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► **To cite this version:**

Guillaume Wille, Didier Lahondère, Ute Schmidt, Jeromine Duron, Xavier Bourrat. Coupling SEM-EDS and confocal Raman-in-SEM imaging: A new method for identification and 3D morphology of asbestos-like fibers in a mineral matrix. *Journal of Hazardous Materials*, 2019, 374, pp.447-458. 10.1016/j.jhazmat.2019.04.012 . hal-02160944

**HAL Id: hal-02160944**

**<https://brgm.hal.science/hal-02160944>**

Submitted on 20 Jun 2019

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# **Coupling SEM-EDS and confocal Raman-in-SEM imaging: a new method for identification and 3D morphology of asbestos-like fibers in a mineral matrix**

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## **Abstract**

Asbestos consists in natural minerals crystallized in a specific habit and possessing in particular properties. In the case of Naturally Occurring Asbestos, usual methods applied to the identification of mineral fibers and the determination of their possible asbestiform nature seems not efficient, especially in the case of mineral fibers included in mineral matrix.

We present a new in-situ method based on the use of confocal Raman-in-SEM imaging implemented in a Scanning Electron Microscope as an efficient method for in-situ mineralogy. The limitation of conventional methods is discussed. We applied 2D-Raman imaging to the identification of sub-micrometric fibers included in different mineral matrix. We were able to identify actinolite fibers down to 400 nm in diameter, included in feldspar, quartz and/or calcite matrix.

Moreover, Confocal Raman allows the collection of 3D data that would provide access to critical information on the morphology of the amphibole fibers in the volume, such as aspect ratio, fibers distribution and amphibole volume fraction.

We performed this method on various examples of rocks containing actinolite fibers of mean structural formula is:  $\text{Na}_{0,04-0,12}\text{Mg}_{2,79-3,73}\text{Al}_{0,29-0,58}\text{K}_{0,01}\text{Ca}_{1,79-1,98}\text{Mn}_{0,01-0,09}\text{Fe}^{2+}_{0,99-1,91}\text{Fe}^{3+}_{0,12-0,25}\text{Si}_{7,64-7,73}\text{O}_{22}(\text{OH})_2$ . We demonstrated that coupling confocal Raman imaging and SEM is a new and efficient in-situ method for identification and morphological characterization of amphibole fibers.

## **Highlights**

New methods are requested for characterizing asbestos fibers in a mineral matrix

SEM-Raman imaging is efficient for characterizing mineral fibers in-situ

Confocal Raman imaging makes 3D analysis possible

3D analysis provides information on the aspect ratio and volume fraction of asbestos

Fibers thinner than 400nm can be identified by confocal Raman in SEM ( $\lambda = 532 \text{ nm}$ )

## **Keywords**

in-situ asbestos diagnosis; Raman-in-SEM imaging; naturally occurring asbestos; 3D analysis; fibrous amphiboles;

## **1. Introduction**

The asbestos group consists of several natural minerals that crystallize according to a specific habit and possess particular properties of flexibility, high tensile strength, and resistance to heat and chemical degradation. Asbestos fibers usually cluster in bundles with separable fibers and/or as long fibers made of small fibrils [1]. The term asbestos refers to a fibrous serpentine called chrysotile and five amphiboles known as the asbestiform varieties of riebeckite (crocidolite), anthophyllite (anthophyllite-asbestos), grunerite (amosite), actinolite (actinolite-asbestos), and tremolite (tremolite-asbestos) [2,3]. In the natural environment, a large set of metamorphic rocks may contain asbestos fibers, such as meta-ophiolitic rocks of basic or ultrabasic compositions (meta-gabbros, meta-basalts, serpentinites) (e.g. [4–6]) and hydrothermally altered dolerites ([7]), more rarely in talc deposits ([8]), metamorphosed dolostones and iron formations ([9]) and subalkaline plutonic rocks ([10]). Asbestos is listed as a Category 1 human carcinogen, because inhalation of asbestos fibers causes respiratory diseases, in particular asbestosis, lung cancers, and malignant mesothelioma (e.g. [2,11–13]). Due to the pathogenicity of asbestos fibers, their use has been banned in most countries around the world. In France, the total ban on asbestos is associated with the decree n° 96-1133 (1997), which notably prohibits the manufacture, processing, sale and import of asbestos fibers. At European level, the ban on asbestos has been the subject of the directive n° 99/77/CE which should be implemented by January, 1<sup>st</sup>, 2005 at the latest. The ban applies to natural materials that are quarried

and used for public works projects. Compliance with existing rules requires accurate diagnosis of the asbestos or non-asbestos nature of materials likely to be exploited in a quarry or involved in the operation of a construction site.

The use of electron dispersive X-ray spectrometry (EDS) or wavelength dispersive X-ray spectrometry (WDS) within a scanning electron microprobe (SEM) or electron probe microanalyzer (EPMA) to analyze asbestiform fibers of serpentines or amphiboles present in a mineral matrix of a mineral mixture is challenging. The main reason is the micrometric to submicrometric diameter of these fibers. In fact, under the usual beam conditions (high voltage = 10 to 20 kV, beam current 5 to 20 nA) used in SEM-EDS or EPMA analysis of silicate minerals, the asbestiform fiber diameter is clearly smaller than the X-ray emission volume (approximately 1.5 – 3  $\mu\text{m}$ ). As a result, a portion of the X-ray emission detected is generated by the neighboring mineral grains along with the fiber being analyzed (mixed analyses).

The Transmission Electron Microscopy (TEM) is well suited for the determination of morphological and dimensional characteristics, and in conjunction with EDS analysis, for chemical characteristics; and, along with electron diffraction, for crystallographic characteristics of mineral fibers. TEM is considered as the reference method for determining the asbestiform character of fibers in air [14,15]. However, in the case of mineral fibers contained in a mineral matrix, the use of the TEM requires a complex preparation including the reduction by fragmentation, sampling and milling of a subsample (1 to 2 g), the calcination of the rock powder to remove organic matter and then an acid attack to solubilize the constituents of the matrix such as calcite or gypsum. The test sample (~ 20 mg) should then be mixed with water, sonicated, filtered through a pre-metallized polycarbonate carbon membrane and covered with a second layer of carbon before being examined. The preliminary crushing step causes many difficulties because it can lead to excessive fragmentation of the non-asbestiform three-dimensional amphibole crystals, and then the creation of somewhat elongated fibriform fragments (cleavage fragments) which can be mistakenly identified as asbestos [16]. An alternative protocol is based on thinning down a piece of the sample by ionic beam or using a focused ion beam (FIB) in an SEM (SEM-FIB) to sample a thin slice [17–21]. These two techniques are efficient but also difficult to achieve and thus costly and not applicable to routine analysis. In addition, only fibers that are elongated parallel to the surface can be investigated. EDS analysis on transmission

electron microscope can be used to analyze submicrometric fibers, but quantitative analysis is not as precise as EPMA analysis.

Specific methods were developed for analysis of submicrometric objects included in a matrix, such as coupling EDS/WDS measurements with Monte-Carlo simulation [22] or development of special calculations [23], but these methods face a major challenge, which is the knowledge of the shape of the analyzed particle (generally unknown in the case of natural mineral particles/ fibers). Special methods based on the mix of bulk analysis and stratified materials make it possible to produce satisfactory results in specific cases such as grain boundary segregated phases in nickel alloys [24]. In addition, these methods are not commercially available for routine analysis.

Lowering the high voltage to  $HV \leq 5$  kV is an analytical method that seems suited to this problem. The use of low voltage is known to notably reduce the analyzed volume down to a submicrometric diameter [25,26]. However, this method encounters/faces major challenges in both EDS and WDS, including the use of L ( $20 < Z < 50$ ) and M ( $Z > 50$ ) lines, changes in the peak shape and position in WDS, heightened sensitivity to surface carbon contamination, and uncertainty regarding the Mass Absorption Coefficient (MAC) at low peak energy [27–29].

Other methods can be applied to the identification of amphiboles, such as X-ray diffraction (XRD), Fourier-transform infrared spectroscopy (FTIR) or thermal analysis [30]. But, these methods do not provide a morphological information needed for the diagnosis, and as mentioned by these authors, since the amosite, crocidolite, actinolite and tremolite are crystallographically very close together, the XRD patterns of the amphibole minerals are similar and not really usable to differentiate amphibole members. For thermal analysis, it can be possible to distinguish the different amphiboles. But, in the case of our samples the objective is to work *in-situ* on natural rocks (i.e. amphiboles mixed with numerous other minerals), several thermal phenomena could occur on the same thermal range and this can significantly complicate the analysis of the DTA (then it makes DTA not really applicable to « routine » asbestos diagnosis).

We present a new and original *in-situ* approach of the asbestos diagnostic in natural samples, based on the combined use of conventional petrographic / mineralogical approach and the use of a fully integrated Raman-in-SEM system to perform analyses on the same areas / amphibole fibers. This paper discusses the efficiency of this in-

situ analytical method. Conventional petrographic and mineralogical approach use polarized light microscopy (PLM), scanning electron microscopy coupled with SEM-EDS, and electron probe microanalysis (EPMA) for the location, morphological description, and chemical analysis of fibrous or particulate amphiboles. The limits of such conventional methods are discussed. The contribution and advantages of the combination of Confocal Raman integrated into a SEM-EDS are presented as a new in-situ method for the chemical, morphological, and structural identification and description of extremely fine mineral fibers (diameter < 0.5  $\mu\text{m}$ ) contained in a natural mineral matrix. We discuss the performance of high-resolution low vacuum Field Emission SEM (LV-FE-SEM) in terms of imaging resolution (down to 1 nm) coupled with EDS qualitative analysis (micrometric resolution), and high-resolution confocal Raman Imaging (resolution close to the diffraction limit, down to 360 nm for a laser wavelength  $\lambda = 532$  nm [31]). We present the data correlation that can be obtained from the results from these techniques in the context of identification, description, and counting of mineral fibers isolated in a natural mineral matrix. We apply this method to multiple samples from various geological environments. We present and discuss 2D (surface) and 3D (volume) analytical results.

## **2. Sampling, petrographic and mineralogical study**

### **2.1. Sampling**

Three samples were collected in France, two from the southern part of the Armorican massif and one from the southwestern part of the Massif Central. The location of the samples is shown on simplified geological map of France (figure 1 – after [32]).

Sample 1 was collected in the southern part of the Armorican massif from a geological formation composed mainly of amphibolites (Pont-Léger and Boufféré Formation [33]). These amphibolites are foliated rocks, weakly affected by greenschist recrystallization. They are locally intersected by feldspathic veins that contain macroscopic crystals of greenish, prismatic amphiboles.

Sample 2 comes from the southern part of the Armorican massif from a basic volcanic complex that is more than 1000 m thick and contains underwater flows, breccias, hyaloclastites, tuffs, cinerites, and sills [34]. In basalts, hydrothermal overprinting led to crystallization of actinolite at the expense of magmatic pyroxenes [35,36].

Sample 3 was collected in a ten meter thick doleritic sill emplaced within Cambrian schists in the southwestern part of the Massif Central (Monts de Lacaune [37]).

Samples were individually stored in a double bagging to avoid cross-contamination and the spread of fibers in case of the presence of asbestos fibers. Since we have used in-situ methods, the samples were prepared according to the usual methods in petrography, namely the preparation of polished geological thin section. In particular, no grinding was applied and no fiber sampling was performed to avoid any contamination or cleavage fragment creation (that could result in an incorrect diagnosis). Indeed, the grinding of an amphibole sample is likely to form fine and elongated particles, of nanometric diameter, which, with the transmission electron microscope, can easily be confused with true asbestos fibers and for which differentiation criteria are not simple [38].

## **2.2. Petrographic study**

The three sample were observed by polarized light microscopy (PLM) to describe the mineralogy of the samples, and to identify areas of interest containing fibrous / fibrous-like amphiboles. Examples of areas of interest are presented in figure 2.

Sample 1 is a dark, banded amphibolite composed of green amphibole (magnesian hornblende), plagioclase (andesine-oligoclase), epidote (clinozoisite), and ilmenite, intersected by a plagioclase-amphibole vein. Matrix amphiboles form large, three-dimensional crystals slightly aligned and arranged flat in the banding. Morphological characteristics of fibrous amphiboles associated with plagioclase-bearing veins are shown on figure 2 (S1-A and S1-B). These amphiboles from the vein have fibrous morphologies and form both moderately dissociated elongate particles and extremely thin and sometimes curved fibrils.

Sample 2 is a hydrothermally altered basalt intersected by an amphibole-chlorite-calcite-K-feldspar vein. Outside the vein, the sample has a pseudomorphic texture characterized by the presence of colorless phenocrysts of clinopyroxene (diopside) partially destabilized in amphibole. Inside the vein, the amphiboles are dispersed and appear completely embedded in calcite and K-feldspar crystals. A view of the contact

between the hydrothermally altered basalt and the quartz-calcite- amphibole vein is shown on figure 2 (S2-A). Clinopyroxene crystals are present in the basalt. The amphiboles from the veins form randomly curved bundles with split ends and fibrils, both extremely long and remarkably thin (Figure 2: S2-B).

Sample 3 is a dolerite intersected by an epidote-quartz-amphibole vein. Outside the vein, the rock retains a recognizable doleritic texture despite a pervasive greenschist overprint. The matrix consists mainly of crystals of altered plagioclase embedded in an essentially chloritic background. Highly altered and partially chloritized pyroxene crystals are preserved. The polymineralic vein appears zoned, with a quartz-epidote central zone, that grades into an intermediate zone constituted by epidote and amphibole ( $\pm$  chlorite) and then a quartz zone ( $\pm$  amphibole, chlorite) towards the borders. Amphiboles from the vein form brownish, polyfilamentous bundles within the intermediate zone and more or less elongated and thinnest bundles within the quartz crystals of the external zones (Figure 2: S3-A). Fiber bundles regularly exhibit splitted ends and frayed borders (Figure 2: S3-B).

### **2.3. Amphibole chemistry (EPMA)**

The general chemical formula of the minerals of the amphibole supergroup can be written as  $A_{0-1}B_2C_5T_8O_{22}W_2$ , where A = Na, K, Ca, Pb, Li; B = Na, Ca,  $Mn^{2+}$ ,  $Fe^{2+}$ , Mg, Li; C = Mg,  $Fe^{2+}$ ,  $Mn^{2+}$ , Al,  $Fe^{3+}$ ,  $Mn^{3+}$ ,  $Cr^{3+}$ ,  $Ti^{4+}$ , Li; T = Si, Al,  $Ti^{4+}$ , Be and W = (OH), F, Cl,  $O^{2-}$ . Minor elements such as Zn,  $Ni^{2+}$ ,  $Co^{2+}$ ,  $V^{3+}$ , Sc and Zr may also be observed as C-site cations [39]. The amphiboles were analyzed with an electron probe microanalyser (EPMA) CAMECA SXFive (CAMECA, Gennevilliers, France) equipped with five wavelength dispersive X-ray spectrometers (WDS) at BRGM (Orleans, France). Ten chemical elements were analyzed (Si, Ti, Al, Cr, Mn, Fe, Mg, Ca, Na, K). The operating conditions were accelerating voltage HV=15 kV and beam current BC=12 nA. Samples were coated with carbon under secondary vacuum (thickness = 20 nm) using a CRESSINGTON 308Carbon (Cressington, Watford, UK). K  $K\alpha$ , Ti  $K\alpha$ , Ca  $K\alpha$  and Cr  $K\alpha$  were measured on PET; Fe  $K\alpha$  and Mn  $K\alpha$ , on LiF; and Si  $K\alpha$ , Al  $K\alpha$ , Na  $K\alpha$  and Mg  $K\alpha$ , on TAP. The phi-rho-Z method X-Phi [40] was used for quantitative calculation. Classification of amphibole chemical analyses was done following the 2012 nomenclature recommended by the International Mineralogical Association [39].  $Fe^{3+}/\Sigma Fe$ ,  $Mn^{3+}/\Sigma Mn$ , OH content, and cation site assignments were determined

using the Excel spreadsheet of Locock [41]. Monte-Carlo simulation has shown (CASINO 2.48 software [42]) that EPMA analyses are possible on fibers whose size exceeds 2 microns in depth / width, i.e. more than 3-4  $\mu\text{m}$  in diameter to account for the polishing effect on fiber dimensions. According to the nomenclature of Hawthorne et al. [39], the analyzed amphibole fibers (larger than 3  $\mu\text{m}$ ) are classified as calcic amphiboles. Detailed analyses of analyzed amphiboles are given in table 1. Magnesio-hornblende and magnesio-ferri-hornblende were mainly identified in sample 1, while actinolite is present in the three samples. Depending of the sample, the actinolite fibers are more or less iron-rich and magnesium-poor. The iron-rich and magnesium-poor actinolite fibers were analyzed in the first sample (15.9-17.8 wt % and 12.5-13.1 wt % respectively). In the others samples, the actinolite fibers have significantly lower iron content (9.8-12.6 wt %) and higher magnesium content (15.9-18.3 wt %).  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$  and  $\text{CaO}$  contents do not vary significantly in the three samples.  $\text{TiO}_2$ ,  $\text{MnO}$ ,  $\text{Cr}_2\text{O}_3$  and  $\text{Na}_2\text{O}$  contents are always less than 1 %.

Sample 1 contains micron-sized fibers from which acceptable EPMA analyses can be obtained. Conversely, in samples 2 and 3, fibers are mostly extremely thin, with a diameter of less than 1 or 2  $\mu\text{m}$ . For these extremely thin and dispersed fibrils, EPMA analyzes are often unsatisfactory from a stoichiometric point of view, because they most likely incorporate a mixture of the analyzed fiber and matrix minerals.

Thus, the EPMA method is quite difficult to use to characterize the chemical composition of asbestiform fibers as defined by EPA [43]. Figure 3 illustrates these difficulties. In this figure, two fibers from sample 1, one thick (Xa) and the other quite thin (Xf), are contained within an albite matrix. The EPMA analyzes of these two fibers are shown in Table 2. The results obtained from the thick fiber (Xa) correspond to actinolite analyzes. The results obtained from the fine fiber (Xf), on the other hand, show abnormally high contents of  $\text{SiO}_2$ ,  $\text{Al}_2\text{O}_3$ , and  $\text{Na}_2\text{O}$  and low contents of  $\text{MgO}$ ,  $\text{CaO}$ , and  $\text{FeO}$ . Thus, actinolite can be identified in Xa but not (or only with great difficulty) in Xf.

### **3. SEM-EDS and Contribution of Confocal Raman imaging integrated within SEM-EDS (RISE)**

#### **3.1. *Methods***

The three samples were observed under SEM using the backscattered detector imaging (BSE) mode. SEM-EDS produces a general description of the sample (matrix, fibers, mineralogical view of the rock), identifies the mineral matrix and areas of interest (areas representative of the sample) for coupled SEM-Raman analysis. SEM-EDS analysis was performed on a LV-FE-SEM TESCAN Mira 3 XMU (TESCAN, Brno, Czech Republic) coupled to an EDAX Team (EDAX, Mahwah, USA) EDS system (EDAX Apollo XPP Silicon Drift Detector).

Raman spectroscopy uses the principle of inelastic scattering of light (monochromatic laser), so-called "Raman effect". Raman spectroscopy is a non-destructive, preparation-free method that can be used to study crystal chemistry and structure. It can be easily applied to thin sections of rock. Because Raman spectra cannot be collected from carbon coated samples, a Raman system integrated in a SEM can be implemented only in a low-vacuum or an environmental SEM [44]. Information on local chemistry can be obtained at a submicrometric scale using Confocal Raman spectroscopy and Imaging [45,46]. Amphibole fibers that have the general formula  $A_0-1B_2C_5T_8O_{22}W_2$  can be identified by confocal Raman spectroscopy using a 532 nm laser wavelength. Several differences are observed on the Raman spectra, depending on the nature of the various cations filling the different sites (A, B, C, T) in the crystal structure [47].

We conducted Raman imaging on three samples in the SEM chamber. The area of interest was located using SEM imaging and EDS microanalysis. Then the SEM stage was used to transfer the sample to the Raman imaging position (automated movement). The advantage of this coupled system is the ability to conduct the different analyses at exactly the same place and on the same fibers (assuming the fact that nanometric fibers cannot be visualized under the optical microscope of a conventional micro-Raman spectroscope). In this way, Raman spectral maps (2 dimensions X,Y (2D)) can be collected and analyzed to identify the mineralogical nature of the fibers. In confocal Raman imaging, Raman spectra are collected point by point in a 2D or 3D array consisting of ten thousands of complete Raman spectra. Multivariate analysis tools are used to extract information from the acquired spectral arrays [48]. Raman maps were collected on the three samples in areas previously defined by SEM and optical microscopy. The array size, number of acquired spectra, integration time per spectrum are listed in the corresponding figure captions.

Coupled SEM observations / Raman imaging in SEM (RISE) were performed on a Tescan-Witec RISE microscope combining a TESCAN Mira 3 GMU LV-FE-SEM coupled to a WITec Confocal Raman Imaging System (WITec, Ulm, Germany). The RISE confocal Raman imaging system is equipped with a UHTS300 spectrometer, a Zeiss 100x vacuum objective (Numerical Aperture 0.75) mounted inside the SEM chamber, using a 532 nm laser radiation wavelength. Coupled SEM-EDS and Raman imaging were performed on non-coated samples under low vacuum at HV = 15kV under Nitrogen pressure  $P = 20$  Pa.

### **3.2. Results**

#### **SEM-EDS:**

Images of the three samples are presented in figure 4. The images were coupled with qualitative EDS analyses. In fact, as pointed out previously for EPMA analytical resolution, EDS resolution is the same, and the precision of EDS quantitative analysis is much less than WDS (on EPMA). As a result, quantitative EDS analysis is not effective for determining the amphibole nature of a thin fiber.

Figure 4 shows SEM images of different areas of the samples 1, 2, and 3, where amphiboles are present.

Sample 1 (figure 4 a,b) has several large areas of amphibole surrounding plagioclase with micrometric to submicrometric elongate amphibole particles. The aspect of these elongated particles is fibrous and generally asbestiform.

In sample 2 (figure 4 c,d), numerous elongate asbestiform fibers can be observed. Some fibers occur as bundles that measure several tens of microns wide, and some are isolated in a K-feldspar matrix. Calcite is observed in places.

In sample 3 (Figure 4 e,f), amphibole fibers are observed within different matrix, composed of quartz, epidote, and calcite.

#### **2D confocal Raman imaging:**

Figure 5 shows an area of sample 1 analyzed by confocal Raman imaging in SEM (RISE). In this area, actinolite fibers are present within a matrix of albite. The width of

the actinolite fibers visible in this area ranges from large fibers of several  $\mu\text{m}$  in diameter to thin fibers of about 400 nm in diameter.

An area of sample 2 analyzed by Raman imaging is presented in figure 6. Sample 2 has fine fibers included in a mineral matrix identified as orthoclase by a combination of qualitative EDS and Raman spectroscopy. Calcite is also present in this area.

The area analyzed in sample 3 (figure 7) looks like a loosely organized bundle. Thin fibers are observed in a quartz matrix in combination with calcite particles. The aspect ratio of these fibers is important, then the thinnest fibers can be considered as asbestos fibers.

#### **4. Contribution of 3D Confocal Raman imaging integrated into a SEM-EDS (RISE)**

##### ***4.1. Introduction and method***

Confocal Raman imaging offers the ability to visualize three-dimensional volumes (3D) of the different phases present in a sample. Due to the confocal setup, the focal plane from which Raman spectra are collected can be varied, leading to an optical nondestructive sectioning of the sample. 2D Raman images are collected from the same sample area successively, by changing the focal plane in z-direction. The primary limitation however is the transparency of the matrix to the laser beam.

The 3D volume analysis has several advantages. The first is the ability to describe the particles in the volume, i.e. the true aspect ratio of the particles detected. In fact, The PLO makes it possible to visualize fibers in a transparent volume at micrometric resolution. In contrast, information obtained from the SEM is nanometric, and is only two-dimensional (surface of the sample). As a result, it is not always easy to discriminate between an elongated particle and a true asbestos fiber. 3D mapping produces a precise description of the shape and aspect ratio of the amphibole, and it also offers of accurately identifies the asbestos-containing character of the material. In addition, calculations conducted on the 3D volume can be used to determine the volume fraction of each phase. The results obtained on the three samples are presented below.

The 3D view is obtained by collecting 2D maps equally spaced in Z. The volume is reconstructed using ImageJ software [49].

## **4.2. Results**

Figure 8 presents a 3D view of the area analyzed by 2D RISE (figure 5) in sample 1. Fibers are visible but the most of them look wide. This can be explained by the presence of a "compact" bundle of fine actinolite fibers or, more likely, the presence of micrometric elongated crystals. In the latter case, a different technique is required to make a determination, for example, either SEM-FIB or TEM observation on an SEM-FIB extracted thin slice. In this case, the 3D view is a useful tool for locating the area of TEM sample extraction.

The Raman volume analysis of sample 2 is presented in figure 9.

The actinolite fibers observed previously in the 2D volume in sample 2 appear to be elongate with a high aspect ratio in the 3D view. This confirms that these are fiber bundles, and the thinnest ones appear to be asbestiform.

The 3D view of the area presented in 2D on figure 10 (sample 3) shows numerous thin fibers with no preferred orientation. The matrix is calcite with quartz. The 3D view shows long fibers and probable fiber bundles, some of which are partially visible at the surface, but others that are not visible. In this case, 3D is useful for revealing the presence of fibers / fiber bundles below the surface of the sample.

## **5. Discussion**

The identification and morphological characterization of fibrous amphiboles in a mineral matrix is of great interest and of major importance for the extraction and commercial exploitation of stones concerned, for prevention of the naturally occurring asbestos (NOA) hazard, and also for safe extraction and manufacturing of building stones and aggregates at the quarry. The chemical and morphological characterization of very/extremely thin isolated fibers in a mineral matrix requires the use of several microscopic and microanalysis techniques.

To address these considerations, EPMA is an efficient tool that can be used to determine the chemistry of amphibole fibers / particles (diameter > 3  $\mu\text{m}$ ). Unfortunately, the maximum diameter of asbestos fibers of amphiboles is 3  $\mu\text{m}$  and a typical diameter is several hundred nanometers; as a result, EPMA can provide only

an approximate composition. Obviously, another tool is necessary to definitively identify mineral fibers.

By extension the combination of polarized light microscopy, SEM coupled to EDS and EPMA analyses is efficient in the identification of amphibole particles and/or fibers larger than at least 3  $\mu\text{m}$ .

FE-SEM appears to be an efficient tool for the identification isolated fibers or submicrometric objects in a mineral matrix. However, because the compositions of amphiboles and other silicate minerals and the various members of the amphibole group are similar, EPMA is required for a precise composition determination, including minor and trace elements.

The use of a SEM coupled to EDS analysis (or EPMA) is an effective way to observe and describe the morphology of actinolite or other elongate amphibole particles in a mineral matrix. However it is inadequate for a complete and indisputable risk diagnosis, because EDS or WDS spatial resolution is not high enough to analyze the submicrometric diameter of asbestos fibers.

Raman spectroscopy is applied to the analysis of asbestos by different authors. In the case of serpentines, Raman spectroscopy is able to differentiate chrysotile (only fibrous, i.e. asbestos) and lizardite or antigorite (usually not fibrous, i.e. not asbestos) [50–52]. However, fibrous antigorite can occasionally be found [53]. In this case, a morphological characterization by a microscopy of nanometric resolution (i.e. SEM or TEM) is necessary for a complete diagnosis. For amphiboles, the problem is more complex, because each variety of amphibole classified asbestos can exist as massive crystal or asbestiform fibers. As mentioned by Bard et al [54], the use of Raman spectroscopy does not, on its own, make it possible to differentiate a massive amphibole from an asbestos amphibole. In this case, the use of Raman spectroscopy with an optical microscope does not allow a complete diagnosis, a morphological characterization by a microscopy of nanometric resolution (i.e. SEM or TEM) is then required for a complete diagnosis. The use of Confocal Raman imaging in SEM (RISE) is an efficient solution to this problem. SEM shows the morphology of actinolite (or other amphibole) fibers, EDS gives an approximate composition, and high resolution. Raman analysis (up to 360 nm @  $\lambda=532\text{nm}$  [31]) let the analyst confirm the

mineralogical nature of the fibers [47,55] and determine whether this mineral is on the list of regulated asbestos mineral fibers.

RISE microscopy also makes it possible to obtain a 3D view of the distribution of each mineral that is present in a volume of several thousand cubic micrometers. This 3D view can be used to determine the elongation/diameter ratio, a decisive parameter for the "asbestiform" nature of an amphibole particle. This is in fact one of the three diagnostic criteria for asbestos (along with chemistry and crystallography, provided by SEM-EDS and Raman spectroscopy, respectively). Moreover, the 3D view obtained by RISE can reveal the presence of subsurface fibers through a non-destructive analytical determination.

This approach can also be used to meet various needs of the extractive industry. The nature and shape of fibers is a valuable indicator of the fiber emission risk during any step of the aggregate production process (as an example, amphibolite rocks are widely used for roadway construction or as ballast in railroad construction). The 3D view is also the initial step in the determination of the volume content of asbestos fibers in a rock (metal ore, for example).

## **6. Conclusion**

This paper presents a new in-situ analytical method for the identification of asbestos fibers in their natural state in rocks, based on a combination - within the same analytical system - of SEM-EDS and confocal Raman imaging in the SEM (RISE). The integration of a confocal micro-Raman system in a SEM makes it possible to determine a precise location and to analyze the exact same area by both SEM-EDS and Raman. The spatial resolution of a confocal Raman microscope is much higher than that of EDS and makes it possible to identify mineral fibers thinner than 400 nm in diameter, which is sufficiently accurate for amphibole fibers identification.

The combination of SEM-EDS and confocal Raman imaging leads to a precise in-situ diagnosis of the nature and morphology of amphiboles fibers contained in a mineral matrix, by determination of their mineralogical nature and their asbestiform (or non-asbestiform) morphology, i.e. the determination of the three criteria required to conclude to the presence of asbestos. This diagnosis is performed on polished

sections or geological thin sections and any fibers sampling or rock grinding is avoided to eliminate the risk of any contamination and creation of cleavage fragments that could result in an incorrect diagnosis. The use of this combined system makes it possible to perform an accurate in-situ diagnosis on the health risk of rocks that contain amphiboles. This method makes it possible to carry out a diagnosis prior to any operation likely to suspend the asbestos fibers in the atmosphere.

In addition, the 3D volume analysis by Raman can be done in the SEM, due to the confocality of the system. The 3D analysis makes it possible to visualize amphibole fibers below the surface.

### **Acknowledgements**

The authors gratefully acknowledge the BRGM research direction for its help and financial support. This study was supported by the French ministry of ecological and solidarity transition. The RISE acquisitions were performed at the application laboratory of the company WITec in Ulm, with the help and support of Dr. Philippe Ayasse. The authors thank M. Alleki for preparation of geological thin sections at the BRGM thin section lab. The authors also gratefully acknowledge F. Chene and J-P Quinquis for the maps and notices.

## References

- [1] PRELIMINARY REGULATORY ECONOMIC ANALYSIS FOR PROPOSED RULE ON ASBESTOS EXPOSURE LIMIT, 2005.  
[https://arlweb.msha.gov/REGS/REA/05-14510\(Asbestos\).pdf](https://arlweb.msha.gov/REGS/REA/05-14510(Asbestos).pdf).
- [2] WHO (World Health Organization), Asbestos and other natural mineral fibres, Environmental Health criteria, (1986).
- [3] Niosh, Asbestos Fibers and Other Elongate Mineral Particles : State of the Science and Roadmap for Research Revised Edition, Curr. Intell. Bull. (2011) 153. <http://www.cdc.gov/niosh/docs/2011-159/pdfs/2011-159.pdf%5Cnhttp://www.cdc.gov/niosh/docs/2011-159/>.
- [4] G. Vignaroli, P. Ballirano, G. Belardi, F. Rossetti, Asbestos fibre identification vs. evaluation of asbestos hazard in ophiolitic rock mélanges, a case study from the Ligurian Alps (Italy), Environ. Earth Sci. 72 (2014) 3679–3698. doi:10.1007/s12665-014-3303-9.
- [5] A. Campopiano, A. Olori, A. Spadafora, M. Rosaria Bruno, F. Angelosanto, A. Iannò, S. Casciardi, R. Giardino, M. Conte, T. Oranges, S. Iavicoli, Asbestiform minerals in ophiolitic rocks of Calabria (southern Italy), Int. J. Environ. Health Res. 28 (2018) 134–146. doi:10.1080/09603123.2018.1453051.
- [6] D. Lahondere, F. Cagnard, Naturally Occurring Asbestos in an Alpine Ophiolitic Complex (Northern Corsica, France), in: XIII IARG Congr., San Francisco, 2018. <http://iaeg.info/events/congresses/xiii-iaeg-congress-engineering-geology-for-a-sustainable-world/>.
- [7] D. Lahondère, F. Cagnard, G. Wille, J. Duron, M. Misseri, TEM and FESEM characterization of asbestiform and non-asbestiform actinolite fibers in hydrothermally altered dolerites (France), Environ. Earth Sci. 77 (2018). doi:10.1007/s12665-018-7549-5.
- [8] B.S. Van Gosen, H.A. Lowers, S.J. Sutley, C.A. Gent, Using the geologic setting of talc deposits as an indicator of amphibole asbestos content, Environ. Geol. 45 (2004) 920–939. doi:10.1007/s00254-003-0955-2.
- [9] B.S. Van Gosen, The geology of asbestos in the United States and its practical applications, Environ. Eng. Geosci. 13 (2007) 55–68. doi:10.2113/gseegeosci.13.1.55.
- [10] R. V Metcalf, B.J. Buck, Genesis and health risk implications of an unusual occurrence of fibrous NaFe<sup>3+</sup>-amphibole, Geology. 43 (2015) 63–66. <http://dx.doi.org/10.1130/G36199.1>.
- [11] IARC, IARC monographs on the evaluation of carcinogenic risks to humans: arsenic, metals, fibres and dusts, International agency for research on Cancer, Lyon, 2012. [http://publications.iarc.fr/\\_publications/media/download/3026/50ed50733f7d1152d91b30a803619022ef098d59.pdf](http://publications.iarc.fr/_publications/media/download/3026/50ed50733f7d1152d91b30a803619022ef098d59.pdf).
- [12] HSE, Asbestos: The analysts' guide for sampling, analysis and clearance

- procedures, 2006. <http://www.hse.gov.uk/pUbns/priced/hsg248.pdf>.
- [13] L. Kazan-Allen, Asbestos and mesothelioma: Worldwide trends, *Lung Cancer*. 49 (2005) S3–S8. doi:10.1016/J.LUNGCAN.2005.03.002.
- [14] D. Steen, M.P. Guillemin, P. Buffat, L. Gilbert, Determination of asbestos fibres in air transmission electron microscopy as a reference method, *Atmos. Environ.* 17 (1983) 2285–2297. doi:10.1016/0004-6981(83)90227-5.
- [15] K.E. Harris, K.L. Bunker, B.R. Strohmeier, R. Hoch, R.J. Lee, Discovering the true morphology of amphibole minerals: complementary TEM and FESEM characterization of particles in mixed mineral dust., in: A. Méndez-Vilas, J. Diaz (Eds.), *Mod. Res. Educ. Top. Microsc. Vol. 2*, Formatex research center, Badajoz, 2007: pp. 643–650. <http://www.formatex.org/microscopy3/pdf/pp643-650.pdf>.
- [16] E. Kauffer, S. Veissiere, P. Brochard, EFFECT OF PREPARATION METHODS ON THE ASSESSMENT OF AIRBORNE CONCENTRATIONS OF ASBESTOS FIBRES BY TRANSMISSION ELECTRON MICROSCOPY, *Ann. Occup. Hyg.* 40 (1996) 321–330. doi:10.1093/annhyg/40.3.321.
- [17] R. Wirth, L. Morales, Focused Ion Beam (FIB) combined with SEM (FIB/SEM) and TEM: Advanced tools for nano-analysis in Geosciences, 2011.
- [18] S. Giffin, R. Littke, J. Klaver, J.L. Urai, Application of BIB–SEM technology to characterize macropore morphology in coal, *Int. J. Coal Geol.* 114 (2013) 85–95. doi:10.1016/j.coal.2013.02.009.
- [19] J. Klaver, J. Schmatz, G. Desbois, S. Hemes, J.L. Urai, Application of BIB – SEM technology to characterize microstructure and pores in mudstone at a range of scales, in: 2nd Petrus-OPERA Conf. Radioact. Waste Manag. Geol. Dispos., Delft, 2016: pp. 55–57. 2nd Petrus-OPERA Conference on Radioactive Waste Management and Geological Disposal.
- [20] A.-M. Seydoux-Guillaume, D. Fougereuse, A.T. Laurent, E. Gardés, S.M. Reddy, D.W. Saxey, Nanoscale resetting of the Th/Pb system in an isotopically-closed monazite grain: A combined atom probe and transmission electron microscopy study, *Geosci. Front.* 10 (2019) 65–76. doi:10.1016/j.gsf.2018.09.004.
- [21] A.-M. Seydoux-Guillaume, J.-M. Montel, R. Wirth, B. Moine, Radiation damage in diopside and calcite crystals from uranothorianite inclusions, *Chem. Geol.* 261 (2009) 318–332. doi:10.1016/j.chemgeo.2008.04.013.
- [22] E. Acosta, X. Llovet, E. Coleoni, J.A. Riveros, F. Salvat, Monte Carlo simulation of x-ray emission by kilovolt electron bombardment, *J. Appl. Phys.* 83 (1998) 6038–6049. doi:10.1063/1.367473.
- [23] J.T. Armstrong, P.R. Buseck, Quantitative chemical analysis of individual microparticles using the electron microprobe. Theoretical, *Anal. Chem.* 47 (1975) 2178–2192. doi:10.1021/ac60363a033.
- [24] J.-C. Tedenac, C. Pascal, C. Merlet, R.-M. Marin-Ayral, B. Boyer, Identification by Electron Probe Microbeam Analysis of Submicron Borides in Joints of Nickel

- Base Superalloys, *Microchim. Acta.* 145 (2004) 147–151. doi:10.1007/s00604-003-0144-8.
- [25] J.A. Small, The analysis of particles at low accelerating voltages ( $\leq 10$  kV) with energy dispersive x-ray spectroscopy (EDS), *J. Res. Natl. Inst. Stand. Technol.* 107 (2002) 555. doi:10.6028/jres.107.047.
- [26] I. Barkshire, P. Karduck, W.P. Rehbach, S. Richter, High-Spatial-Resolution Low-Energy Electron Beam X-Ray Microanalysis, *Mikrochim. Acta.* 132 (2000) 0113–0128. doi:10.1007/s006040050052.
- [27] C. Merlet, X. Llovet, Uncertainty and capability of quantitative EPMA at low voltage – A review, *IOP Conf. Ser. Mater. Sci. Eng.* 32 (2012) 012016. doi:10.1088/1757-899X/32/1/012016.
- [28] P. Gopon, J. Fournelle, P.E. Sobol, X. Llovet, Low-Voltage electron-probe microanalysis of Fe-Si compounds using soft X-rays, *Microsc. Microanal.* 19 (2013) 1698–1708. doi:10.1017/S1431927613012695.
- [29] P. Jonnard, F. Brisset, F. Robaut, G. Wille, J. Ruste, Inter-laboratory comparison of a WDS-EDS quantitative X-ray microanalysis of a metallic glass, *X-Ray Spectrom.* 44 (2015) 24–29. doi:10.1002/xrs.2573.
- [30] R. Kusiorowski, T. Zaremba, J. Piotrowski, J. Adamek, Thermal decomposition of different types of asbestos, *J. Therm. Anal. Calorim.* 109 (2012) 693–704. doi:10.1007/s10973-012-2222-9.
- [31] J. Jiruše, M. Haničinec, M. Havelka, O. Hollricher, W. Ibach, P. Spizig, Integrating focused ion beam–scanning electron microscope with confocal Raman microscope into a single instrument, *J. Vac. Sci. Technol. B, Nanotechnol. Microelectron. Mater. Process. Meas. Phenom.* 32 (2014) 06FC03. doi:10.1116/1.4897502.
- [32] S. Denner, D. Rambourg, Les roches dominantes de la France - carte lithologique simplifiée (the dominant rocks of France - simplified lithological map), (2008).
- [33] P.D. GODARD G., BOUTON P., Explanatory Note, French geological map. France (1/50 000), Montaignu sheet (536) - Geological map par Godard G., Bouton P., Poncet D., Carlier G., Chevalier M. (2007), BRGM, BRGM, Orleans (France), 2010.
- [34] R. WYNS, Lablanche G, A. Lefavrais-Raymond, Explanatory note and geological map (1/50 000) of Chantonay (563). Orléans : BRGM, 76 p. Geological map by R. Wyns, G. Lablanche, A. Lefavrais-Raymond (1984)., BRGM, BRGM, Orleans (France), 1988.
- [35] D. Thieblemont, bruno Cabanis, Découverte d'une association de volcanites d'arc et de basaltes de type "MORB" dans la formation paléovolcanique silurienne de La Meilleraie, Vendée, *Comptes Rendus l'Académie Des Sci. Série 2, Mécanique, Phys. Chim. Sci. l'univers, Sci. La Terre.* 1986-01 (1986). <https://gallica.bnf.fr/ark:/12148/bpt6k6296984t>.
- [36] D. Thiéblemont, Le magmatisme paleozoique en vendee : apport de la

geochimie des elements traces et de la petrologie du metamorphisme a la comprehension du developpement orogenique varisque, Paris, 1987.

- [37] M. Demange, J. Guerange-Lozes, B. Guerange, Explanatory note and geological map (1/50 000) of Lacaune (987). Orléans : BRGM, 153 p. Geological map by M. Demange, J. Guérangé-lozes et B. Guérangé, BRGM, BRGM, Orleans (France), 1995.
- [38] D.R. Van Orden, K.A. Allison, R.J. Lee, Differentiating Amphibole Asbestos from Non-Asbestos in a Complex Mineral Environment, *Indoor Built Environ.* 17 (2008) 58–68. doi:10.1177/1420326X07087006.
- [39] F.C. Hawthorne, R. Oberti, G.E. Harlow, W. V. Maresch, R.F. Martin, J.C. Schumacher, M.D. Welch, Nomenclature of the amphibole supergroup, *Am. Mineral.* 97 (2012) 2031–2048. doi:10.2138/am.2012.4276.
- [40] C. Merlet, An accurate computer correction program for quantitative electron probe microanalysis, *Mikrochim. Acta.* 114–115 (1994) 363–376. doi:10.1007/BF01244563.
- [41] A.J. Locock, An Excel spreadsheet to classify chemical analyses of amphiboles following the IMA 2012 recommendations, *Comput. Geosci.* 62 (2014) 1–11. doi:10.1016/j.cageo.2013.09.011.
- [42] D. Drouin, A.R. Couture, D. Joly, X. Tastet, V. Aimez, R. Gauvin, CASINO V2.42—A Fast and Easy-to-use Modeling Tool for Scanning Electron Microscopy and Microanalysis Users, *Scanning.* 29 (2007) 92–101. doi:10.1002/sca.20000.
- [43] R.L. Perkins, B.W. Harvey, Method for the Determination of Asbestos in Bulk Building Materials, (1993) 99.
- [44] G. Wille, X. Bourrat, N. Maubec, A. Lahfid, Raman-in-SEM, a multimodal and multiscale analytical tool: Performance for materials and expertise, *Micron.* 67 (2014) 50–64. doi:10.1016/j.micron.2014.06.008.
- [45] G. Wille, U. Schmidt, O. Hollricher, RISE: Correlative confocal raman and scanning electron microscopy, 2018. doi:10.1007/978-3-319-75380-5\_23.
- [46] M. Fries, A. Steele, Raman Spectroscopy and Confocal Raman Imaging in Mineralogy and Petrography, in: 2010: pp. 111–135. doi:10.1007/978-3-642-12522-5\_6.
- [47] L. Leissner, J. Schlüter, I. Horn, B. Mihailova, Exploring the potential of Raman spectroscopy for crystallochemical analyses of complex hydrous silicates: I. Amphiboles, *Am. Mineral.* 100 (2015) 2682–2694. doi:10.2138/am-2015-5323.
- [48] T. Dieing, W. Ibach, Software Requirements and Data Analysis in Confocal Raman Microscopy, in: T. Dieing, O. Hollricher, J. Toporski (Eds.), *Confocal Raman Microsc.*, Springer Berlin Heidelberg, Berlin, Heidelberg, 2011: pp. 61–89. doi:10.1007/978-3-642-12522-5\_4.
- [49] J. Schindelin, C.T. Rueden, M.C. Hiner, K.W. Eliceiri, The ImageJ ecosystem: An open platform for biomedical image analysis, *Mol. Reprod. Dev.* 82 (2015)

518–529. doi:10.1002/mrd.22489.

- [50] C. Rinaudo, D. Gastaldi, E. Belluso, CHARACTERIZATION OF CHRYSOTILE, ANTIGORITE AND LIZARDITE BY FT-RAMAN SPECTROSCOPY, *Can. Mineral.* 41 (2003) 883–890. doi:10.2113/gscanmin.41.4.883.
- [51] C. Groppo, C. Rinaudo, S. Cairo, D. Gastaldi, R. Compagnoni, Micro-Raman spectroscopy for a quick and reliable identification of serpentine minerals from ultramafics, *Eur. J. Mineral.* 18 (2006) 319–329. doi:10.1127/0935-1221/2006/0018-0319.
- [52] J.R. Petriglieri, E. Salvioli-Mariani, L. Mantovani, M. Tribaudino, P.P. Lottici, C. Laporte-Magoni, D. Bersani, Micro-Raman mapping of the polymorphs of serpentine, *J. Raman Spectrosc.* 46 (2015) 953–958. doi:10.1002/jrs.4695.
- [53] V. Cardile, L. Lombardo, E. Belluso, A. Panico, S. Capella, M. Balazy, Toxicity and Carcinogenicity Mechanisms of Fibrous Antigorite, *Int. J. Environ. Res. Public Health.* 4 (2007) 1–9. doi:10.3390/ijerph2007010001.
- [54] D. Bard, J. Yarwood, B. Tylee, Asbestos fibre identification by Raman microspectroscopy, *J. Raman Spectrosc.* 28 (1997) 803–809. doi:10.1002/(SICI)1097-4555(199710)28:10<803::AID-JRS151>3.0.CO;2-7.
- [55] R. Petry, R. Mastalerz, S. Zahn, T.G. Mayerhöfer, G. Völksch, L. Viereck-Götte, B. Kreher-Hartmann, L. Holz, M. Lankers, J. Popp, Asbestos Mineral Analysis by UV Raman and Energy-Dispersive X-ray Spectroscopy, *ChemPhysChem.* 7 (2006) 414–420. doi:10.1002/cphc.200500303.