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Understanding the high temperature reaction sequence during the thermal treatment of cement-asbestos slates

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Introduction

- After a long *incubation* time, the promulgation of the law D.M. 19/07/2004, nr. 248 opened a new scenario in the management and treatment of asbestos waste

- Because of the lack of waste plants devoted to the confinement of ACM on the Italian territory, and the reorganization of the existing ones to withstand restrictive legislative scheme, the promulgation of this law was **a prompt to solve this critical and urgent issue**

- The importance of alternative ways of treating ACM is witnessed by the number of existing research (lab, industrial, semi-industrial) projects that have been developed in Italy in the last decade but not applied to an industrial scale because of the lack of a regulation act

- Although the Italian projects were the first to be chronologically conceived, neighbour countries such as France and Germany were faster in converting ideas into industrial plants

Introduction

•we are exploring the viability of an industrial heating process to directly transform the cement-asbestos slates, as an alternative to their confinement in waste plants (**Patent Req. Nr. MO2006A000205**), developed within the granted project "**CONVENZIONE DI RICERCA CON LA SOCIETA' ZETADI s.r.l."** entitled "*Progettazione ed avviamento di un impianto per l'inertizzazione termica dell'amianto e riciclo del prodotto di trasformazione*"

•The study of the transformation of cement-asbestos slates must consider the complexity of the system and the fact that the high temperature reactions taking place within that system greatly differ from the reaction path of the pure asbestos minerals.

Pure chrysotile in the 700-800 °C range:

$Mg_3(OH)_4Si_2O_5 \Rightarrow Mg_2SiO_4$ (*forsterite*) + $MgSiO_3$ (*enstatite*) + $2H_2O$

Pure riebeckite at 1100 °C, a complex reaction path which includes iron oxidation:

$Na_2MgFe''_2Fe'''_2Si_8O_{22}(OH)_2 \Rightarrow 2NaFe'''Si_2O_6$ (*pyroxene*) + $MgSiO_3$ (*enstatite*) + Fe_2O_3 (*hematite*) + $3SiO_2$ (*cristobalite*) + H_2O

Experimental

- Packages of commercial cement-asbestos slates to be dumped were used for the study

- Their phase composition was: **clinochrysotile (10 wt%), calcite, quartz, gypsum, illite, kaolinite, and minor CHS phases** and **portlandite**. The low content of cement phases is due to the well known reaction of **carbonation in air**, a slow process which leads to the formation of calcite from portlandite and from the CHS phases

- The thermal treatments of commercial cement-asbestos slates were conducted using a discontinuous industrial kiln in different firing cycle up to 1200 °C

- The monitoring of the phase evolution was possible on samples that experienced various temperatures using optical microscopy, electron microscopy, X-Ray powder diffraction, FTIR. *In situ* high temperature XRPD and ESEM experiments were also conducted on powdered specimen

The reaction sequence

In the cement-asbestos slate system up to the maximum firing temperature 1200 °C:

- kaolinite undergoes dehydroxylation in the range 400-600 °C according to the: $Al_2(OH)_4Si_2O_5 \Rightarrow Al_2Si_2O_7$ (*metakaolinite*) + $2H_2O$

- chrysotile decomposes in the range 700-800 °C to directly form forsterite and enstatite. Forsterite is stable up to the maximum firing temperature whereas enstatite is readily decomposed to form later Ca- and Mg-rich silicates such as merwinite ($Ca_3MgSi_2O_8$) and akermanite ($Ca_2MgSi_2O_7$)

- calcite decomposition ($CaCO_3 \Rightarrow CaO + CO_2$) at about 900 °C is accompanied by the decomposition of minor phases such as illite and gypsum. The latter has been previously converted to anhydrite at about 350 °C. Anhydrite decomposition ($CaSO_4 \Rightarrow CaO + SO_3$) releases molecular groups useful for the formation at high temperature of the stable phase silicocarnotite ($Ca_5(SiO_4)_2SO_4$)

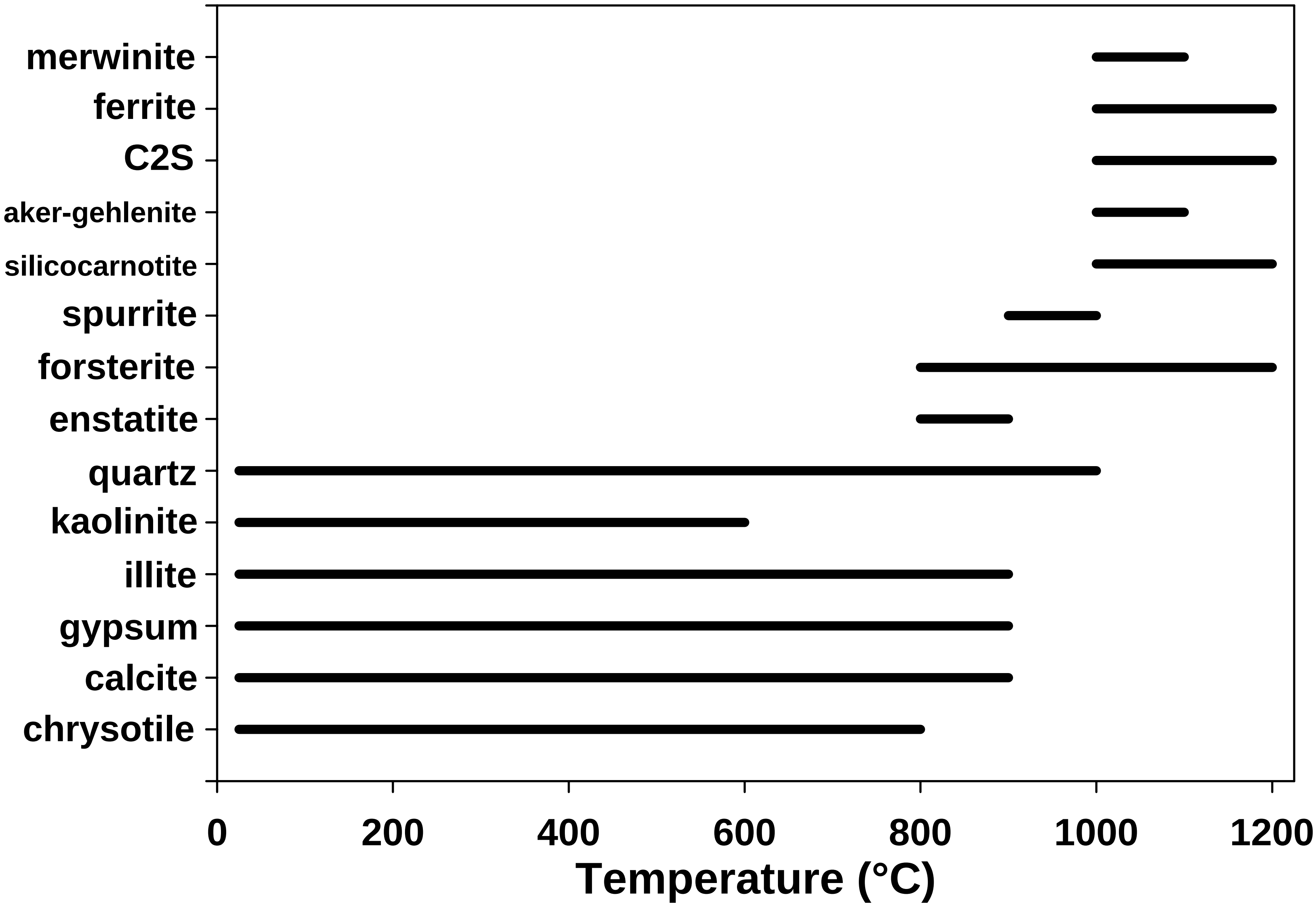
The reaction sequence

In the cement-asbestos slate system up to the maximum firing temperature 1200 °C:

- the decomposition of minor illite makes available Al, Mg, Si, and K for the high temperature reactions. K is likely to form a very low amount of amorphous (glassy) phase

- the large amount of lime available after the decomposition of calcite combines with silica (quartz is then no longer stable at T>1000 °C), magnesium, and iron to form the typical clinker phases: C2S ($2CaO \cdot SiO_2$) with a larnite structure; ferrite (brownmillerite, $Al_2Ca_4Fe_2O_{10}$); merwinite. Only the latter is not stable up to the maximum firing temperature (1200 °C)

The reaction sequence



Verification of the thermal transformation: Protocol of Analysis?

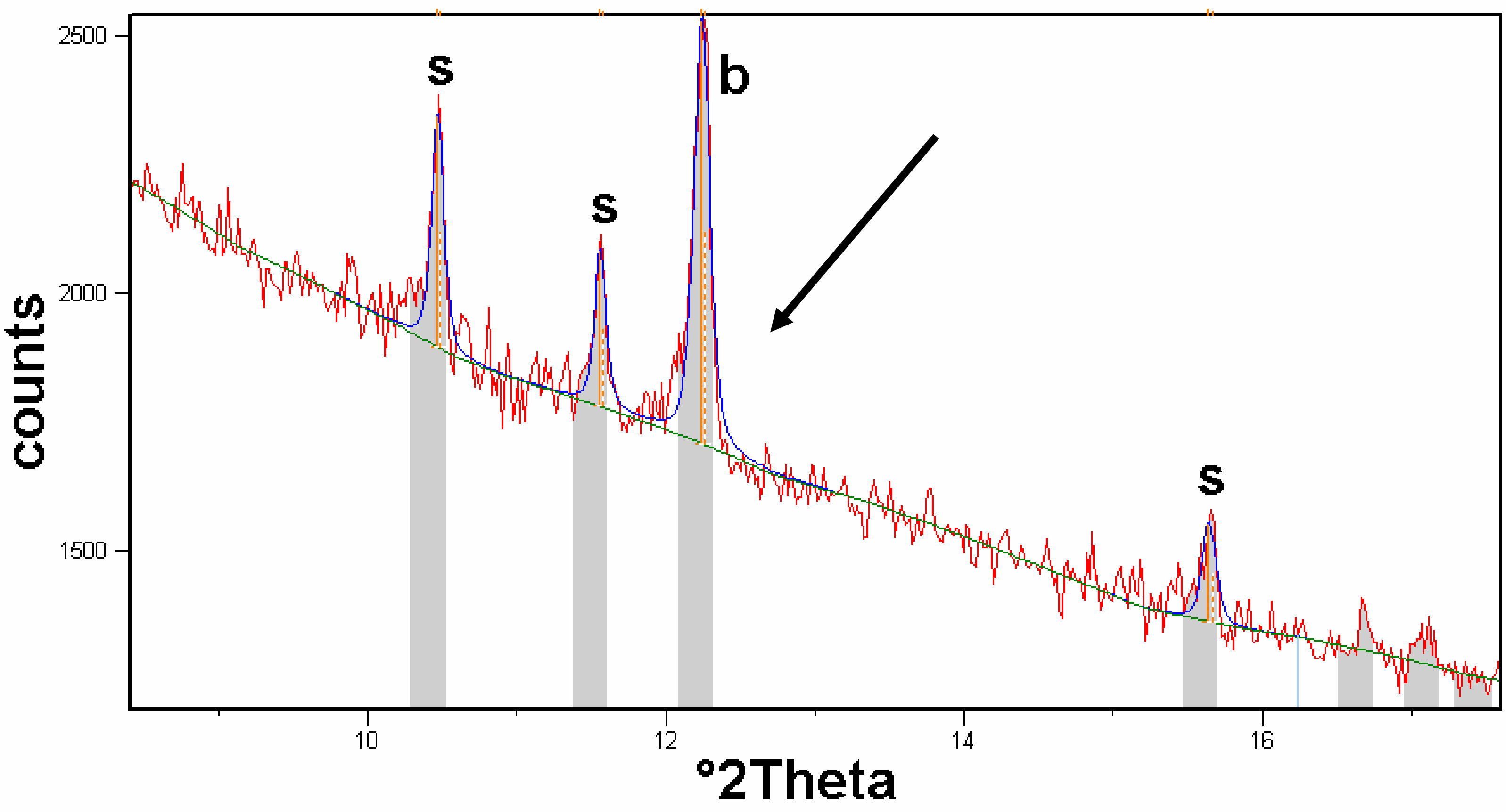
- D.M. 19/07/2004 clearly states that the full transformation of asbestos minerals due to thermal treatment must be achieved: no residual asbestos fibres should be present in the treated material = "*I trattamenti che, come effetto, conducono alla totale trasformazione cristallochimica dell'amianto, rendono possibile il riutilizzo di questo materiale come materia prima*."

Need of a verification analytical protocol: XRPD?

⇒Certainly useful to indirectly cross-check the phase composition but it should be used as complementary technique as the phase detection limit is around 0.5-1 wt% (the same applies to **FTIR, RAMAN spectroscopy**…)

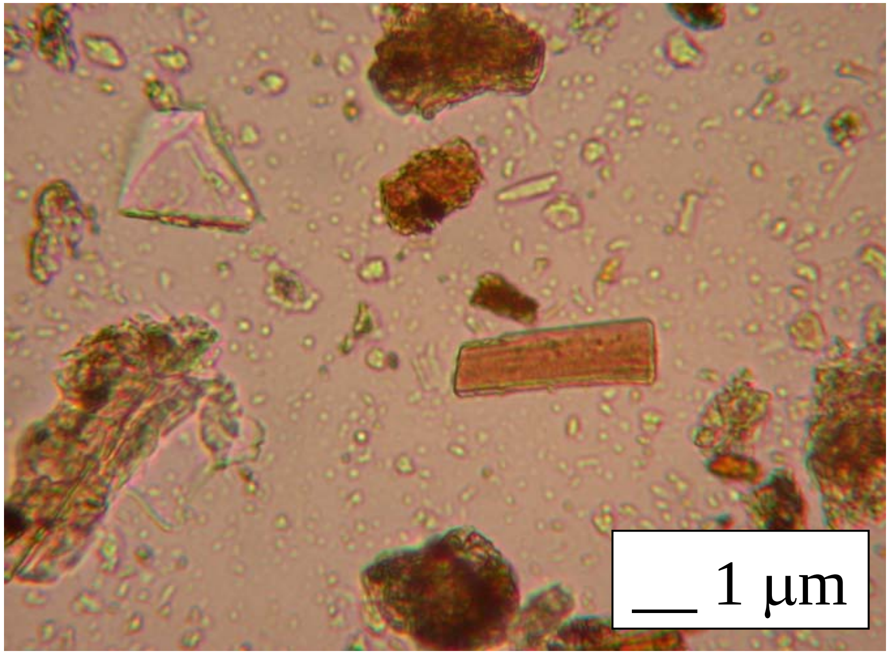
Protocol of Analysis? XRPD

- XRPD invalidated! Diffraction peaks of the high temperature phases may overlap with those of the asbestos phases and invalidate the sole application of this technique

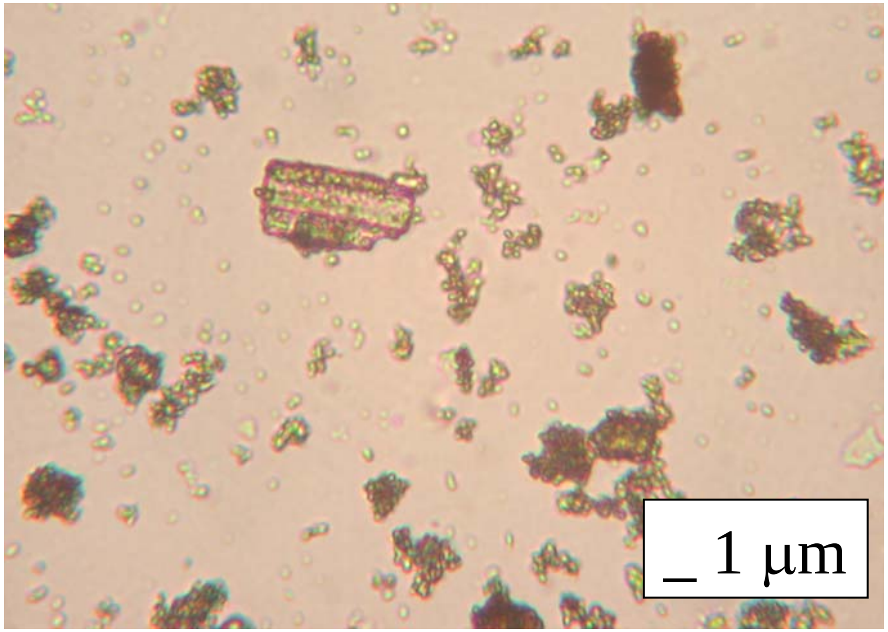


Low angle region of powder pattern of a sample of cement-asbestos slate fired at 1200 °C with the presence of the brownmillerite (**b**) and silicocarnotite (**s**) peaks

Protocol of Analysis? Optical microscopy



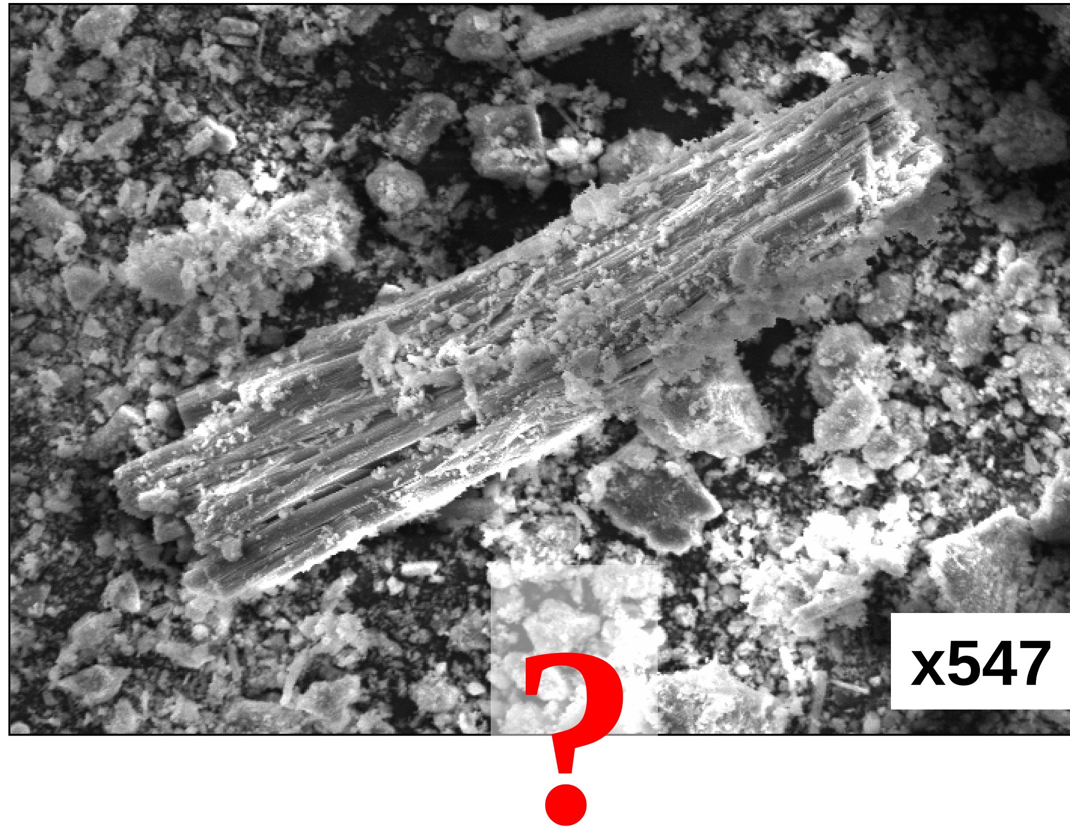
- Because of the low resolution (max 50x here), it has a limited use because of the intrinsic difficulties to ascertain whether a fibre is transformed or not.
- Capability to observe variation of the crystal habit and changes of the optical properties (e.g. pleocroism, extinction, and dispersion) of the transformed fibres with respect to those of the original ones.



Protocol of Analysis? SEM

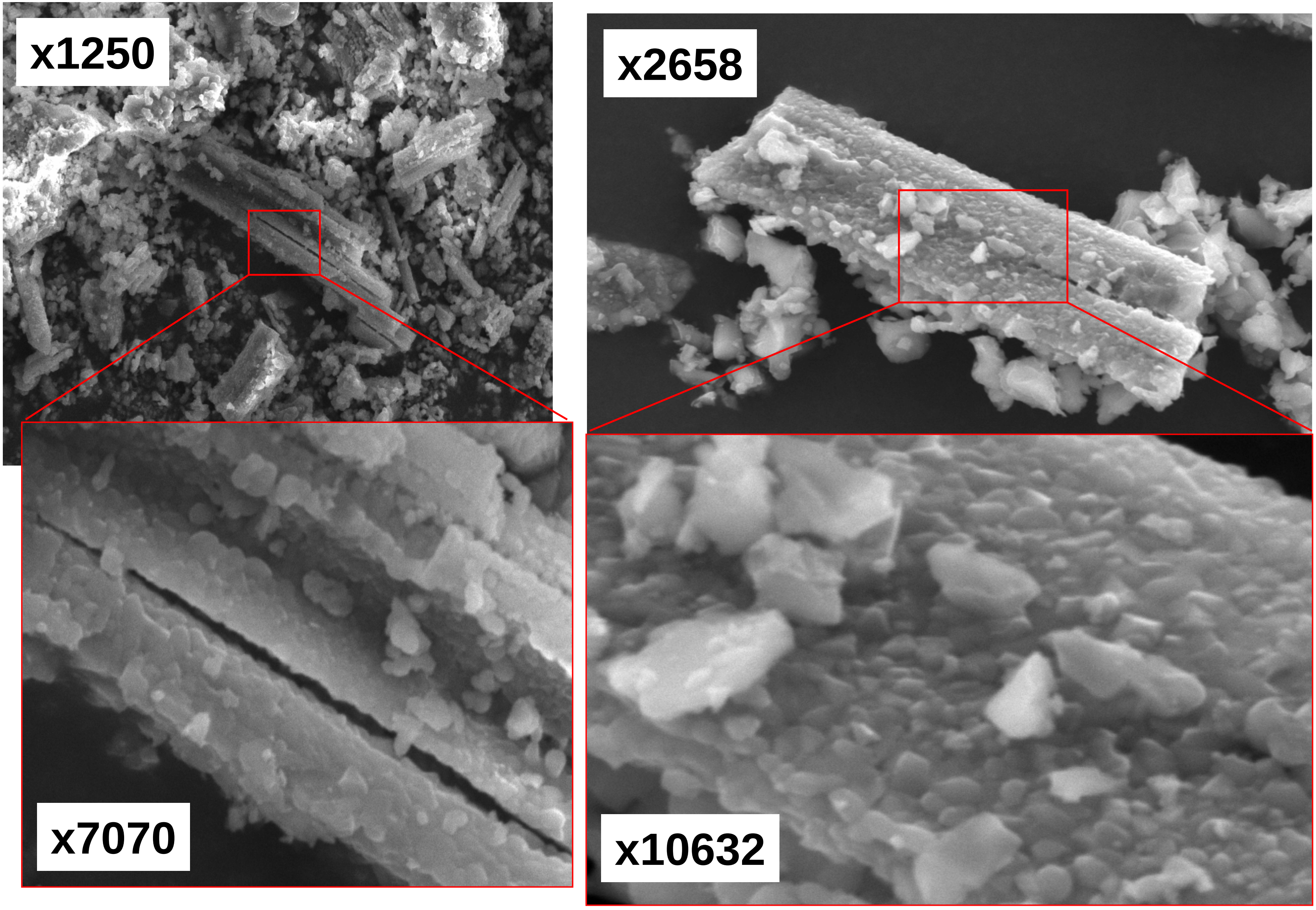
- SEM+EDS performed with imaging at high magnification may reveal the very nature of the microstructure of the thermally treated fibres

- The fibres which underwent a full transformation exhibit a totally different microstructure with respect to the original ones with an evident intergrowth of newly-formed crystals

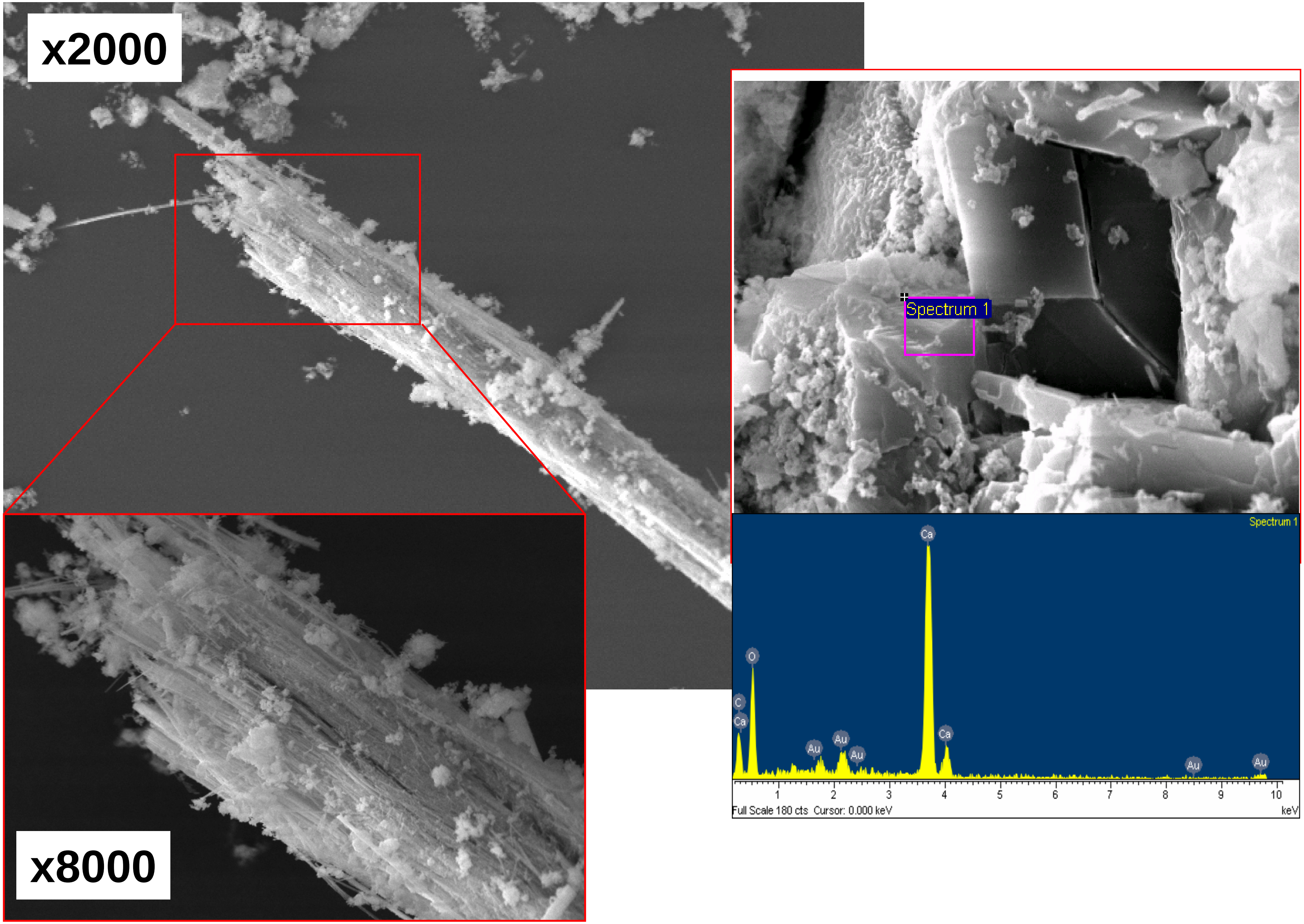


- At low magnification the microstructure of a thermally treated fibre is not revealed and doubts may arise on the effectiveness of the thermal treatment. At higher magnification the issue may be unravelled

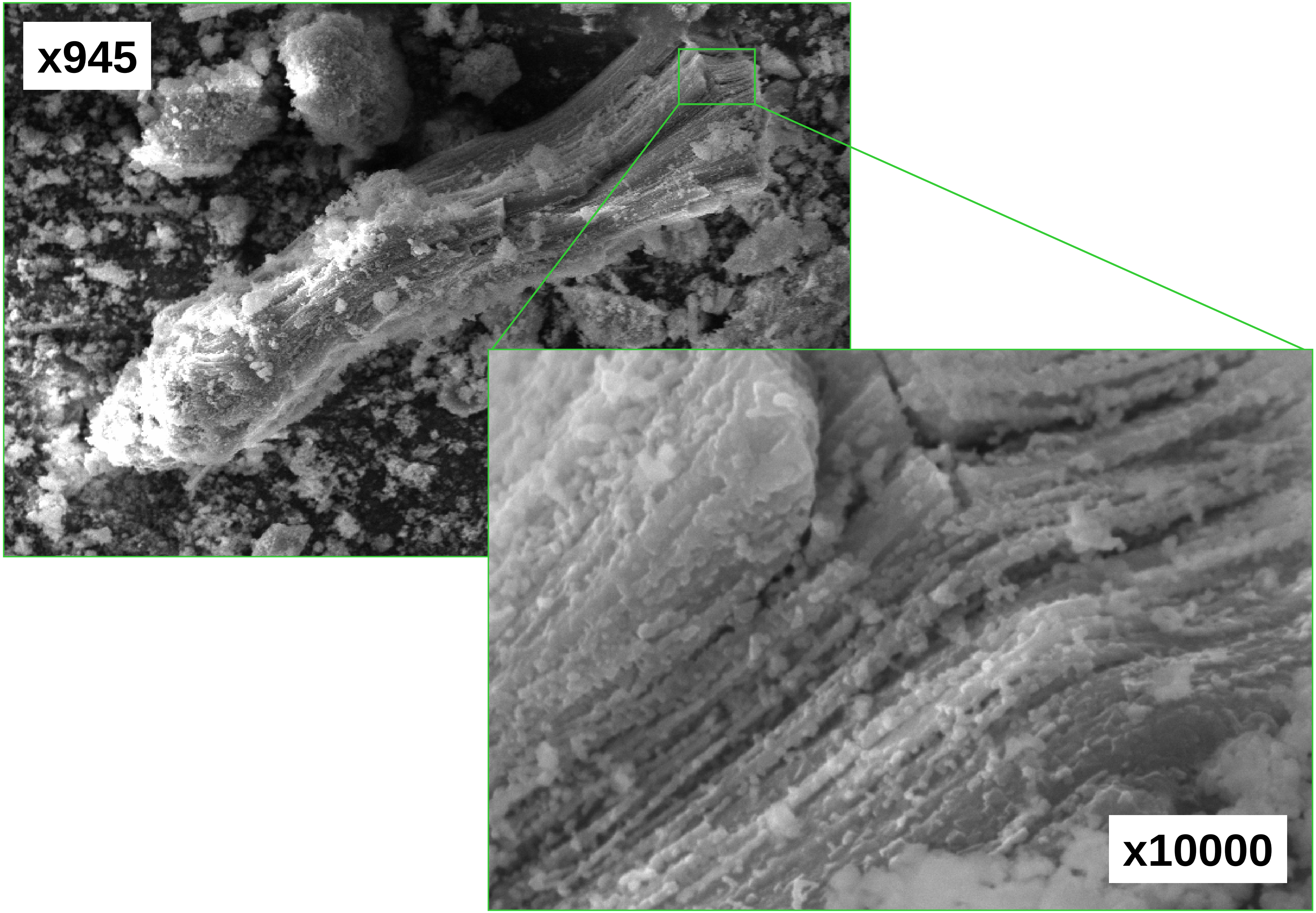
Protocol of Analysis? SEM



Protocol of Analysis? SEM

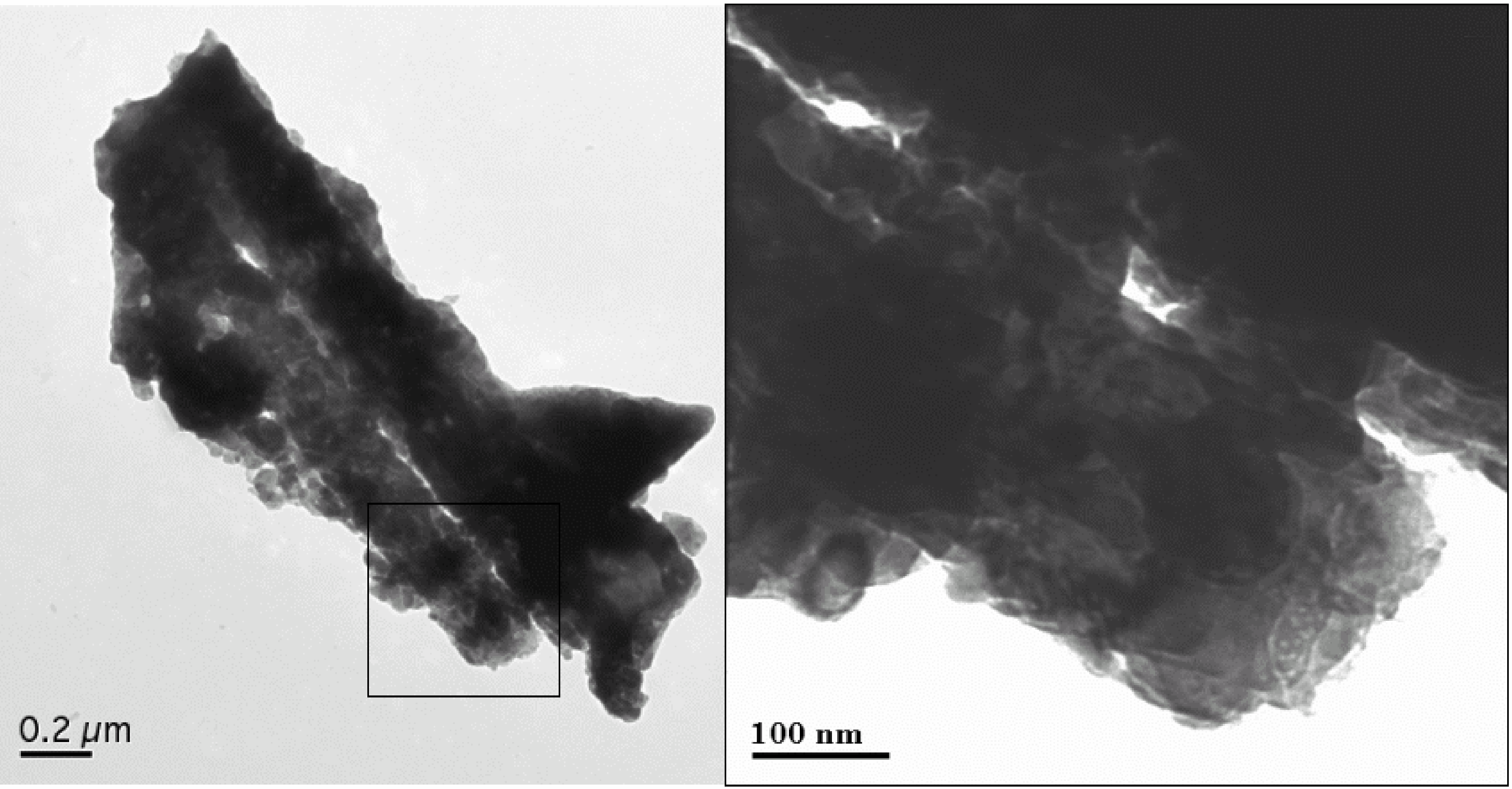


Protocol of Analysis? SEM



Protocol of Analysis? TEM

TEM of a thermally treated chrysotile bundle showing a complete recrystallization of the original fibres into newly-formed high temperature silicates



Protocol of Analysis? Indications

D.M. 19/07/2004: the yield of transformation of asbestos minerals due to thermal treatment should be **complete**

⇩

We believe that the analytical protocol utilized to verify the completeness of the transformation reaction should embrace a combination of different experimental techniques:

OPTIONAL

XRPD

FTIR (eventually RAMAN)

MOCF

MOLP

MANDATORY

SEM at high resolution/magnification

TEM

Concluding remarks and future perspectives

- The study of the transformation of cement-asbestos slates must consider the complexity of the system as the high temperature reactions taking place greatly differ from the reactions regarding the pure asbestos minerals

- Because of the expected development of industrial processes for the thermal treatment of asbestos containing materials, an analytical protocol for the assessment of the completeness of the transformation reaction is requested. Our findings indicate that the analytical protocol may embrace a combination of various experimental techniques and must include SEM at high resolution/magnification or TEM

- At an applicative level, the complexity of the inertization process requires a mathematical model for its optimization. The possibility to apply a simple **multiple regression analysis system** to predict the optimal thermal cycle for a specific cement-asbestos slates typology is under investigation:

$$\mathbf{R = a_1X_1 + a_2X_2 + \dots\ a_nX_n}$$