



Aggregates and naturally occurring asbestos: the need of a correct analytical approach

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Aggregates...

- **Sand & gravel** used to make concrete, asphalt, roads, blocks & bricks...
- Every year each person (including babies) uses **more than 4,500 kg** of aggregates!
- In the US, 1.33 billion tons of crushed stone valued at more than \$15 billion was produced by an estimated 1,400 companies operating 3,700 quarries and 187 sales/distribution yards in 50 States.



Aggregates...

The most common suitable rock types are:

- carbonatic rocks
- basalts
- porphyries
- orthogneisses
- granites
- “green stones”



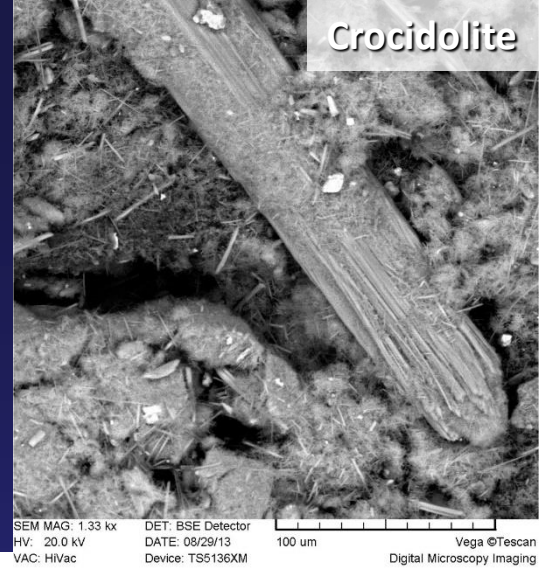
“Green Stones”...may contain asbestos!

Rock type	Main rock-forming minerals
Serpentinites	Atg, Ol, Cpx, Opx, Tlc, Mag, Chr, <u>Ctl</u> , <u>Tr</u> , (Dol), Grt)
Prasinites	Pl (Ab), Ep, <u>Tr – Act</u> , <u>Gln</u> , Cpx, WM
Eclogites	Cpx, Grt, Rt, <u>Gln</u>
Amphibolites	Pl, Hbl, Ep, Chl, <u>Ath – Ged</u>
Actinolitic schists	<u>Act</u> , Tlc, Chl, Ep, Ol
Tl, Chl and Srp schists	Tlc, Chl, <u>Tr – Act</u> , Srp, Ctl, Dol, Rt, Ttn, Grt
Opicalcites	Atg, Ol, Cal, Dol, Tlc, <u>Tr</u> , <u>Ctl</u>

Chrysotile



Crocidolite



Asbestos

Chrysotile

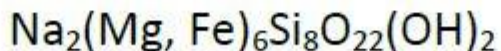
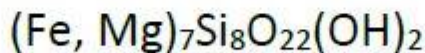
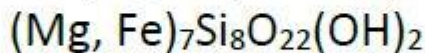
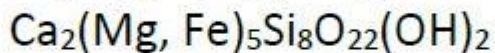
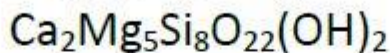
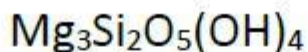
Tremolite

Actinolite

Anthophyllite

Grunerite (amosite)

Riebeckite (crocidolite)



n. CAS 12001-29-5

n. CAS 77536-68-6

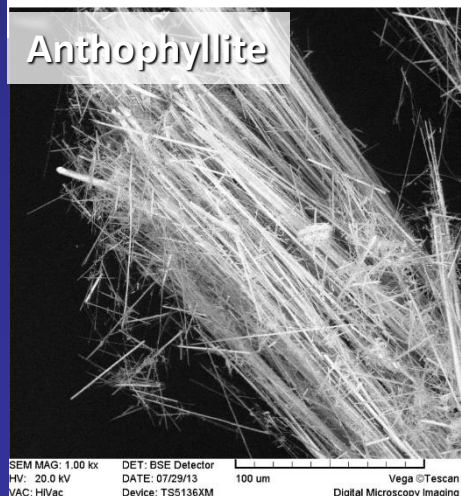
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n. CAS 77536-67-5

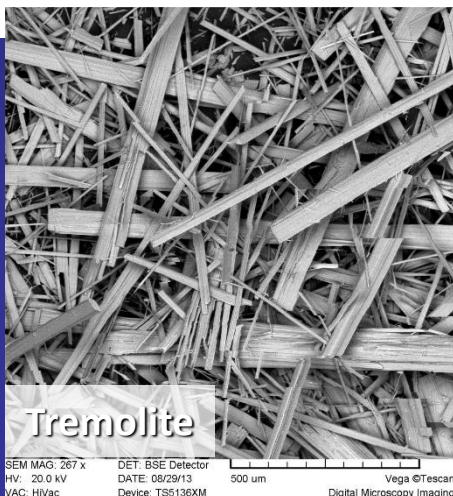
n. CAS 12172-73-5

n. CAS 12001-28-4

Anthophyllite



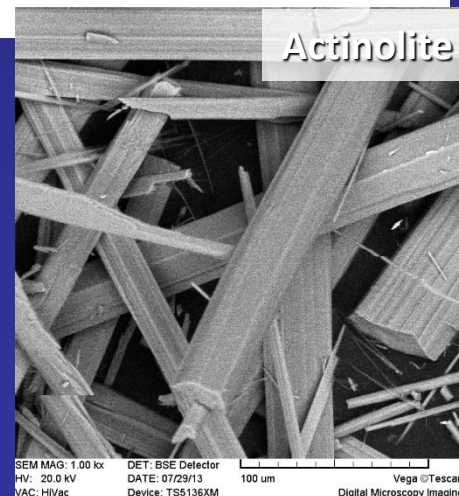
Tremolite



Amosite



Actinolite

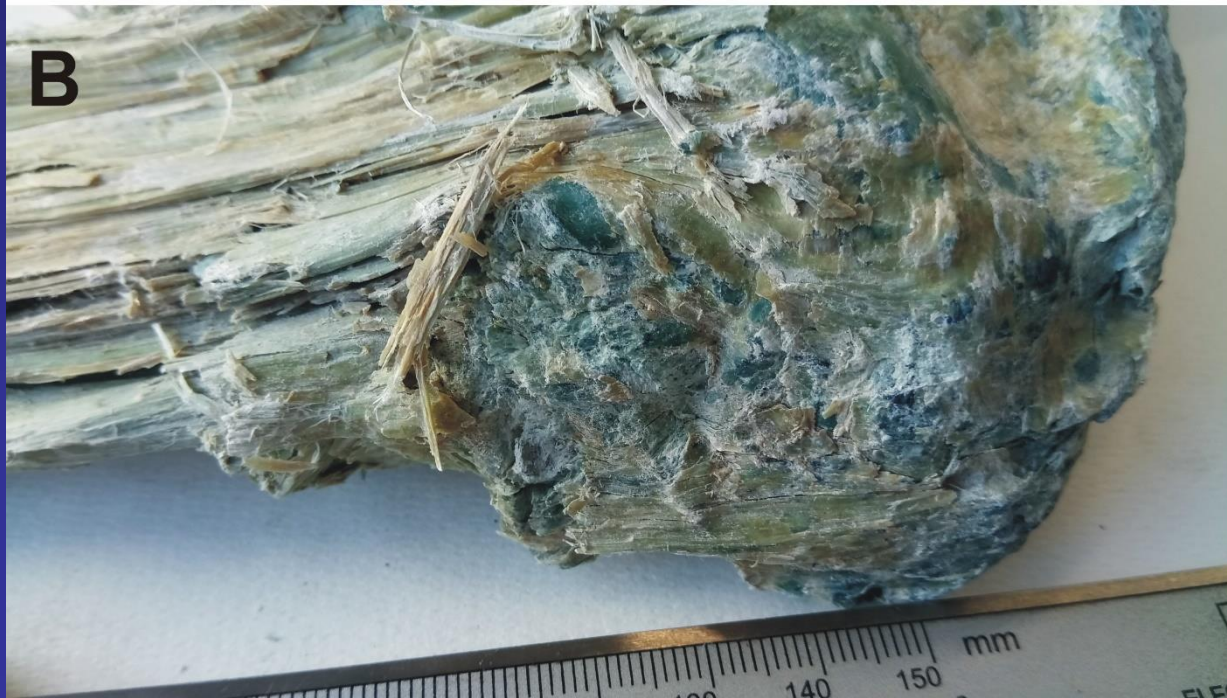


A



Some “dirty”
green stones

B



The starting point? The quarries!



Detailed preliminary **geological investigations** needed:

- source rocks?
- Fine fraction? Sand and silt?
- Facies variations?

- The importance of a **representative sampling** → consider lateral and vertical facies variation, relative abundances of different lithologies, grain size, planar and linear anisotropies...



Asbestos quantification: analytical techniques suggested by law



Legal threshold
0.1 % wt. – 1000 ppm

NO!

- LOD $\approx$ 0.5 – 1.0% wt.
- Interferences (polymorphs)
- NO information about crystal habit

Step 1: macroscopic petrographic description

- How many “green stones”?
- Visible fibers?
- Preliminary evaluation with **portable Raman!**



Step 2: sample preparation (gravel)

A. “self-crushing” (similar to *Los Angeles rattle test*)



< 2 mm: «self-crushing» powders



SEM-EDS

B. complete crushing and grinding of the bulk sample



Bulk sample: «self-crushing»
powders + remaining rock
fragments



XRPD-QPA

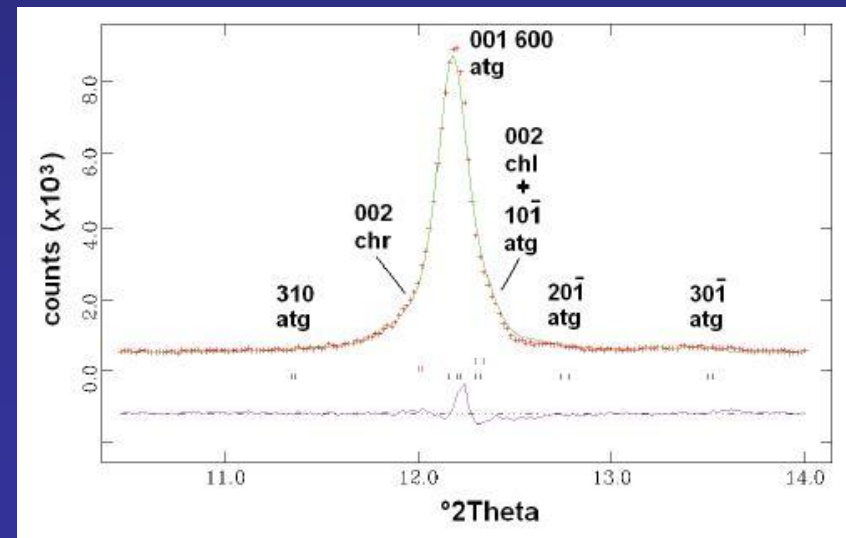
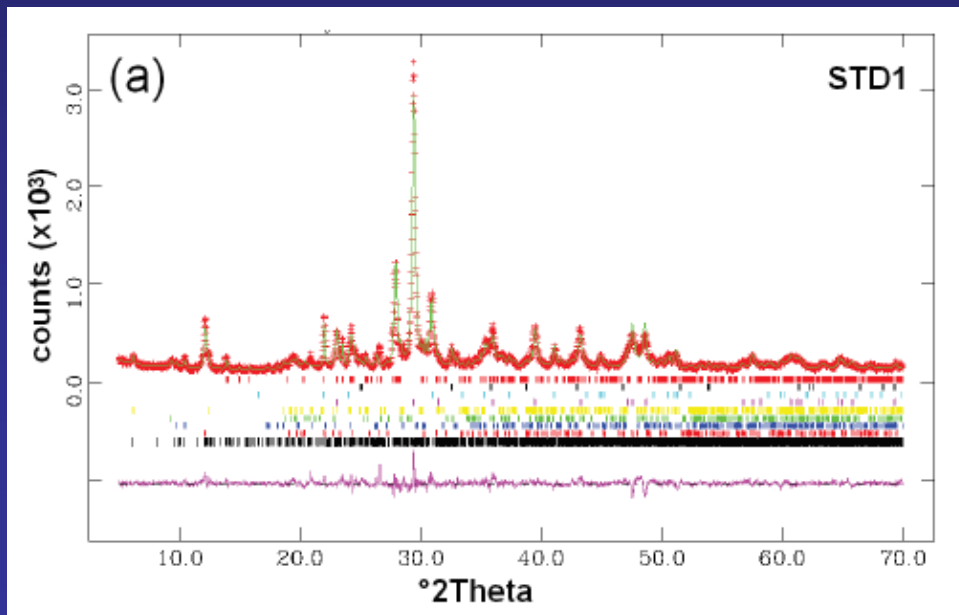


SEM-EDS



Step 3: qualitative and quantitative XRPD

- main rock-forming minerals (LOD $\approx$ 0.5 – 1% wt.) of **bulk samples**
- **RIR** (*Reference Intensity Ratio*) and **Rietveld method** for quantitative analysis
- Rietveld method is effective in the discrimination between Ctl and Atg **only in high-grade samples** (> 2% wt.) - *Gualtieri et al., 2014*.

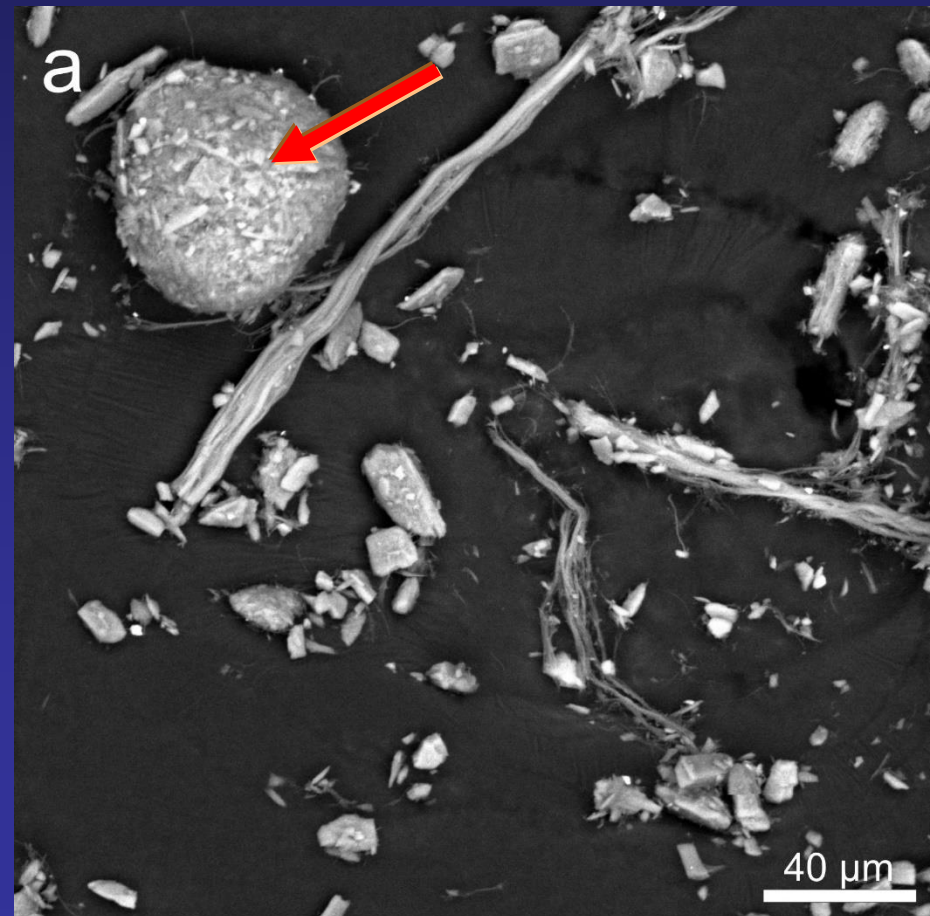


Step 4: quantitative SEM-EDS

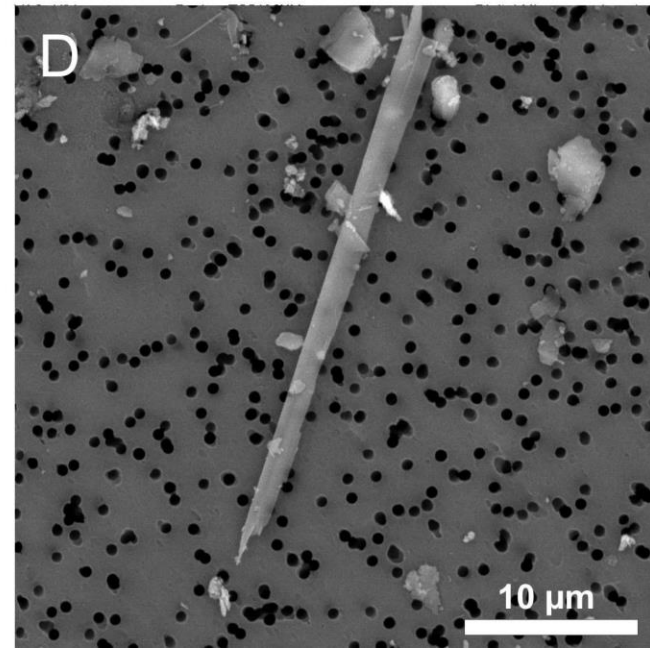
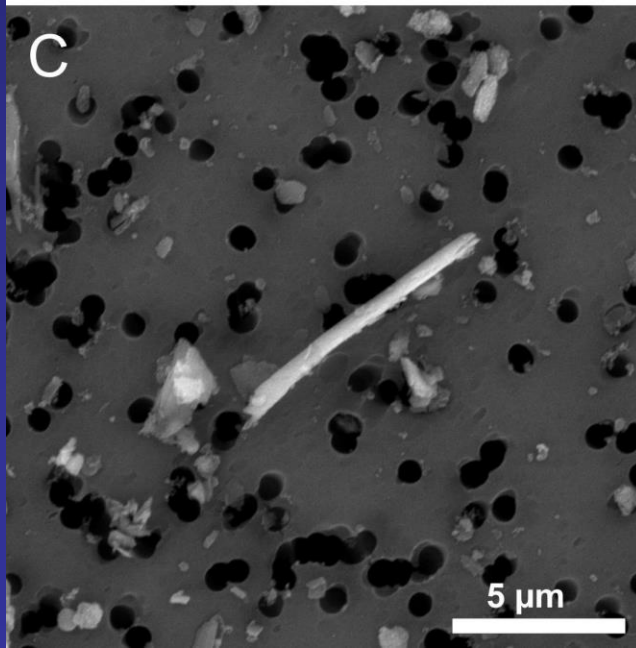
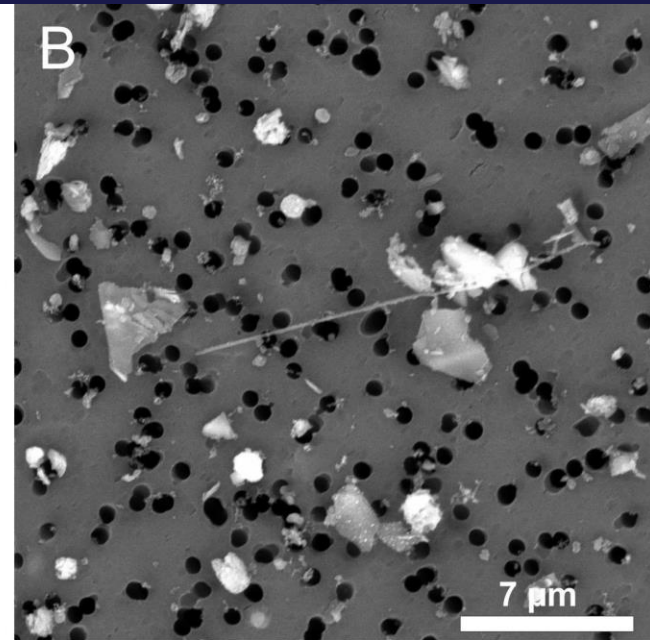
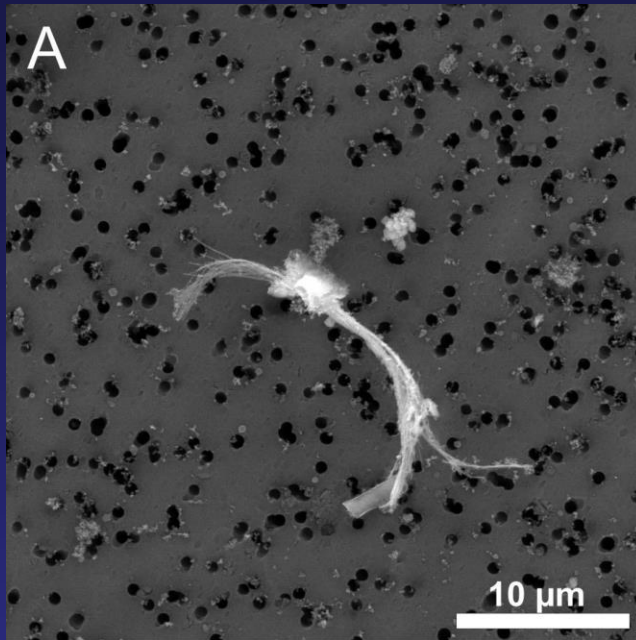
- optimized **sample preparation** and **fiber counting criteria for NOA** (*Cattaneo et al, 2012; Cavallo & Rimoldi, 2013; Gualtieri et al., 2014; Gualtieri et al., 2018*).
- report **ALL fibers, regulated** and **non regulated**!

$$C = \left[A \frac{(w_c + w_a)}{n a W} \right] 10^6$$

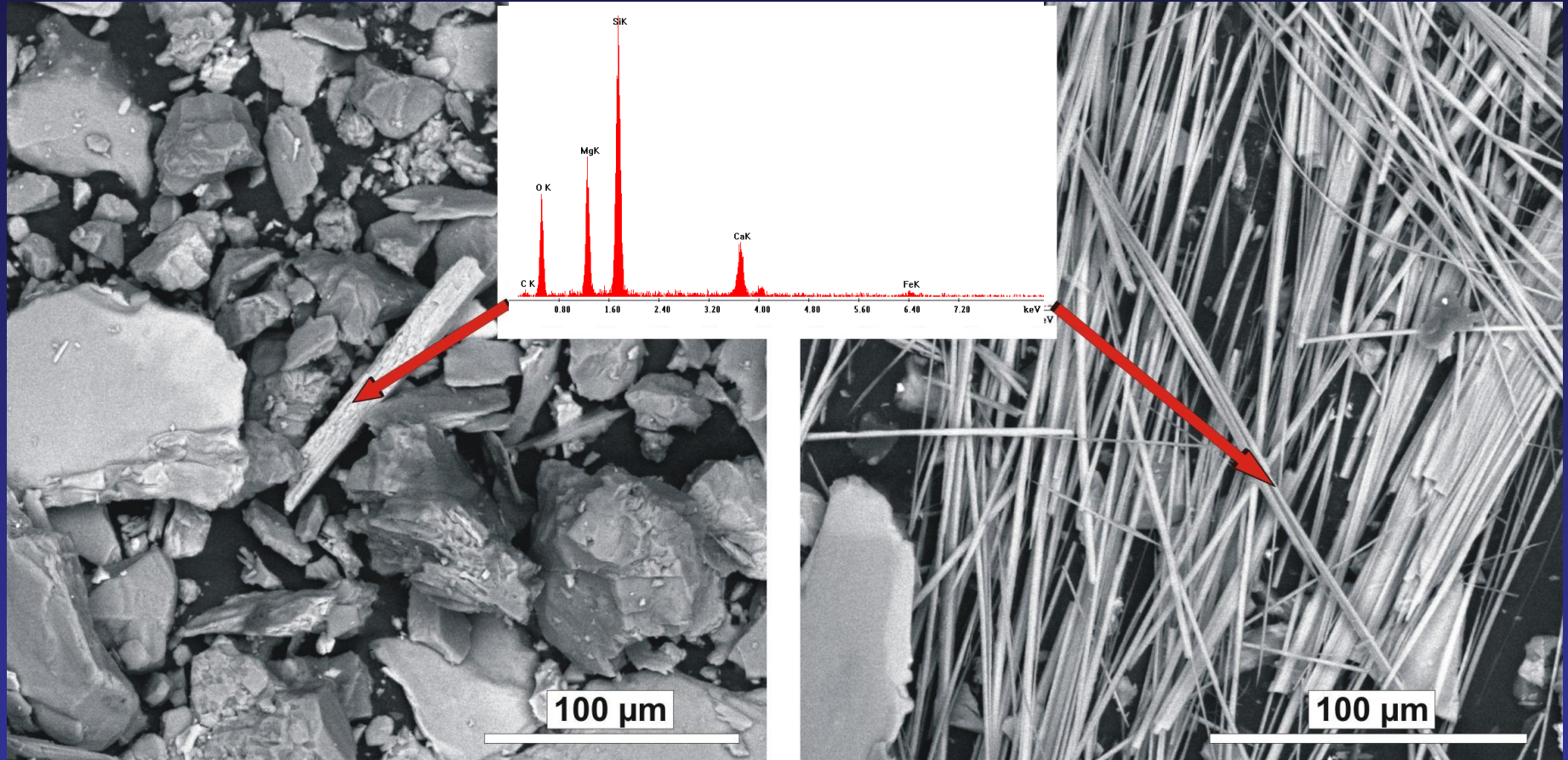
C = fiber concentration (mg/kg = ppm);
 A = membrane area (mm²);
 w_c = total weight of chrysotile fibers;
 w_a = total weight of amphibole fibers;
 n = number of examined fields under SEM;
 a = area of the single examined field (mm²);
 W = sample weight on the membrane (mg).



Chrysotile vs. “fibrous” antigorite



Asbestiform and non asbestiform tremolite



Conclusive remarks

- **Lithologies**  highly variable lithological and mineralogical composition.
Serpentinites are critical for chrysotile!
- **Asbestos content**  238 samples out of a total of 457 contain asbestos, mainly chrysotile, range 65 – 7300 ppm. **35 samples exceed the legal threshold of 1000 ppm!**
- **Bulk vs. «self crushing»**  «self-crushing» powders have a systematically higher asbestos content than bulk samples.
- **Amphibole asbestos**  Asbestiform tremolite relatively rare, asbestiform actinolite uncommon.

Future challenges

- *HR μ -Raman spectroscopy for quantitative analysis?*
- *Fibrous zeolites (e.g. erionite) from volcanic rocks!*
- *The future legal threshold will be only 100 ppm?*

