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

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

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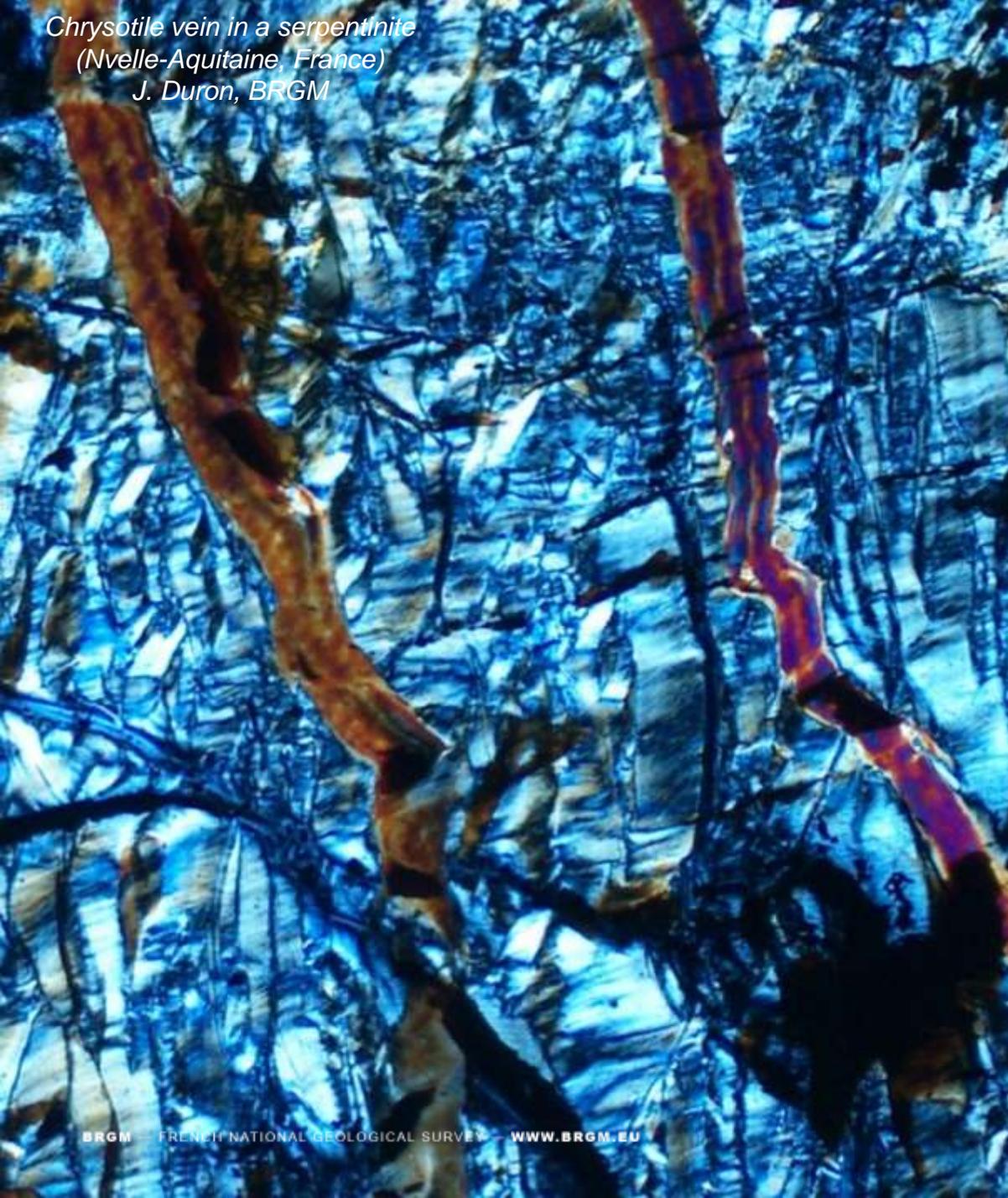
³ TESCAN France, Fuveau, France



*Actinolite-asbestos vein
interspersed with ophiolytic
metabasalts (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 occurring asbestos (NOA)
- Conclusion

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



Introduction: Interest of multimodal analysis in geosciences

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

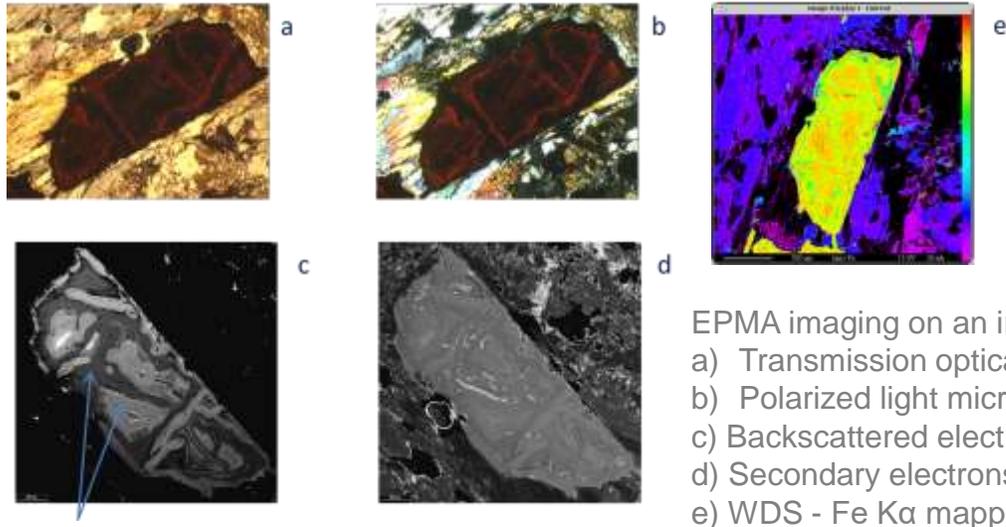
MULTIMODAL APPROACH

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

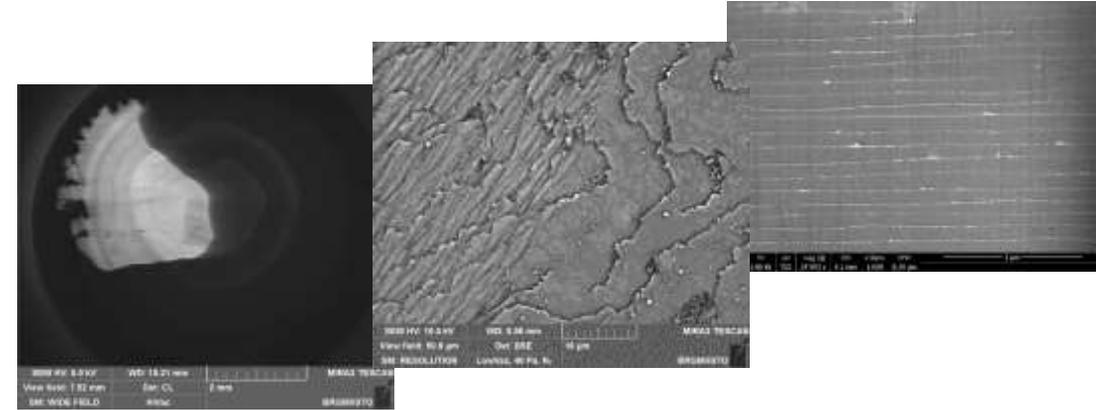
Complementary analytical data

Co-location of physical and chemical data

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



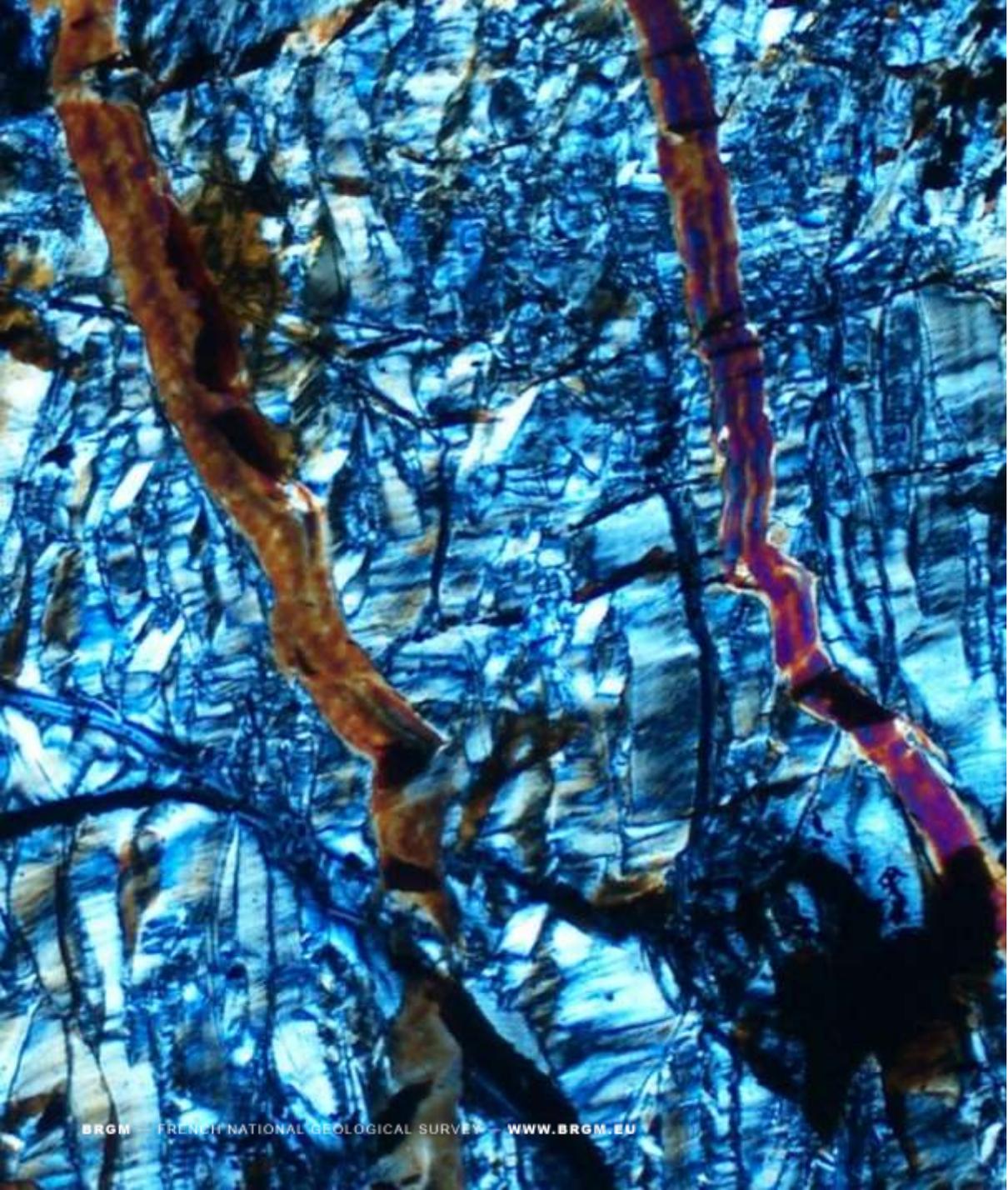
EPMA imaging on an iron oxide grain
a) Transmission optical microscopy
b) Polarized light microscopy
c) Backscattered electrons imaging
d) Secondary electrons imaging
e) WDS - Fe K α mapping



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

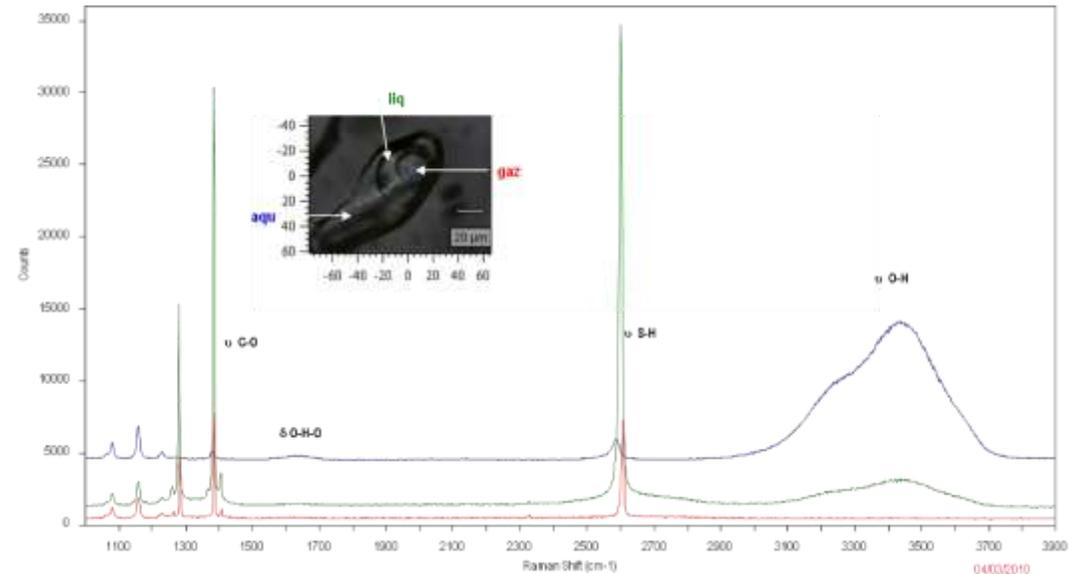
Co-located multi-scale data

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



Coupling SEM-EDS and Raman spectroscopy

Why ? How ?



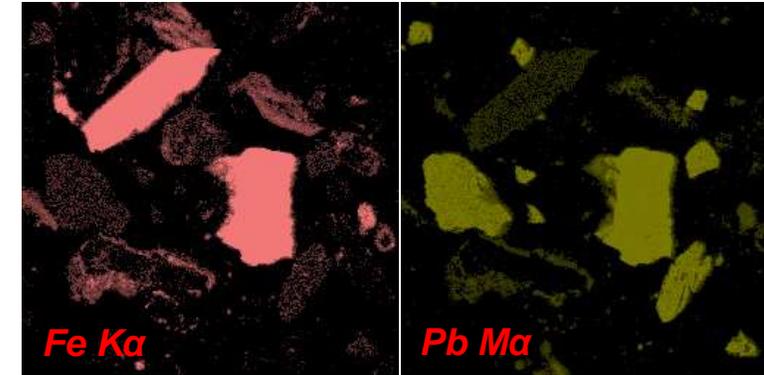
μ -Raman spectroscopy analysis of a fluid inclusion in a quartz grain

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

Scanning Electron Microscopy

SEM

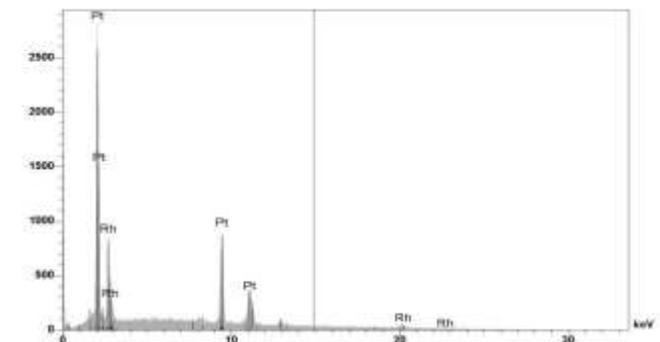
- Electron beam generated by an electron gun, accelerated and focused in an « electron column »
- Various imaging modes (matter / electron beam interactions):
 - Secondary electrons imaging (topography)
 - Backscattered electrons imaging (chemical contrast \pm crystal orientation contrast)
 - Other imaging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



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

EDS

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



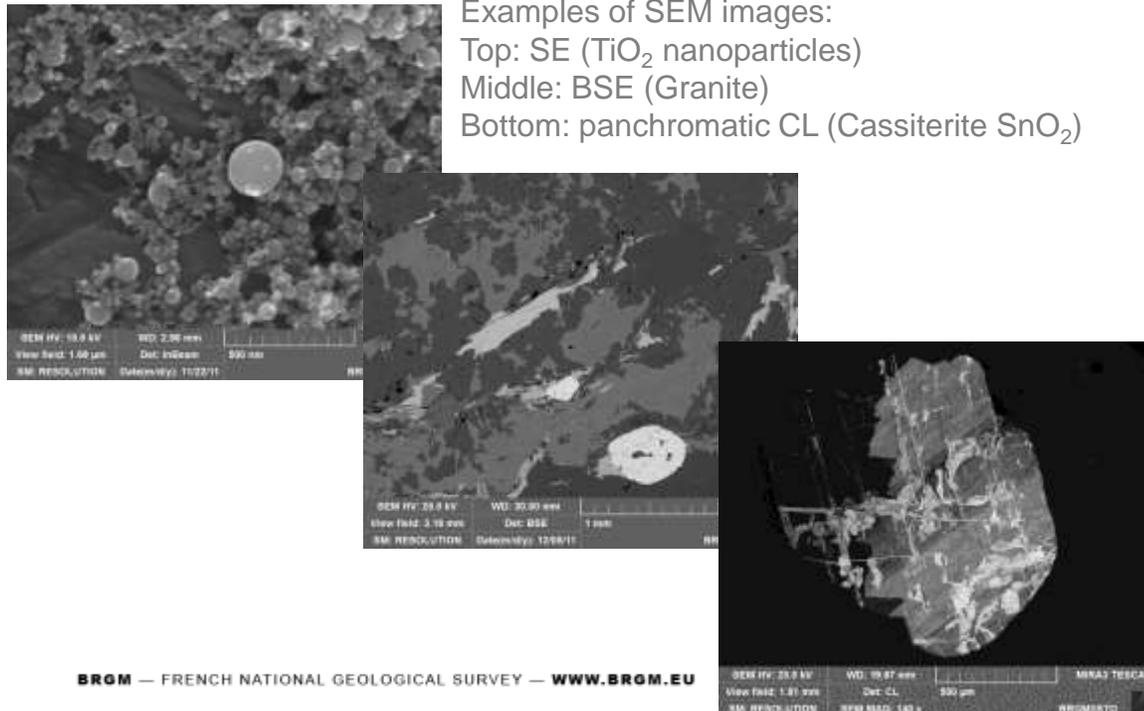
EDS spectra of Pt / Rh alloy

Examples of SEM images:

Top: SE (TiO₂ nanoparticles)

Middle: BSE (Granite)

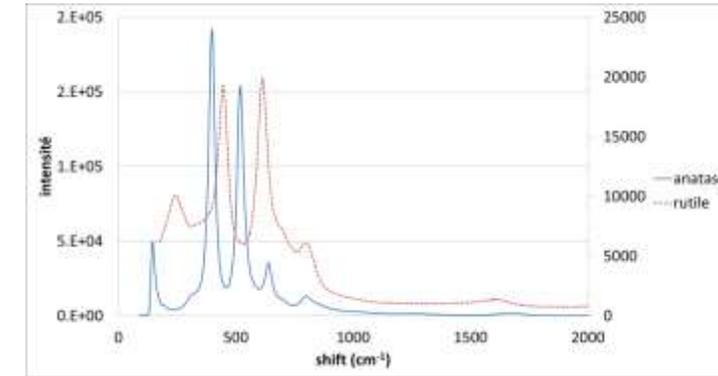
Bottom: panchromatic CL (Cassiterite SnO₂)



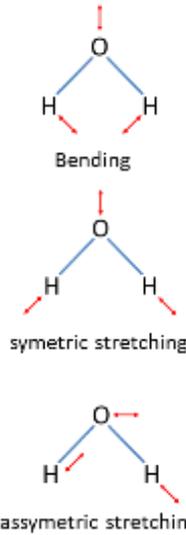
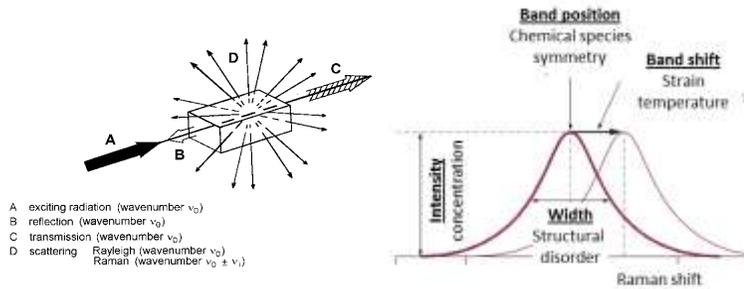
Micro-Raman spectroscopy

Principe

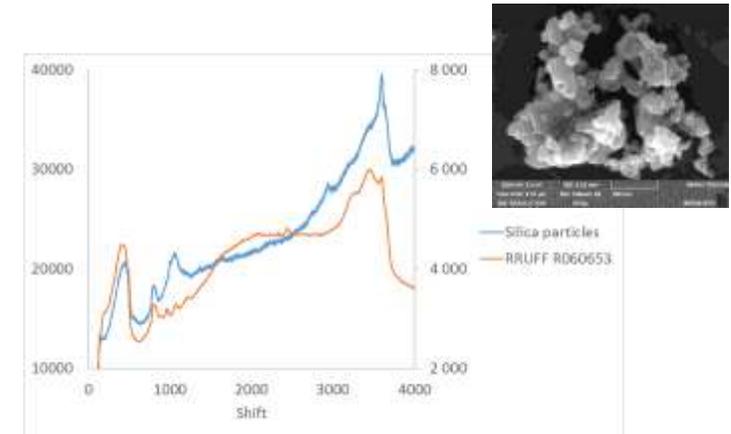
- Vibrational spectroscopy based on the inelastic diffusion of monochromatic light (laser beam)
- Various structural information:
 - Crystal structure, degree of crystallinity
 - Presence de chemical groups (-OH, -CO3, etc ...)
 - Amorphous materials



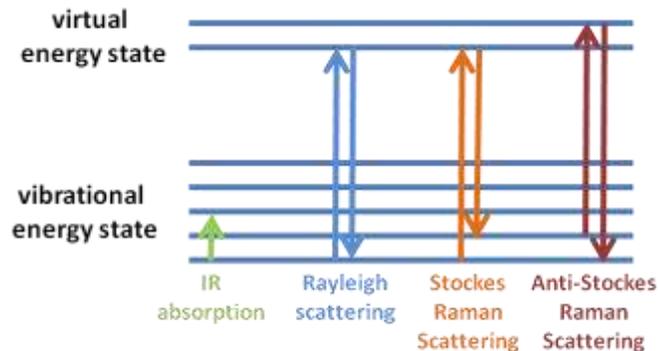
Raman spectra of TiO₂ rutile (quadratique P) and anatase (quadratique C)



Vibration modes of the water molecule H₂O



Raman spectrum of SiO₂ nanoparticles compared to the Raman spectrum of opal (hydrated amorphous form of silica) (RUFF database - <http://ruff.info/>)



Coupling SEM-EDS and Raman

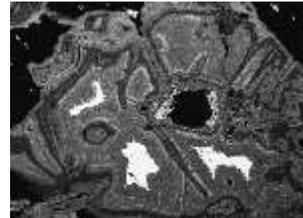
A case study, the mineral

Composition

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

In the SEM

EDS, WDS



Minéral

Pyrite (FeS_2)

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

Cristallography

Crystal structure
+
Distortions (defects, dislocations...)

In the SEM

**EBSD / TKD
Raman**

Morphology, shape

Automorphs crystals,
surface roughness...

In the SEM

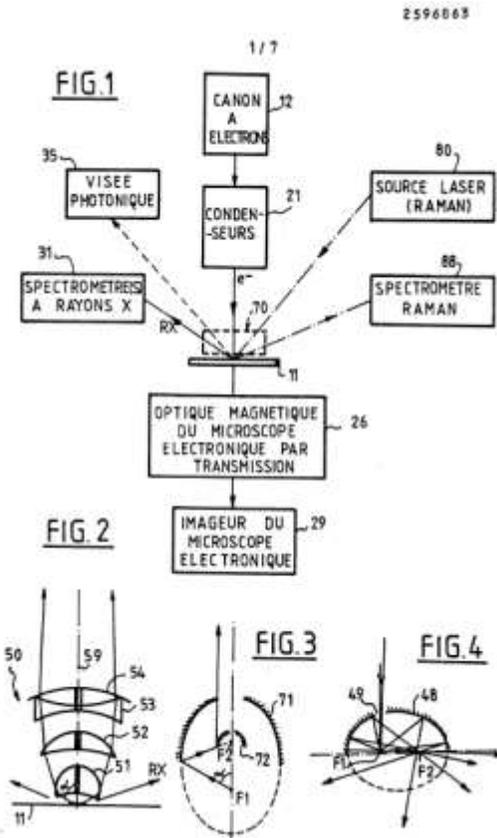
**Imaging Modes
(SE, BSE, CL...)**

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, 147-176

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

Michel TRUCHET* et Michel DELHAYE**

* Laboratoire d'Histophysiologie fondamentale et appliquée, U.R.A. 660, C.N.R.S., Université Pierre et Marie Curie, 12, rue Curier, 75005 PARIS, France

** Laboratoire de Spectrochimie Infrarouge et Raman, L.P.C.R.S. 3831 Université des Sciences et Techniques de Lille-Flandres-Artois, 59655 VILLENEUVE D'ASCQ Cedex, France

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 ellipsoidal mirror associated with a plane mirror, 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

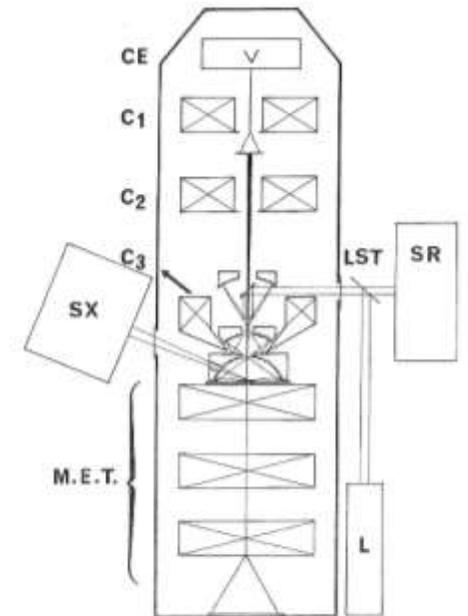
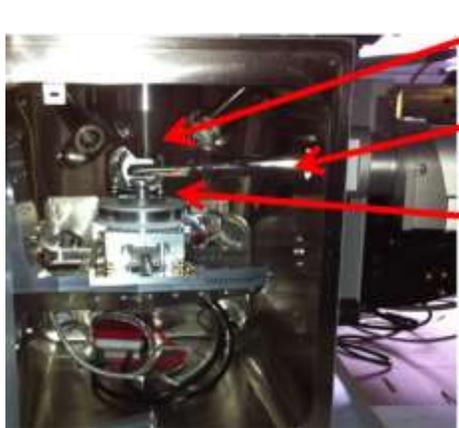
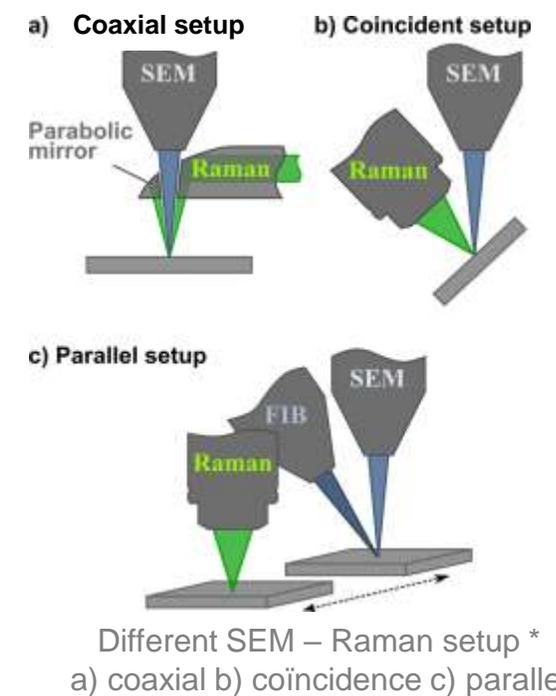


FIG. 4 - Coupe verticale très schématisée d'une colonne de microscope électronique à transmission équipé pour la spectroscopie des rayons X en dispersion de longueur d'onde selon le montage de Castaing, et pourvu d'un dispositif de collecte de flux photoniques permettant l'analyse moléculaire par spectroscopie Raman. Ce dispositif comprend deux objectifs ellipsoïdaux selon la Figure 3, associés en cascade, et associés à un objectif de Casagrande. CE : canon à électrons. C1, C2 et C3 : condenseuses. M.E.T. : microscope électronique à transmission (partie large). SX : spectromètre à rayons X. SR : spectromètre Raman. L : laser. LST : lame semi-transparente.

Micro-Raman spectroscopy

SEM-Raman

- 2 types of SEM-Raman coupling : coaxial or parallel
- Coaxial setup
 - Resolution: $\sim 2.5 \mu\text{m}$ @ $\lambda = 514 \text{ nm}$
 - Spectral analysis: loss of intensity (compared to conventional Raman spectroscopy)
 - Imaging mode: possible but limited (time / pixel)
- Parallel setup
 - Resolution: $< 400 \text{ nm}$ @ $\lambda = 532 \text{ nm}$
 - Spectral analysis: comparable with a conventional Raman spectroscopy
 - Imaging: comparable with a conventional Raman spectroscopy ($250 \times 250 \mu\text{m}$)



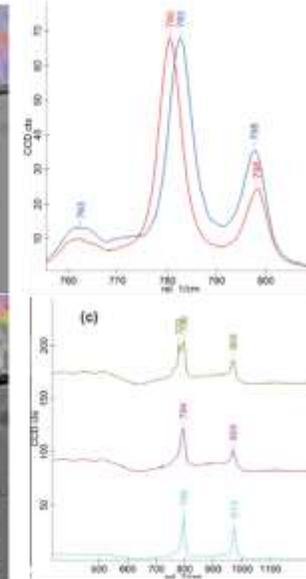
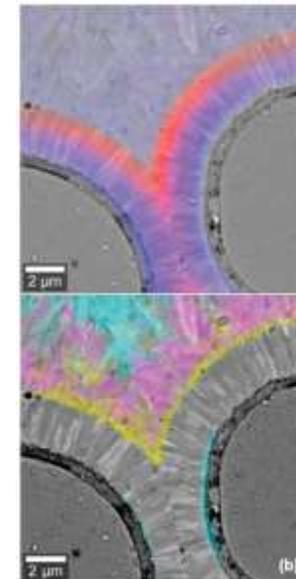
SEM pole piece

Raman mirror

Sample

Co-axial setup
Renishaw SEMScA / Tescan MIRA

Parallel setup
WITec RISE / Tescan MIRA

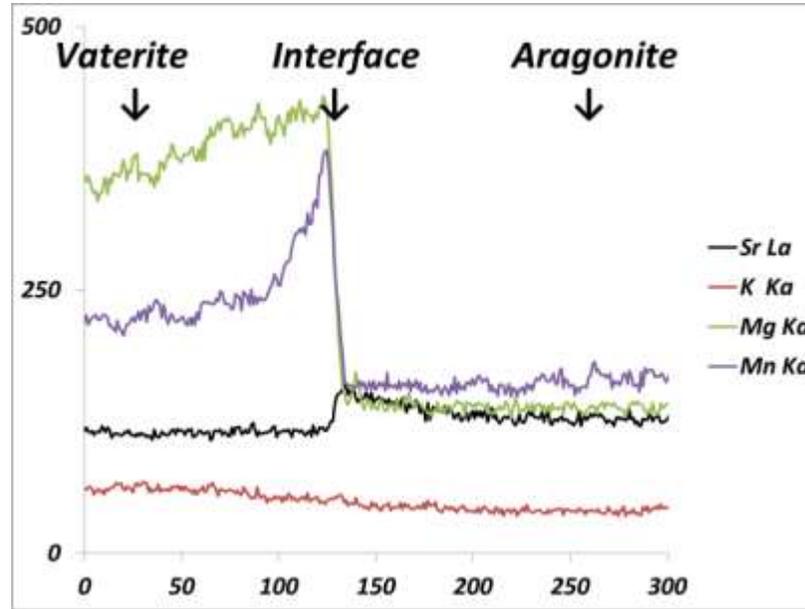
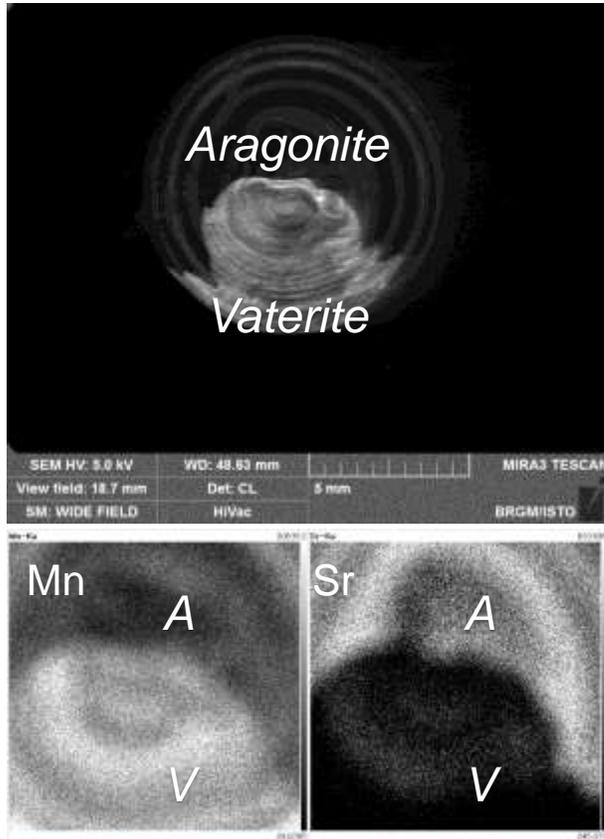
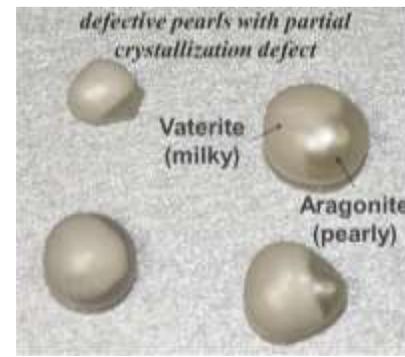


SEM-Raman analysis of a composite Carbon / SiC (Tescan – WITec RISE)

*Jiruse et al, 2014

Coupling SEM-EDS and Raman

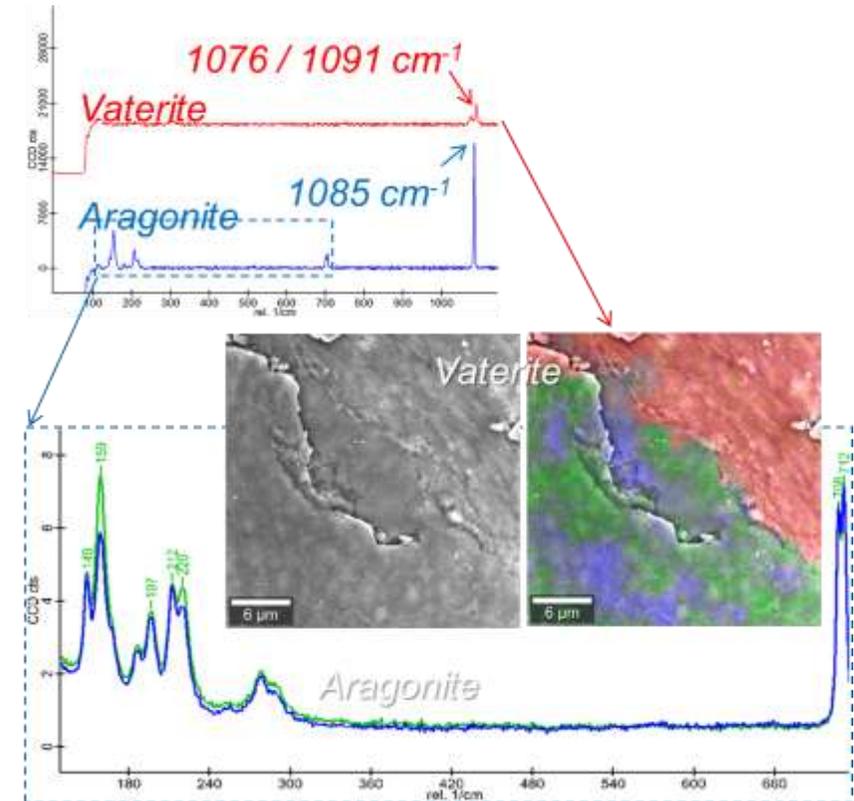
Example: polymorphs of calcium carbonates in a defective pearl

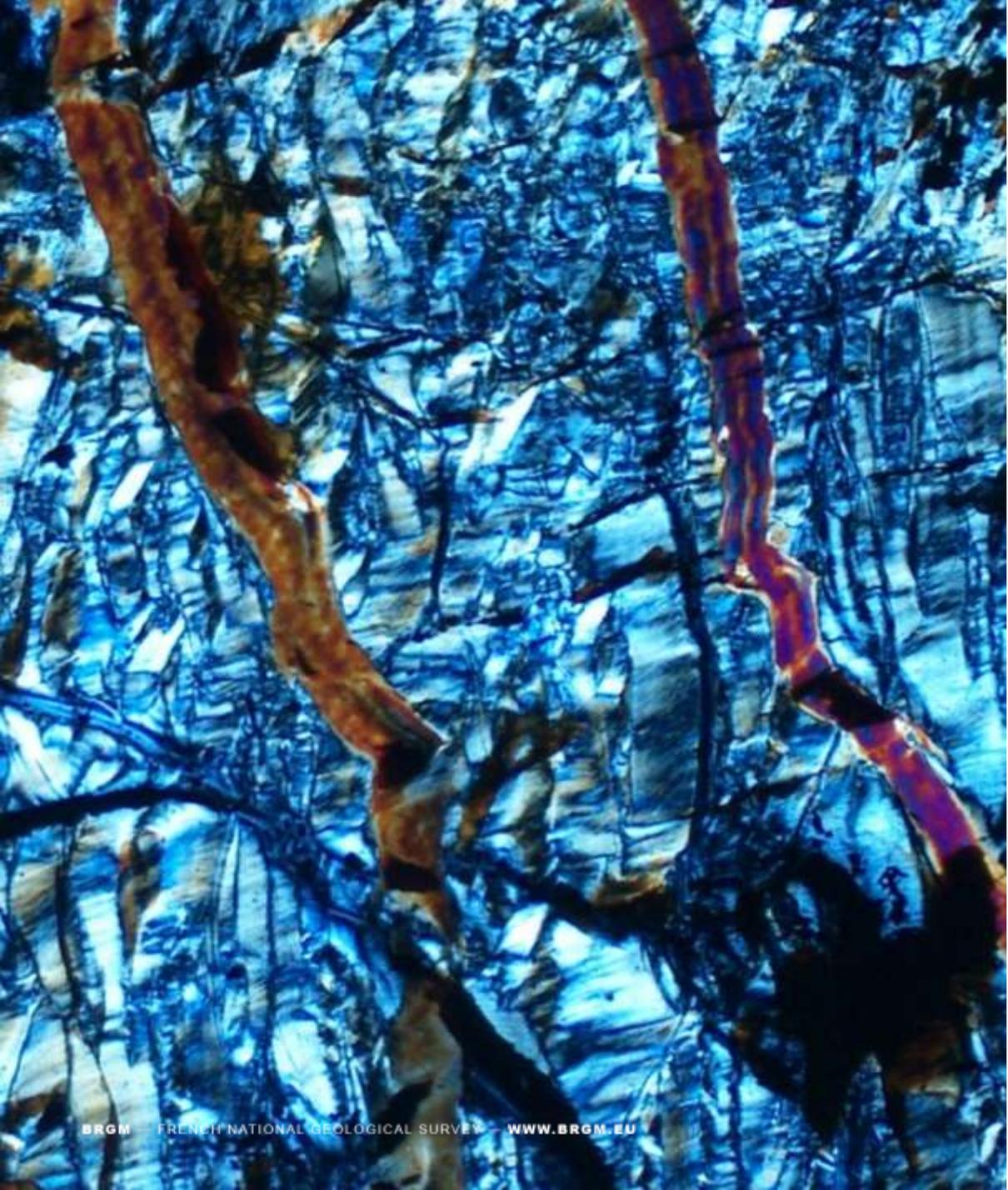


WDS profile (EPMA) on both sides of the interface

SEM - panchromatic CL and μ-XRF maps

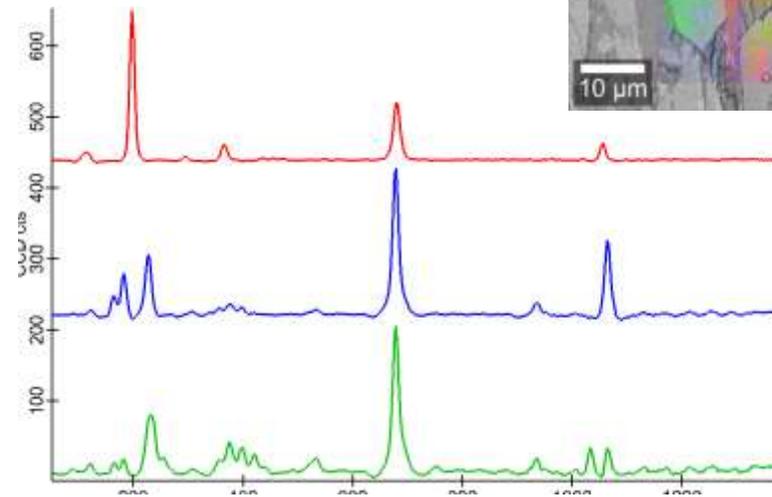
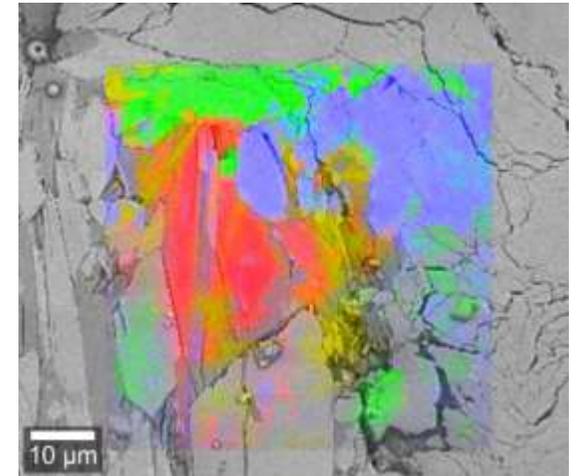
Raman map on both sides of the interface





Coupling SEM-EDS and Raman spectroscopy

Examples



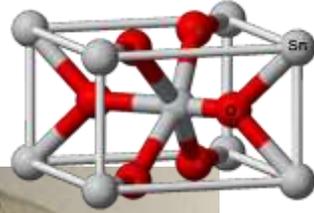
SEM-Raman on a transverse section of an actinolite fibers bundle

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: $\text{Sn}^{4+} \leftrightarrow \text{Ti}^{4+}$
 - Heterovalent: $2.(\text{Nb},\text{Ta})^{5+} + (\text{Fe},\text{Mn})^{2+} \leftrightarrow 3.\text{Sn}^{4+}$



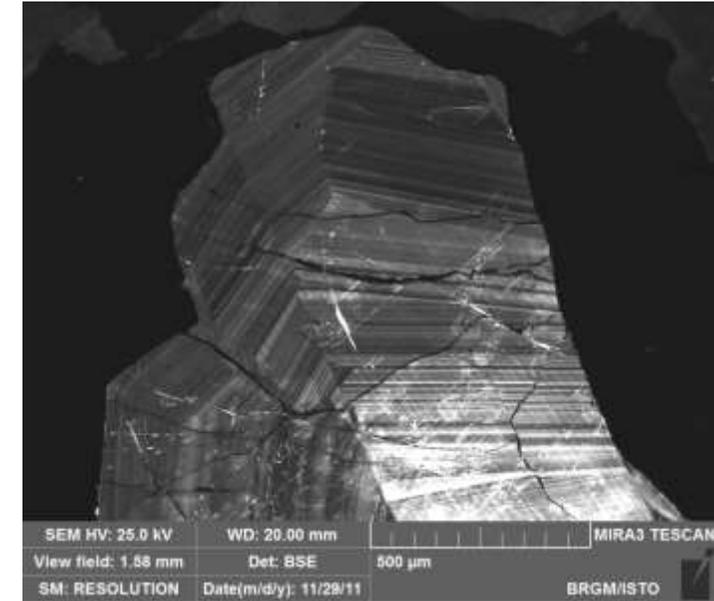
Tin ore from the Montbelleux mine
(Luitré, Ille-et-Vilaine - France)

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

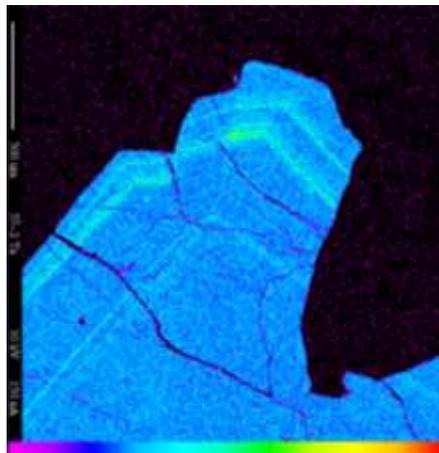
Ex. 1 – Zonation in tin oxide cassiterite

SEM - Raman - EBSD - WDS

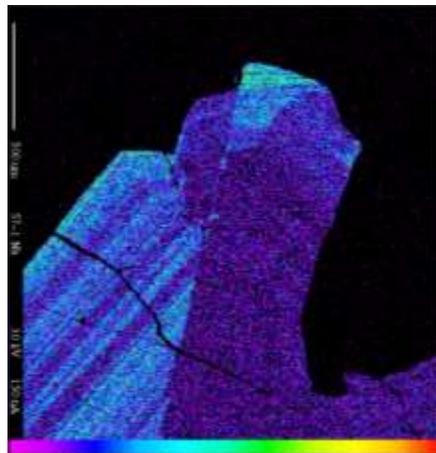
- SEM - CL shows a strong contrast that may be associated with trace elements distribution and / or crystal orientation
- EPMA (WDS) analysis is applied for mapping and quantification of trace elements content – Some CL contrasts can be linked to EPMA data
- EBSD provide 2 informations on the crystallography of cassiterite grains
 - Millimetric monocrystalline grains
 - Elbow twin ($\sim 70^\circ$) commonly encountered in rutile structure



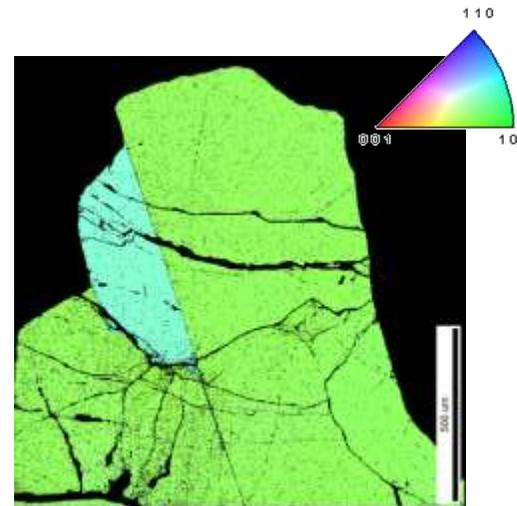
SEM - CL



Ta



Nb



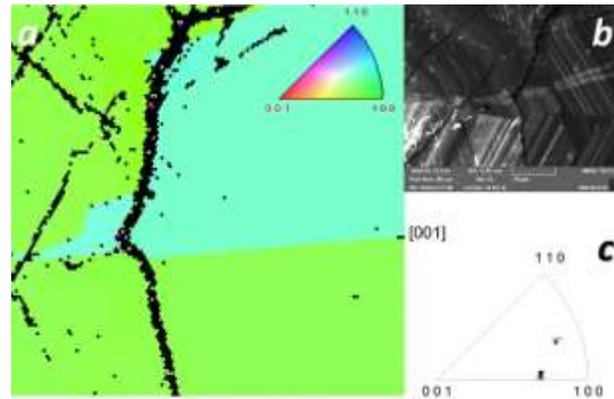
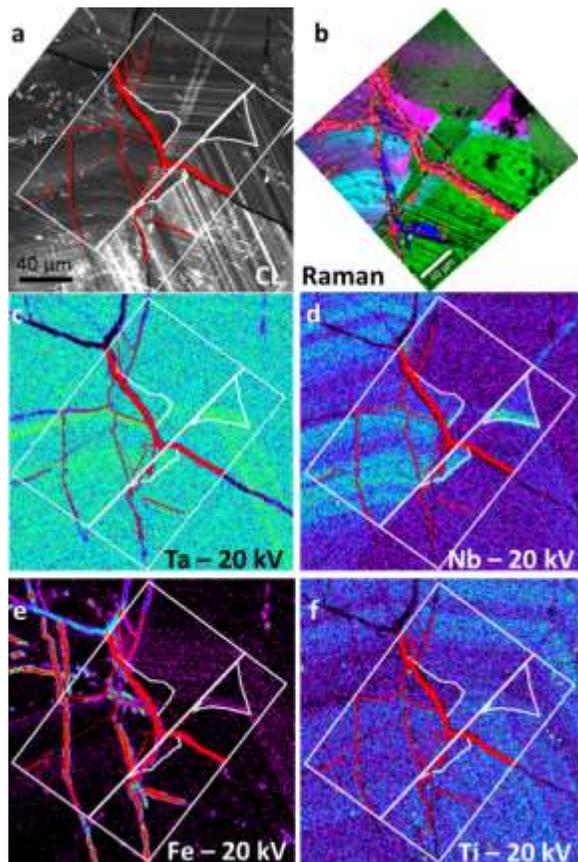
EBSD

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

Ex. 1 – Zonation in tin oxide cassiterite

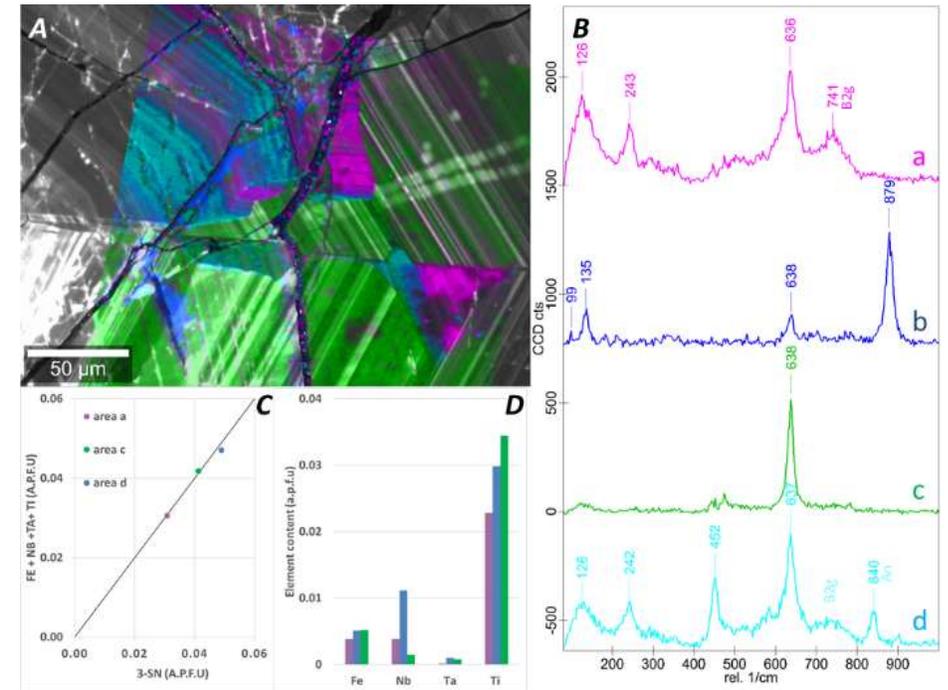
SEM - Raman - EBSD - WDS

- 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



EBSD

EPMA(WDS)



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

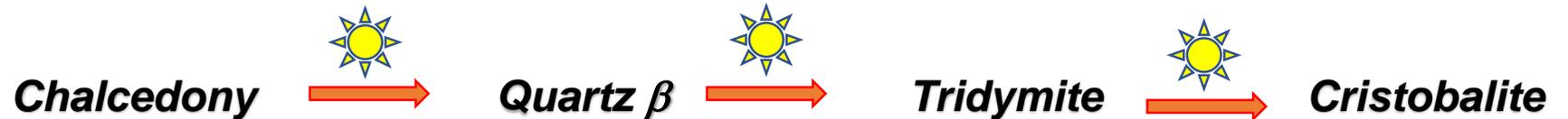
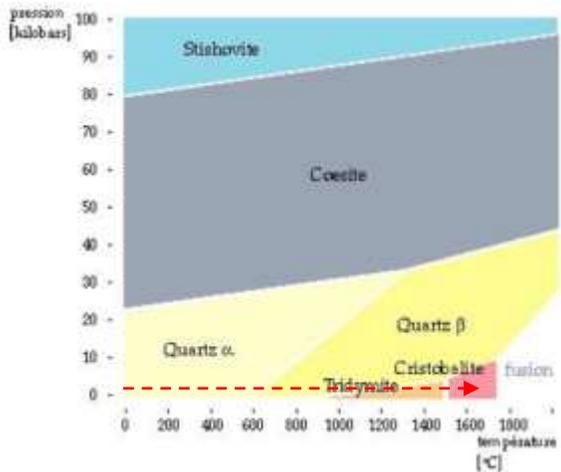
Ex. 2 – Industrial process for the obtention of white pigments

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)

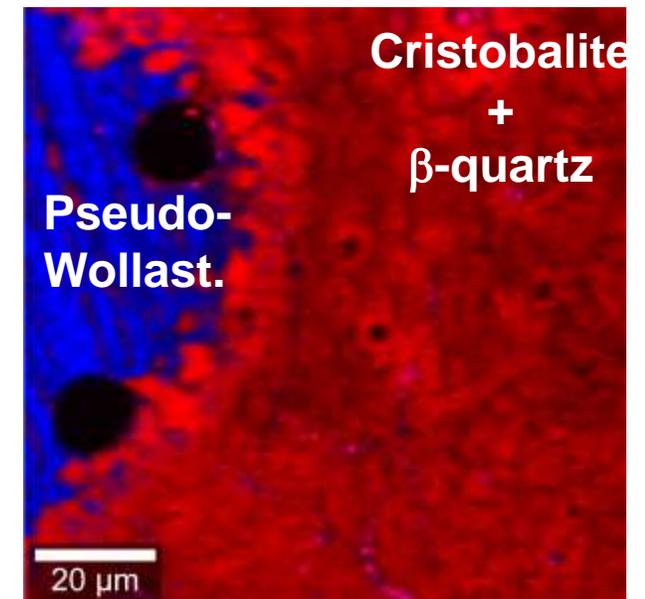
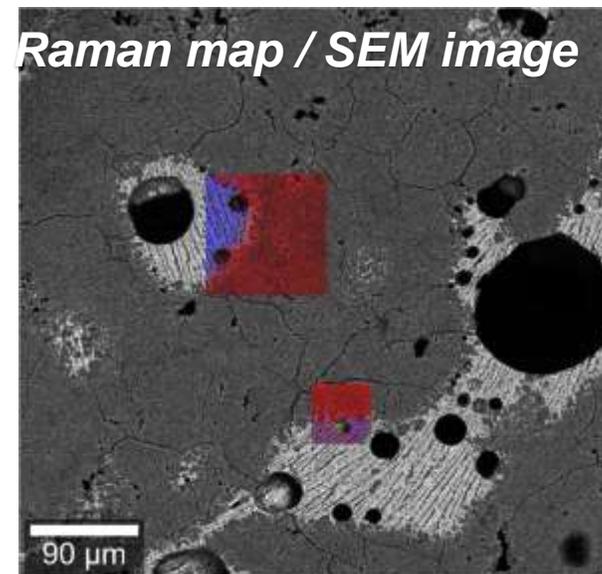
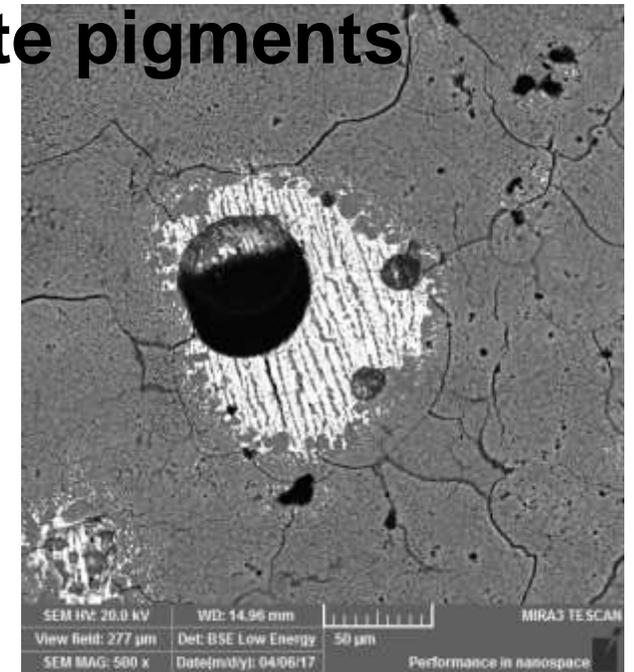
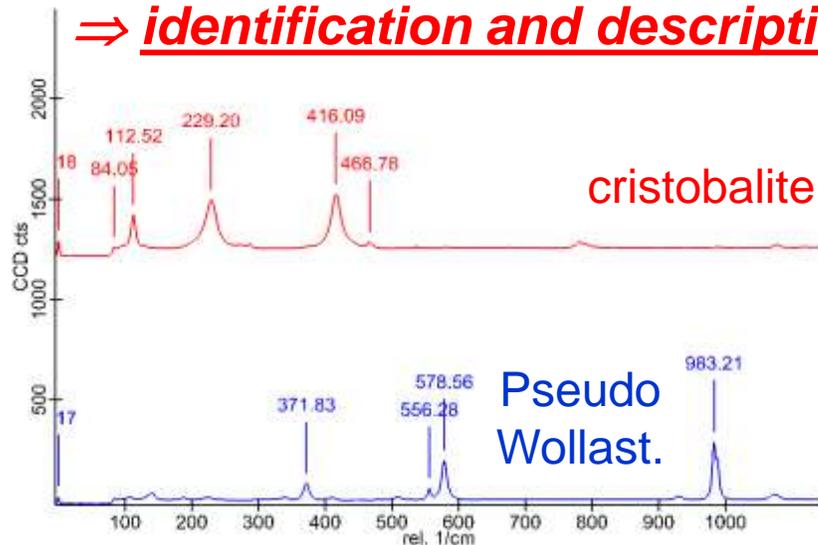


Ex. 2 – Industrial process for the obtention of white pigments

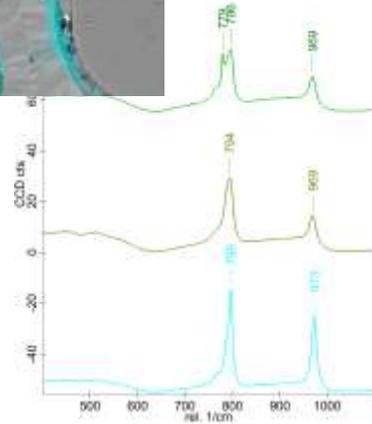
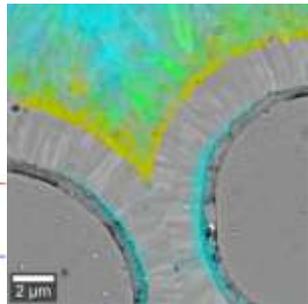
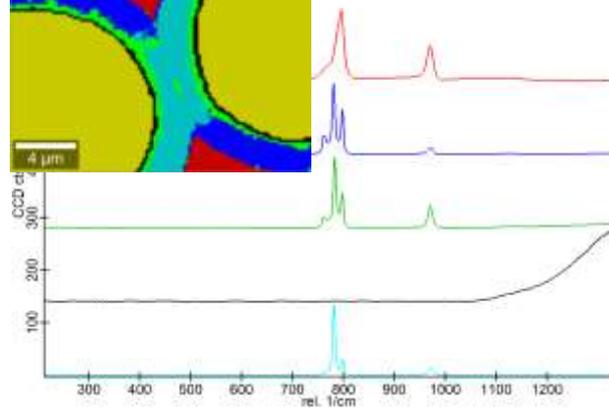
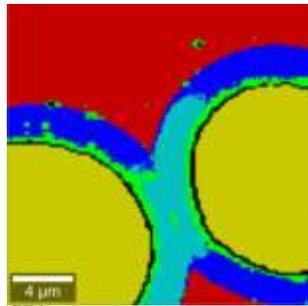
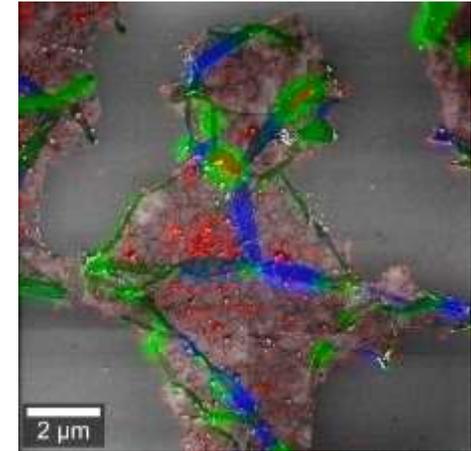
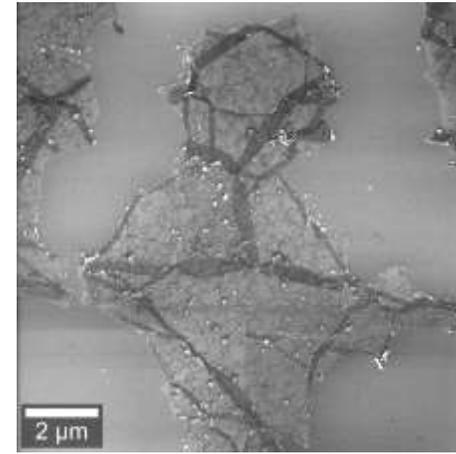
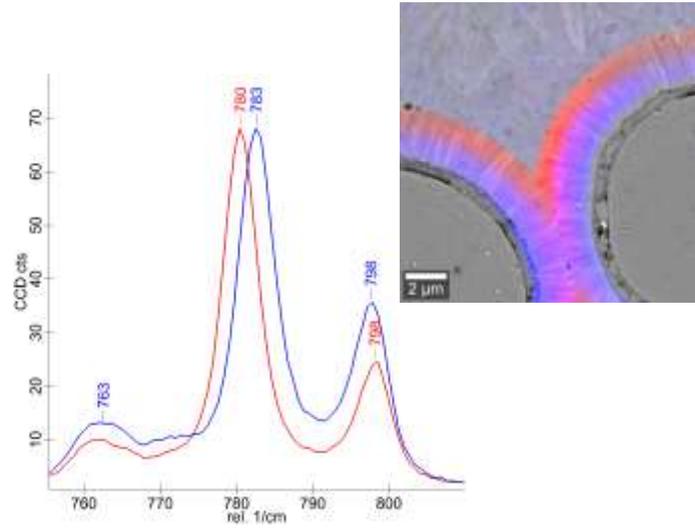
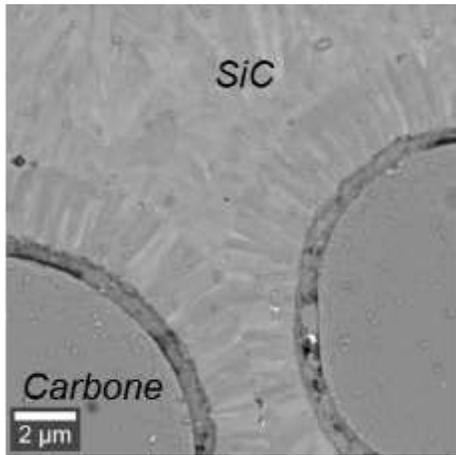
Industrial process for the production of high quality white pigments from natural silica stones (beach pebbles)

- 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**



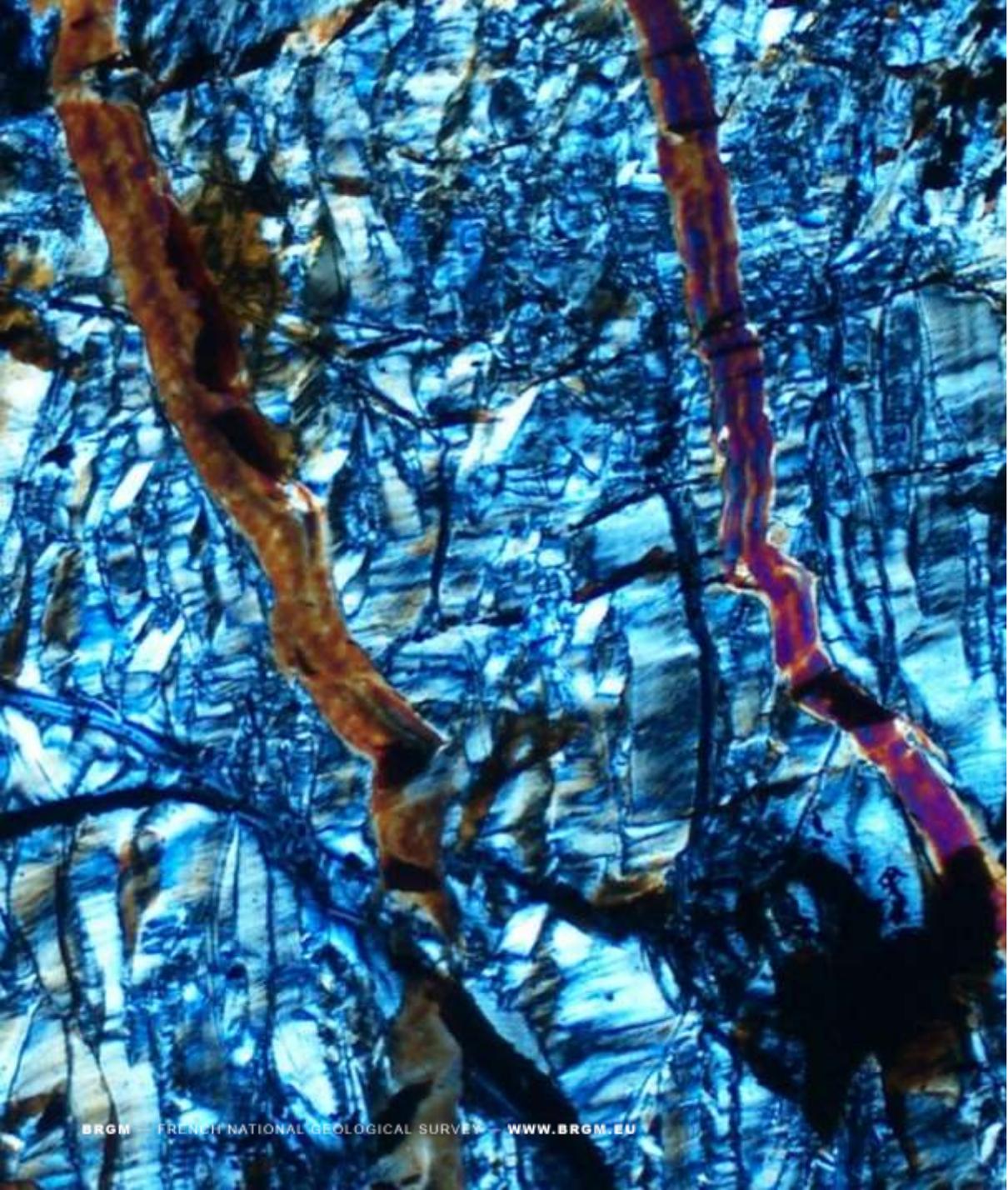
Application – other examples



Composite Carbon / SiC

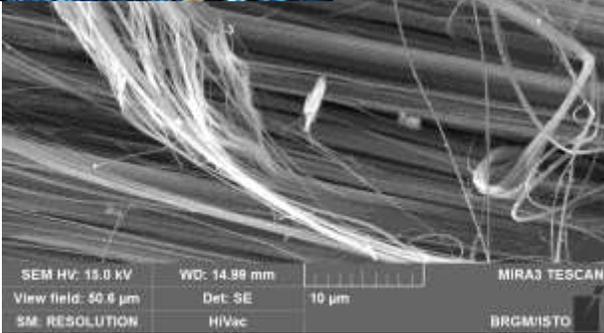
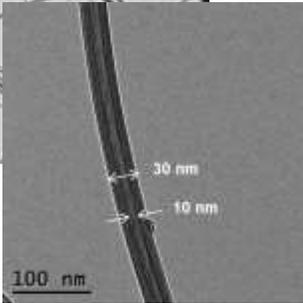
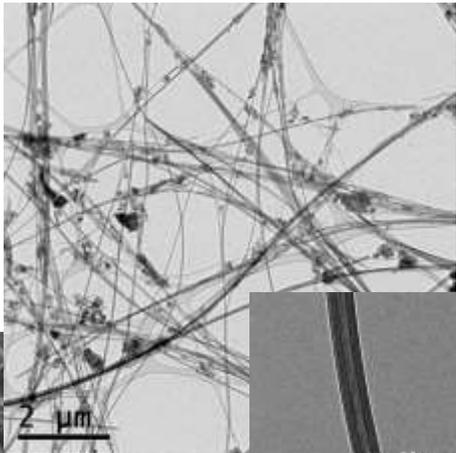
CVD deposition of graphene on silicium

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 occurring asbestos (NOA)



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).

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

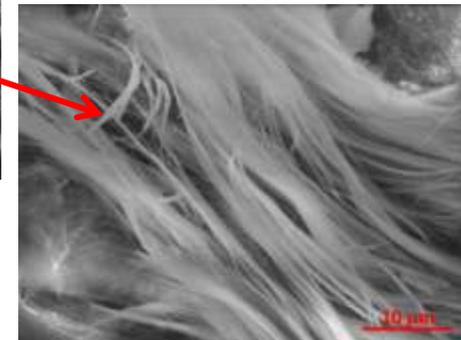
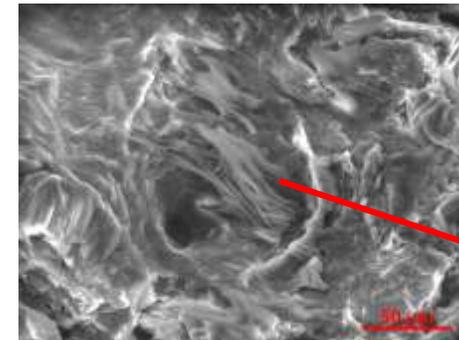
commercial definition → limited to the varieties exploited industrially

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

Breathable Fiber (WEO 1998) = $L > 5 \mu\text{m}$; $D < 3 \mu\text{m}$; $L/D > 5$

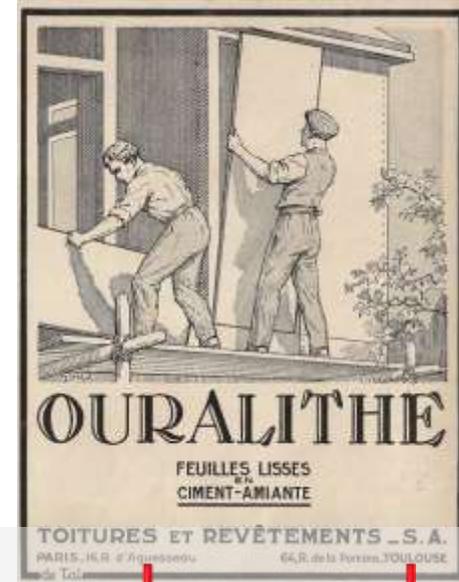
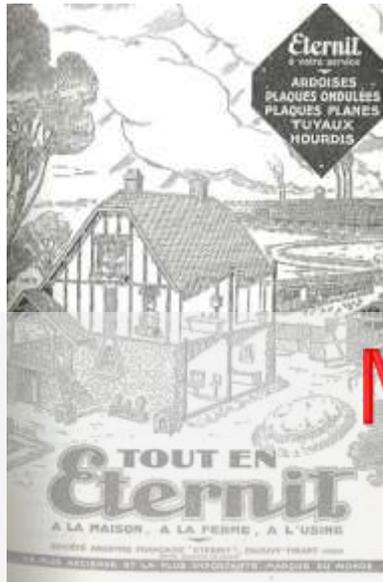
Asbestiform fiber (EPA) = $L/D > 20$, fine fibers ($< \mu\text{m}$)

Serpentines	
Chrysotile	$\text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4$
Amphiboles	
Tremolite	$\text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Actinolite	$\text{Ca}_2(\text{Mg,Fe})_5\text{Si}_8\text{O}_{22}(\text{OH})_2$
Anthophyllite	$(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
Amosite	$(\text{Mg,Fe})_7\text{Si}_8\text{O}_{22}(\text{OH})_2$
Crocidolite	$\text{NaFe}_5\text{Si}_8\text{O}_{22}(\text{OH})_2$



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

Asbestos



More than 3000 manufactured good containing asbestos

Asbestos Toaster
No. 7313702 Crown Asbestos Toaster consists of an asbestos disc covered with steel mesh, the lower surface being covered with sheet steel. Has a corrugated steel handle 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, 8 3/4 inches. Weight, 10 ounces. Price, each 90



Naturally Occuring Asbestos

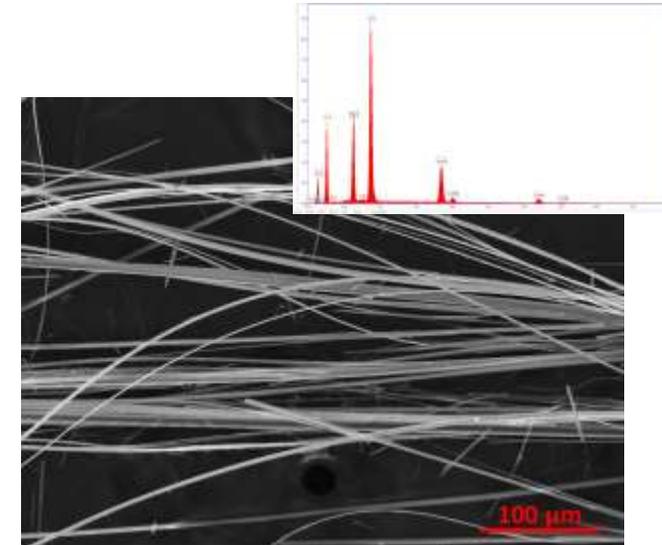
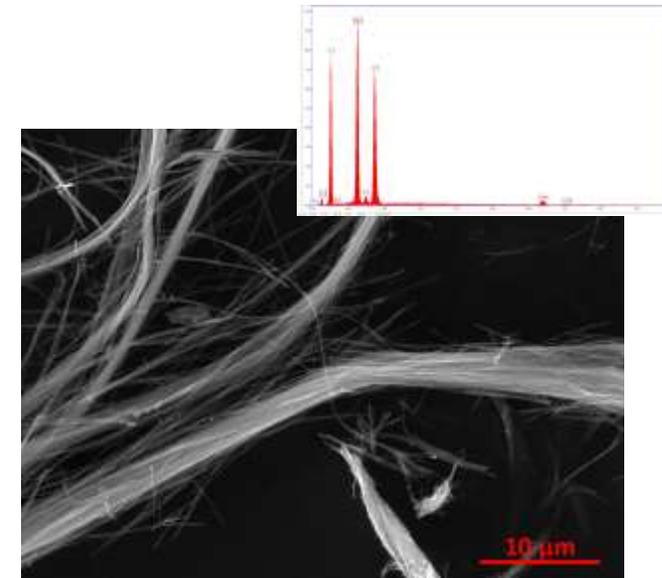
The geologist point of view

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

:

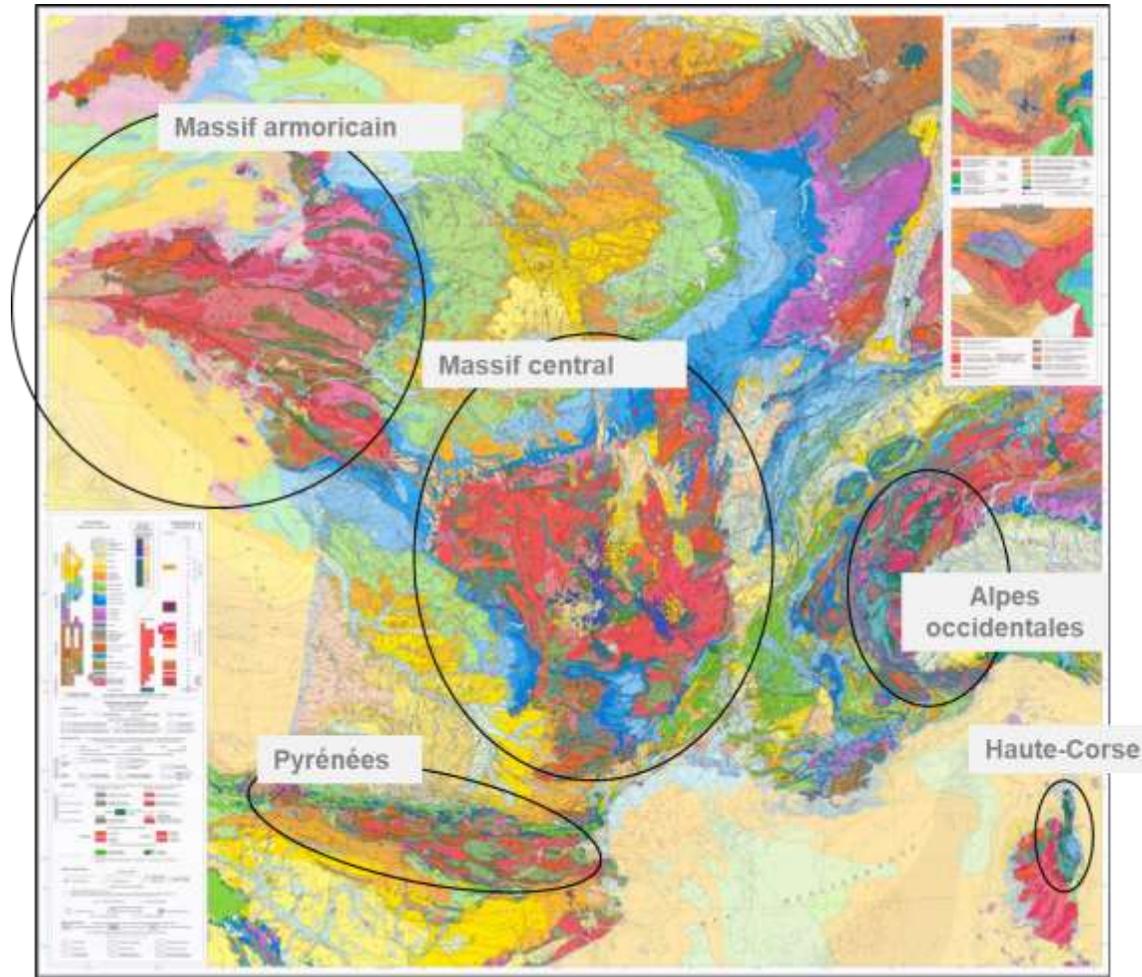
- Ultrabasic rocks: peridotite, serpentized peridotites, serpentinite, (méta)-pyroxenite
- Basic metamorphized rocks: amphibolites, metabasalts, metagabbro, metadolerits, prasinites, spilites, etc...
- Some metaphorphized carbonated rocks

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

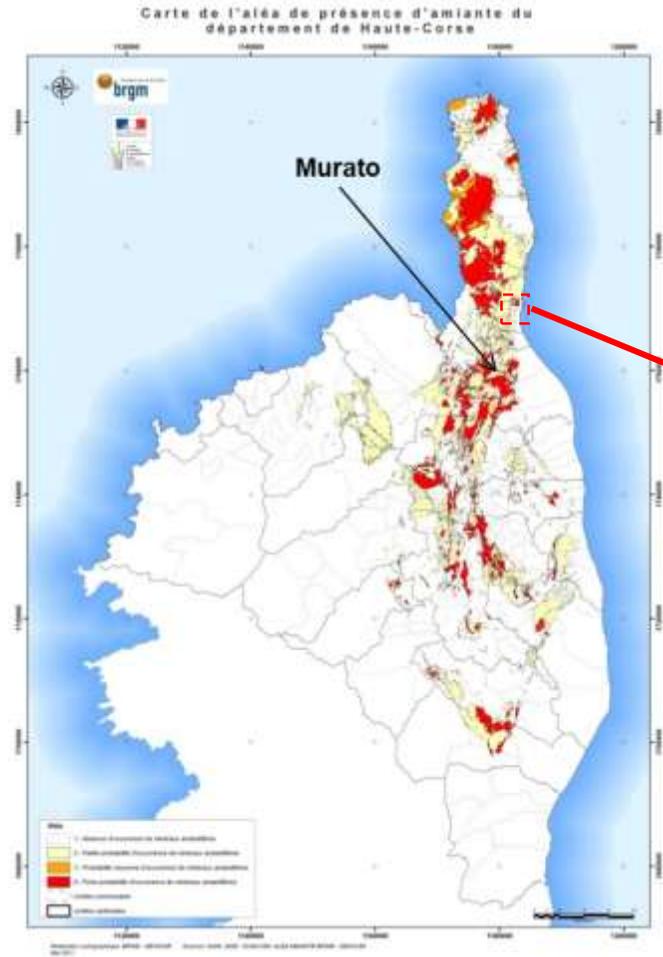


top: chrysotile
bottom Tremolite-asbestos

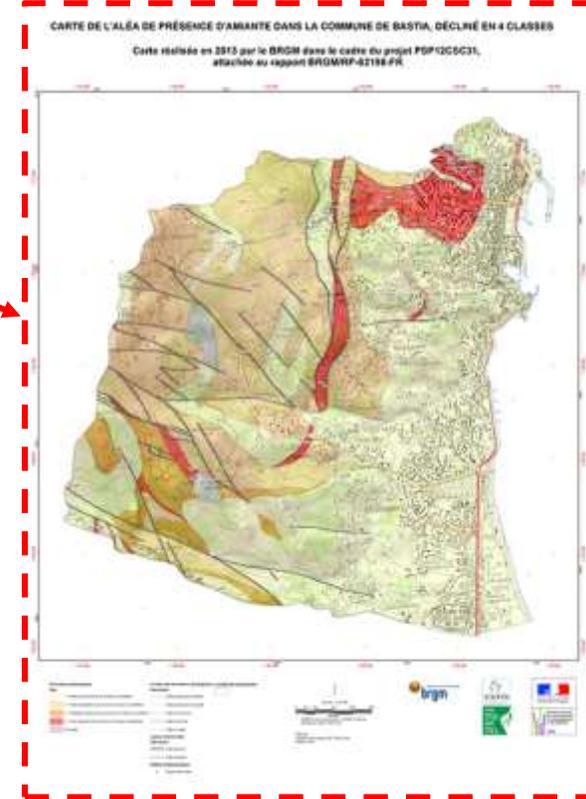
Naturally Occuring Asbestos in France



Main area
(D. Lahondere, BRGM)



North of Corsica
(D. Lahondere, BRGM)



Bastia and around
(D. Lahondere, BRGM)

Naturally Occuring Asbestos in France

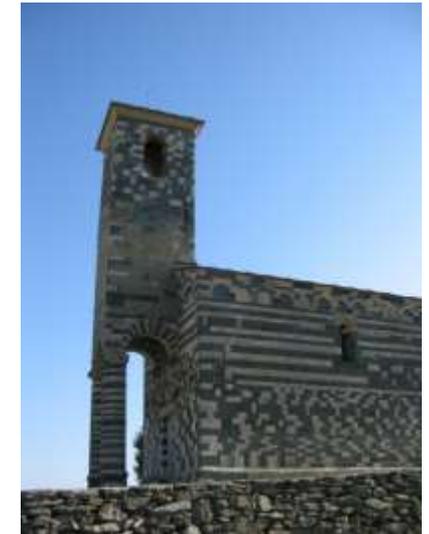
Main risks

- 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 engineering (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

Extent	Location					
	Diaphragm		Chest wall		Pericardium/mediastinum	
	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.

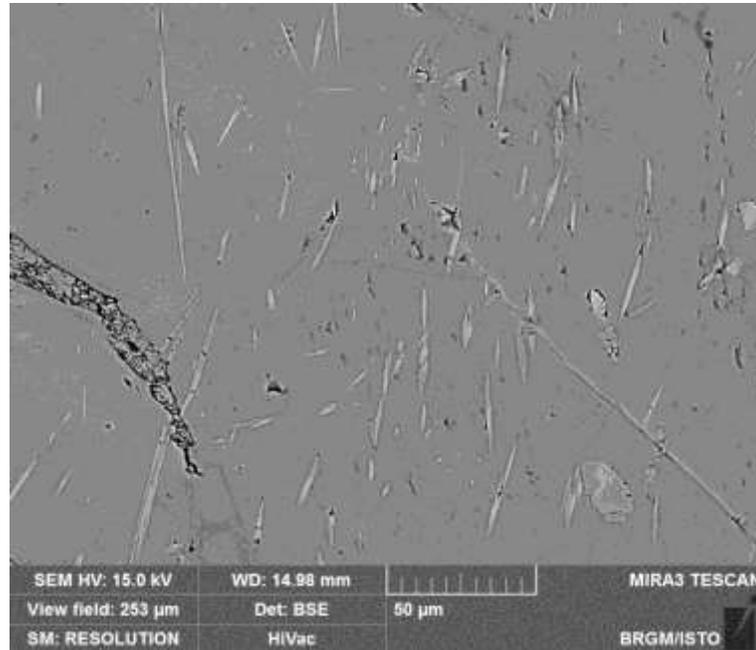
Table 3. - Airborne asbestos pollution as assessed using transmission electron microscopy ($\times 10^3$ g m⁻³)

	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, median, low); ns: not significant. *: Murato values versus Vezzani.

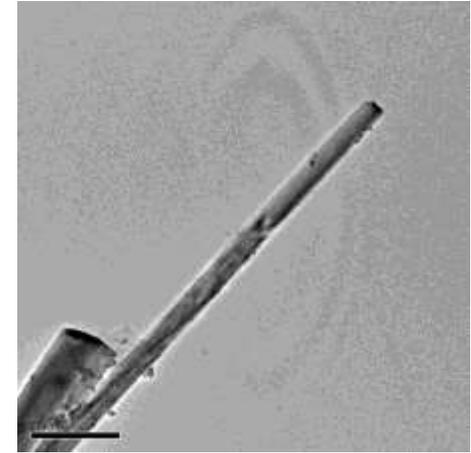
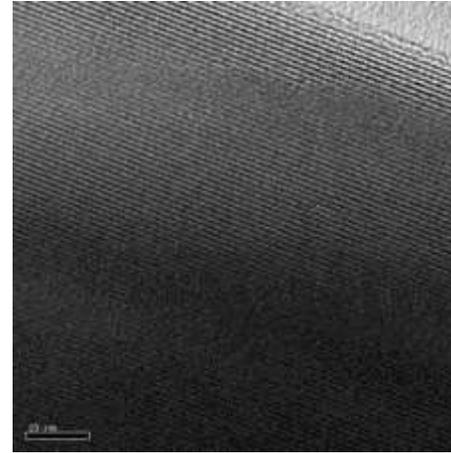
Health hazard of NOA
the example of the north of Corsica
F. Rey et al, *Eur. Respir. J.*, (1993), 6, 978-982

Naturally Occuring Asbestos



SEM (BSE)

TEM

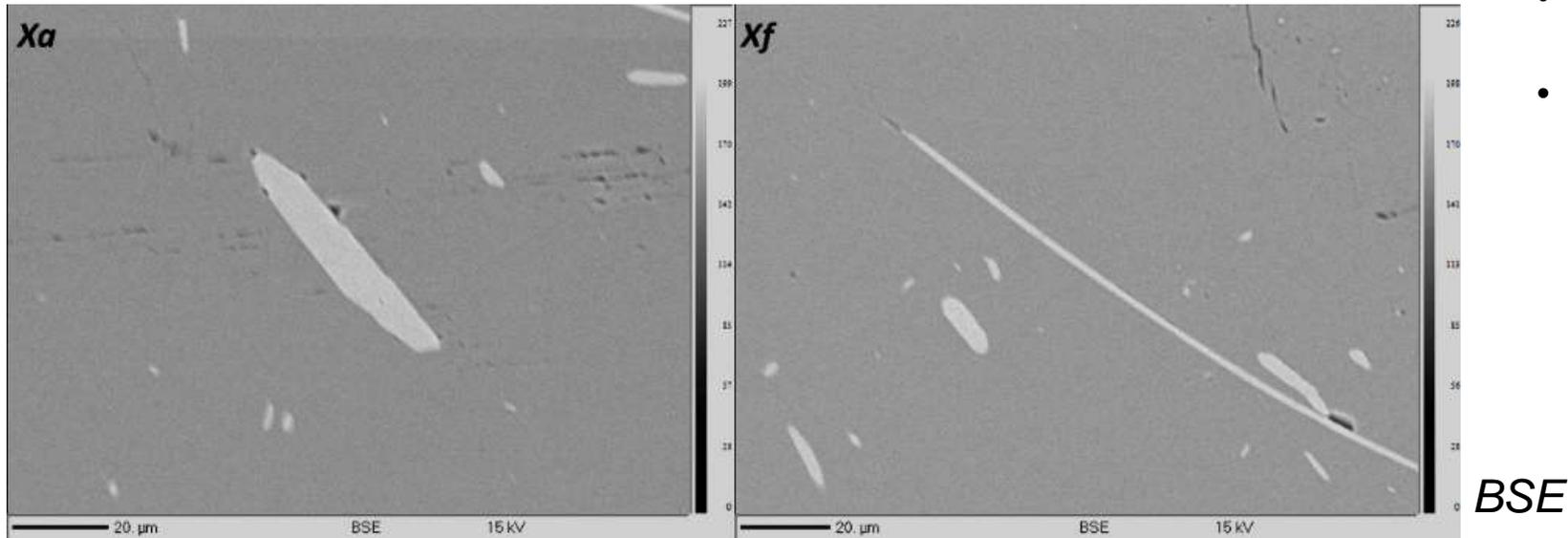


Naturally Occuring Asbestos

EPMA analysis

- Large particles ($> 3\mu\text{m}$) \rightarrow ok
- Thin fibers ($< 3\mu\text{m}$) \rightarrow result not usable - contribution of the matrix in the result

\Rightarrow For thin fibers, another technique is requested for the identification



	SiO ₂	TiO ₂	Al ₂ O ₃	Cr ₂ O ₃	FeO	MnO	MgO	CaO	Na ₂ O	K ₂ O	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

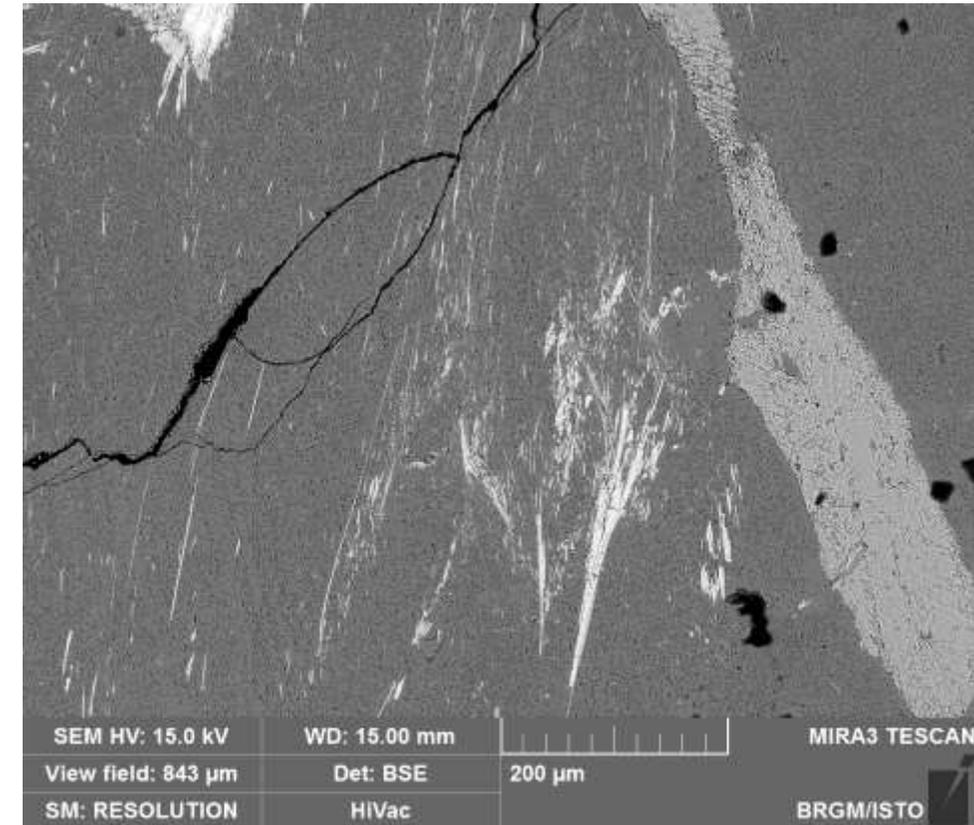
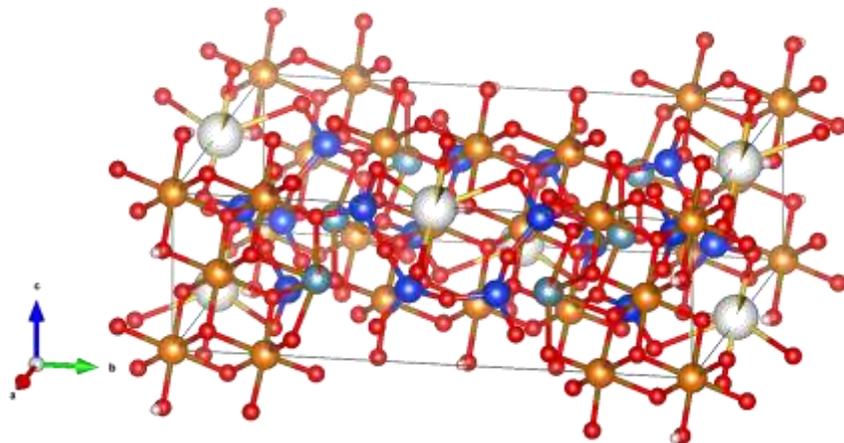
EPMA (WDS)

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

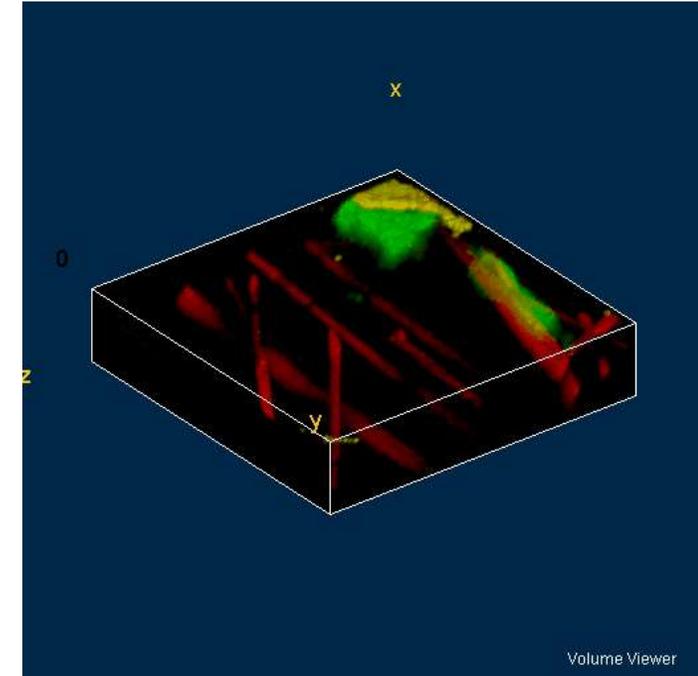
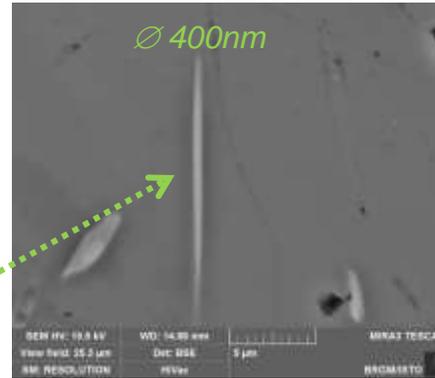
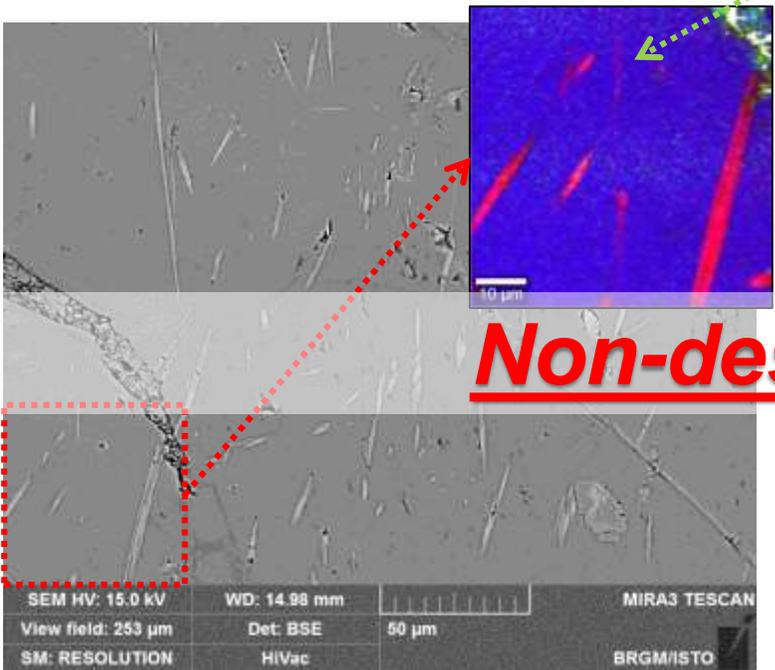


Thin section of a blue micro-diorite containing fibrous actinolite in a quartz matrix (Sainte Florence, France)

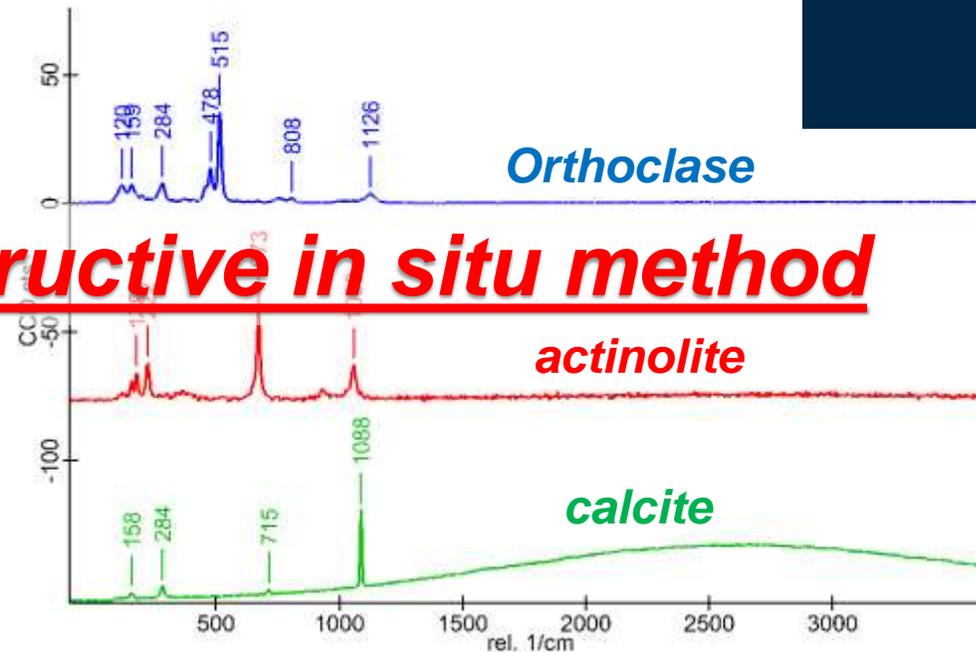
Naturally Occuring Asbestos - In Situ characterization

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



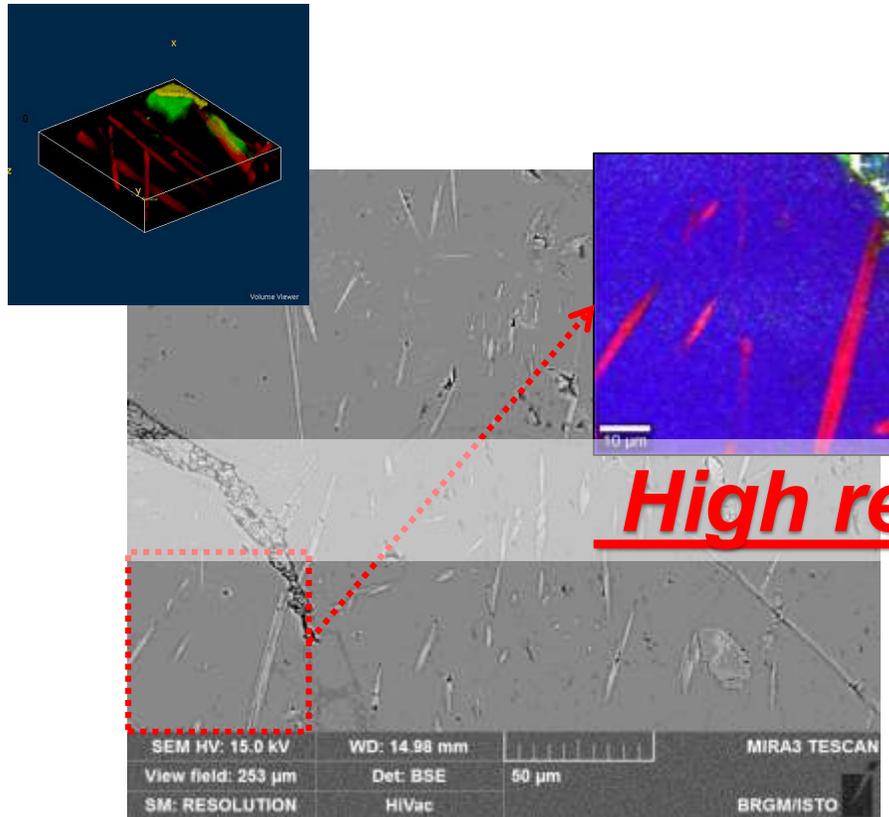
Raman 3D

120 µm x 120 µm x 20 µm

Naturally Occuring Asbestos - In Situ characterization

Fibers < 400 nm → SEM-FIB 3D analysis

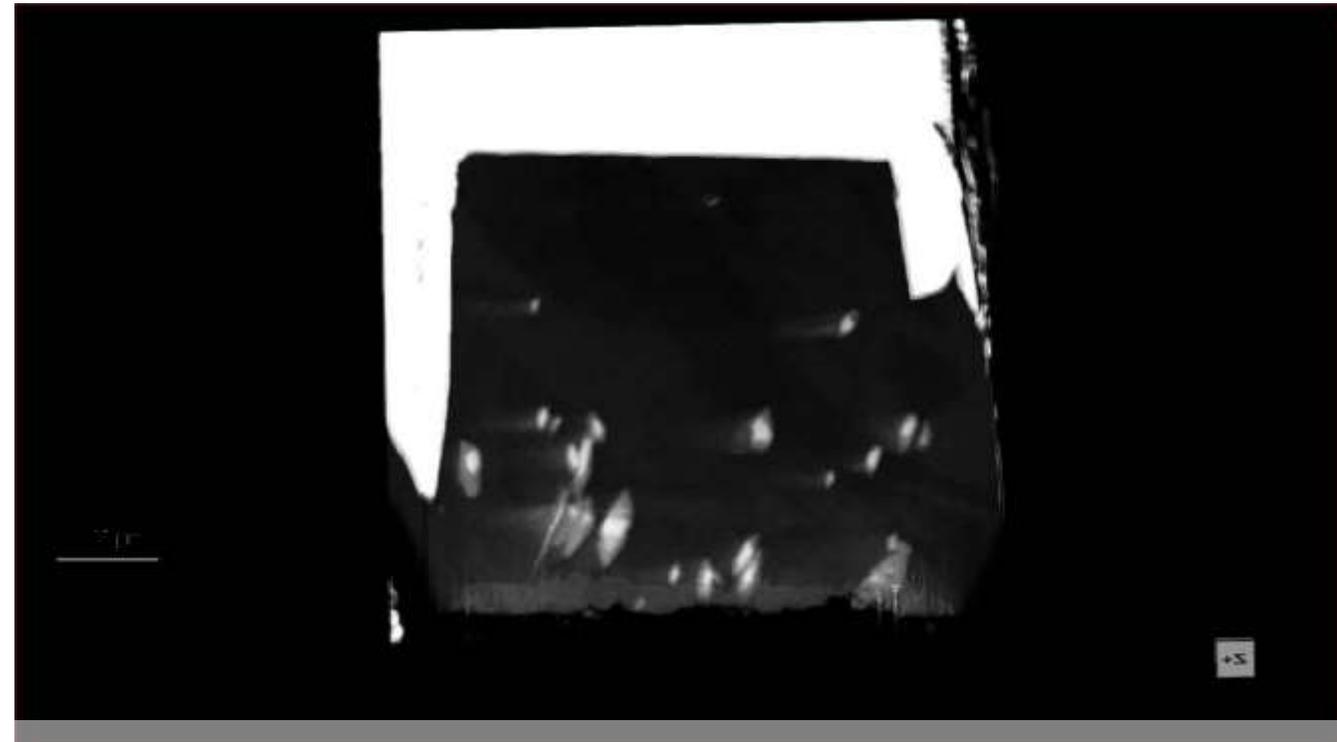
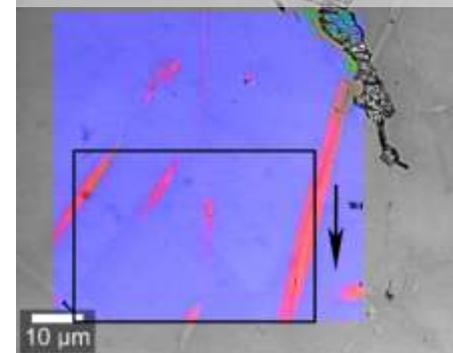
- 3D Fibrous morphology and distribution of actinolite fibers in the analyzed volume up to 100 nm (or better)



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)



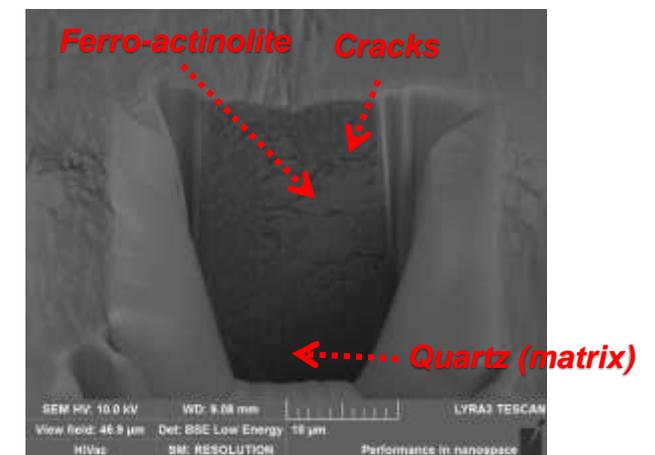
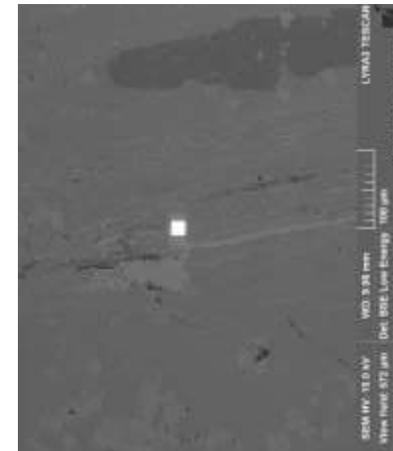
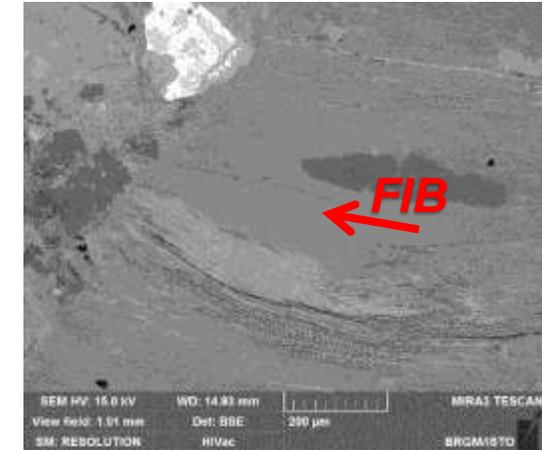
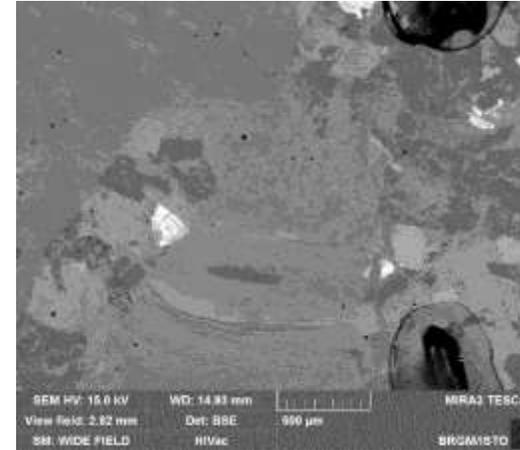
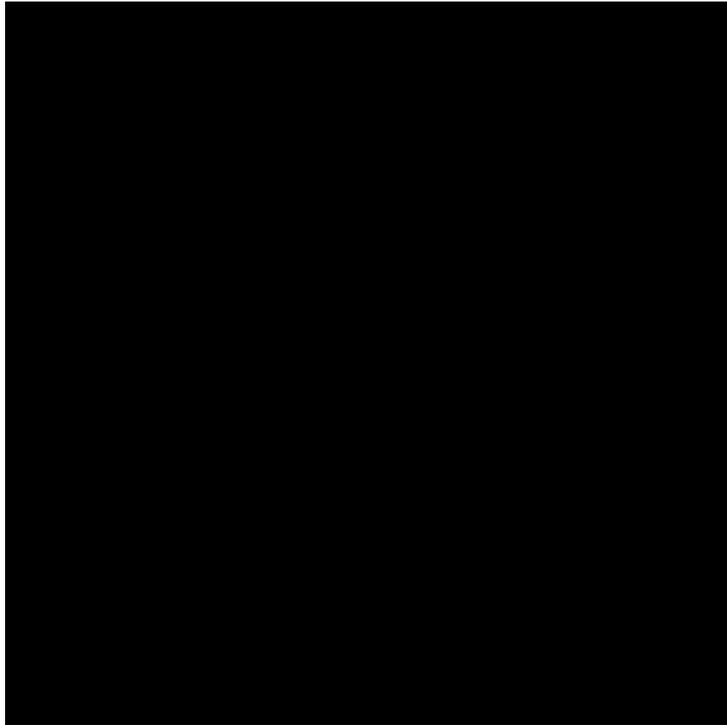
Volume
76274 µm³

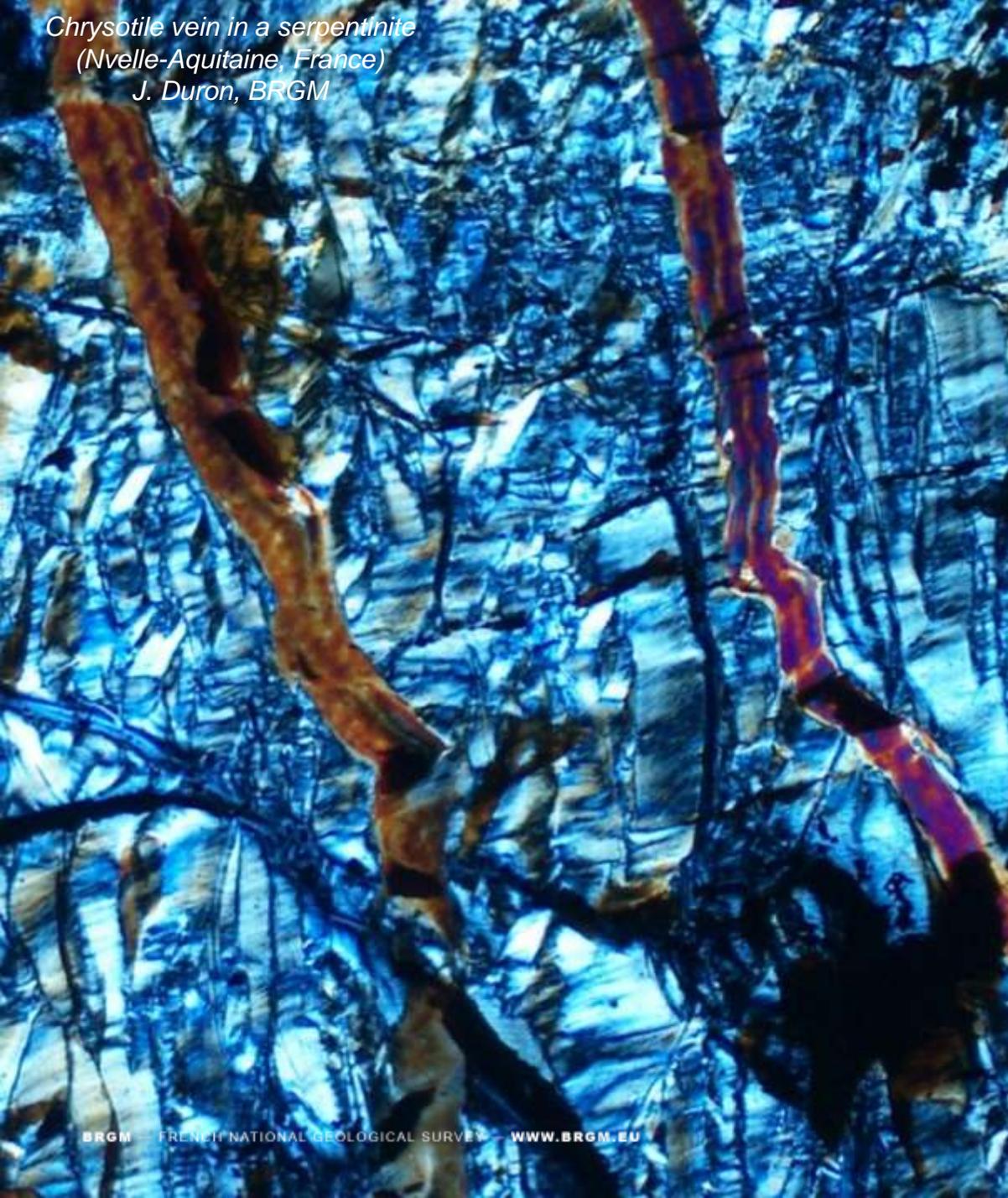
Fibers
1464,40 µm³ soit 1.94 % du volume

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





Coupling SEM-EDS and Raman spectroscopy

Conclusion

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

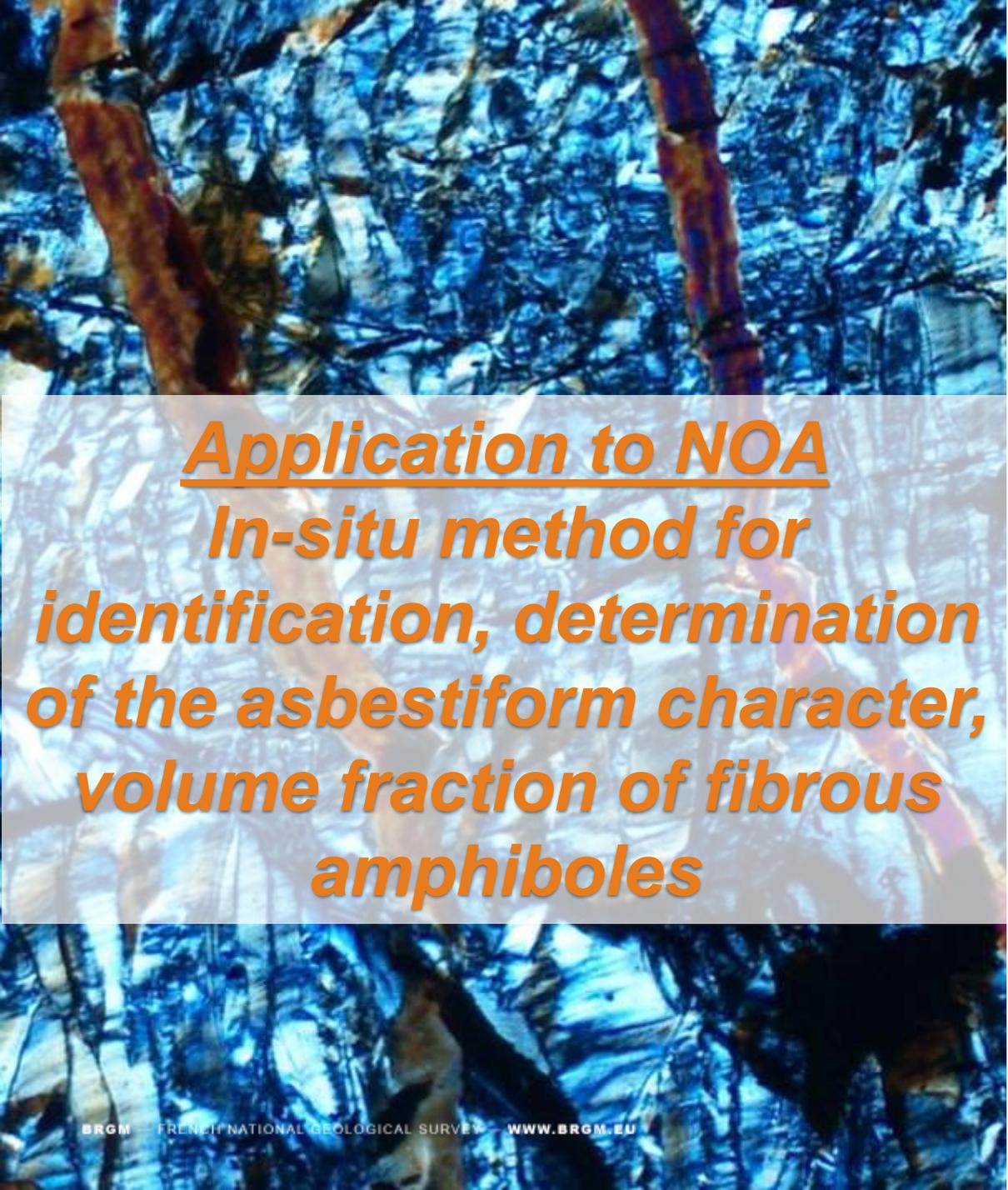
The characterization of geo-materials usually requires various informations: Chemistry (major / trace elements), cristallography, morphology

⇒ *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*



Application to NOA
In-situ method for identification, determination of the asbestiform character, volume fraction of fibrous amphiboles

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*

THANK YOU
Questions ?