Contribution of Image correlation SEM-EDS-Raman to the study of geomaterials: a promising approach

Guillaume Wille

Actinolite – Asbestos form
PLM (J. Duron, BRGM)

CONTRIBUTION OF IMAGE CORRELATION SEM-EDS-RAMAN TO THE STUDY OF GEOMATERIALS
a promising approach

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Geoscience for a sustainable Earth
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Geoscience for a sustainable Earth

Actinolite-asbestos vein interspersed with ophiolytic metabasaltes (Corsica, France)
D. Lahondere, BRGM

- Introduction: Interest of multimodal analysis in geosciences
- Coupling SEM-EDS and Raman spectroscopy
  - Why ? How ?
- Coupling SEM-EDS and Raman spectroscopy
  - Examples
- Coupling SEM-EDS and Raman spectroscopy
  - A case study: application to the identification and characterization of the natural occuring asbestos (NOA)
- Conclusion

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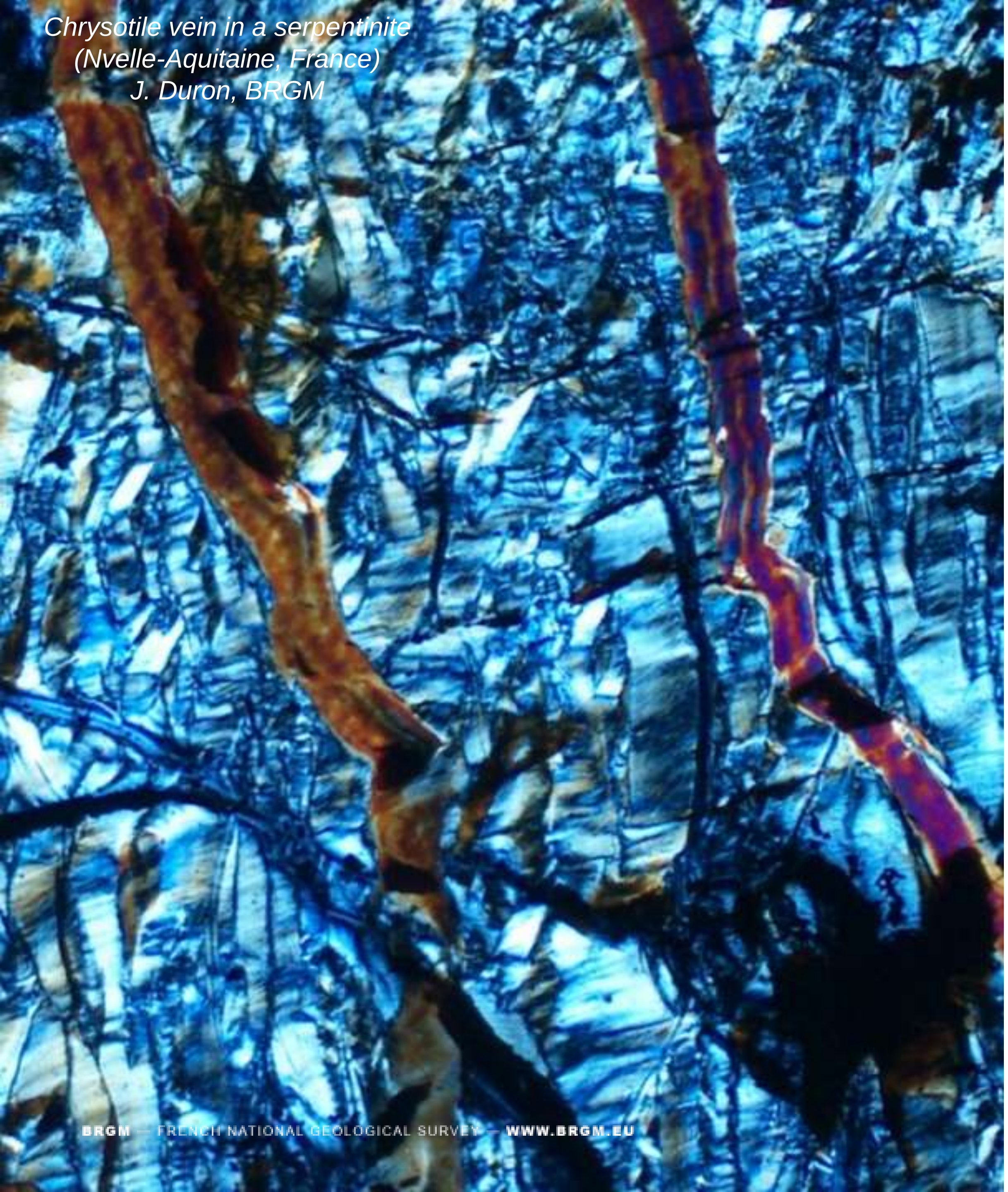


Introduction: Interest of multimodal analysis in geosciences

SEM and all associated techniques is of great interest in the analysis and characterization of geomaterials

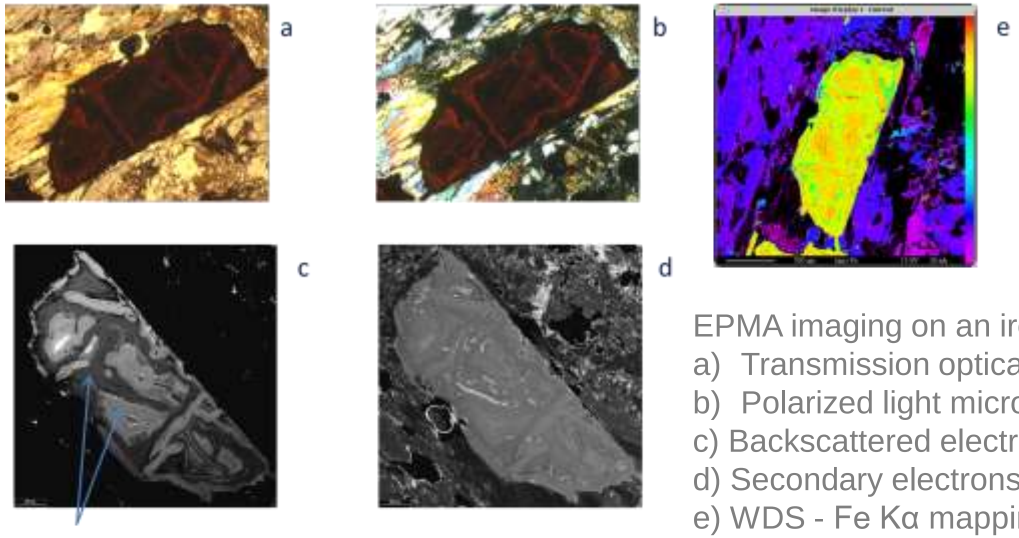
MULTIMODAL APPROACH

A multimodal approach is the combined use – synchronously or asynchronously – of several analytical techniques, each of which can provide a part of a set of physical and chemical data

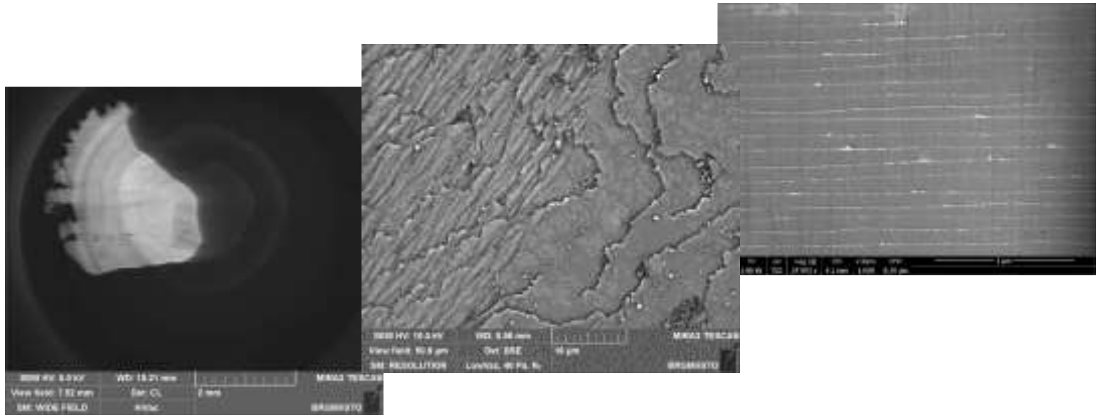
Complementary analytical data

Co-location of physical and chemical data

- Morphology
- chemistry
- Crystallography, atomic / molecular organization
- Etc…



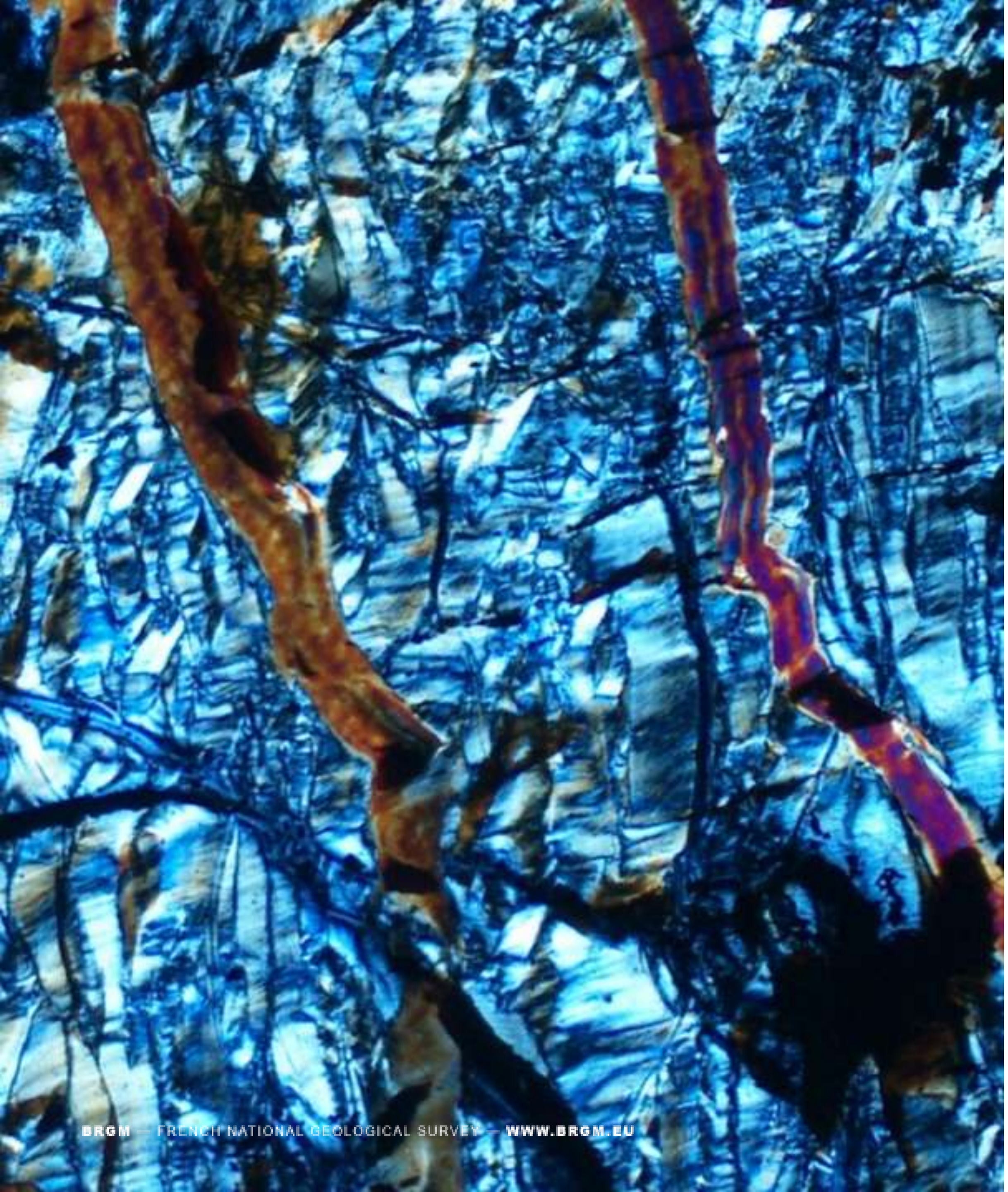
EPMA imaging on an iron oxide grain
a) Transmission optical microscopy
b) Polarized light microscopy
c) Backscattered electrons imaging
d) Secondary electrons imaging
e) WDS - Fe Kα mapping



« Milky » pealrs (vaterite defect) (SEM CL / BSE / SE on FIB slice)

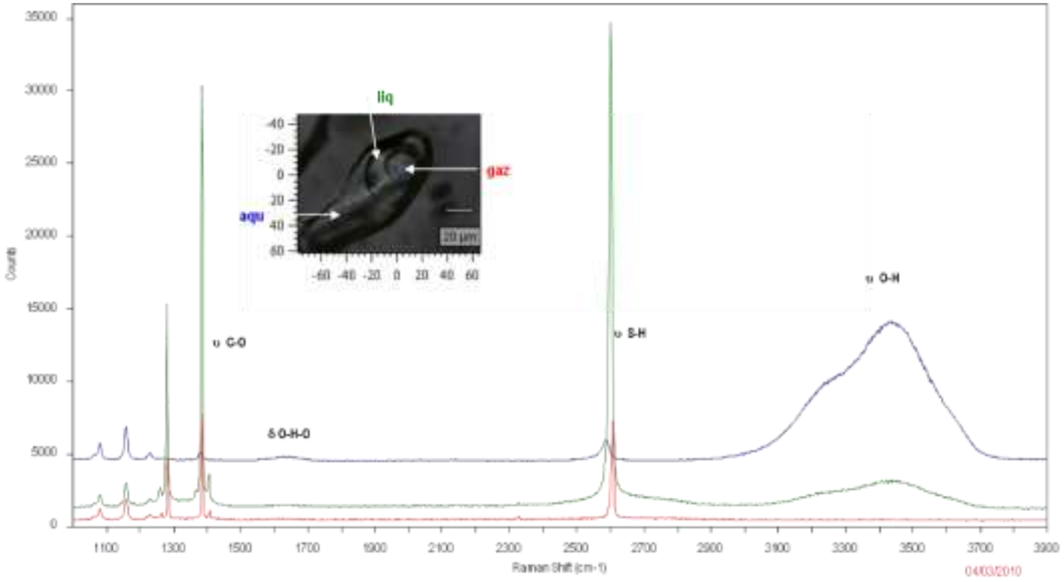
Co-located multi-scale data

- Multi-scale coupled data
- Microscopy:
  - Macroscopy (cm / mm)
  - Visible Light Microscopy (µm)
  - Scanning electron microscopy (nm)
  - Transmission electron microscopy (Å)
- Analytical capacities
  - Various scales and spatial resolution
  - Various detection limits / sensitivity



Coupling SEM-EDS and Raman spectroscopy

Why ? How ?



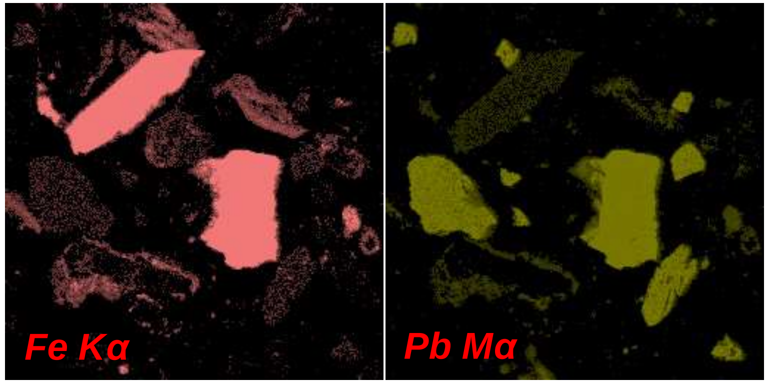
µ-Raman spectroscopy analysis of a fluid inclusion in a quartz grain

After *C. Beny et al., Chemical Geology 37 (1982) 113--127*

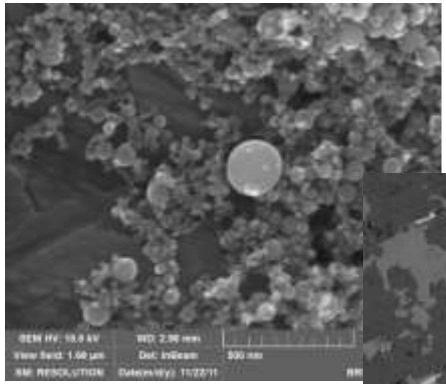
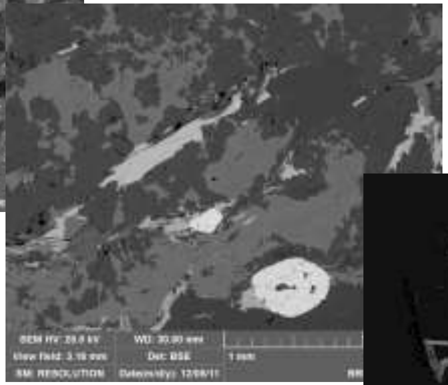
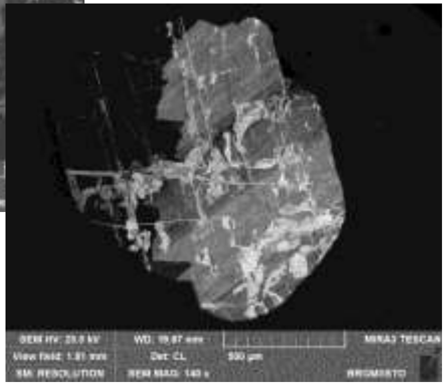
Scanning Electron Microscopy

SEM

- Electron beam generated by an electron gun, accelerated and focused in an « electron column »
- Various imaging modes (matter / electron beam interactions):
  - Secondary electrons imaging (topography)
  - Backscattered electrons imaging (chemical contrast ± crystal orientation contrast)
  - Other imaging modes (cathodoluminesence, transmitted electron…)



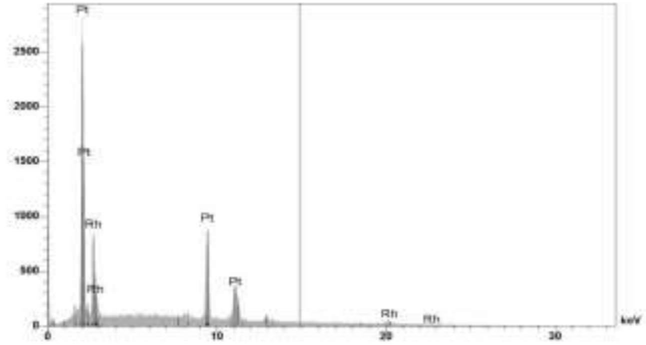
EDS mapping of Iron and Lead in a lead ore (Pontgibaud mine, France)

Examples of SEM images:
Top: SE (TiO_2 nanoparticles)
Middle: BSE (Granite)
Bottom: panchromatic CL (Cassiterite SnO_2)

EDS

- Emission of characteristic X-ray
- Elemental analysis:
  - Qualitative (identification of elments)
  - Quantitative (Wt%)
  - Imaging (elements distribution)

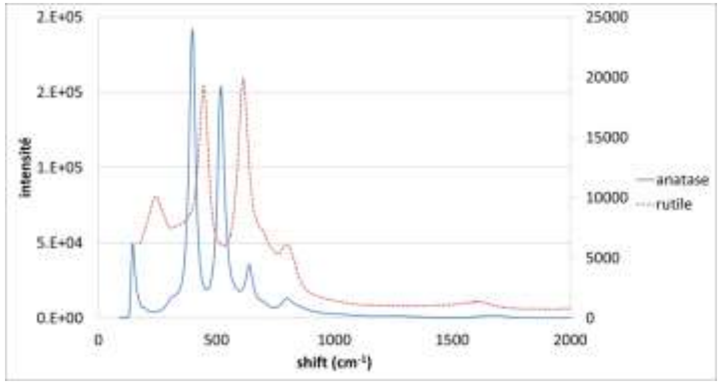


EDS spectra of Pt / Rh alloy

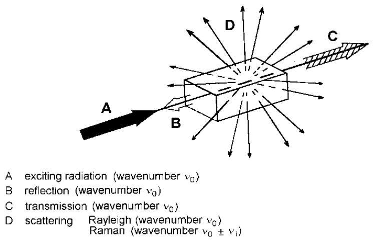
Micro-Raman spectroscopy

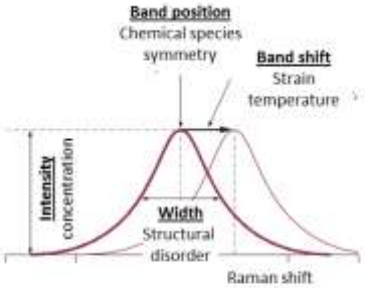
Principe

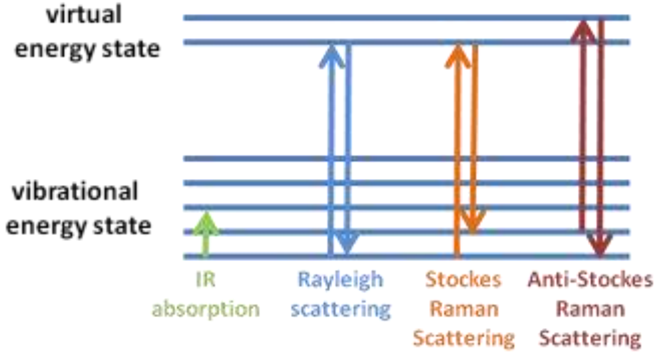
- Vibrational spectroscopy based on the inelastic diffusion of monochromatic light (laser beam)
- Various structural information:
  - Crystal structure, degree of crystallinity
  - Presence de chemical groups (-OH, -CO3, etc ...)
  - Amorphous materials

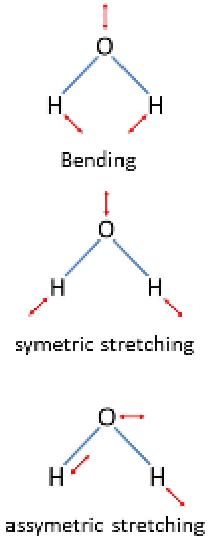


Raman spectra of TiO_2 rutile (quadratique P) and anatase (quadratique C)

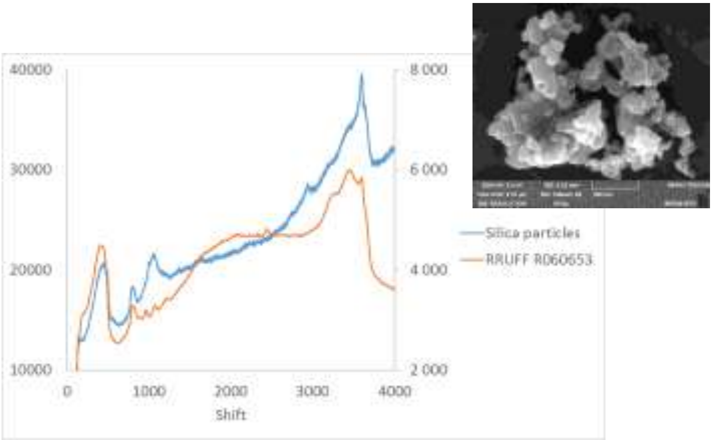








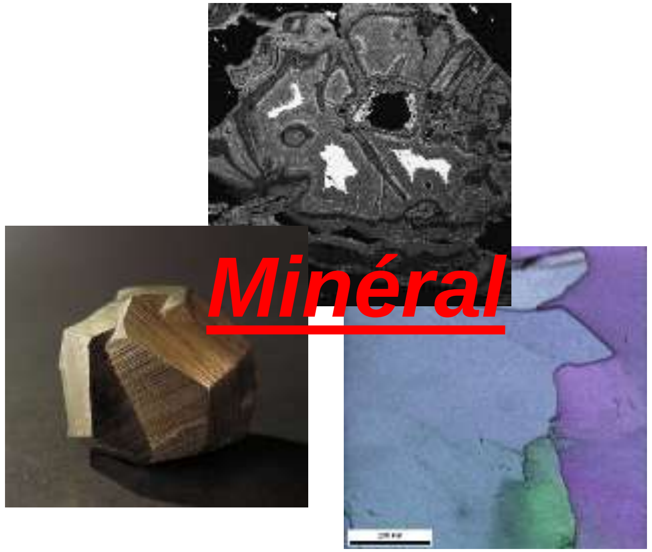
Vibration modes of the water molecule H_2O



Raman spectrum of
SiO_2 nanoparticles compared to the Raman spectrum of opal (hydrated amorphous form of silica)
(RUFF database - http://rruff.info/)

Coupling SEM-EDS and Raman

A case study, the mineral



Minéral

Pyrite (FeS_2)
*a) Pyrite inclusions in Iron oxide - BSE**
*b) Centimetric pyrite (Elba, Italie)***
*c) Orientation map in a pyrite - EBSD**

Composition

« textbook » composition
+
"deviations" dues to the presence of minor / trace elements

In the SEM

EDS, WDS

Cristallography

Crystal structure
+
Distortions (defects, dislocations…)

In the SEM

EBSD / TKD
Raman

Morphology, shape

Automorphs crystals, surface roughness…

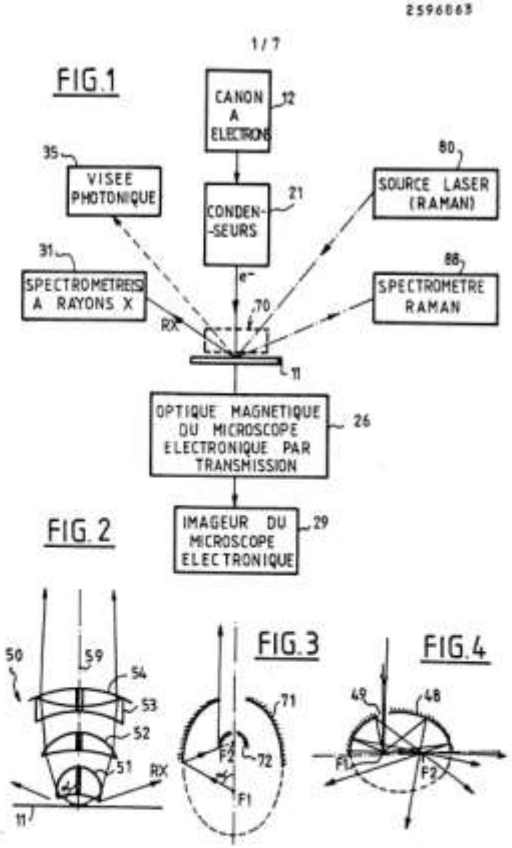
In the SEM

Imaging Modes (SE, BSE, CL...)

*Images * G. Wille / ** U. De Cayeux, BRGM*

Coupling SEM-EDS and Raman

The origin



1986 - M. Delhaye & M. Truchet: Patent for an analytical microscope coupling electron microscopy and Raman microscopy

J. Microsc. Spectrosc. Electron., Vol. 13, 1988, 167-175

COUPLAGE D'UNE SONDE RAMAN LASER ET D'UNE SONDE DE CASTAING DANS UN MICROSCOPE ELECTRONIQUE

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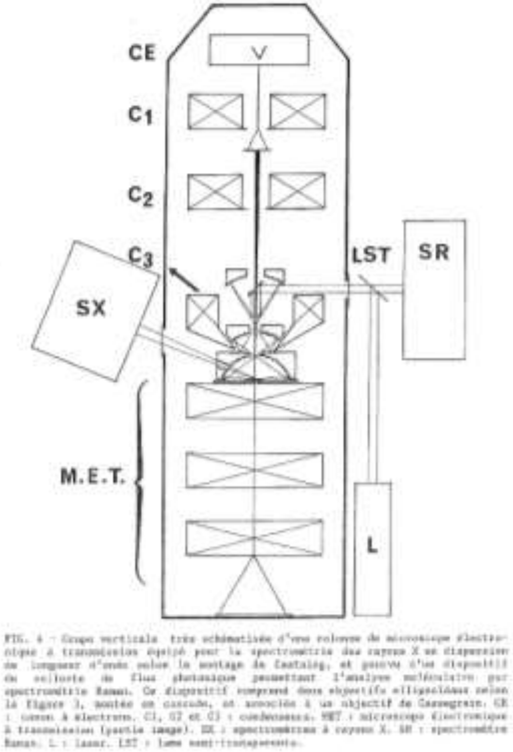
accepté en février 1988

ABSTRACT
The photon microscope of the Raman microprobe limits the spatial resolution to the micrometer scale, and the wavelength width to the visible light. In this paper is described a new objective, made of an ellipsoïdal miror associated with a plane miror, at the first focus. This device allows a numerical aperture of 0.99, a total achromatism from U.V. to I.R. and makes possible molecular Raman analysis of samples into the column of an electron microscope and/or a Castaing's electron microprobe, for simultaneous elemental analysis at submicronic scale.

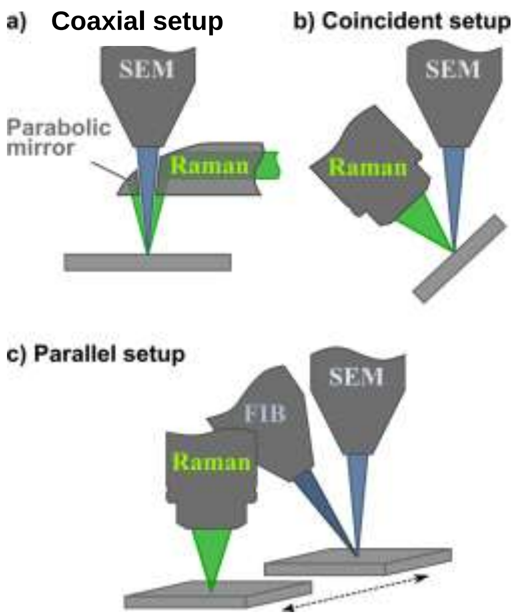
1988 - M. Truchet & M. Delhaye : 1st publication



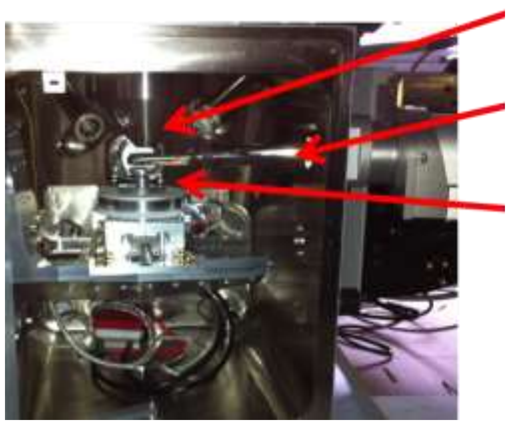
Micro-Raman spectroscopy

SEM-Raman

- 2 types of SEM-Raman coupling : coaxial or parallel
- Coaxial setup
  - Resolution: ~ 2.5 µm @ λ = 514 nm
  - Spectral analysis: loss of intensity (compared to conventional Raman spectroscope)
  - Imaging mode: possible but limited (time / pixel)
- Parallel setup
  - Resolution: < 400 nm @ λ = 532 nm
  - Spectral analysis: comparable with a conventional Raman spectroscope
  - Imaging: comparable with a conventional Raman spectroscope (250 x 250 µm)



Different SEM – Raman setup *
a) coaxial b) coïncidence c) parallel



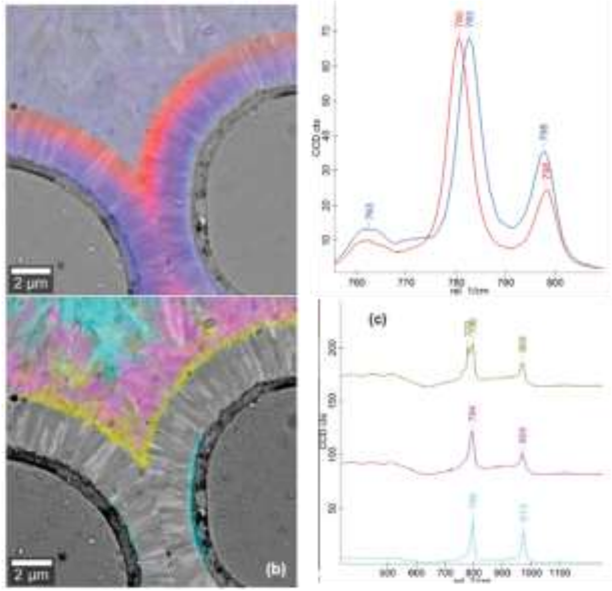
SEM pole piece

Raman mirror

Sample

Co-axial setup
Renishaw SEMSca / Tescan MIRA

Parallel setup
WITec RISE / Tescan MIRA



SEM-Raman analysis of a composite Carbon / SiC (Tescan – WITec RISE)

Jiruse et al, 2014

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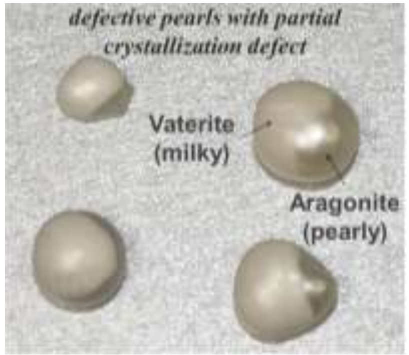
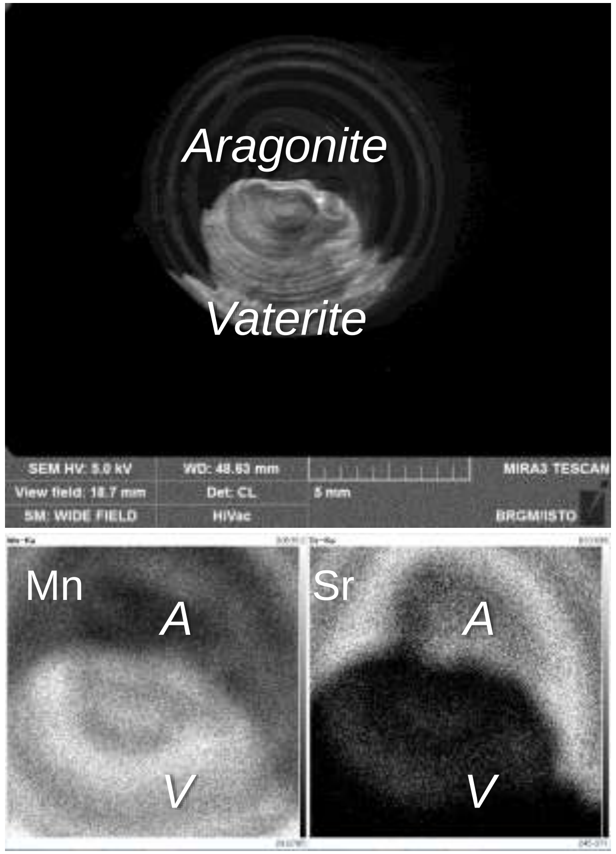
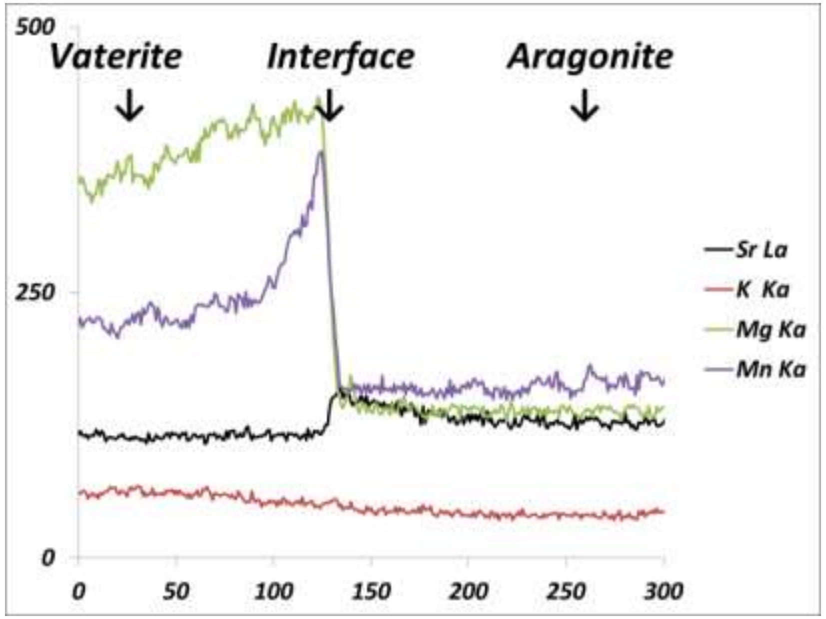
Coupling SEM-EDS and Raman

Example: polymorphs of calcium carbonates in a defective pearl



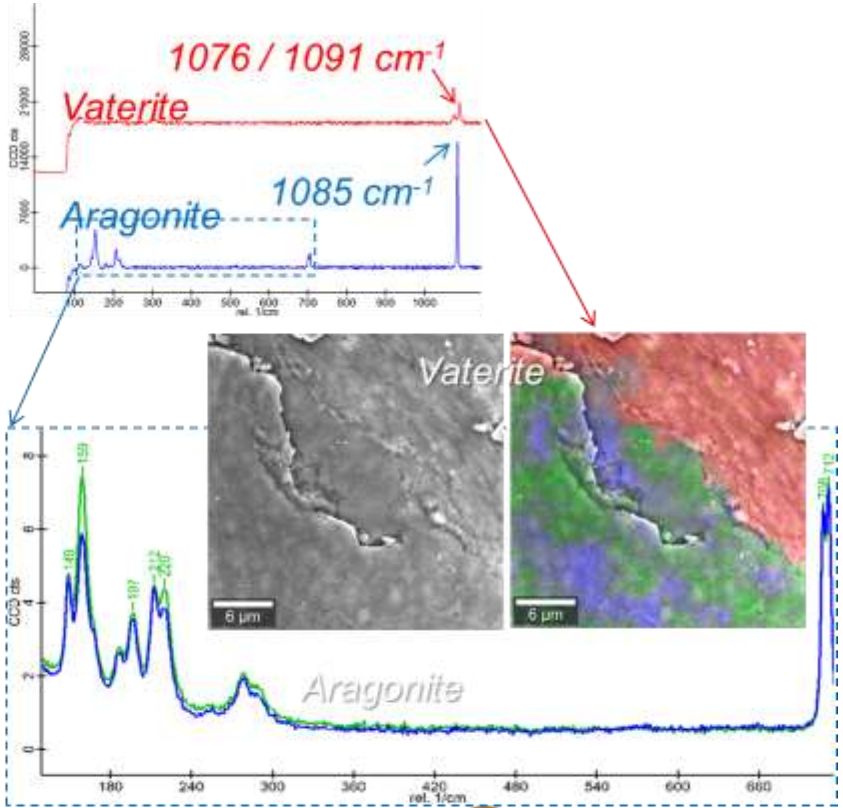


SEM - panchromatic CL and µ-XRF maps



WDS profile (EPMA) on both sides of the interface

Raman map on both sides of the interface



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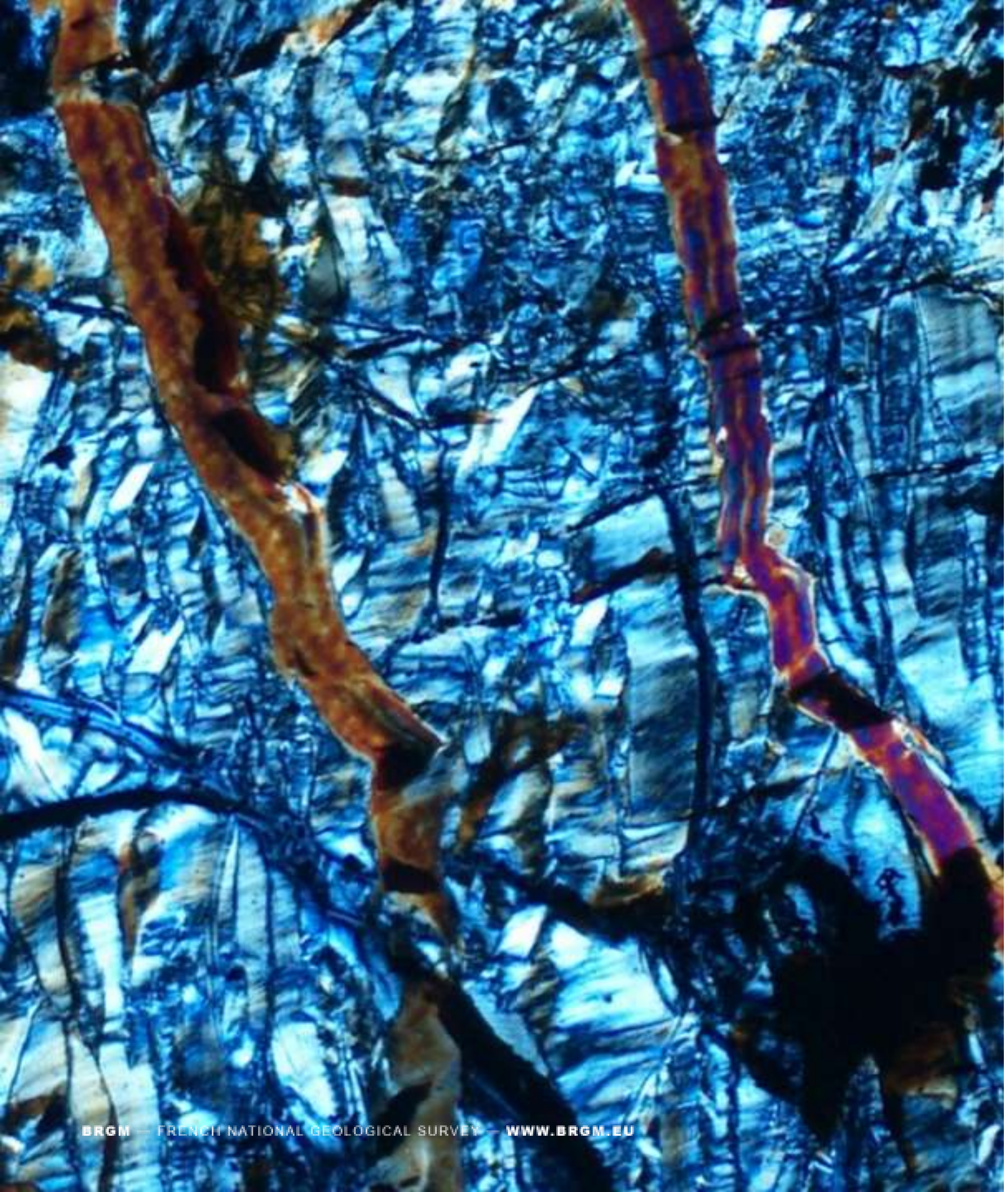
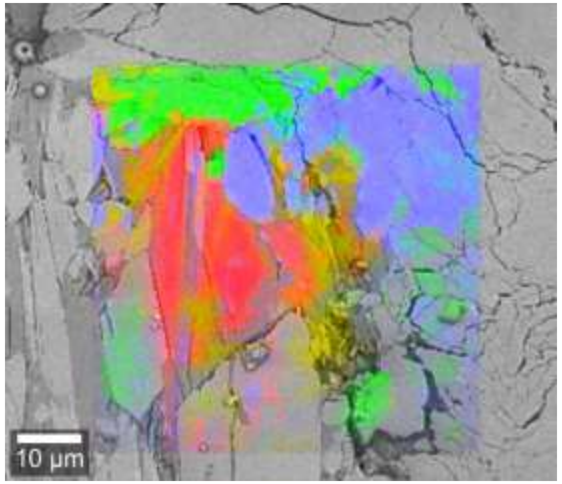
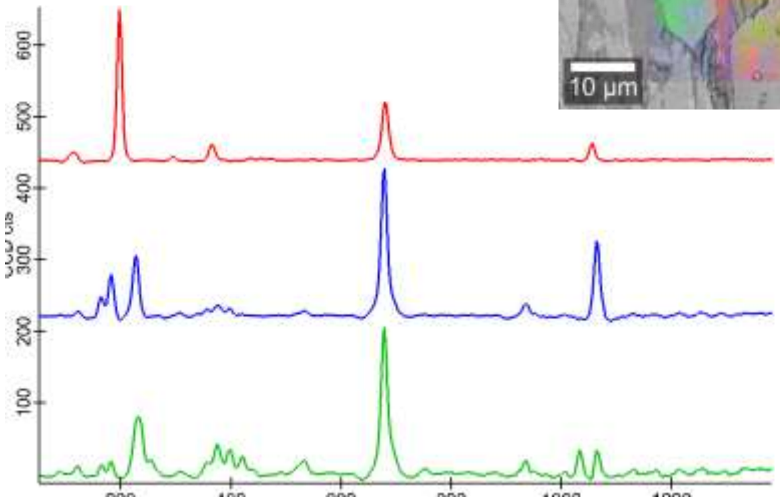


Coupling SEM-EDS and Raman spectroscopy

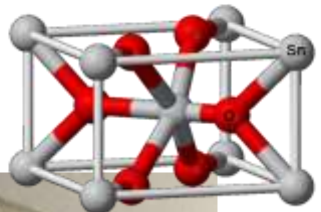
Examples





SEM-Raman on a transverse section of an actinolite fibers bundle

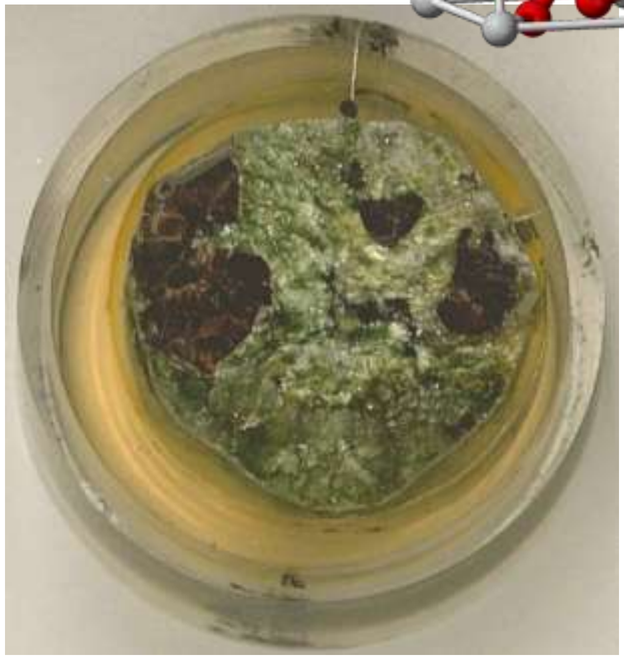
Ex. 1 – Zonation in tin oxide cassiterite



SEM - Raman - EBSD - WDS

G. Wille, C. Lerouge (BRGM), U. Schmidt (WITec)

- Cassiterite SnO_2 is the main tin ore (Sn)
- SnO_2 crystal structure similar to Rutile (TiO_2)
- Various possible trace elements: Ti, Fe, Ta, Nb, Zn, W, Mn, Sc, Ge, In, Ga...
- The knowledge of chemistry is required for:
  - Understanding of the geological context of the mineral resource
  - Feasibility of the tin production process
  - Waste recycling / treatment
- 2 possible substitution:
  - Homovalent: $Sn^{4+} \leftrightarrow Ti^{4+}$
  - Heterovalent: $2.(Nb,Ta)^{5+} + (Fe,Mn)^{2+} \leftrightarrow 3.Sn^{4+}$



Tin ore from the Montbelleux mine
(Luitré, Ille-et-Vilaine - France)

C. Lerouge et al. European Journal of Mineralogy, 2018, 29(4), p. 739-753

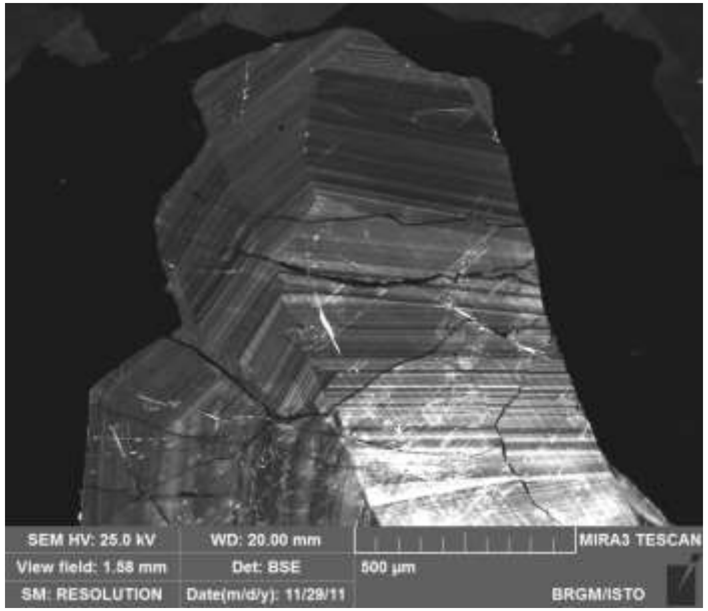
Ex. 1 – Zonation in tin oxide cassiterite

SEM - Raman - EBSD - WDS

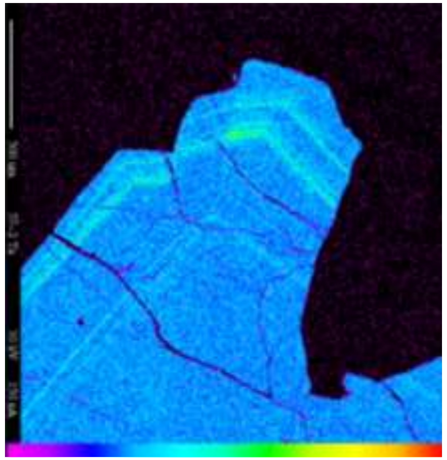
- SEM - CL shows a strong contrast that may be associated with trace elements distribution and / or crystal orientation

- EPMA (WDS) analysis is applied for mapping and quantification of trace elements content – Some CL contrasts can be linked to EPMA data

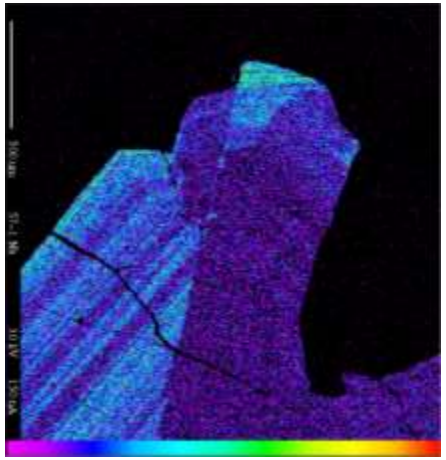
- EBSD provide 2 informations on the crystallography of cassiterite grains
  - Millimetric monocrystalline grains
  - Elbow twin (~ 70°) commonly encountered in rutile stucture



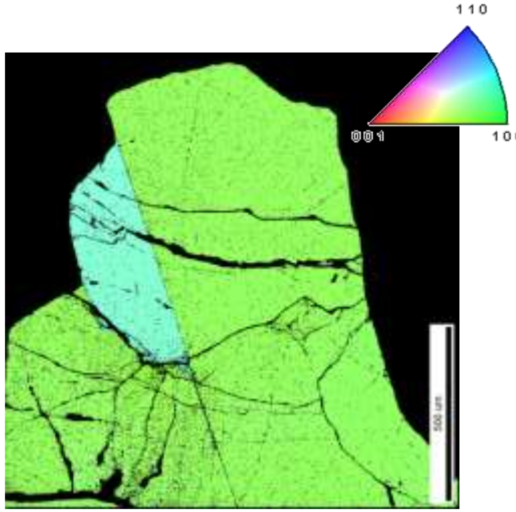
SEM - CL



Ta



Nb



EBSD

WDS maps (EPMA) and EBSD orientation map of the same area

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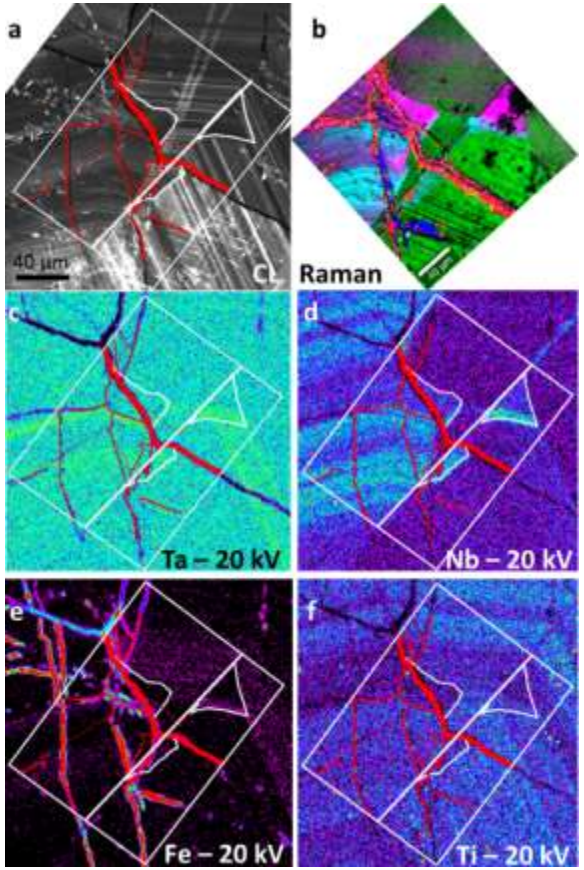
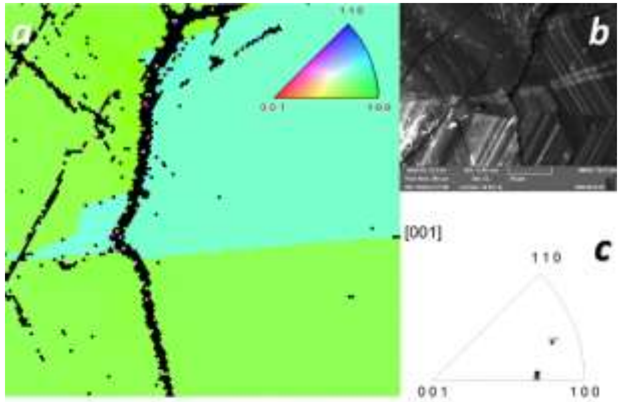
Ex. 1 – Zonation in tin oxide cassiterite

SEM - Raman - EBSD - WDS

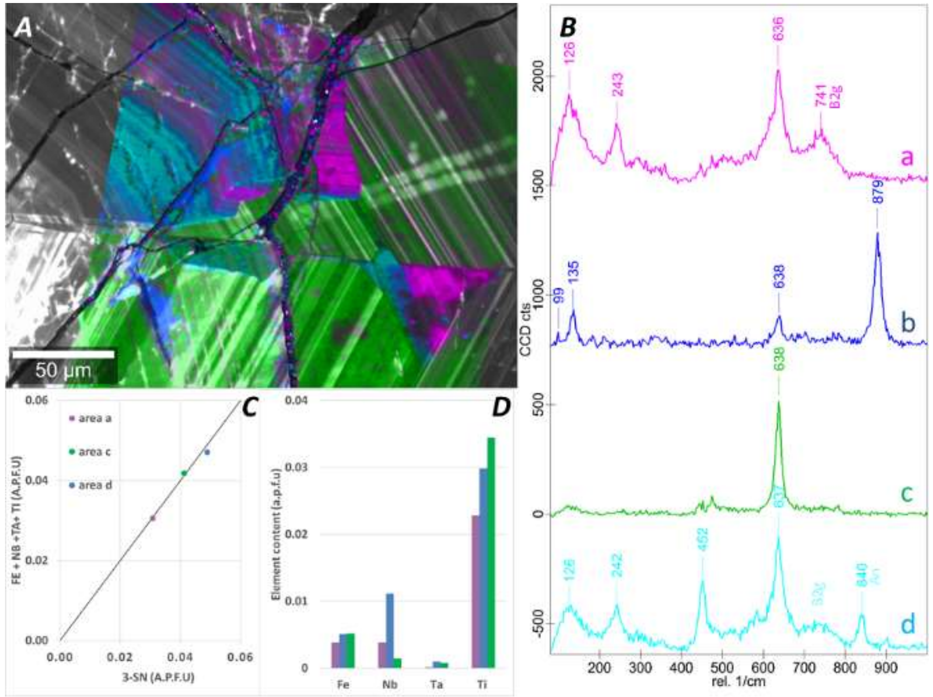
- The correlation of the data obtained from the different techniques on the same area of the sample allow a fine analysis of the substitution of Sn by the other elements



EPMA(WDS)



EBSD



Raman mapping and Raman spectra extracted
Comparison with EPMA data (structural formula)

G. Wille et al. J Microsc. 2018 Jun;270(3):309-317,

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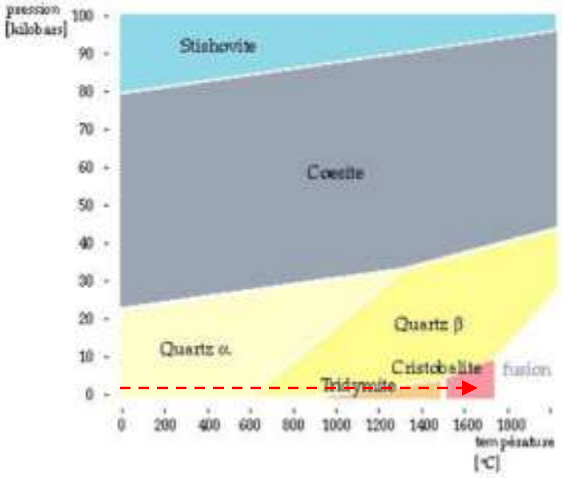
Ex. 2 – Industrial process for the obtention of white pigments

Industrial process for the production of high quality white pigments from natural silica stones (beach pebbles)

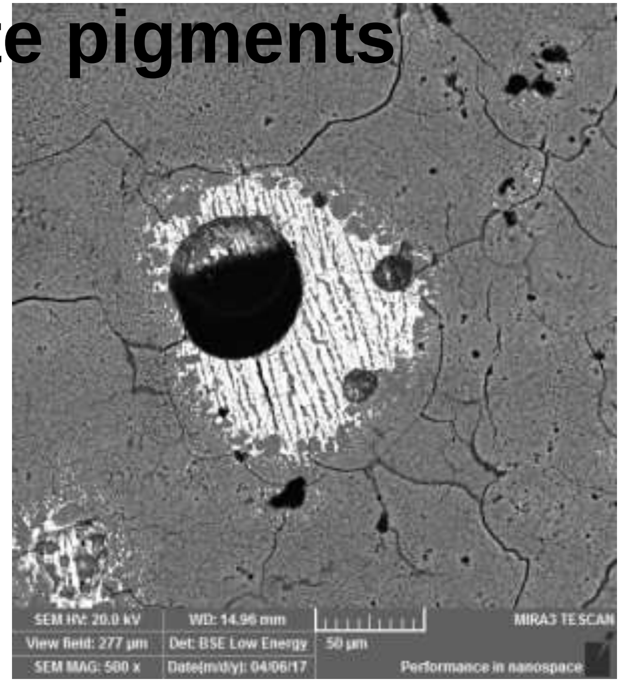
- White pigments obtained from high temperature heating of silica pebbles
- Improvement of the product quality by studying different parameters
  - Source of the raw materials
  - Composition of the final product: % main phase / secondary phases
- ⇒ Overall characterization (XRD, chemistry)
- ⇒ Micro-characterisation: morphology, chemistry, cristallography

Blue flint in a Limestone cliff
(Normandy, France)



Chalcedony → ***Quartz β*** → ***Tridymite*** → ***Cristobalite***

Ex. 2 – Industrial process for the obtention of white pigments

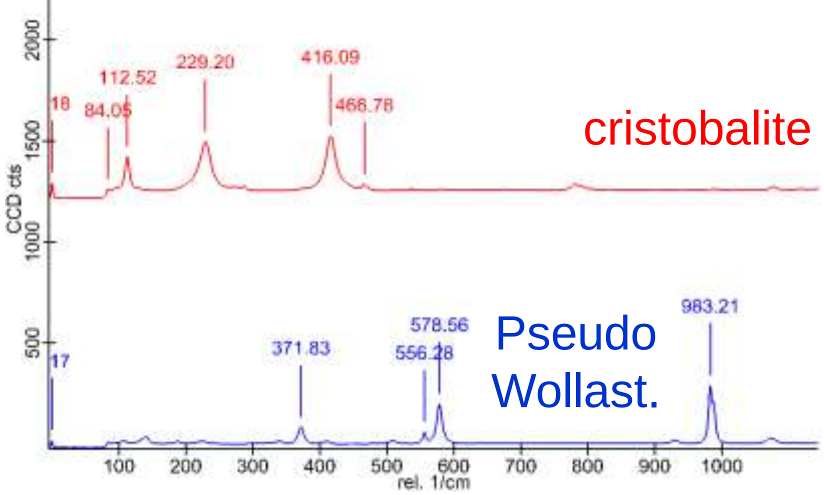


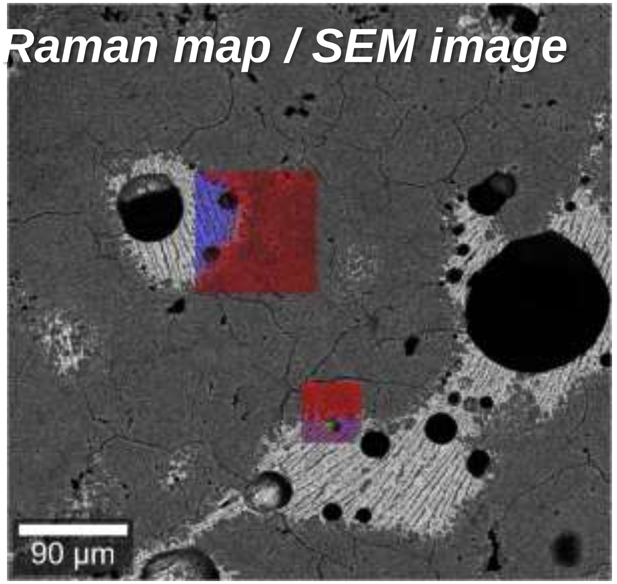
Industrial process for the production of high quality white pigments from natural silica stones (beach pebbles)

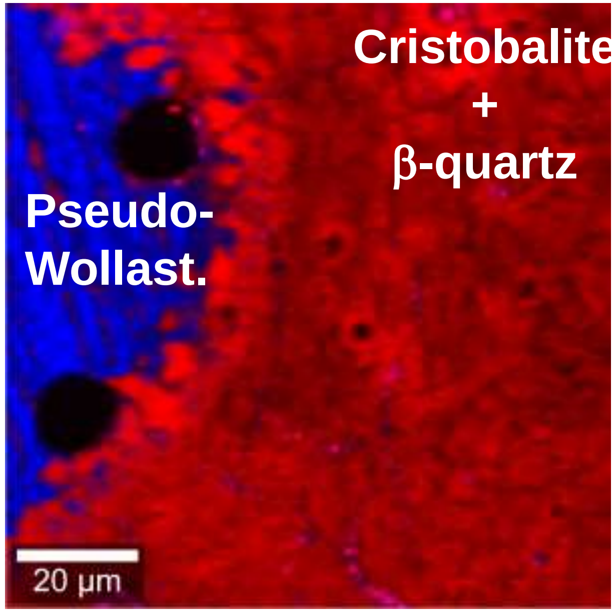
- Final composition: cristobalite, présence de quartz β
  - Distribution of the phases ? → *EBSD doesn't work (poorly crystallized)*

- SEM observation : evidence of a phase containing Ca and Si
  - Lamellar structure
  - Alternance of lamella and Silica
  - EPMA: composition $CaSiO_3$ → *Wollastonite not stable at the process temperature*

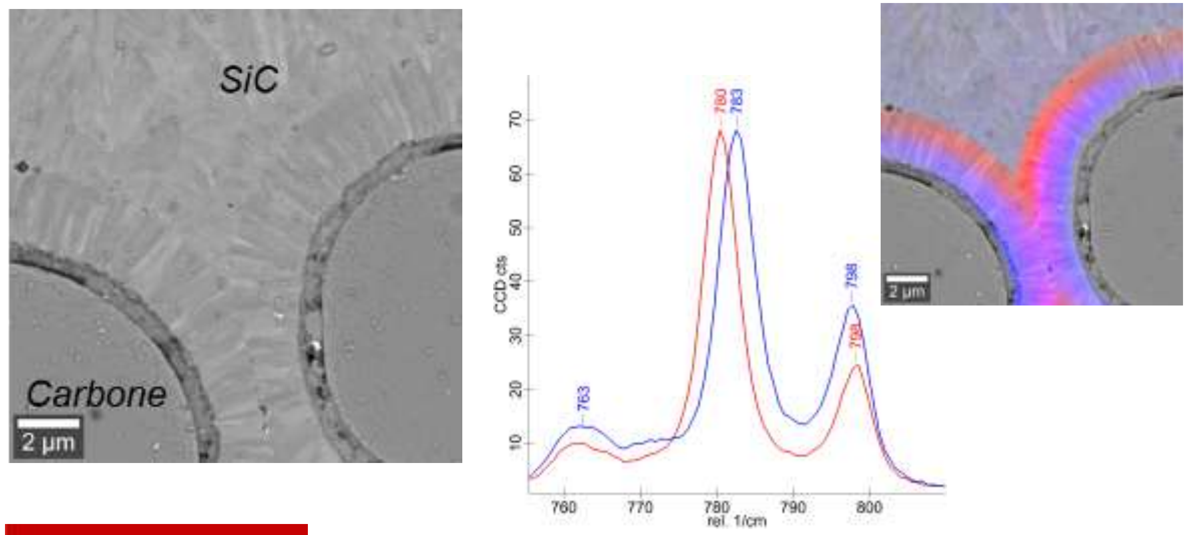
⇒ ***identification and description by Raman imaging in the SEM***

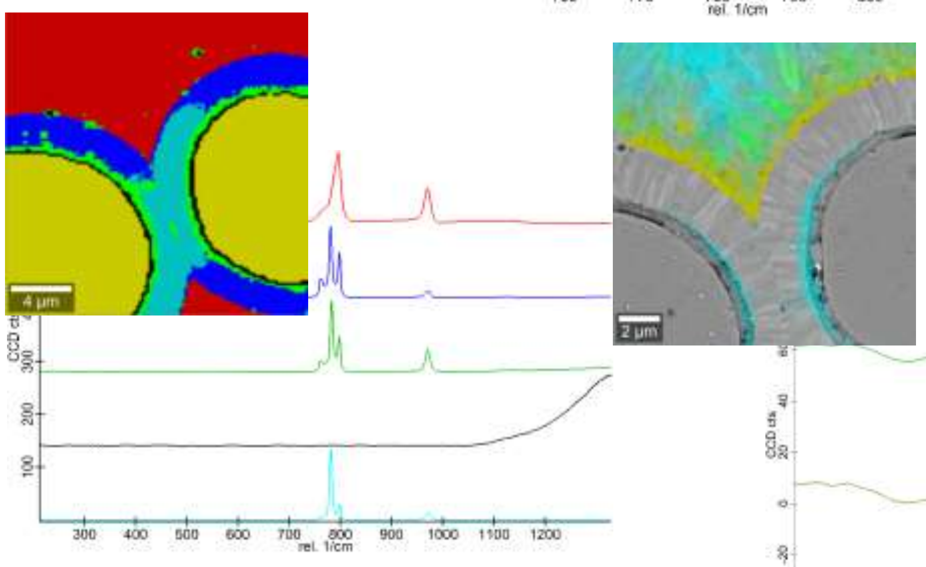


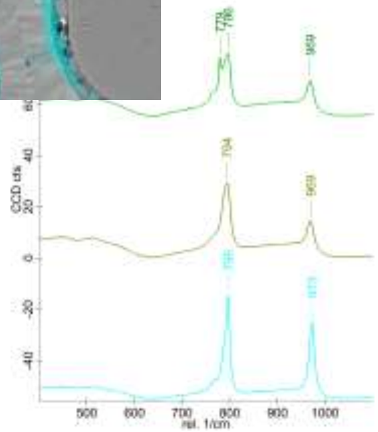




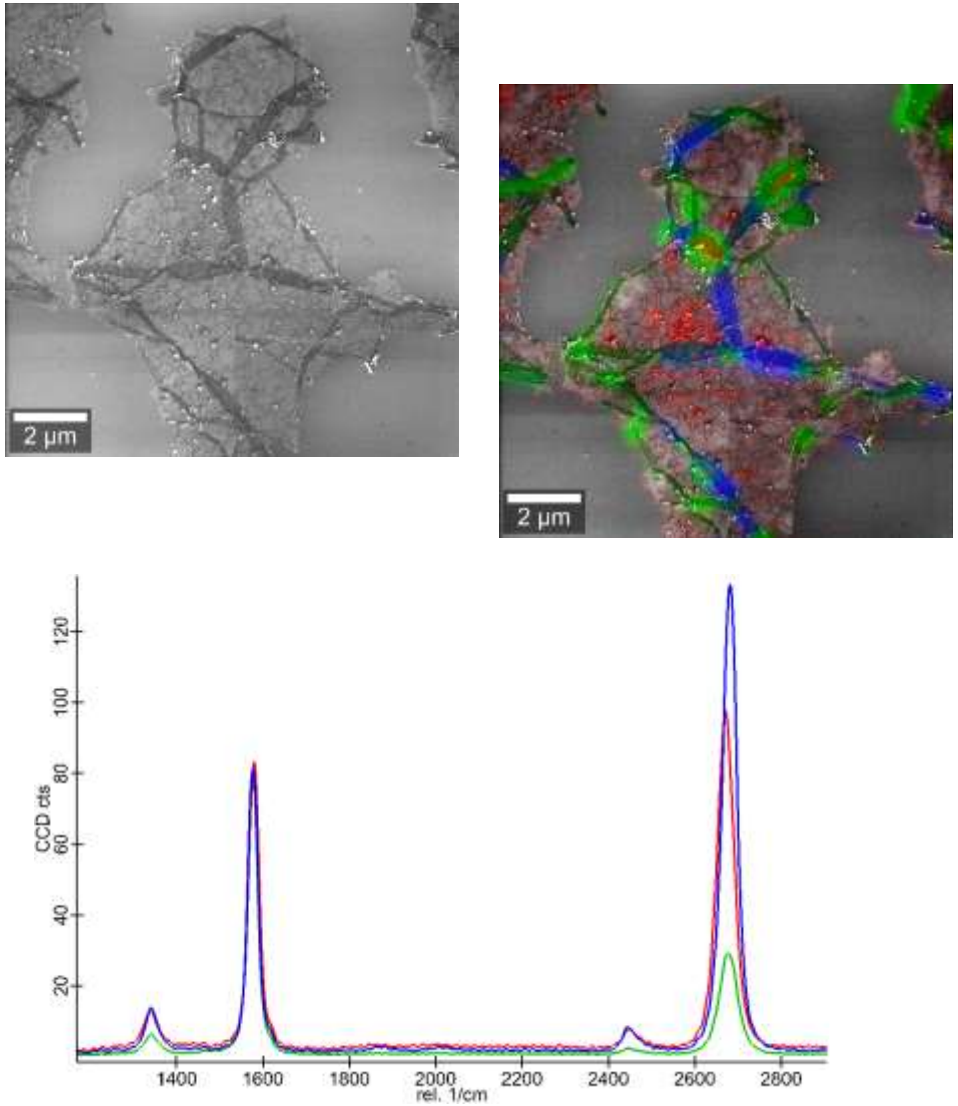
Application – other examples





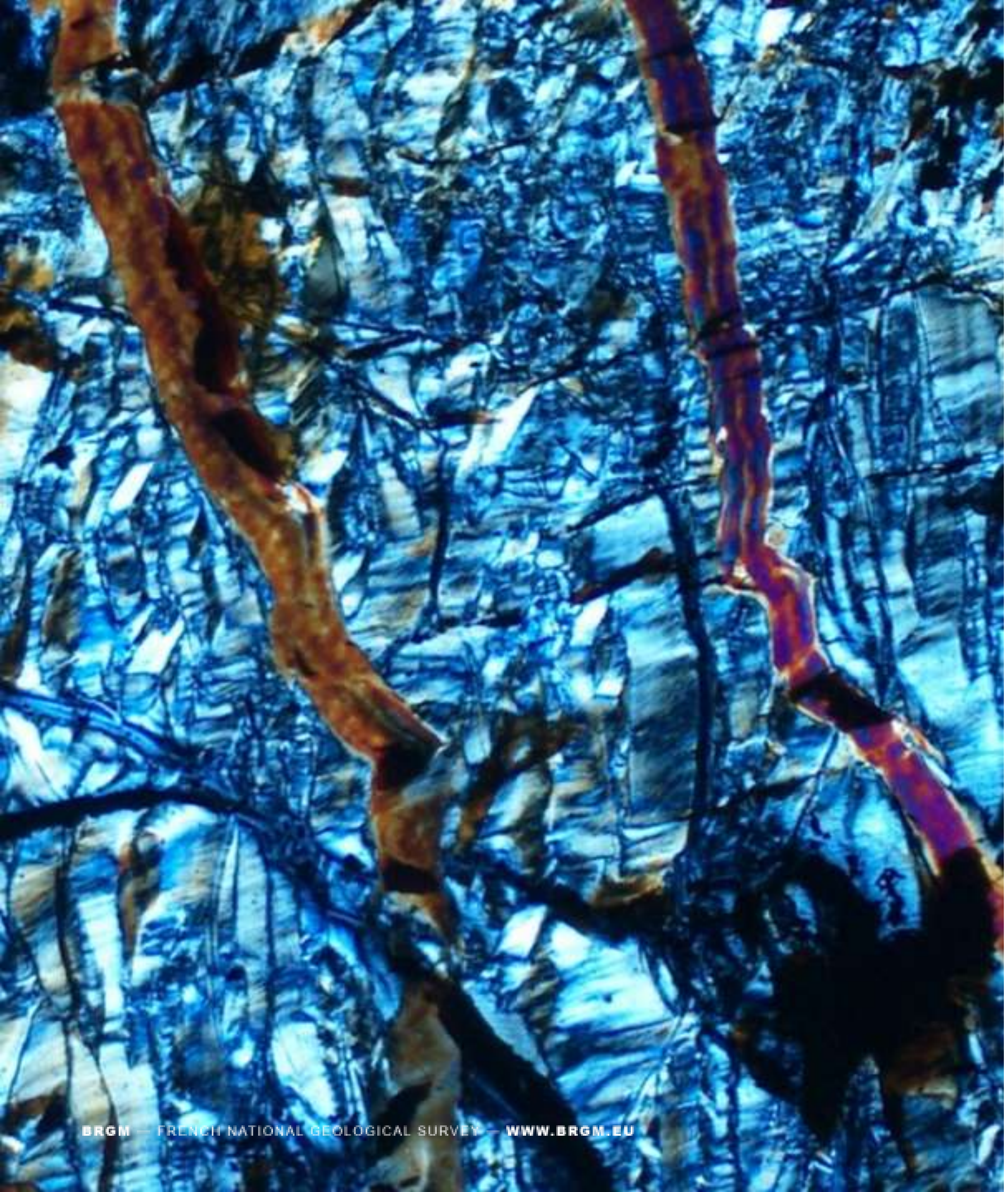


Composite Carbon / SiC



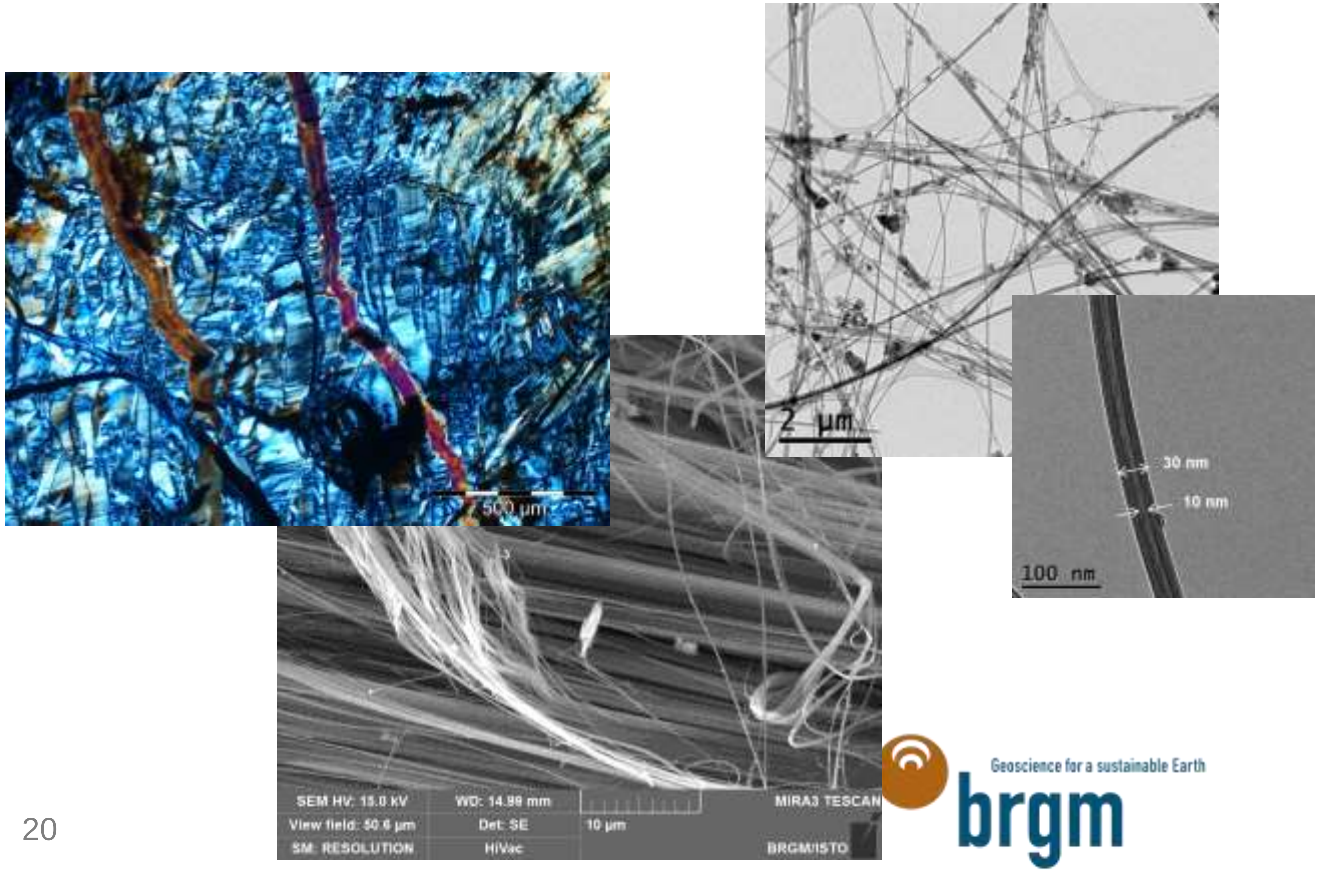
CVD deposition of graphene on silicium

Image SEM (SE) + Raman IG'/IG
Blue, red: NLG <3
green: NLG ≥ 3



Coupling SEM-EDS and Raman spectroscopy

A case study: application to the identification and characterization of the natural occuring asbestos (NOA)



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Asbestos

Asbestos

From the greek word *Asbestos* (incombustible)

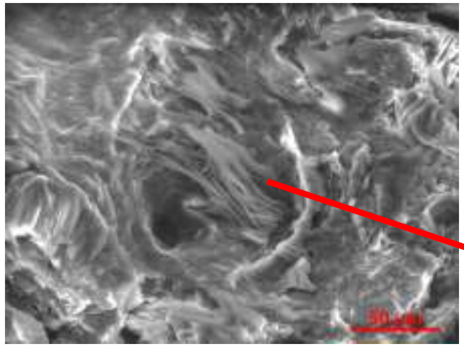
This term refers to a group of 6 natural fibrous silicates (as well as any mixture of these fibers).

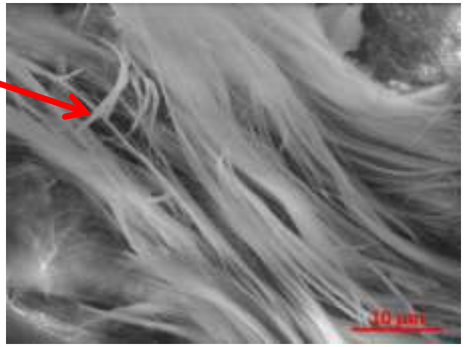
Serpentines	
Chrysotile	$Mg_3Si_2O_5(OH)_4$
Amphiboles	
Tremolite	$Ca_2Mg_5Si_8O_{22}(OH)_2$
Actinolite	$Ca_2(Mg,Fe)_5Si_8O_{22}(OH)_2$
Anthophyllite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$
Amosite	$(Mg,Fe)_7Si_8O_{22}(OH)_2$
Crocidolite	$NaFe_5Si_8O_{22}(OH)_2$

Known and used since the greek and roman antiquity, for their physical and chemical properties.

commercial definition → limited to the varieties exploited industrially

legal and regulatory definition → defined in each country or group of countries. Ex. in the european union 2009/148/EC on the protection of workers from the risk related to exposure to asbestos at work



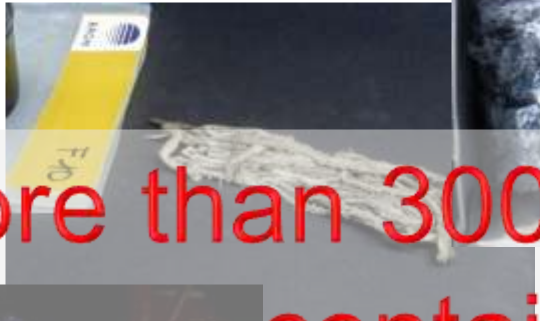


Chrysotile fibers in a vynil floor tile (SEM – SE –low vacuum mode)

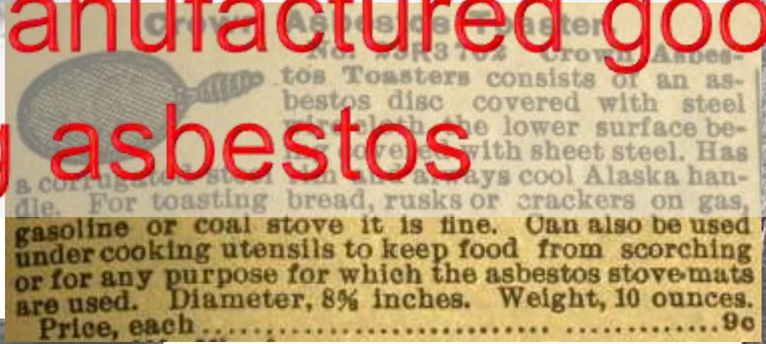
Breathable Fiber (WEO 1998) = L > 5 µm ; D < 3 µm ; L/D > 5

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

Asbestos



More than 3000 manufactured good containing asbestos


tos Toasters consists of an asbestos disc covered with steel ... the lower surface be... with sheet steel. Has ... always cool Alaska handle. For toasting bread, rusks or crackers on gas, gasoline or coal stove it is fine. Can also be used under cooking utensils to keep food from scorching or for any purpose for which the asbestos stove-mats are used. Diameter, 8⅝ inches. Weight, 10 ounces. Price, each 9c

Sources: BRGM; Wikipedia

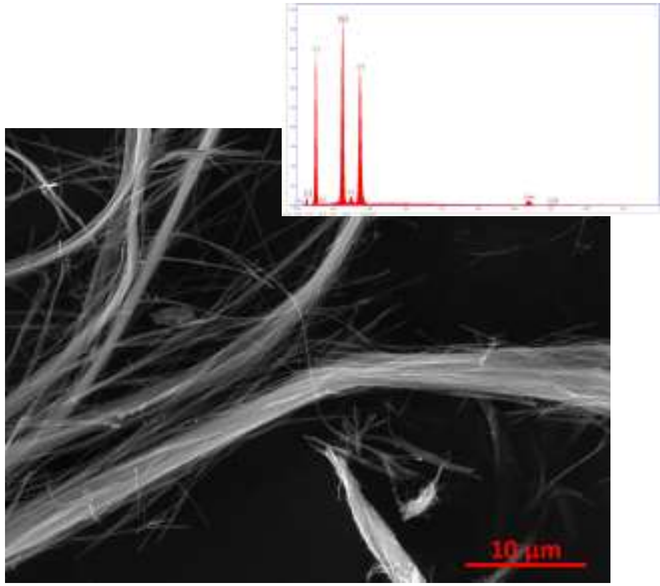
Naturally Occuring Asbestos

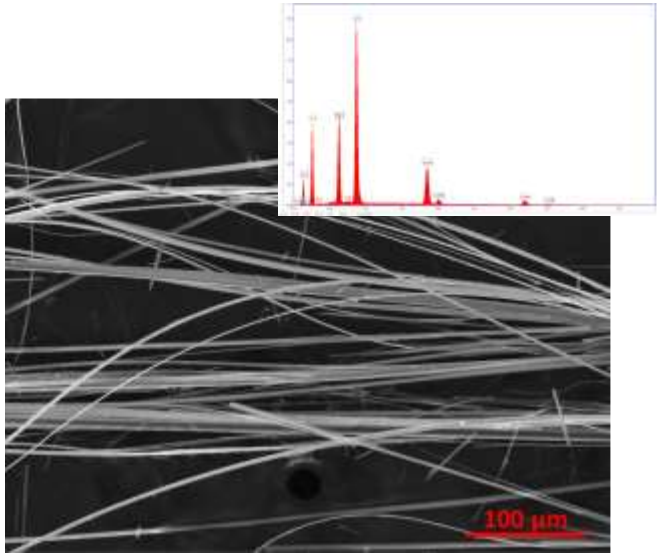
The geologist point of view

The chemical composition of several rocks allows the crystallisation of serpentines or amphiboles able to crystalline in an asbestiform shaphe.
:

- Ultrabasic rocks : peridotite, serpentinized peridotites, serpentinite, (méta)-pyroxenite
- Basic metamorphized rocks : amphibolites, metabasalts, metagabbro, metadolerits, prasinites, spilites, etc...
- Some metaphorphized carbonated rocks

Asbestiforms minerals / fibers can also be found in soils and sediments resulting from the alteration and erosion of these rocks.





top: chrysotile
bottom Tremolite-asbestos

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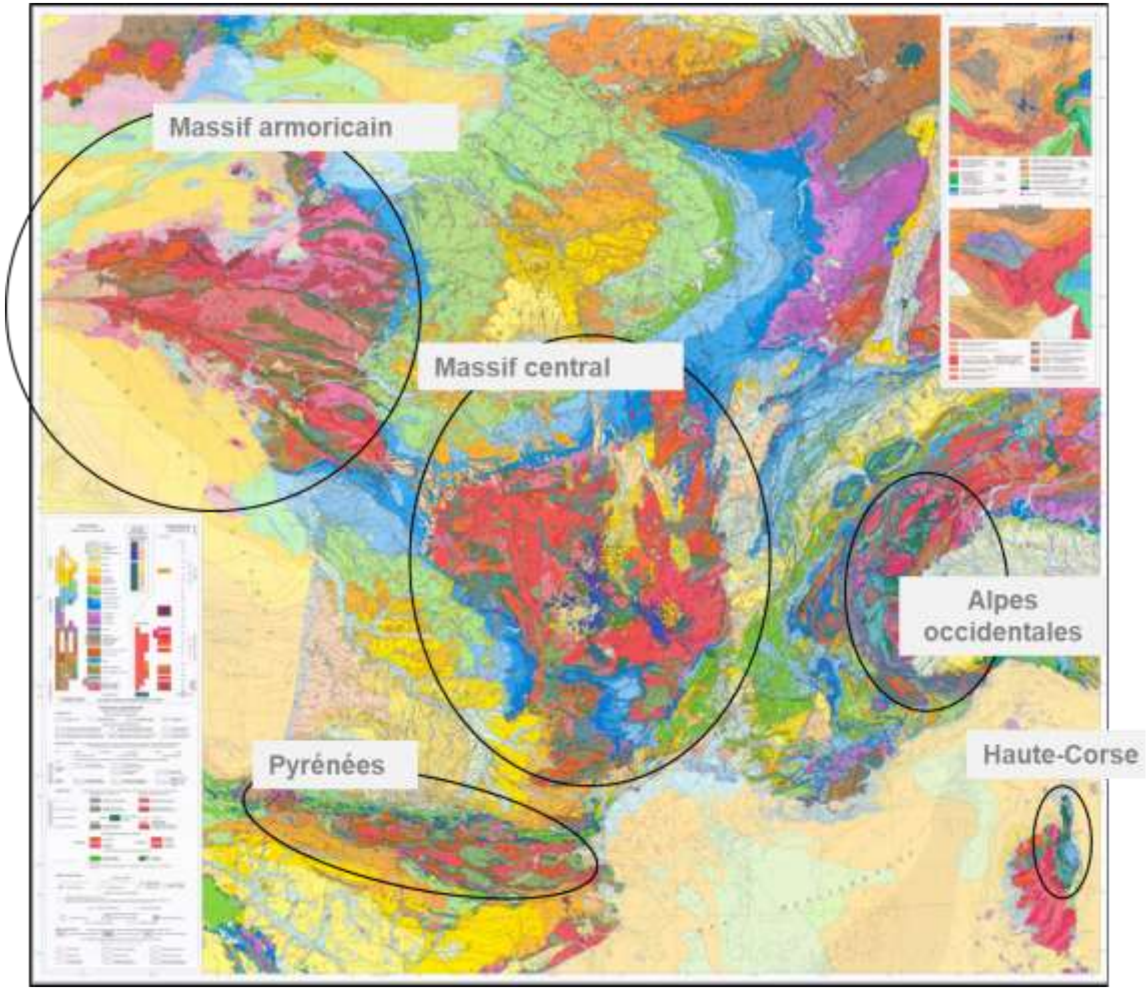
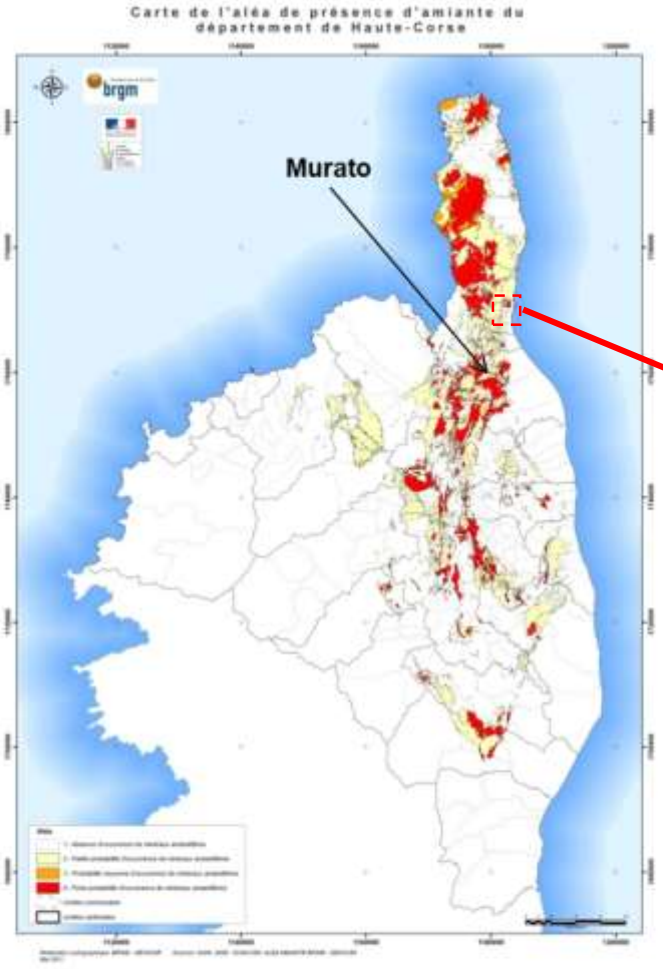
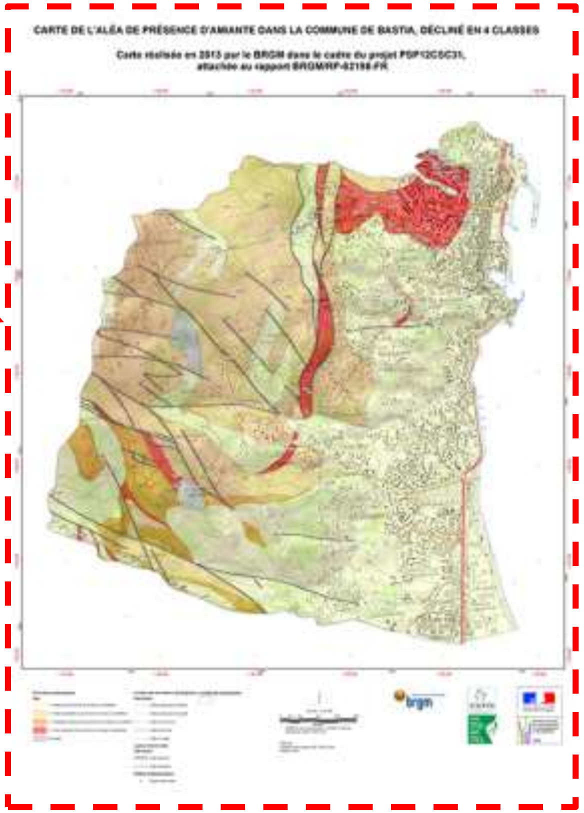
Naturally Occuring Asbestos in France



Main area
(D. Lahondere, BRGM)



North of Corsica
(D. Lahondere, BRGM)



Bastia and around
(D. Lahondere, BRGM)

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Naturally Occuring Asbestos in France

Main risks

- Natural erosion of rocks / soils releasing fibers
- (traditionnal) Use of local rocks for building construction, embankment…
- Civil engineering (road construction, tunnel drilling...)
- Materials quarried for civil engneering (railway ballast, aggregates etc...)

Analytical challenge

- Complex material, purely mineral and natural
- Presence of non-asbestos minerals with similar compositions
- Differentiation fiber / cleavage fragments

The usual standards and methods are often unsuited

Murato church
(D. Lahondere, BRGM)

Table 2. – Location and extent of pleural calcifications observed in Murato, according to the 1980 ILO International Classification

	Location					
	Diaphragm		Chest wall		Pericardium/mediastinum	
Extent	Right	Left	Right	Left	Right	Left
1	3	8	12	6	1	3
2	12	13	13	15	6	4
3	0	0	7	7	3	0
Total	15	21	32	28	10	7
%	47	66	100	88	31	22

ILO: International Labour Office.

Table 3. – Airborne asbestos pollution as assessed using transmission electron microscopy (×10[illegible] g·m[illegible])

	Murato				Vezzani				
	I	H	M	L	I	H	M	L	
Chrysotile	0.6	1	0.4	0.3	0.3	-	0.2	0.1	ns
Tremolite	44	34	6	72	1	-	-	0.4	p<0.05*

I: indoors; H, M, L: outdoors at different levels in the village (high, medium, low); ns: not significant. *: Murato values versus Vezzani.

Health hazard of NOA
the example of the north of Corsica
F. Rey et al, Eur. Respir. J., (1993), 6, 978-982

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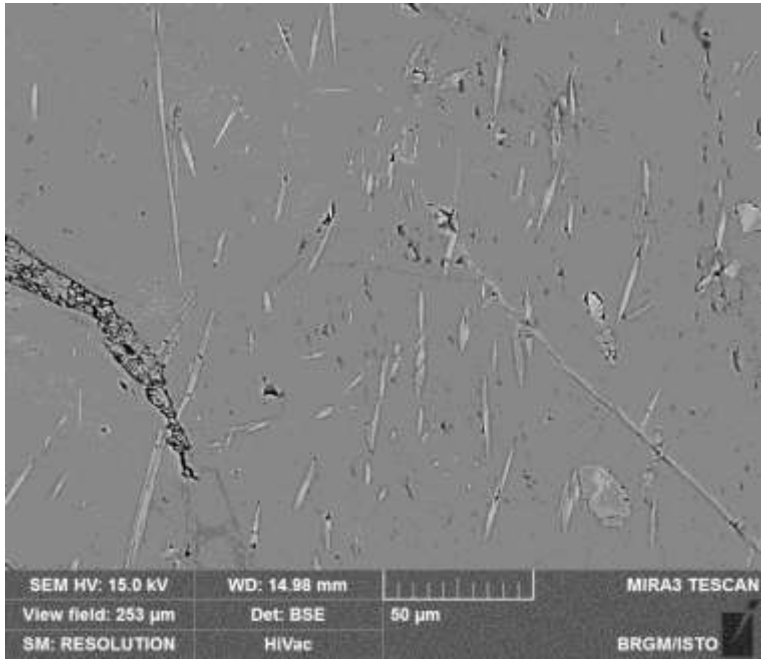
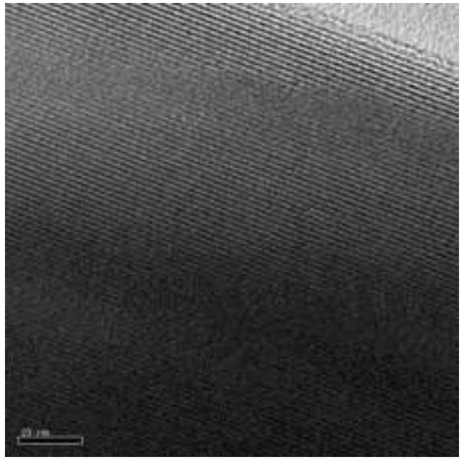
Naturally Occuring Asbestos



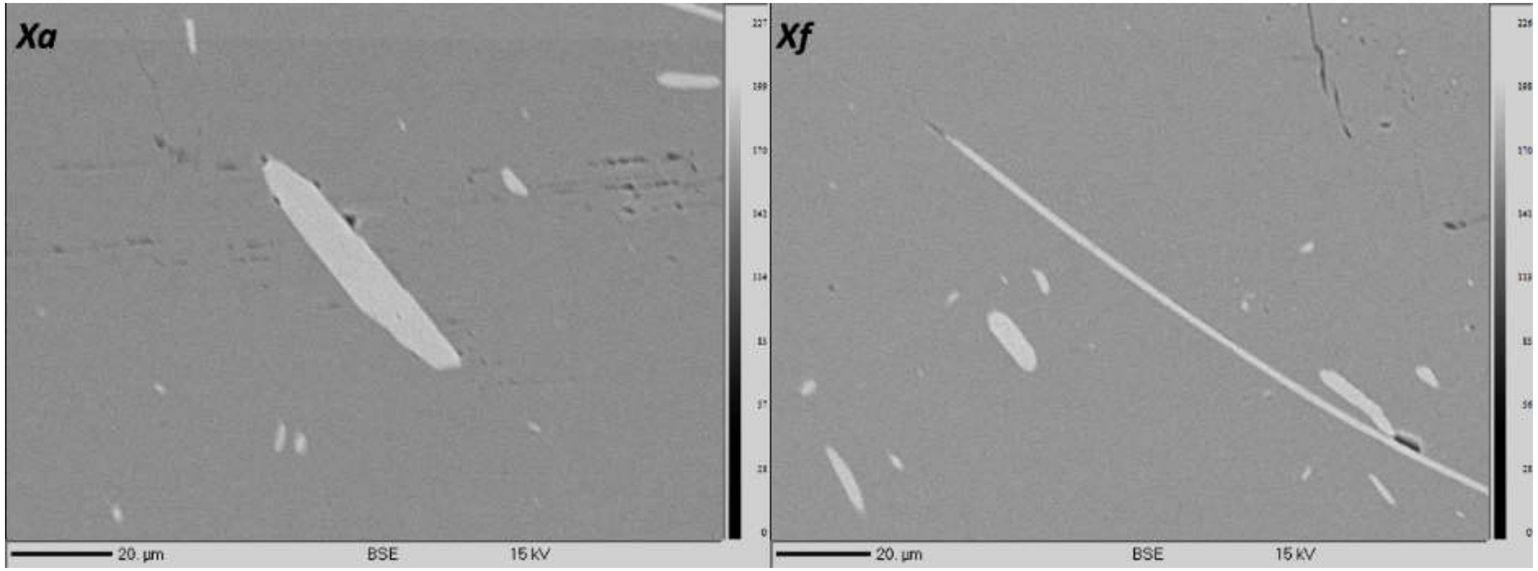
SEM (BSE)

TEM



PLM

Naturally Occuring Asbestos



BSE

EPMA analysis

- Large particles (> 3µm) → ok
- Thin fibers (< 3µm) → result not usable - contribution of the matrix in the result

⇨ For thin fibers, another technique is requested for the identification

	SiO2	TiO2	Al2O3	Cr2O3	FeO	MnO	MgO	CaO	Na2O	K2O	Total
Xa	52.343	0.048	2.691	0.000	17.652	0.738	12.642	11.334	0.291	0.007	97.747
Xf	54.258	0.000	6.863	0.000	15.198	0.481	10.966	10.814	1.661	0.066	100.308
matrix	60.115	0.000	25.032	0.009	0.164	0.000	0.000	6.246	8.195	0.087	99.849

EPMA (WDS)

Naturally Occuring Asbestos - In Situ characterization

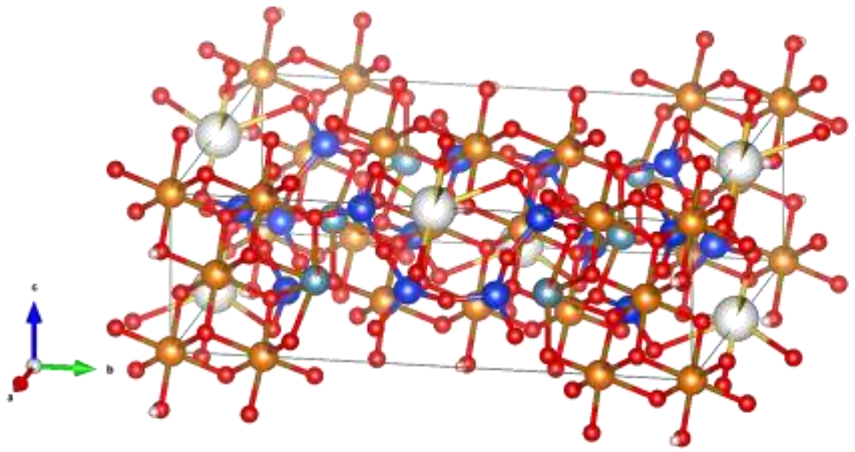
SEM - Raman / SEM – FIB complementarity

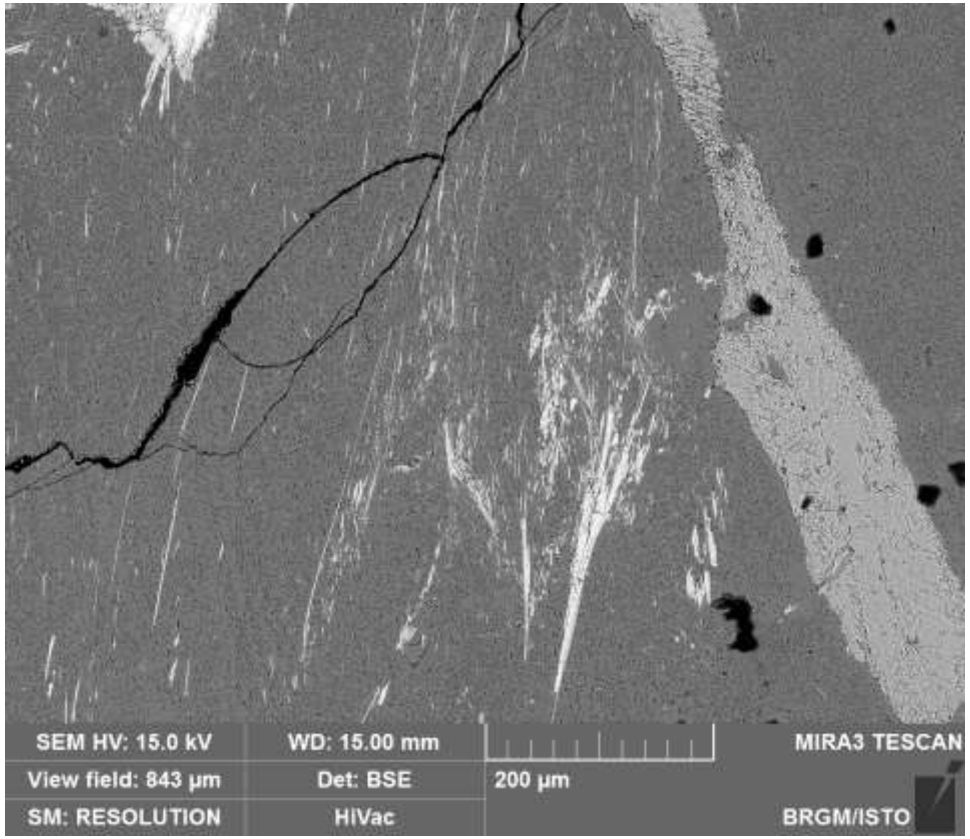
G. Wille, D. Lahondere, J. Duron, X. Bourrat (BRGM), J. Silvent (Tescan), U. Schmidt (WITec)

- Amphibole fibers dispersed in a mineral matrix

- In-situ diagnosis with a limited sample preparation
  - Chushing: risk of cleavage fragments (non-fibrous amphiboles)
  - Amphibole identification
  - Asbestiform / non asbestiform morphology

- Distribution of fibers in the sample
  - 3D analysis





Thin section of a blue micro-diorite containing fibrous actinolite in a quartz matrix
(Sainte Florence, France)

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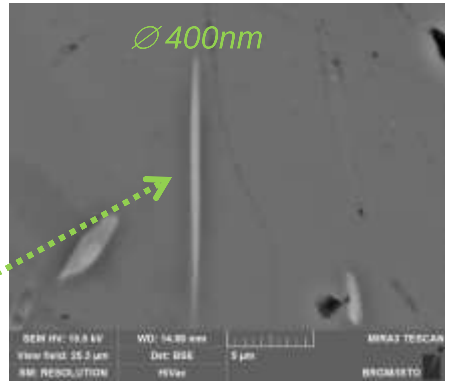
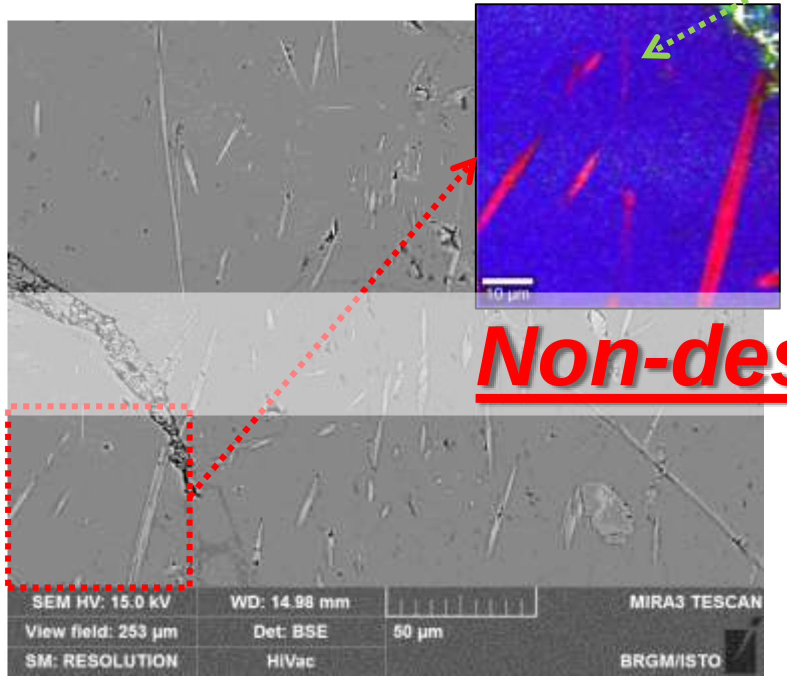
Naturally Occuring Asbestos - In Situ characterization

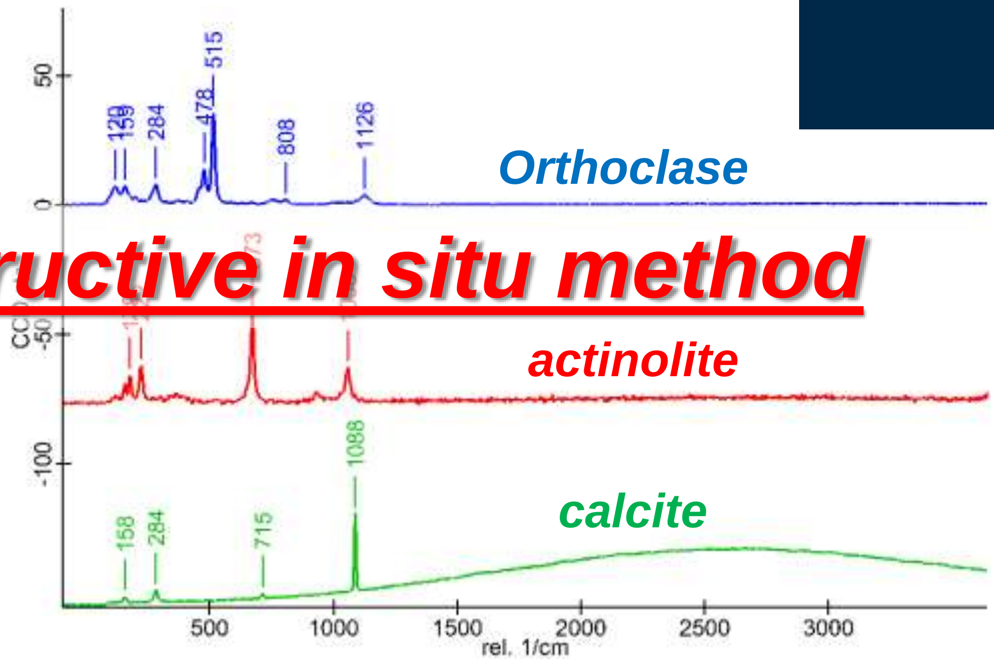
Raman in SEM: 2D / 3D analysis

- 2D: identification of actinolite fibers up to 400 nm in diameter + approximation of the Mg/Fe ratio *(Bersani et al, 2019)*

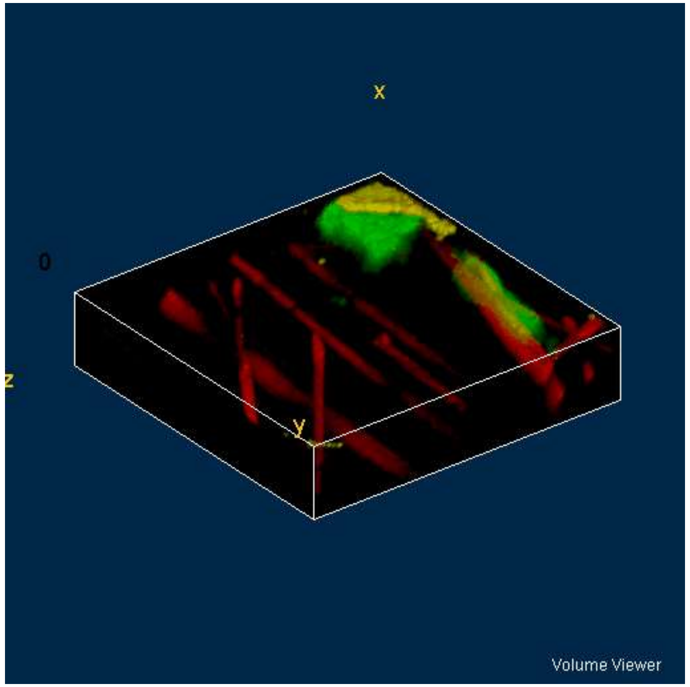
- 3D: Fibrous morphology and distribution of actinolite fibers in the analyzed volume







Non-destructive in situ method



Raman 3D

120 µm x 120 µm x 20 µm

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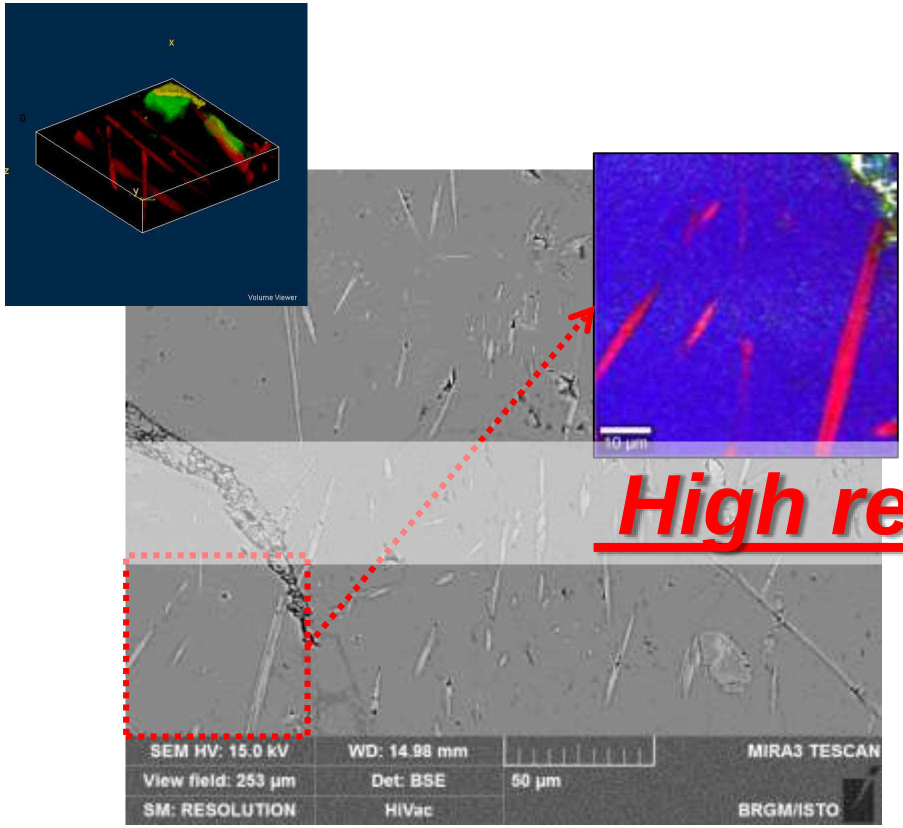
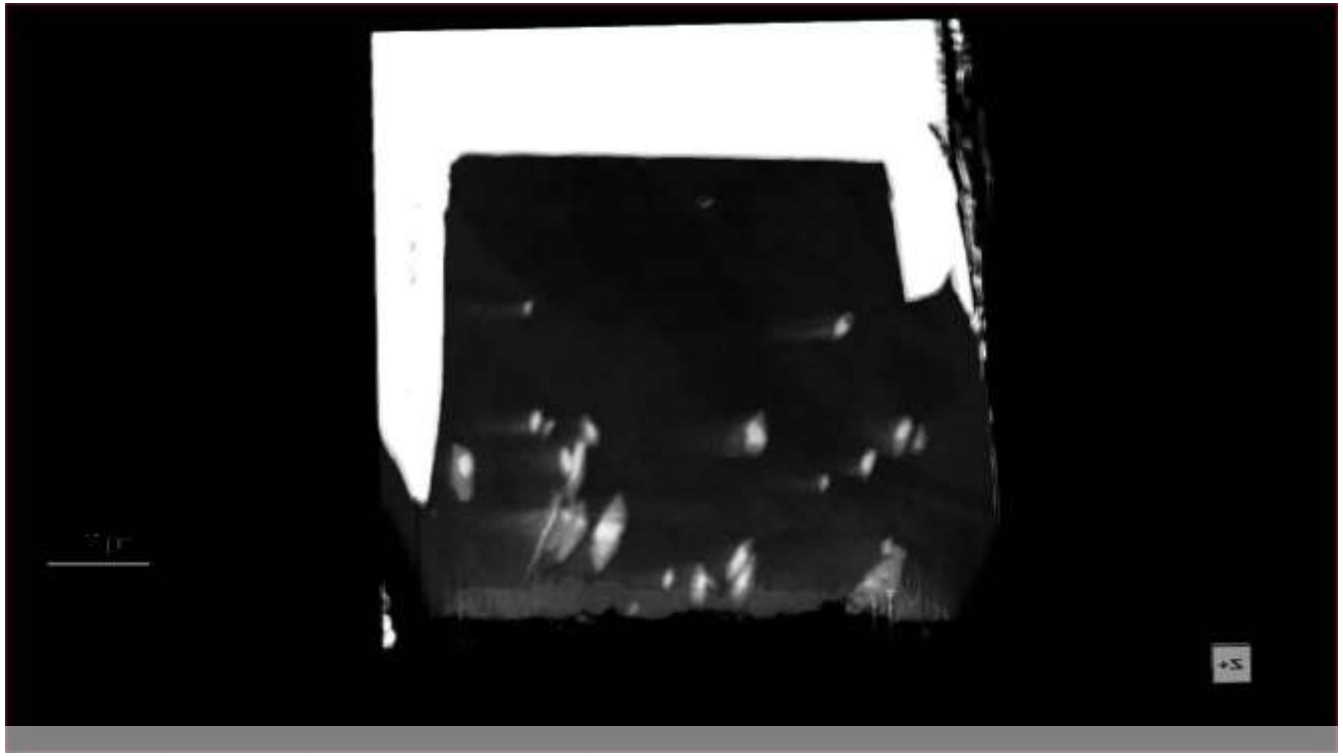
Naturally Occuring Asbestos - In Situ characterization

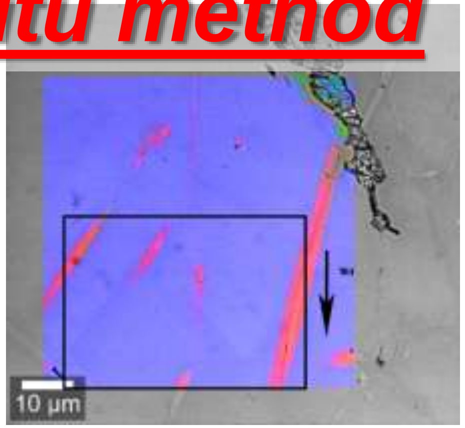
Fibers < 400 nm → SEM-FIB 3D analysis

- 3D Fibrous morphology and distribution of actinolite fibers in the analyzed volume up to 100 nm (or better)





High resolution in situ method



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)

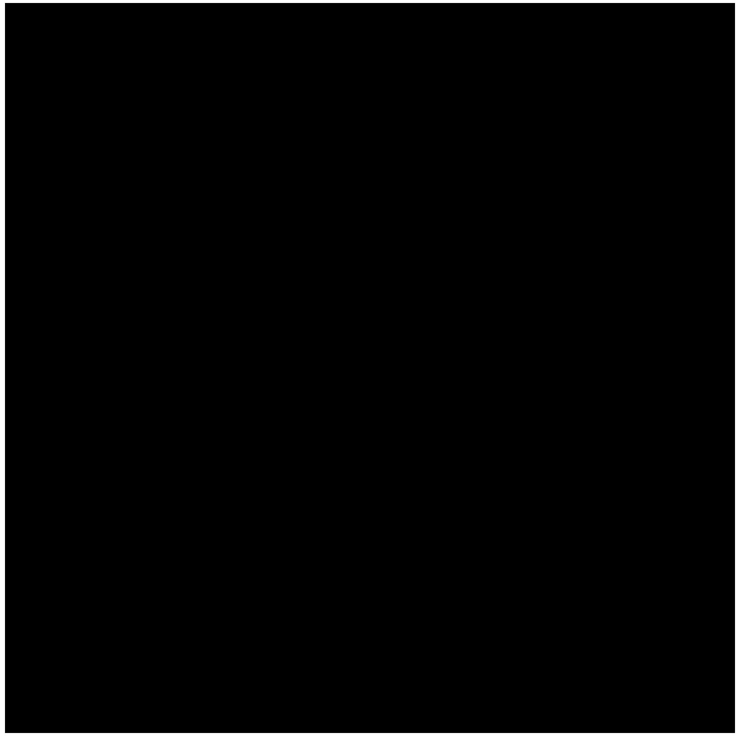
Volume
76274 µm³

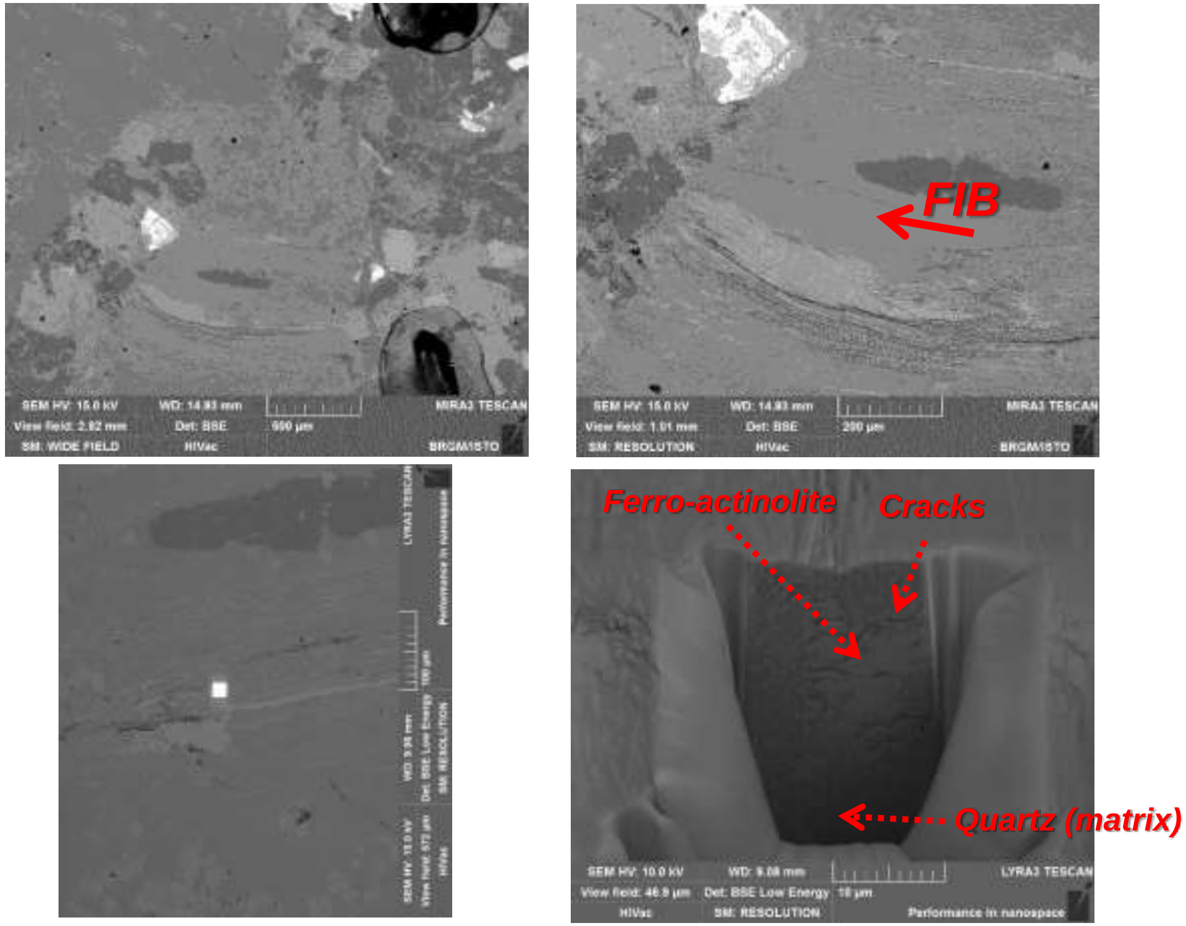
Fibers
1464,40 µm³ soit1.94 % du volume

Naturally Occuring Asbestos - In Situ characterization

Ferro-actinolite fibers bundle - SEM-FIB 3D

- Asbestiform morphology
- Numerous parallel fibers = bundle
- Defects (cracks)
- Location of TEM slice sampling in the SEM-FIB





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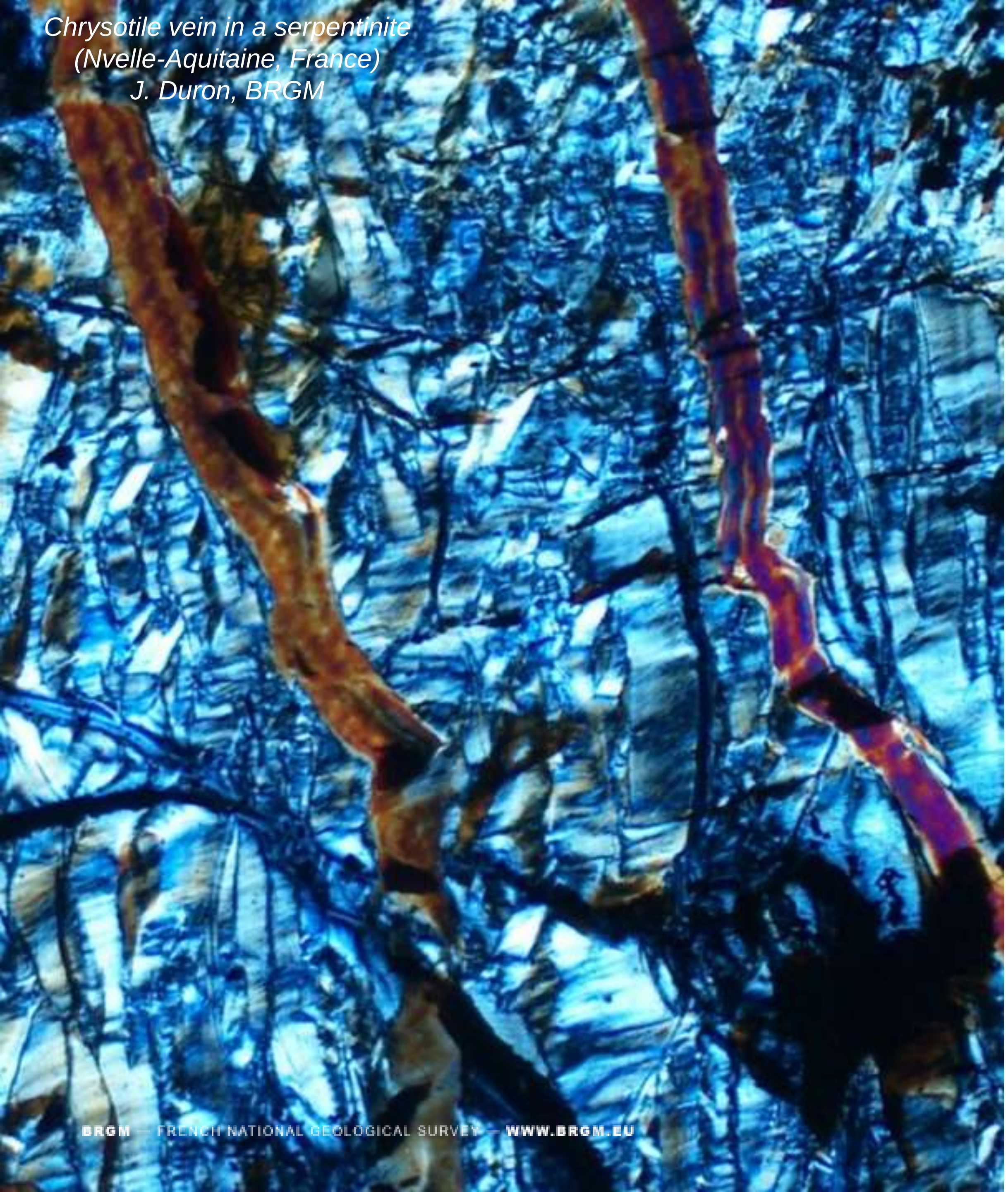

Chrysotile vein in a serpentinite
(Nvelle-Aquitaine, France)
J. Duron, BRGM

Coupling SEM-EDS and Raman spectroscopy

Conclusion

A unique tool for a complete mineralogical characterization of the geological samples

The characterization of geo-materials usually requires various informations: Chemistry (major / trace elements), cristallography, morphology

⇒ Need for multimodal / multitechniques approach

SEM + EDS + Raman

Combination of data, collected at the same time, at the same place, at the same scale

⇒ Multi-parameters, co-localized

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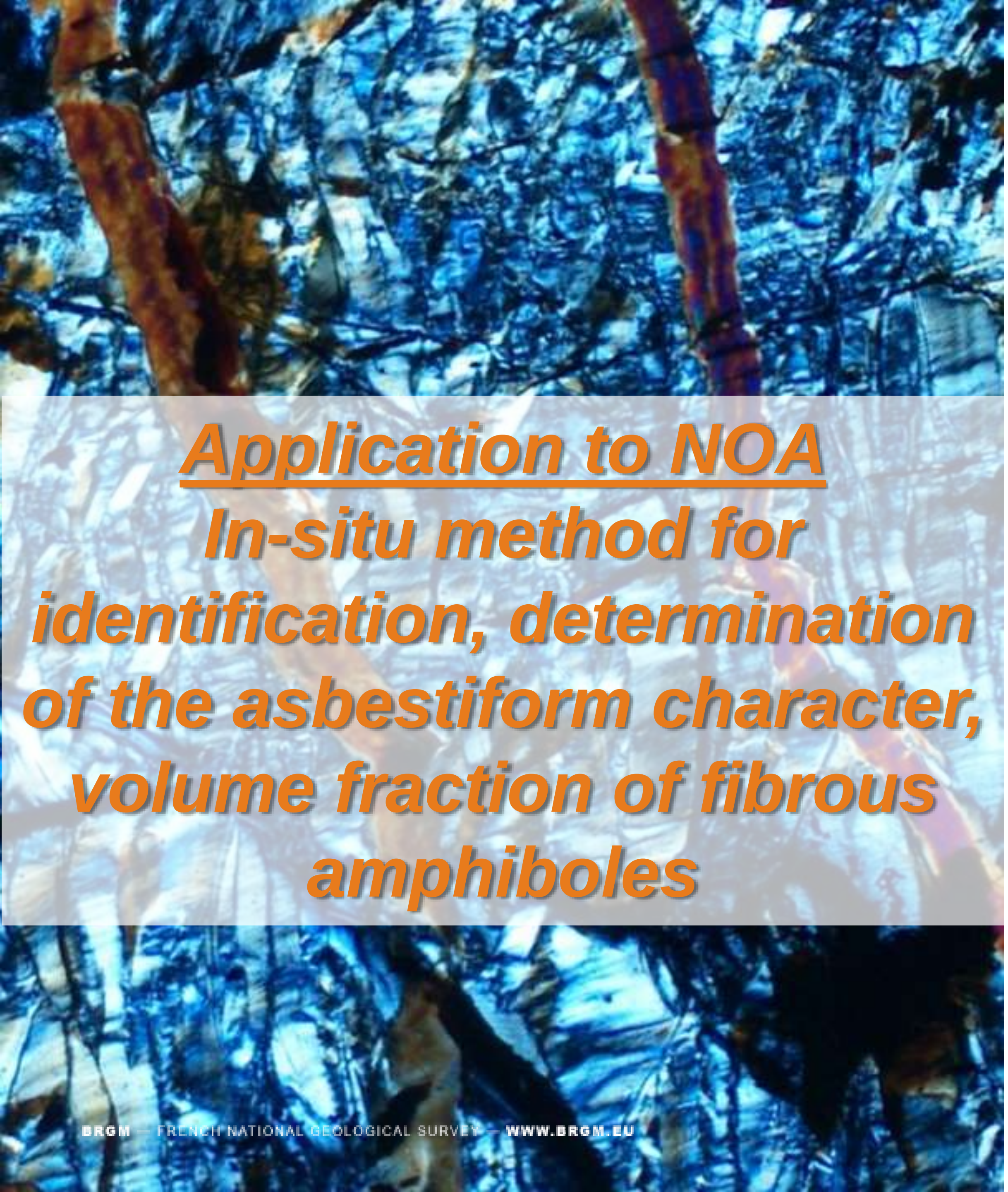

Coupling SEM-EDS and Raman spectroscopy

Conclusion

Confocal Raman imaging in the SEM

Coupling morphology (SEM), chemistry (EDS) and structure (Raman)
Raman in the SEM: 2D / 3D capacities
Non-destructive in-situ method

⇒ Surface / volume information

SEM-Raman and FIB-SEM

FIB 3D: higher resolution but destructive
FIB for TEM: Raman 3D can help

⇒ Complementarity

Asbestos actinolite veins in ophiolitic metabasaltes – north of Corsica (D. Lahondère – BRGM)