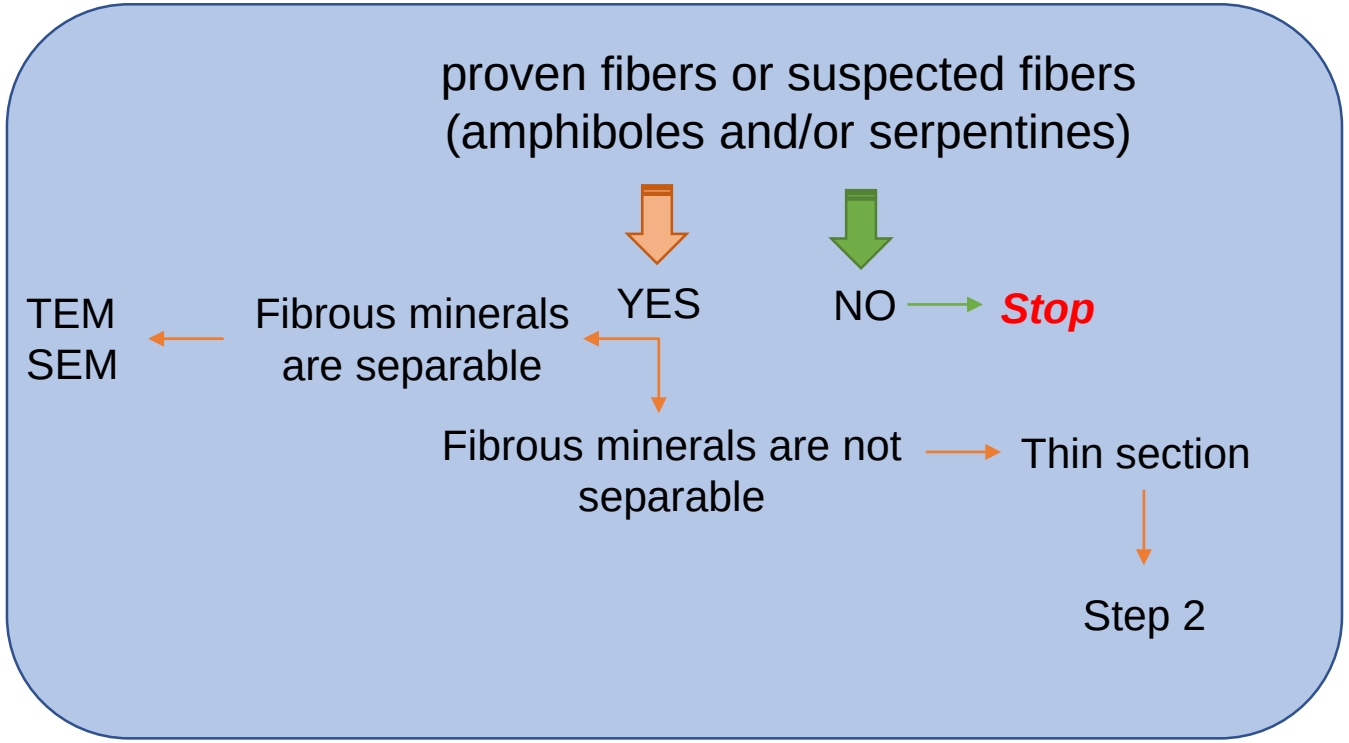
5) 3D morphological characteristics (3D SEM-FIB and/or 3D Raman in SEM)

Analytical techniques of the new protocol

Step 1) Field observation / Macroscopic observations

2 objectives

- Description of the petrographic nature of the sample
- Detection of the presence of fibrous amphiboles and/or serpentines (proven fibers or suspected fibers) ?



Evidence of Tremolite – asbestos fibers (New Caledonia - France)

Suspected presence of chrysotile veins in peridotite (Vosges – France)

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Analytical techniques of the new protocol

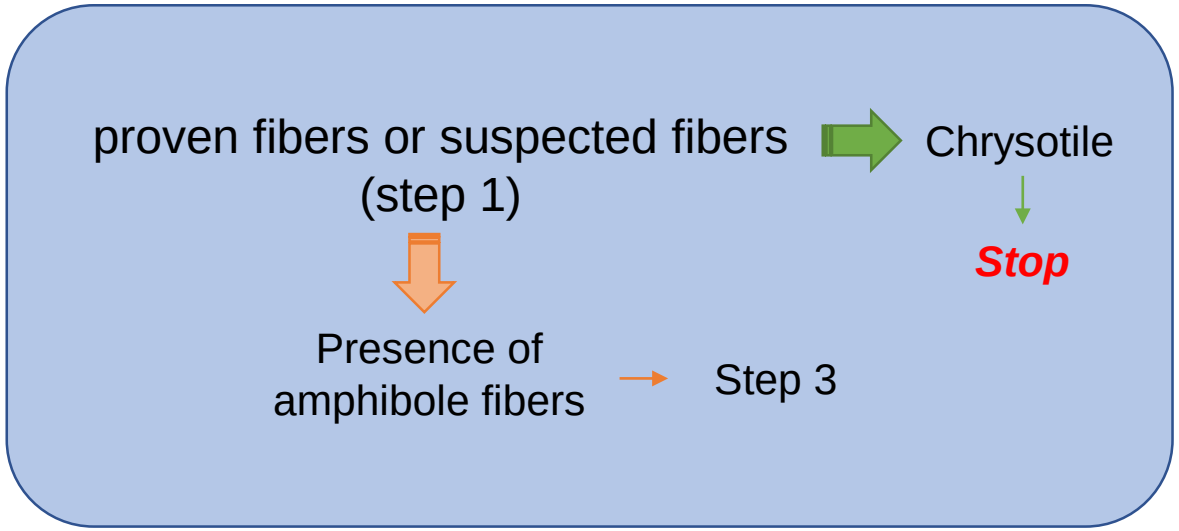
Step 2) Natural Light Microscopy (NLM) / Polarized Light Microscopy (PLM)

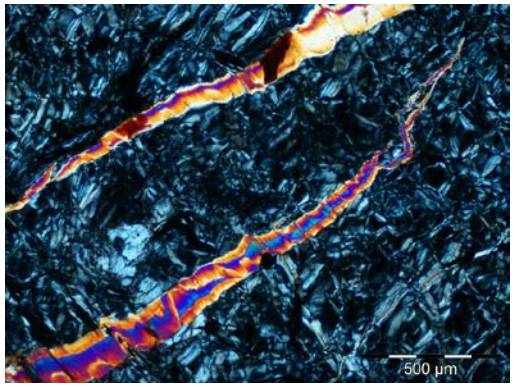
Objectives

- Determination of the constituent minerals and the petrographic nature of the rock
- Description of the microstructures (texture, foliation, veins, etc.)
- Observation of minerals included in the thickness of the thin section is possible (when fibres like amphibole are incorporated into matrices made up of translucent minerals)
- The presence of (potentially) asbestiform fibers can be already detected/suspected from this method

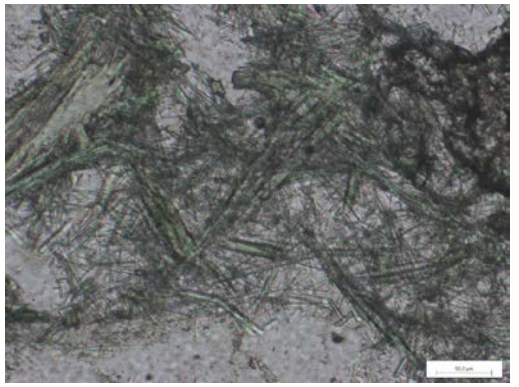
Limitation of this method

- Fibrous minerals with diameter < 3 µm can't be observed and characterized under good conditions





chrysotile veins (PLM)



actinolite fibers (NLM)

Analytical techniques of the new protocol

Step 3) 2D morphological characteristics and chemical composition (Scanning Electron Microscopy)

Objectives

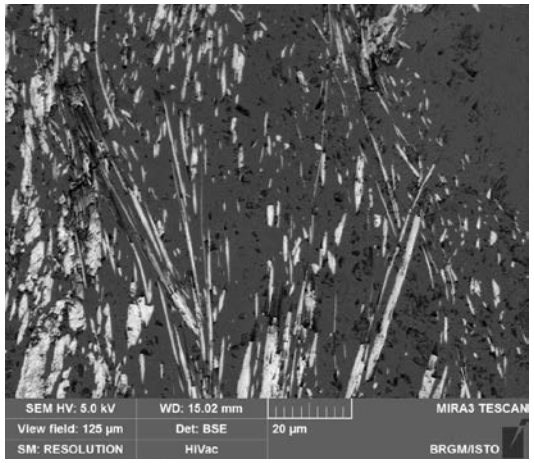
- Determination of the dimensions and morphologies of the fibrous minerals
- Determination of the chemical composition by EDS quantification

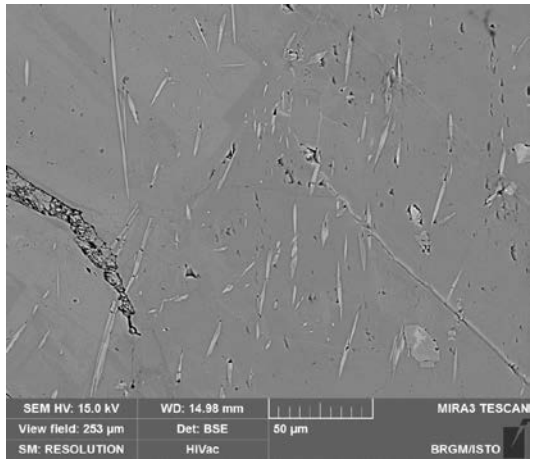
Limitations of this method

- EDS standardized quantification precision may be insufficient to identify the mineral species (depending on measurement precision)
- EDS spatial resolution for the thinnest fibers (D < 1 - 2 µm) – result affected by matrix contribution

Presence of amphiboles with asbestiform morphology
EDS quanti vs composition of the regulated amphiboles

Yes (Meas. Uncertainty)	Possible (Meas. Uncertainty)	
YES	YES	NO
Stop	Step 4	***Stop***





Examples of SEM (BSE) images

Analytical techniques of the new protocol

Step 4) Chemical composition (Electron Probe Microanalyzer)

Objective

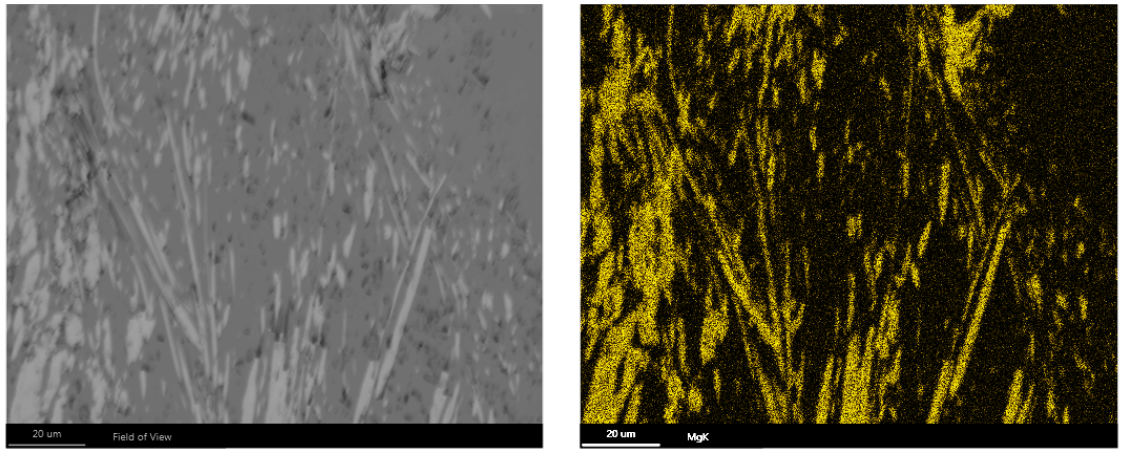
- Precise quantitative analysis of amphiboles for the determination of the mineralogical species of the fibers

Limitation of this method

- WDS spatial resolution for the thinnest fibers (D < 1 - 2 µm) – result affected by matrix contribution
- Spatial resolution / image quality of the SEM images (thermoionic electron gun, analytical conditions) for the thinnest fibers (< 1 µm) ⇒ Preliminary SEM observation may be necessary

Presence of amphiboles with asbestiform morphology
EDS quanti vs composition of the regulated amphiboles

Yes	Possible (spatial resolution)	
YES	YES	NO
Stop	Step 5	***Stop***



EPMA (BSE) image and Mg WDS map

Analytical techniques of the new protocol

Step 5) 3D morphological characteristics (Raman in SEM and/or SEM-FIB)

Objectives

- Informations about the 3D morphology of fibrous amphiboles using 3D techniques (Raman-in-SEM, FIB-SEM
- Critical information on the morphology of the amphibole fibers in the mineral mass (aspect ratio, fiber distribution, and fibrous amphibole volume fraction).
- Fibers included within different types of mineral matrix (feldspar, quartz and/or calcite matrix) may be identified

- Method 1: Raman in SEM
  - Spatial resolution: fibers with diameter about 400 nm may be identified
  - Non-destructive technique

OR

- Method 2: SEM FIB
  - Spatial resolution: fibers with diameter about 100 nm may be identified
  - Destructive technique

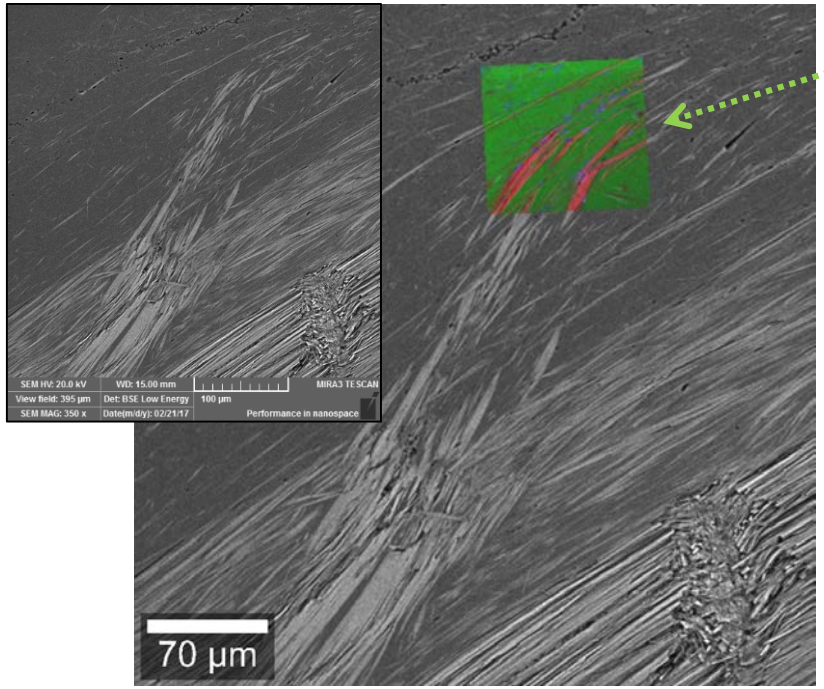
OR

- Method 1 followed by application of the method 2 on selected areas (presence of very thin fibers suspected)
  - Combination of the two techniques for a more precise description

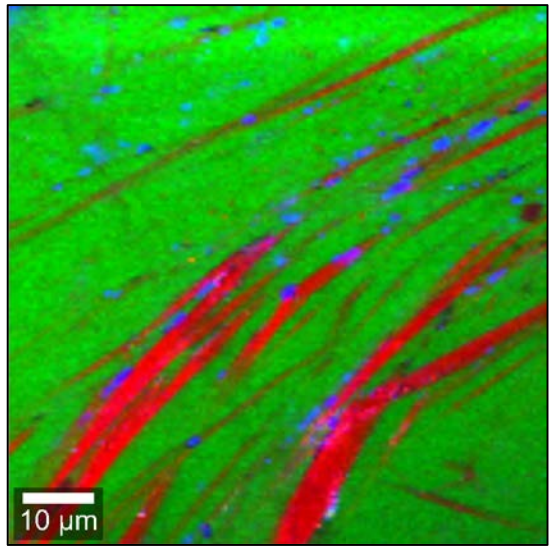
Analytical techniques of the new protocol

Step 5) 2D / 3D morphological characteristics by confocal Raman in SEM imaging (RISE)

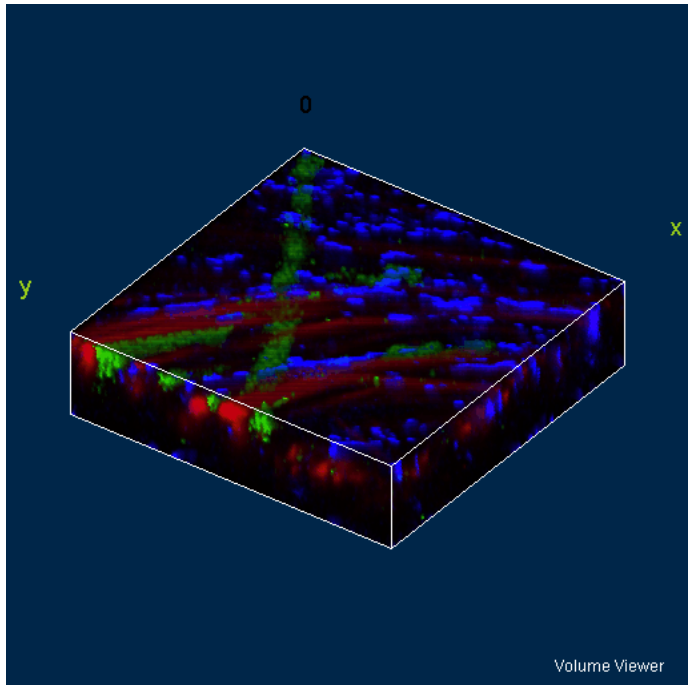
SEM (BSE) images

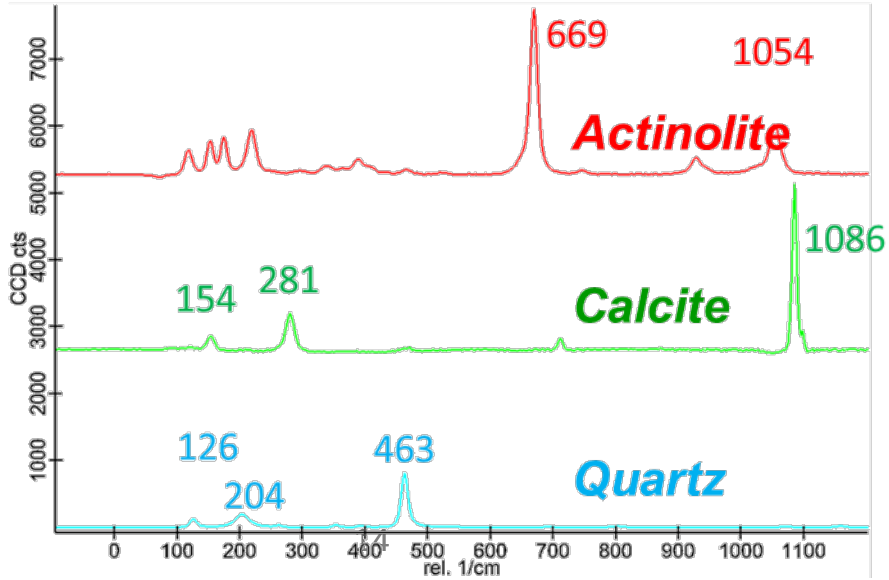


Raman map (2D)



Raman volume (3D)





Raman spectra obtained from the hyperspectral map

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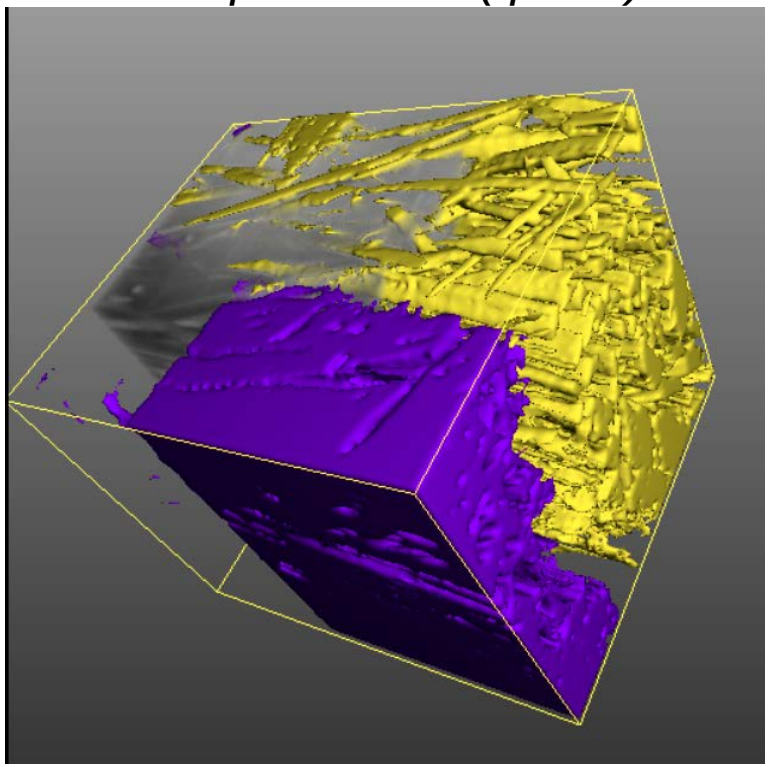
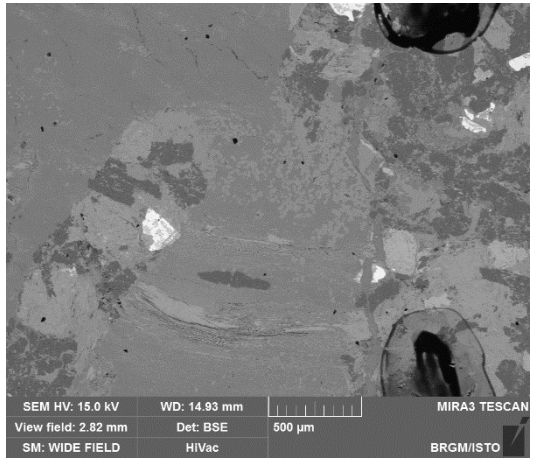
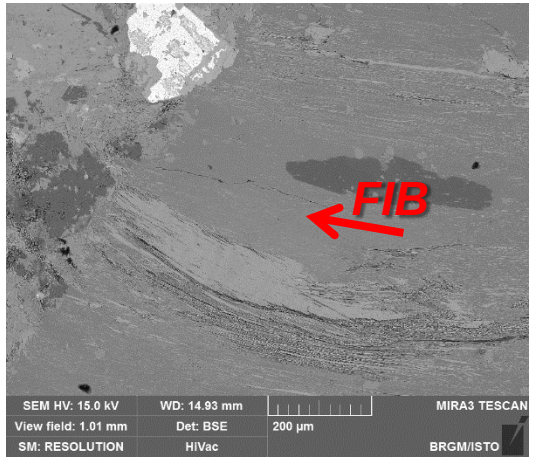
Analytical techniques of the new protocol

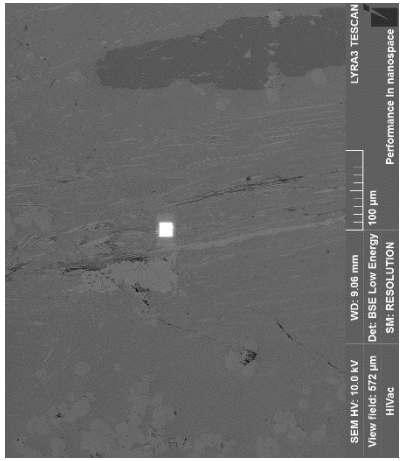
Step 5) 3D morphological characteristics by SEM-FIB

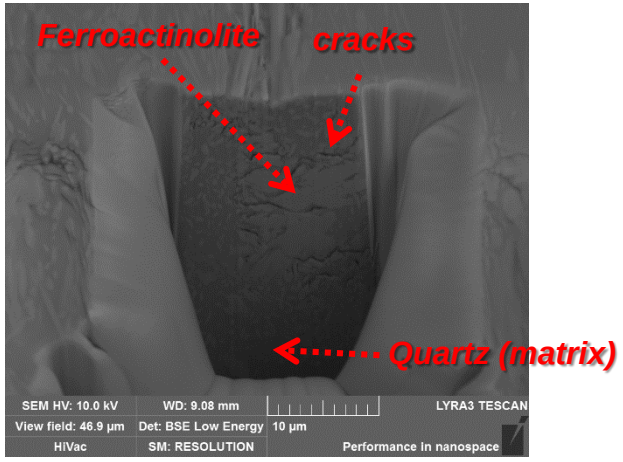
FIB volume (3D)
Yellow : amphibole fibers
Purple : matrix (quartz)

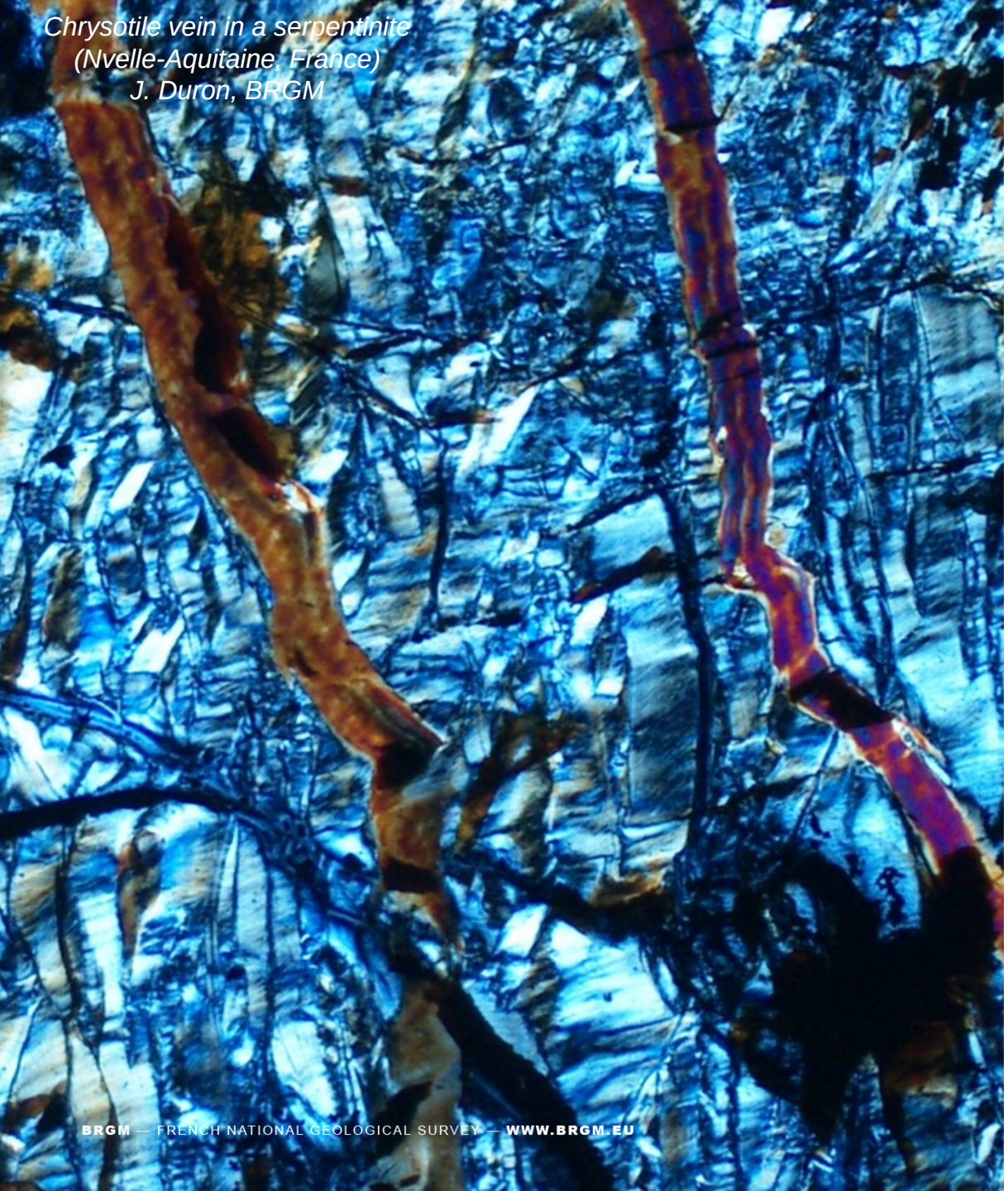












Chrysotile vein in a serpentinite (Nvelle-Aquitaine, France) J. Duron, BRGM

Part II

Towards a 5-steps analytical protocol for an in-situ diagnosis

Application to natural rock samples

Sample 1

Garnet-bearing amphibolite

This rock type is generally appreciated by the extractive industry because of their geotechnical characteristics

Sample 1 corresponds to a **garnet-bearing amphibolite pebble** taken from a geological formation made up of fluvio-glacial alluviums

1) Macroscopic observations

No metamorphic veins is observed.

Production of a thin section
- in a plane perpendicular to the planar anisotropy (metamorphic foliation)
- parallel to the preferential orientation of the fibers (mineral lineation)

This plan therefore makes it possible to observe the fibers in their greatest elongation

Sample 1

Garnet-bearing amphibolite

2) Microscopy / petrographic observation (Light Microscopy)

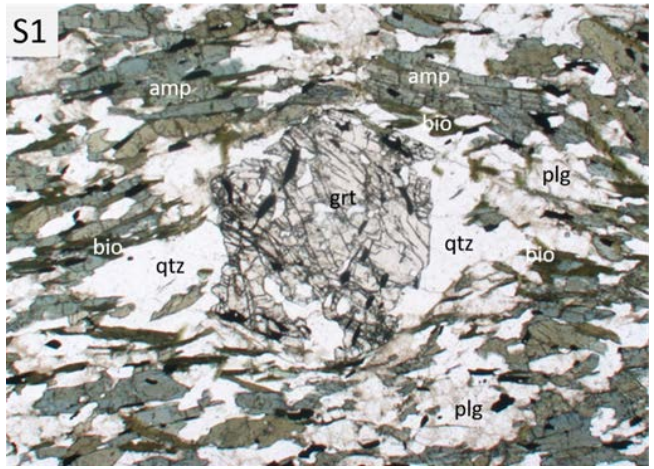
- Presence of amphiboles
  - large crystals parallel to each other, relatively thick low aspect ratio
  - appear homogeneous within the same crystal and from one crystal to another

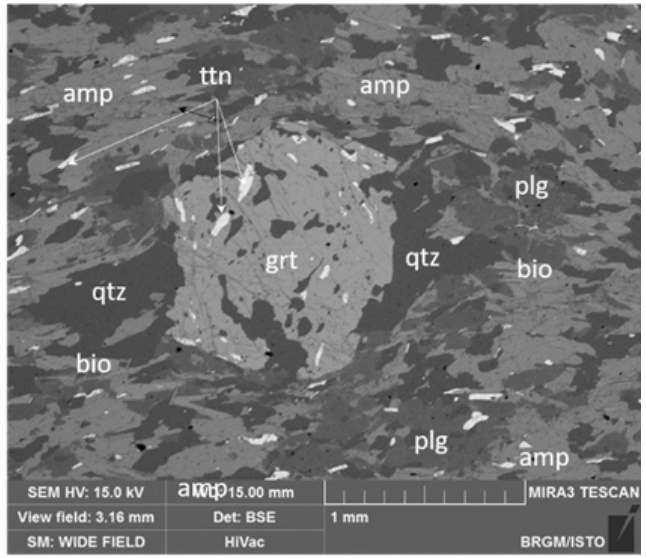
- associated with :
  - non-chloritized biotite lamellae which are laid flat in the metamorphic foliation.
  - Garnets free from any retrograde process, indicating that the rock has not been subjected to late-metamorphic (e.g.: greenschist recrystallizations)

3) SEM – EDS observation

- No fibrous amphibole
- calcic, silica-poor amphiboles
  - ferro-tschermakites and ferro-hornblendes types (6.1 < Si apfu < 6.4)

⇒ No more investigation is necessary – No asbestos detected





Sample 2

Actinolite metadolerite

Sample 2 is a pebble taken from the alluvium deposited by the Durance River
It corresponds to a **greenish metabasic rock** which does not present any preferential planar or linear anisotropy

1) Macroscopic observations

- the presence of fibers only suspected: petrographic nature, hydrothermal character (presence of epidote)
- No planar or linear structure being identifiable

2) Microscopy / petrographic observation (Light Microscopy)

- Presence of large, partially altered, automorphic feldspar crystals
  - Presence of epidote grains, Plagioclase slats, of all sizes, abundant and often contiguous
  - Pyroxene crystals between the plagioclase slats
  - $\Rightarrow$ thin grain metadolerite $\rightarrow$ the asbestos potential has been recently illustrated (Lahondere et al. 2018)

- Fibers:
  - Constitute the extension of matrix pyroxene crystals $\rightarrow$ most certainly amphiboles resulting from the destabilization of magmatic pyroxenes
  - Sometimes very long or only observed in the form of lozenge sections $\rightarrow$ not aligned in a preferential direction

Sample 2

Actinolite metadolerite

3) SEM – EDS observation

- Fibers observation
  - Very heterogeneous morphologies and dimensional characteristics
  - large fibers (D > 50 µm) coexisting with very thin fibers (D < 1 µm)

- EDS analyses
  - Variable weight percent contents for SiO_2 (48.8 – 55.7), Al_2O_3 (1.1 – 6.1), MgO (13.8 – 19.7) and FeO (11.6 - 21.2)
  - CaO content is relatively stable (11.8 - 13.2)
  - ⇒ EPMA analyses are required for higher precision in chemical composition

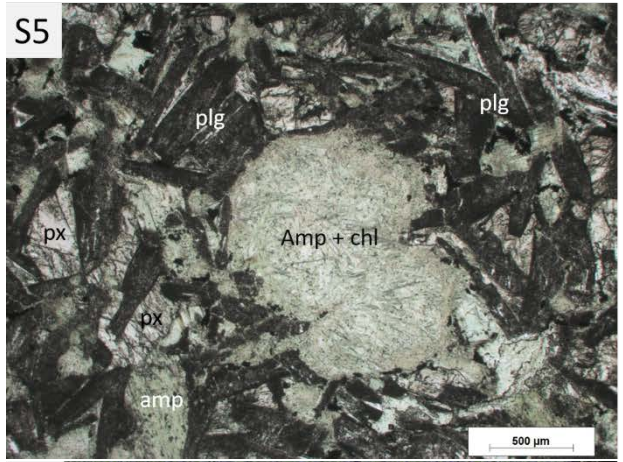
4) EPMA analyses

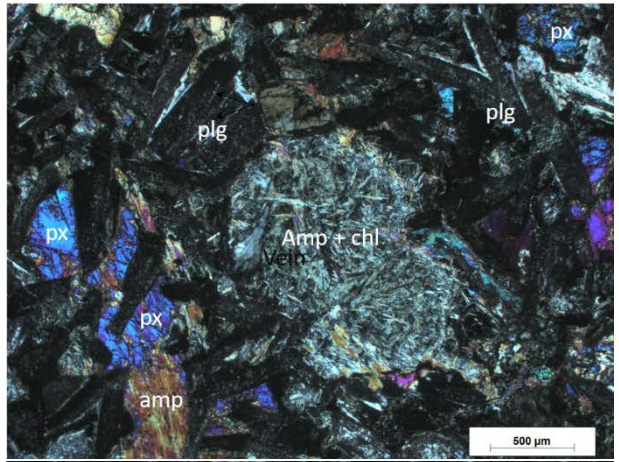
- All calcic amphiboles
  - Analyses cover a wide compositional field from moderately siliceous hornblendes (Mg, Fe) to actinolites and tremolites

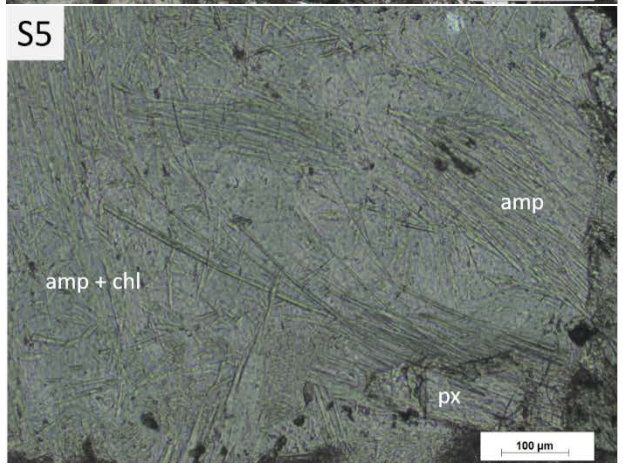
⇒Asbestiform actinolite fibers detected – 3D not necessary but possible if required

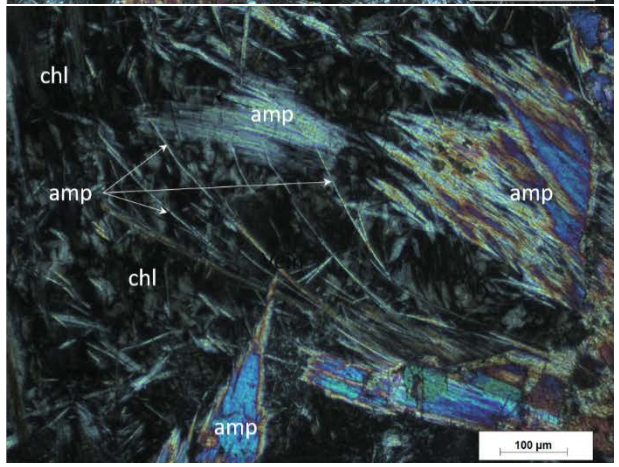
Sample 2

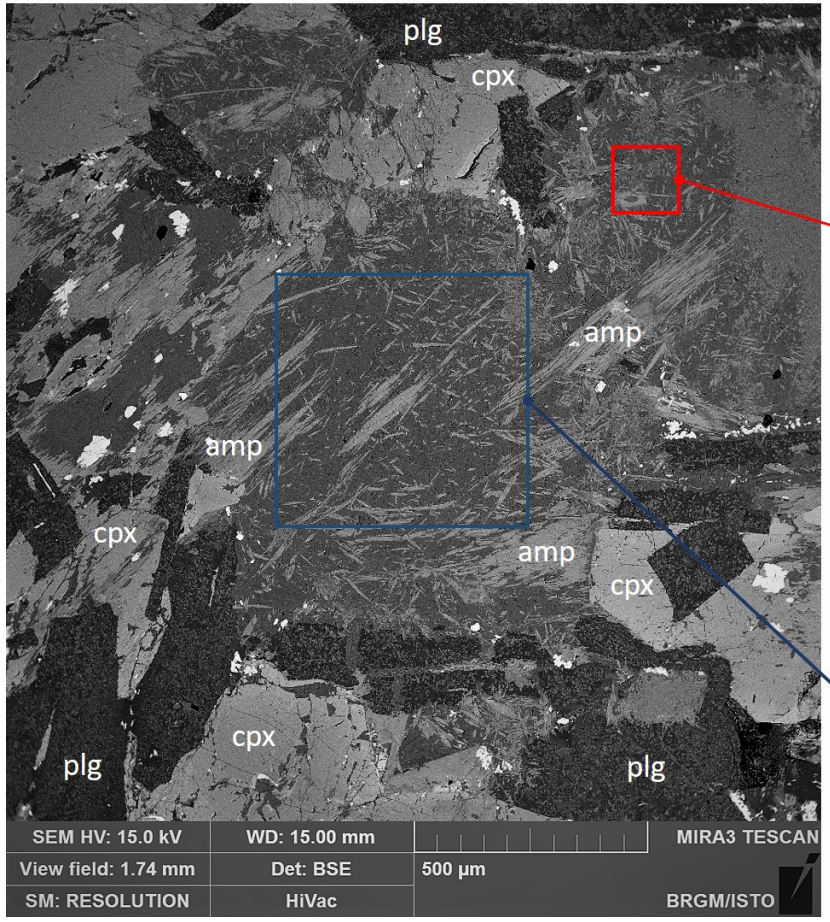
Actinolite metadolerite

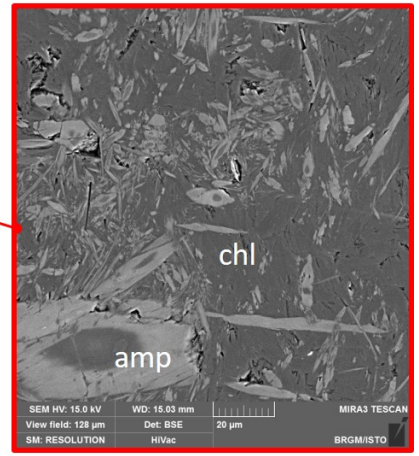


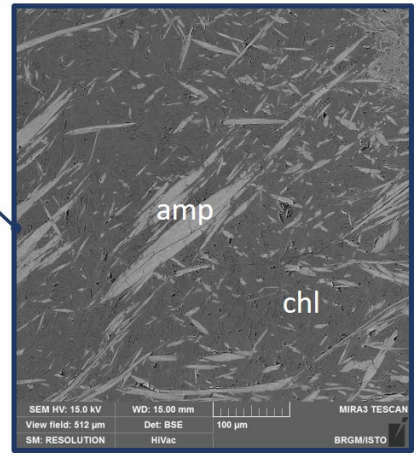












Sample 3

Actinolite metadolerite

Sample 3 comes from the southern part of the Armorican massif from a basic volcanic complex
It corresponds to hydrothermally altered basalt intersected by an amphibole-chlorite-calcite-K-feldspar vein
Inside the vein, the amphiboles are dispersed and appear completely embedded in calcite and K-feldspar crystals

1) Macroscopic observations

- Presence of fibers suspected due to the petrographic nature of the sample

2) Microscopy / petrographic observation (Light Microscopy)

- Presence of large, partially altered, automorphic feldspar crystals
  - Outside the vein, pseudomorphic texture characterized by the presence of colorless phenocrysts of clinopyroxene (diopside) partially destabilized in amphibole
  - Amphiboles from the veins form randomly curved bundles with split ends and fibrils, both extremely long and remarkably thin
- Fibers:
  - Amphibole fibers are clearly visibles by NLM / PLM

Sample 2

Actinolite metadolerite

3) SEM – EDS observation

- Fibers observation
  - Long and thin fibers observed. Some losangic particles are observed (possibly perpendicular sections of fibers
  - Presence of thin to very thin fibers (D < 1 µm)

- EDS analyses
  - Composition possibly corresponds to actinolite
  - ⇒ EPMA analyses are required for higher precision in chemical composition

4) EPMA analyses

- Analyses correspond to the composition of actinolite

⇒Asbestiform actinolite fibers detected – 2D and 3D Raman is necessary to define the mineral nature of the submicrometric fibers and the morphology of losangic particles

Sample 2

Actinolite metadolerite

5a) 2D / 3D Confocal Raman in SEM (RISE)

- 2D Raman imaging
  - Raman imaging confirms the nature of the fibers and losangic particles as actinolite
  - The Raman spectrum of orthoclase and calcite are extracted from the Raman map

- 3D Raman
  - 3D confirms that losangic particles observedd by SEM correspond to perpendicular section of thin actinolite fibers
  - Actinolite is clearly fibrous in the analyzed volume
  - Fibers thinner than 400 nm are observed – SEM-FIB is required for high resolution 3D

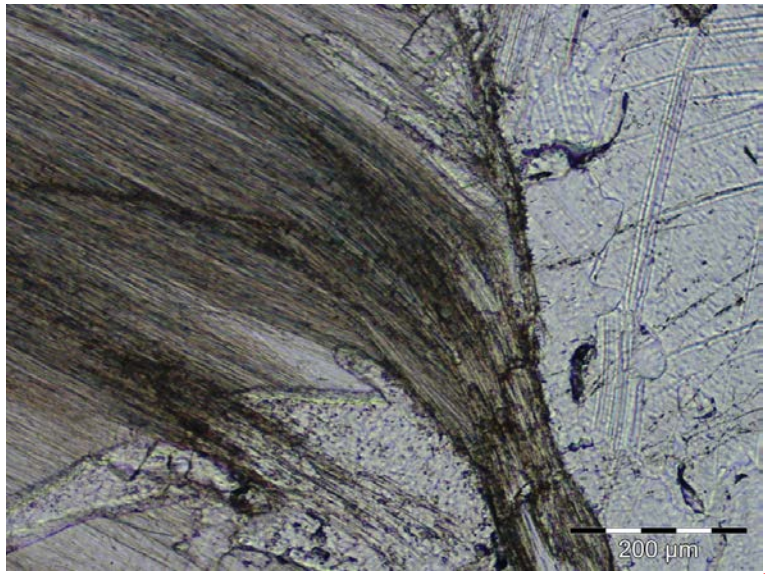
5b) 3D SEM-FIB

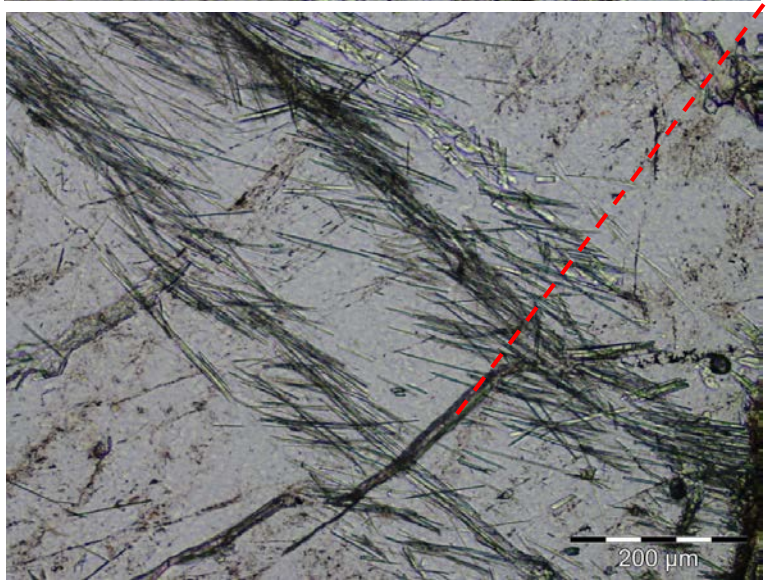
- Very thin fibers of actinolite can be observed in the volume
  The morphology confirms the presence of asbestiform fibers of actinolite in the sample
- Volumic fraction of actinolite can be given by the analysis of the 3D volume

⇒Asbestiform actinolite fibers detected – Presence of asbestos fibers confirmed by 3D

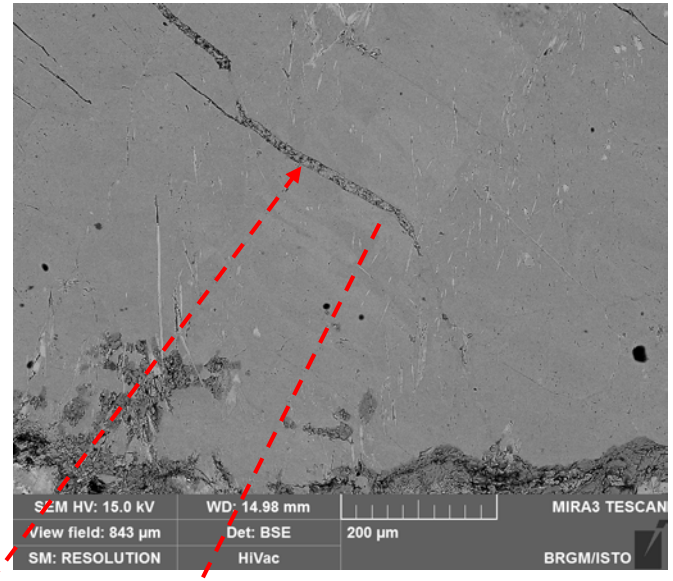
Sample 3

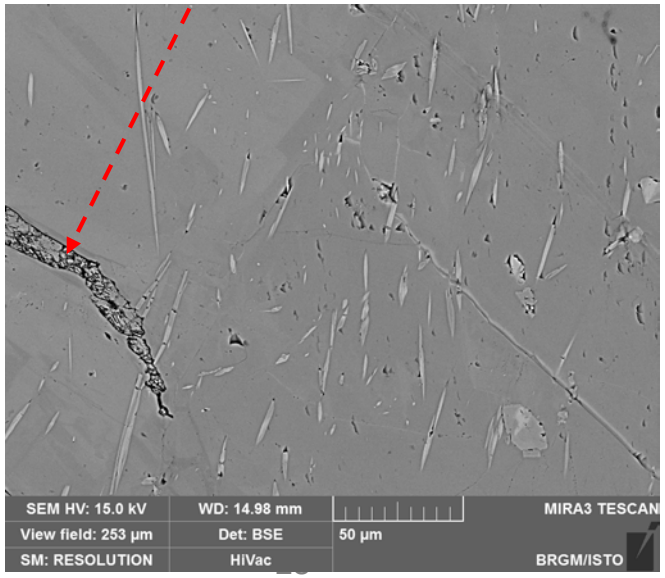
Light microscopy

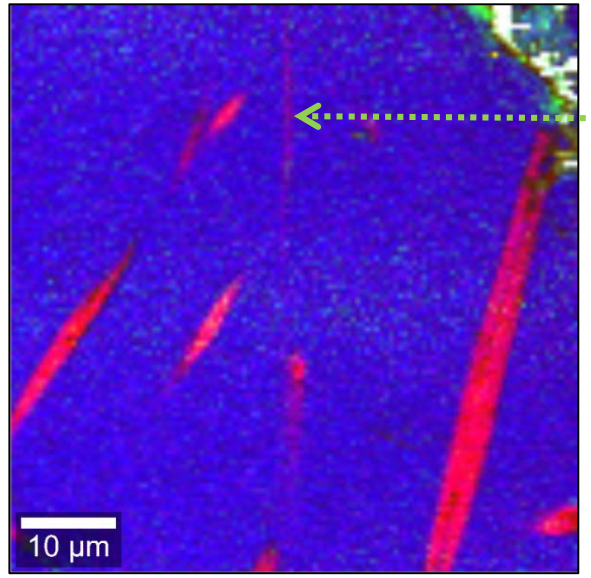


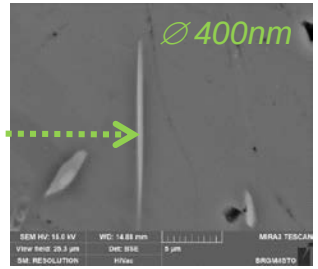


SEM

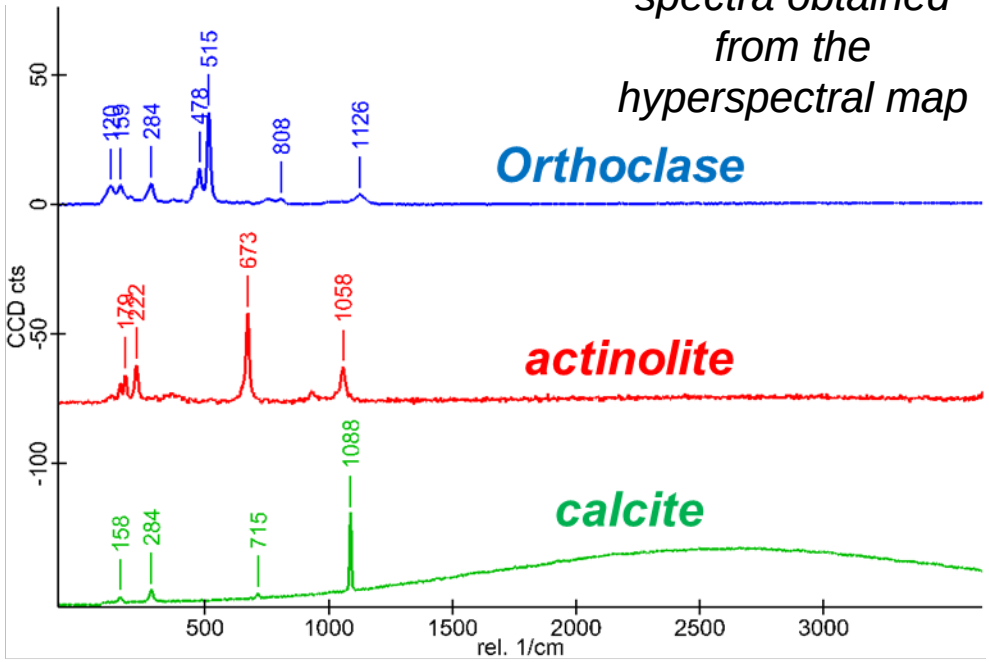




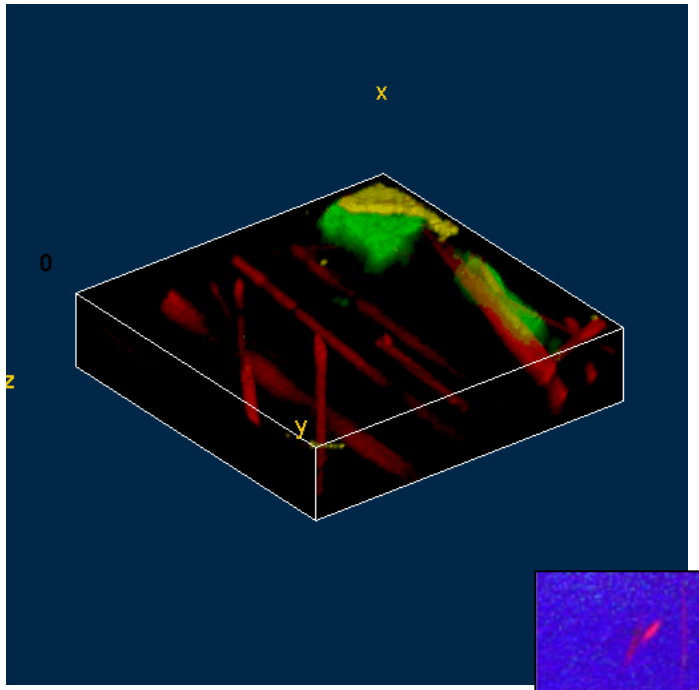




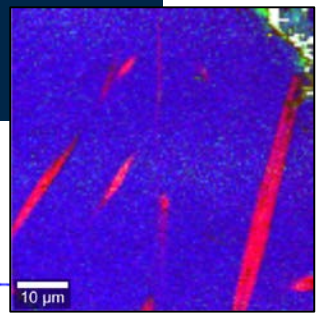
Raman map and spectra obtained from the hyperspectral map

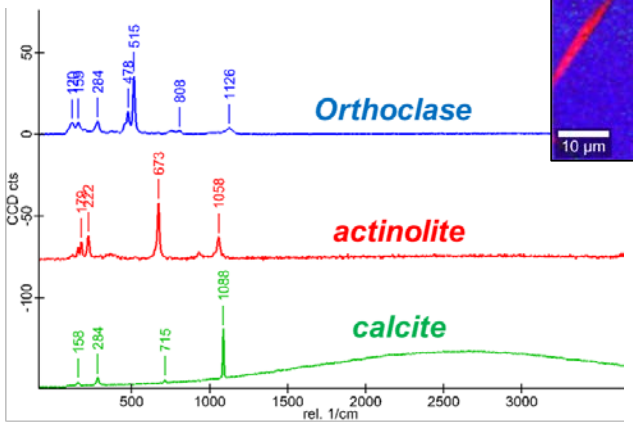


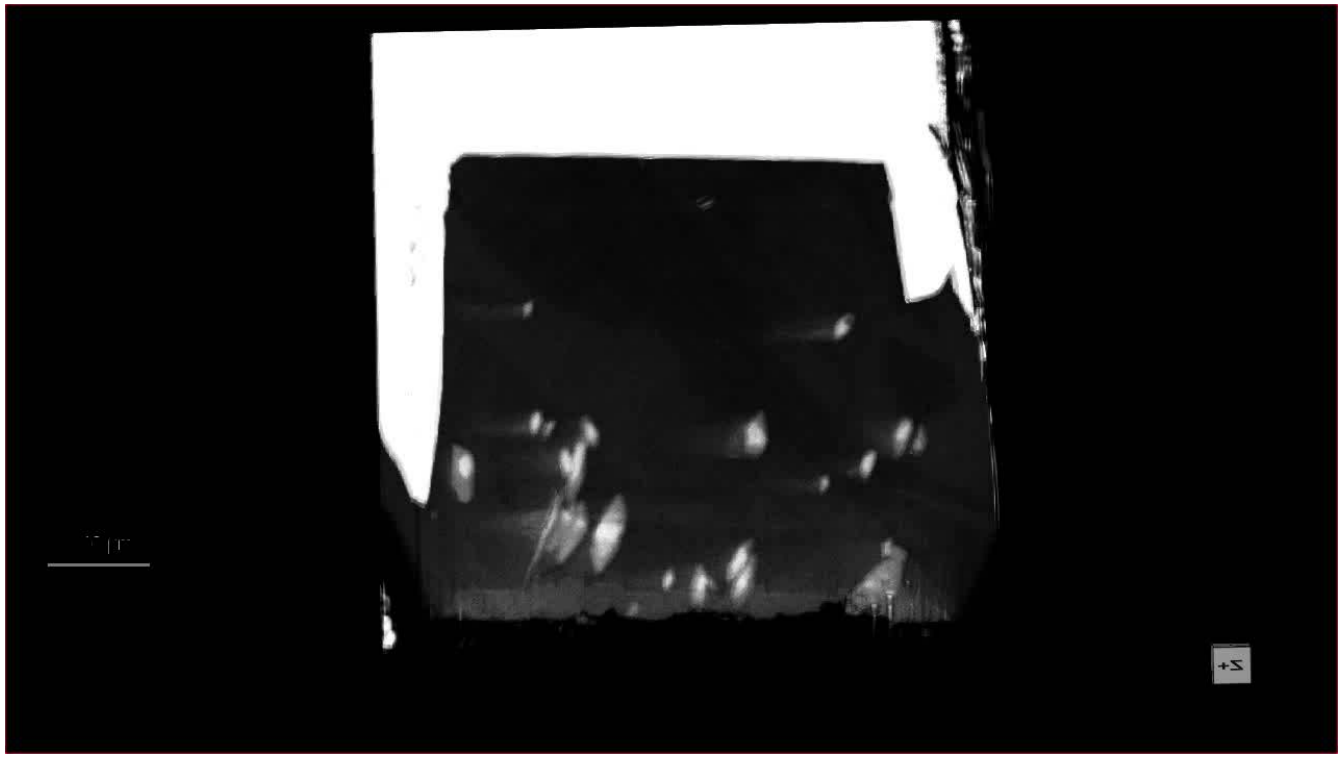
Sample 2



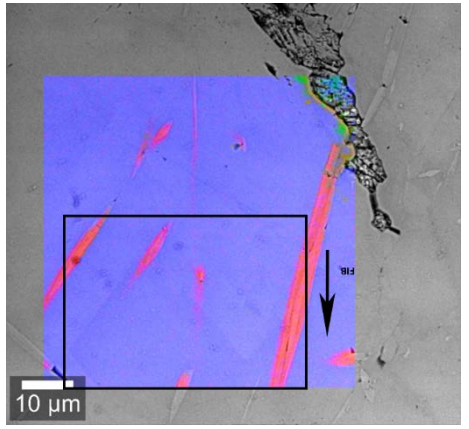
Raman 3D
120x120x20 µm
Z-step 0.5 µm







FIB 3D
563 slices / Voxel 60 µm
Width: 785 px (47.10 µm)
Height: 799 px (47.94 µm)
Depth: 563 px (33.78 µm)



Volume
76274 µm^3

Fibers
1464,40 µm^3 = 1.94 % volume

Geoscience for a sustainable Earth
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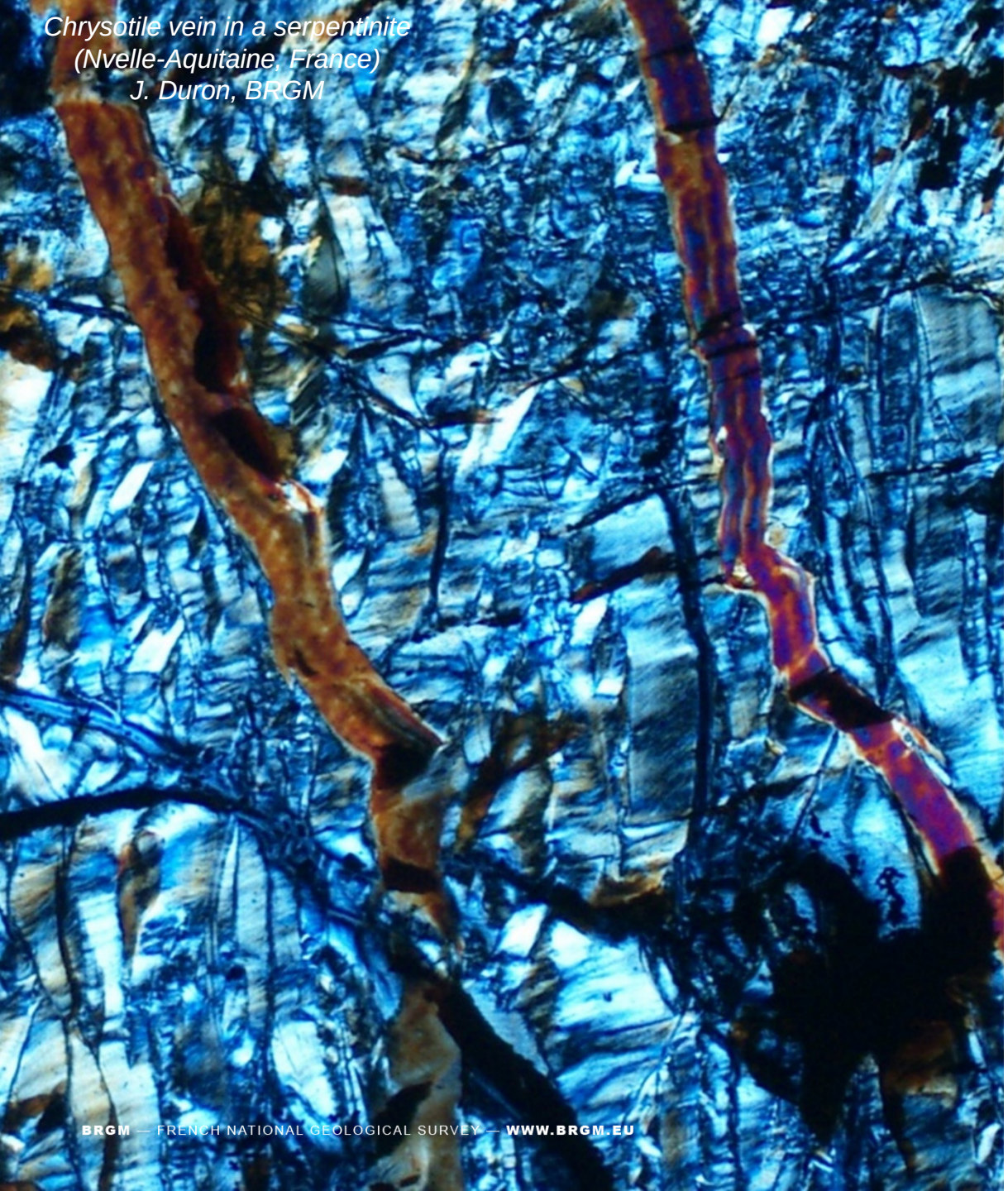


Chrysotile vein in a serpentinite
(Nvelle-Aquitaine, France)
J. Duron, BRGM

Conclusion

Conclusion

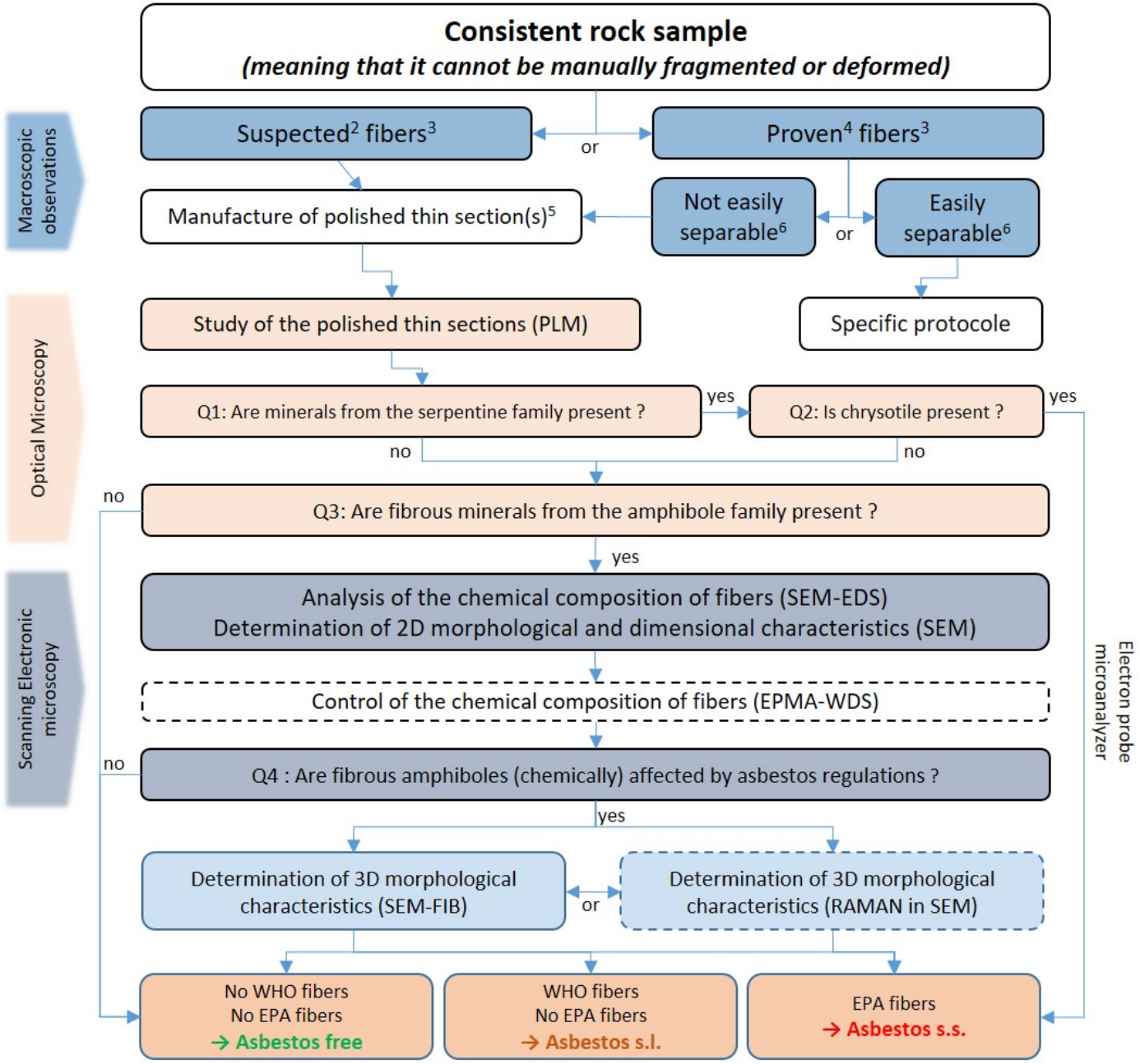
- This protocol **uses a single analytical support (geological thin section)**
  - The manufacture of thin sections is a well-controlled operation, rapid and not very expensive. ⇒ undeniable and important advantage for a standardized analytical method.
  - All steps are performed ***in situ***.

- No preliminary grounding and subsampling steps, **the sample is kept in its natural state for analysis**.
  - **Its limits diagnostic errors and avoids controversies related to the natural / artefact naturel of the morphology** (true asbestiform vs fibriform cleavage fragments).

- This protocol **can be stopped at the end of each step**, as soon as the information collected is sufficient to allow the operator to establish a reliable and justified diagnosis.
  - Only the most complex samples should follow the full protocol.

- The main part of the protocol is based on **proven and robust analytical methods**
  - The last step of the protocol is based on new analytical capacities offered by the use of **high performance advanced techniques implemented within the high-resolution SEM** (Field-Emission SEM)
  - **New technical developments** on theses techniques will offer new capacities in the near future (example : recent developments on xenon plasma focused ion beam for fast and large 3D FIB-SEM)

Protocol
Flow chart



Thank you for your attention

Questions ?

Actinolite-asbestos vein intersecting ophiolitic metabasalts – North of Corsica (France) (D. Lahondère – BRGM)