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

• Introduction: Context and objectives

• Part I: Robust methods for mineralogical characterization and innovative techniques for improved characterization

• Part II: Towards a new 5-steps analytical protocol for an in-situ diagnosis

• Conclusion and perspectives
Introduction

Context and objectives
Asbestos

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

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

**Commercial definition** → limited to the varieties exploited industrially

**Legal and regulatory definition** →


Definition: In the European Union directive 2009/148/EC (protection of workers from the risk related to exposure to asbestos at work)

**Breathable Fiber (WHO 1998)** = \( L > 5 \, \mu m \); \( D < 3 \, \mu m \); \( L/D > 5 \)

**Asbestiform Fiber (EPA)** = \( L/D > 20 \), fine fibers (< \( \mu m \))

<table>
<thead>
<tr>
<th>Serpentines</th>
<th>Amphiboles</th>
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</table>
| Chrysotile          | \( \text{Mg}_3\text{Si}_2\text{O}_5(\text{OH})_4 \) |}

| Tremolite           | \( \text{Ca}_2\text{Mg}_5\text{Si}_8\text{O}_{22}(\text{OH})_2 \) |
| Actinolite          | \( \text{Ca}_2(\text{Mg,Fe})_2\text{Si}_8\text{O}_{22}(\text{OH})_2 \) |
| 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)
Context

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

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

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

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

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

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

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

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

New protocol

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

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

Robust methods for mineralogical characterization and innovative techniques for improved characterization
Analytical techniques of the new protocol

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

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

⇒ Acquisition of precise data about:

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

1) Macroscopic observations

2) Microscopy / petrographic observation (Polarized Light Microscopy)

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

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

5) 3D morphological characteristics (3D SEM-FIB and/or 3D Raman in SEM)
Analytical techniques of the new protocol

Step 1) Field observation / Macroscopic observations

2 objectives

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

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

Suspected presence of chrysotile veins in peridotite
(Vosges – France)
Analytical techniques of the new protocol

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

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

Limitation of this method
• Fibrous minerals with diameter < 3 µm can’t be observed and characterized under good conditions

proven fibers or suspected fibers (step 1) ➔ Chrysotile ➔ Presence of amphibole fibers ➔ Step 3

Stop

chrysotile veins (PLM)

actinolite fibers (NLM)
Analytical techniques of the new protocol

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

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

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

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

Yes (Meas. Uncertainty)  Possible (Meas. Uncertainty)

YES  YES  NO

Stop  Step 4  Stop

Examples of SEM (BSE) images
Analytical techniques of the new protocol

Step 4) Chemical composition (Electron Probe Microanalyzer)

Objective
• Precise quantitative analysis of amphiboles for the determination of the mineralogical species of the fibers

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

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

Yes

Possible
(spatial resolution)

YES

YES

NO

Step 5

Stop

Stop

EPMA (BSE) image and Mg WDS map
Step 5) 3D morphological characteristics (Raman in SEM and/or SEM-FIB)

Objectives
• Informations about the 3D morphology of fibrous amphiboles using 3D techniques (Raman-in-SEM, FIB-SEM)
• Critical information on the morphology of the amphibole fibers in the mineral mass (aspect ratio, fiber distribution, and fibrous amphibole volume fraction).
• Fibers included within different types of mineral matrix (feldspar, quartz and/or calcite matrix) may be identified
• Method 1: Raman in SEM
  ◦ Spatial resolution: fibers with diameter about 400 nm may be identified
  ◦ Non-destructive technique

OR

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

OR

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

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

SEM (BSE) images

Raman map (2D)

Raman volume (3D)

Raman spectra obtained from the hyperspectral map
Analytical techniques of the new protocol

Step 5) 3D morphological characteristics by SEM-FIB

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

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

Application to natural rock samples
Sample 1

Garnet-bearing amphibolite

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

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

1) Macroscopic observations

No metamorphic veins is observed.

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

This plan therefore makes it possible to observe the fibers in their greatest elongation.
Sample 1

Garnet-bearing amphibolite

2) Microscopy / petrographic observation (Light Microscopy)

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

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

3) SEM – EDS observation

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

⇒ No more investigation is necessary – No asbestos detected
Sample 2

Actinolite metadolerite

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

1) Macroscopic observations

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

2) Microscopy / petrographic observation (Light Microscopy)

- Presence of large, partially altered, automorphic feldspar crystals
  - Presence of epidote grains, Plagioclase slats, of all sizes, abundant and often contiguous
  - Pyroxene crystals between the plagioclase slats
  - ⇒ thin grain metadolerite → the asbestos potential has been recently illustrated (Lahondere et al. 2018)
- Fibers:
  - Constitute the extension of matrix pyroxene crystals → most certainly amphiboles resulting from the destabilization of magmatic pyroxenes
  - Sometimes very long or only observed in the form of lozenge sections → not aligned in a preferential direction.
Sample 2

Actinolite metadolerite

3) SEM – EDS observation

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

• EDS analyses
  • Variable weight percent contents for SiO2 (48.8 – 55.7), Al2O3 (1.1 – 6.1), MgO (13.8 – 19.7) and FeO (11.6 - 21.2)
  • CaO content is relatively stable (11.8 - 13.2)
  ⇒ EPMA analyses are required for higher precision in chemical composition

4) EPMA analyses

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

⇒ Asbestiform actinolite fibers detected – 3D not necessary but possible if required
Sample 2

Actinolite metadolerite
Sample 3

Actinolite metadolerite

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

1) Macroscopic observations

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

2) Microscopy / petrographic observation (Light Microscopy)

• Presence of large, partially altered, automorphic feldspar crystals
  • Outside the vein, pseudomorphic texture characterized by the presence of colorless phenocrysts of clinopyroxene (diopside) partially destabilized in amphibole
  • Amphiboles from the veins form randomly curved bundles with split ends and fibrils, both extremely long and remarkably thin
• Fibers:
  • Amphibole fibers are clearly visibles by NLM / PLM
Sample 2

Actinolite metadolerite

3) SEM – EDS observation

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

* EDS analyses
  * Composition possibly corresponds to actinolite
  * \( \Rightarrow \) EPMA analyses are required for higher precision in chemical composition

4) EPMA analyses

* Analyses correspond to the composition of actinolite

\( \Rightarrow \text{Asbestiform actinolite fibers detected – 2D and 3D Raman is necessary to define the mineral nature of the submicrometric fibers and the morphology of losangic particles} \)
Sample 2

Actinolite metadolerite

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

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

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

5b) 3D SEM-FIB

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

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

**Light microscopy**

**SEM**

Raman map and spectra obtained from the hyperspectral map

Orthoclase

actinolite

calcite
Sample 2

Raman 3D
120x120x20 µm
Z-step 0.5 µm

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

Volume
76274 µm³

Fibers
1464,40 µm³ = 1.94 % volume

Orthoclase

calcite

actinolite

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Conclusion
Conclusion

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

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

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

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

Questions?