Raman investigation of mineral fibres and iron compounds in asbestos materials

PRIN 2017 3X8WA4

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Outline

- Fibres-cells systems investigation with μ-Raman spectroscopy
  - Chrysotile (Balangero, Italy), Erionite (New Jersey, USA) and Crocidolite UICC (South Africa, Africa)
  - THP1 and A-549 cells

- μ-Raman identification of iron compounds in Chrysotile from Balangero: presence of both Fe(II) and Fe(III) species in micrometric-crystals to be considered in metal release and fibres toxicity

μ-Raman spectroscopy on fibres-cells systems

- Identification of fibres which undergo **phagocytosis**
- Identification of accessory minerals and **iron compounds**

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Fibres:

- Chrysotile, Balangero (Italy)
- Erionite, New Jersey (USA)
- Crocidolite, UICC South Africa (Africa)

Cells:

- A549
- THP1 no differentiation
- THP1 M0, M1, M2
- THP1 24h, 48h (M0), 72h (M0), 96h (M0)

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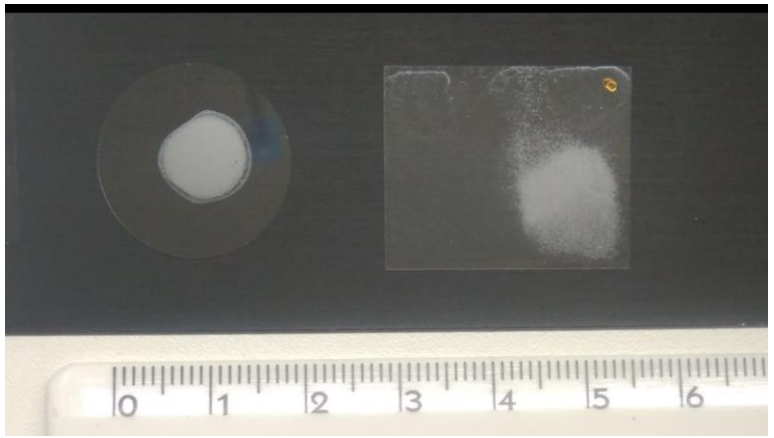
Experimental Setup



Sample preparation

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- Fibres concentration: 50 μg/ml
- Different treatment time: 24, 48, 72, 96h
- Centrifugation and washing with distilled water
- Deposition on a coverslip glass substrate
- Air-drying and RT conservation

μ-Raman analysis

Physics and Chemistry Departments, University of Parma

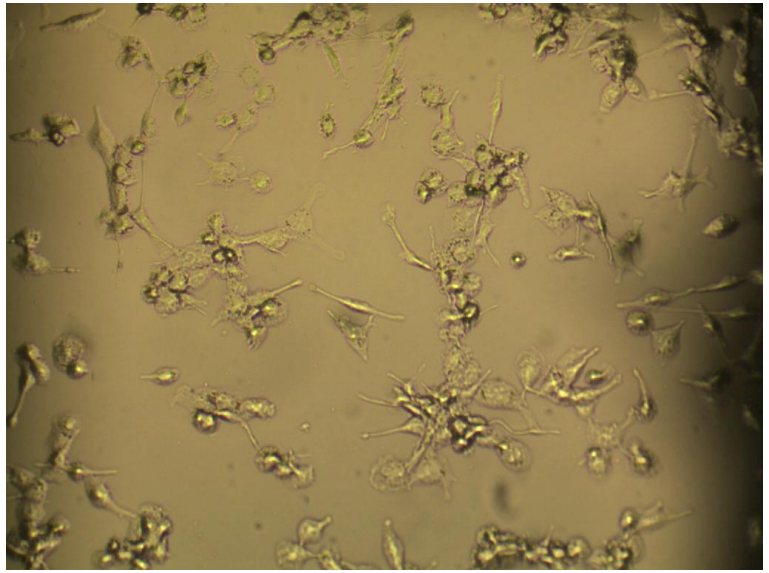
- LabRam and LabRam HR Horiba spectrometers
- Confocal microscope with objective 100x: few microns spot size
- Laser excitations: He-Ne 632.8 nm, diode 785 nm, Nd:YAG 532 nm, Nd:YAG 473.1 nm
- Density filters to reduce laser power and avoid heating effects

Preliminar results on A549 and THP1

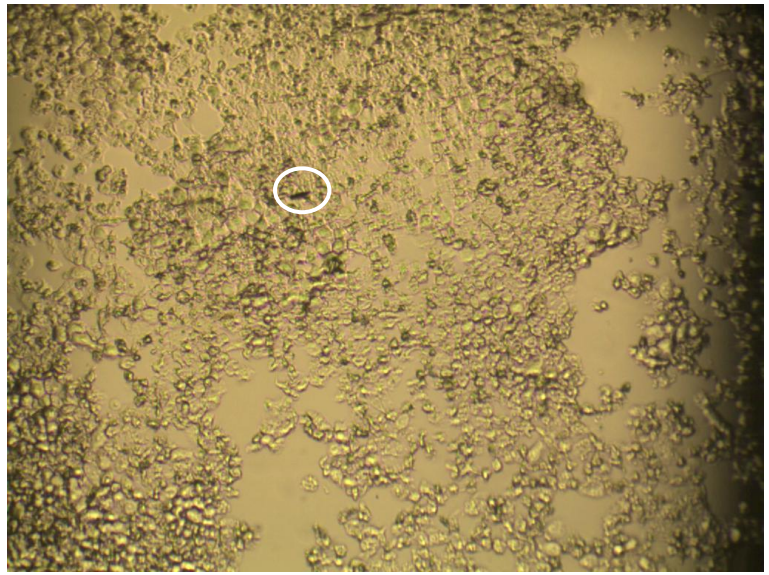
- Raman identification of the three fibres in both A549 and THP1 systems
- Higher concentration of fibres in THP1 systems compared to A549 systems: **phagocytosis**

(Selected areas are about 500 x 600 μm^2)

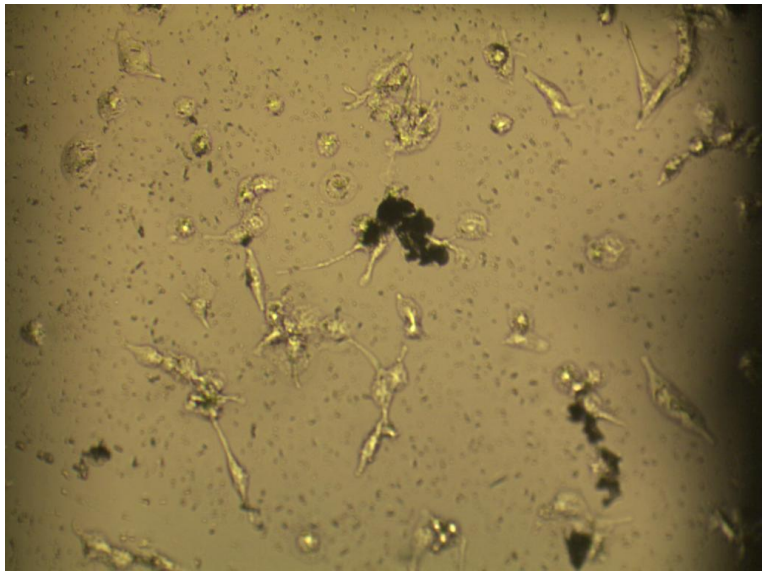
THP1-Untreated 10x



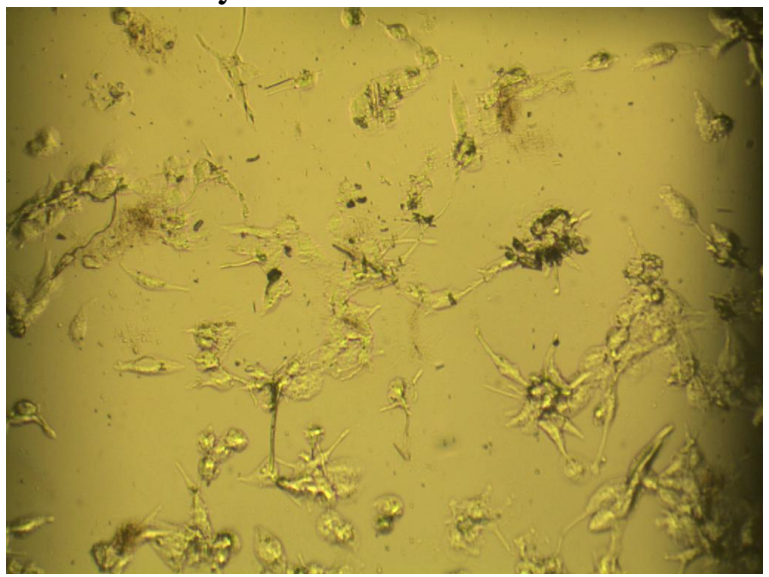
A549-Chrysotile 10x



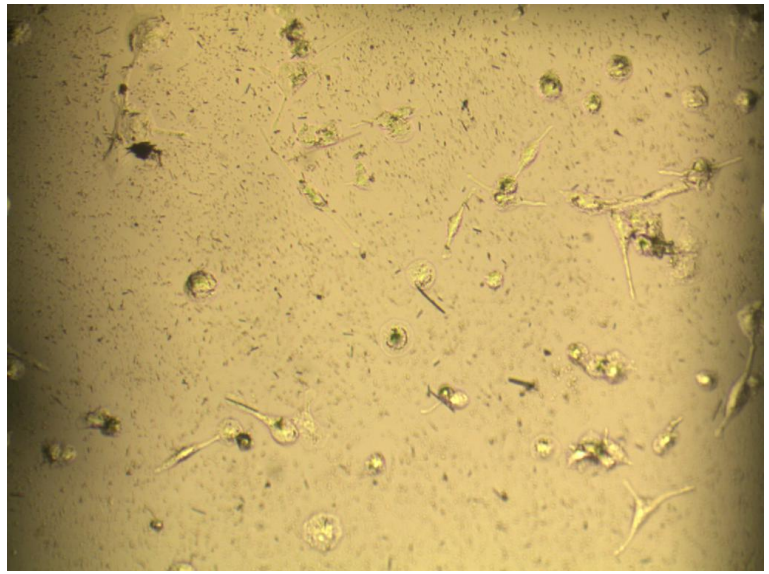
THP1-Erionite 10x



THP1-Chrysotile 10x



THP1-Crocidolite 10x

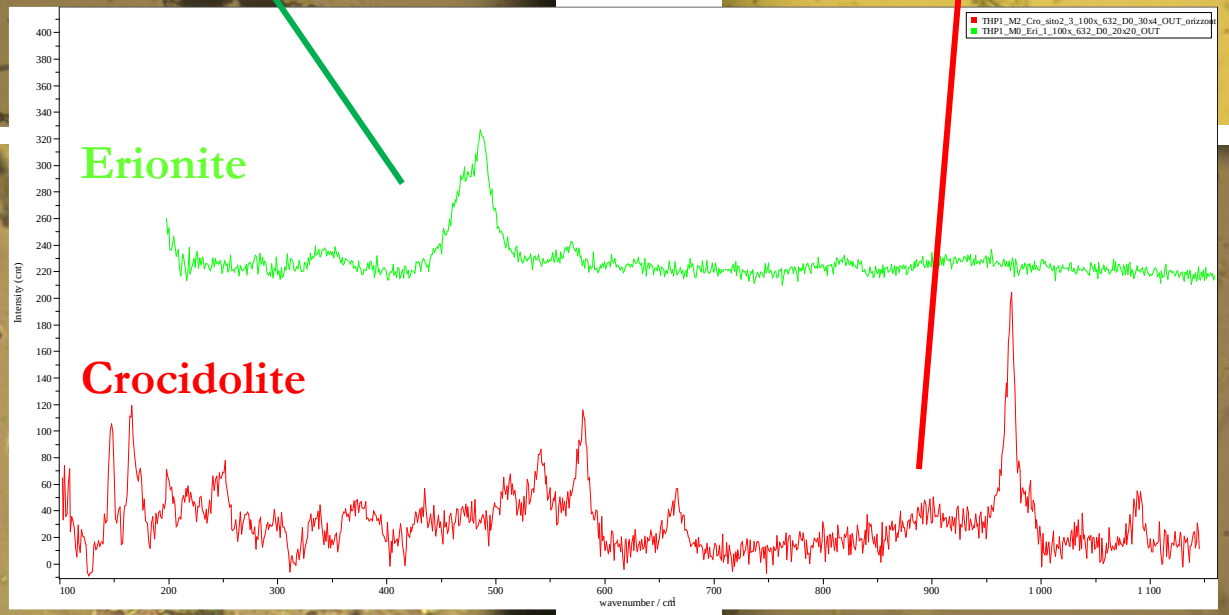


Different morphologies for different fibres

Erionite | **Crocidolite** | **Chrysotile**

50x ~100x120 μm²

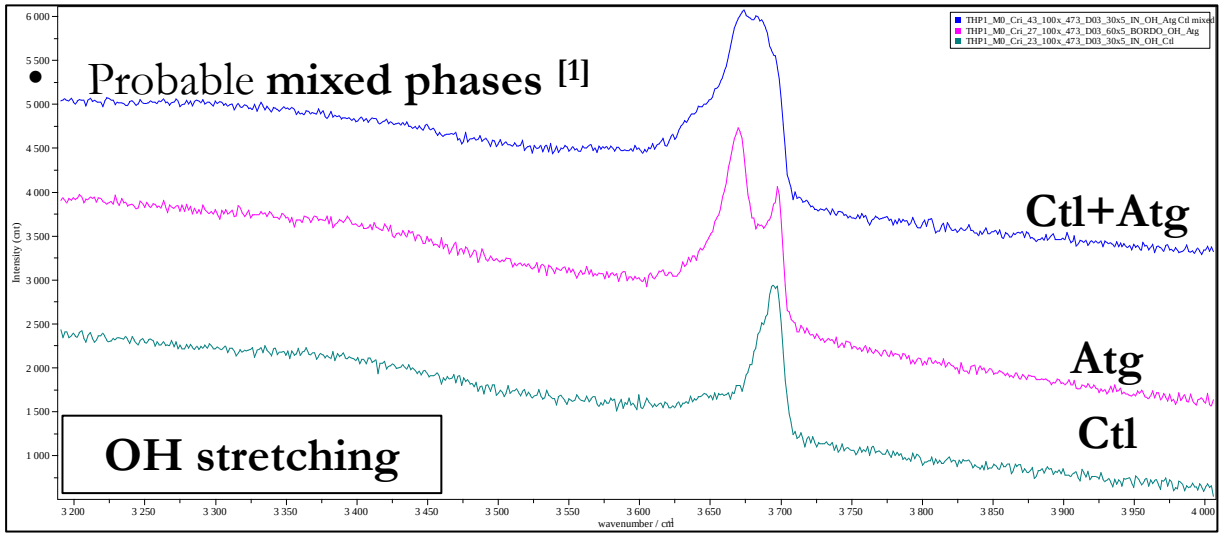
100x ~50x60 μm²

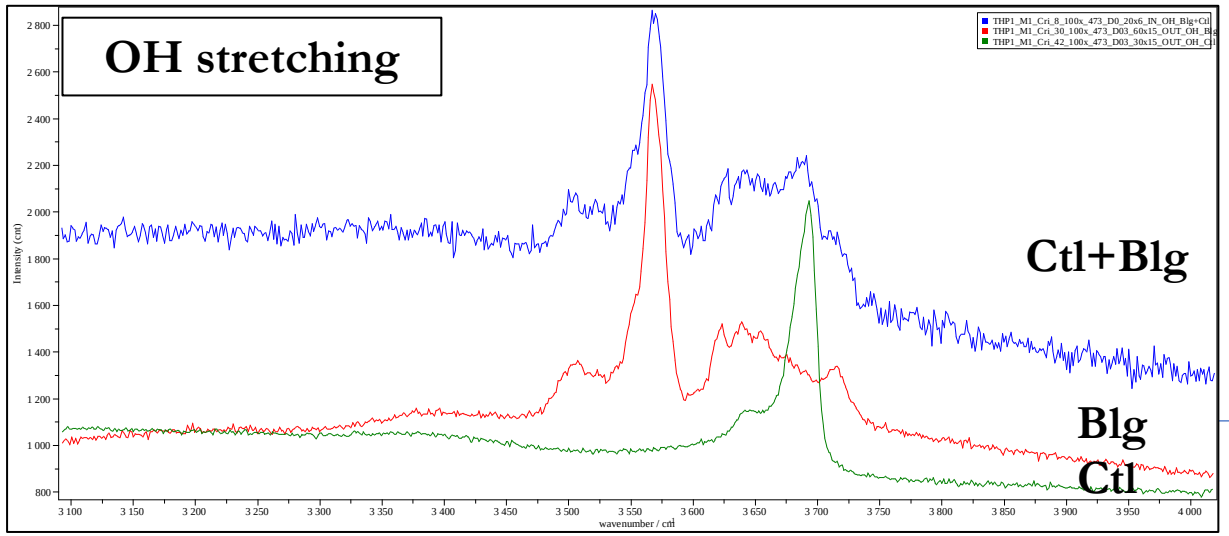


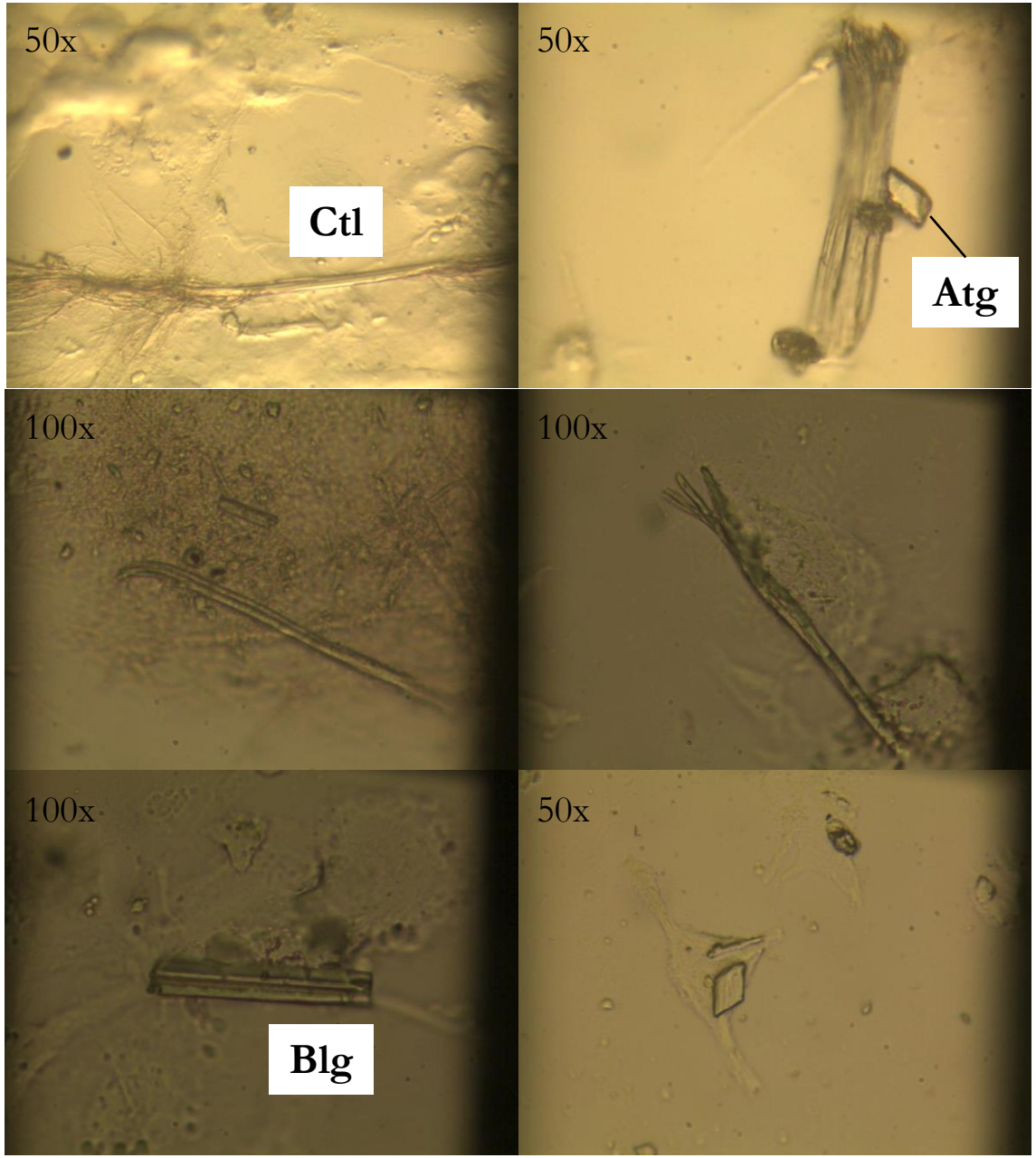
Different spectra

Even more different morphologies in THP1-chrysotile systems

- Curve, elongated, flexible fibres: **Chrysotile**
- Squat, less elongated fibres: **Antigorite**
- Rigid, straight, thin fibres: **Balangeroite**

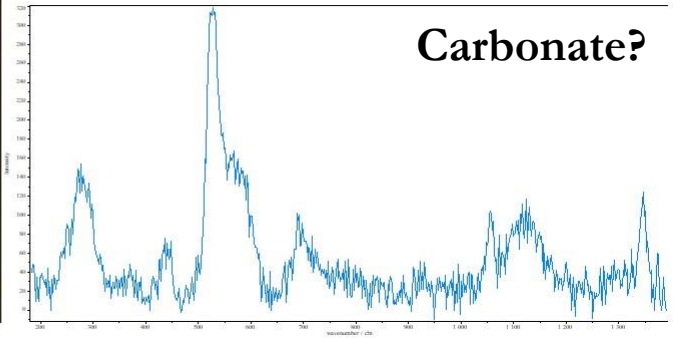


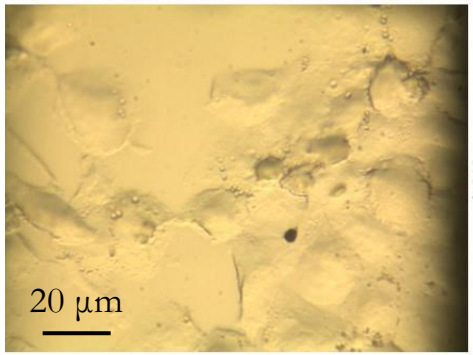


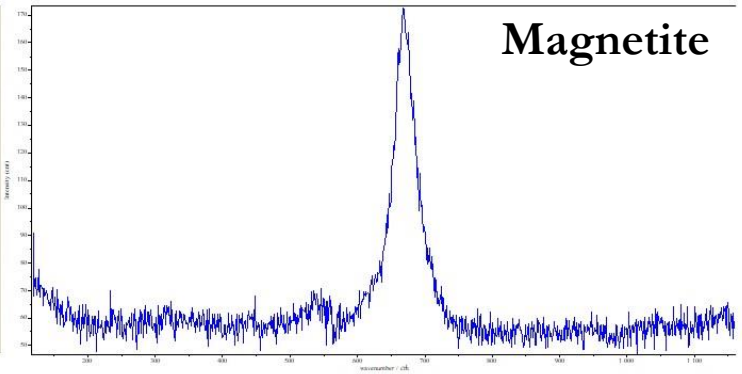


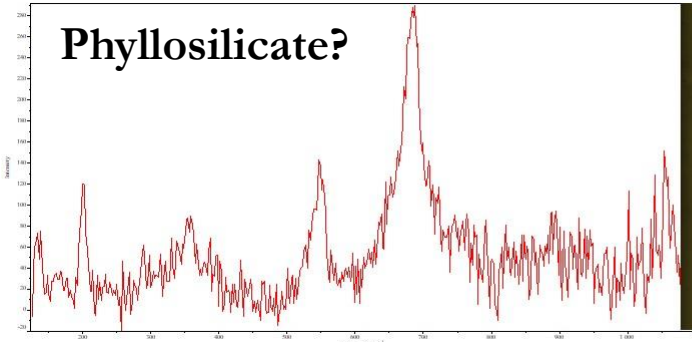
[1] Petriglieri J.R., Bersani D. et al. *Appl. Sci.* 11 (2021) 287

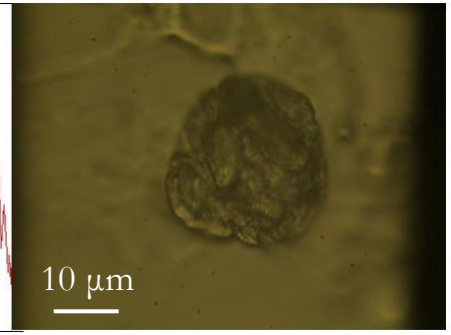
Accessory minerals in THP1-chrysotile systems

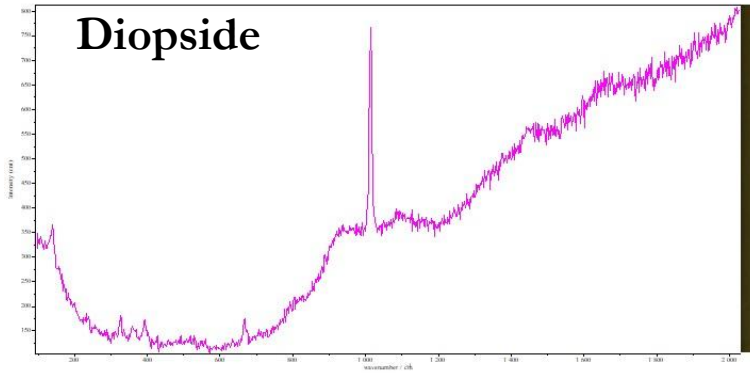


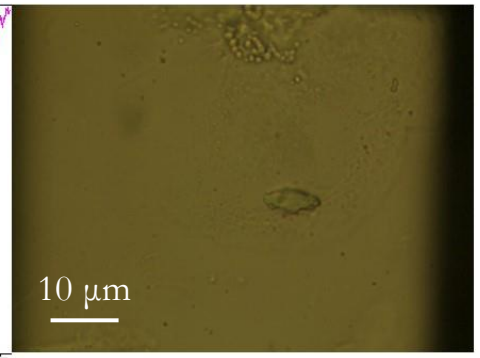










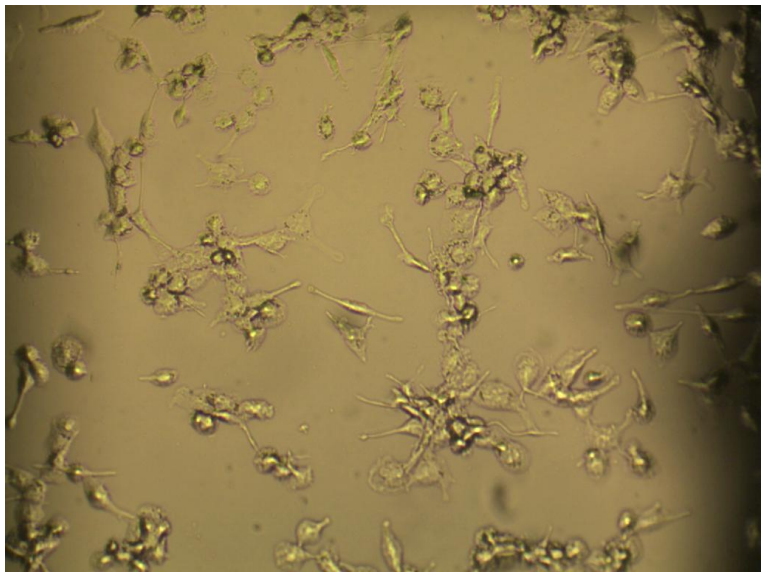


- Micrometric crystals, sometimes found inside cells
- Not fibrous, rounded or irregular shapes
- Presence of **magnetite** as the most frequent phase, rare presence of **diospide**, not identified carbonate and not identified phyllosilicate

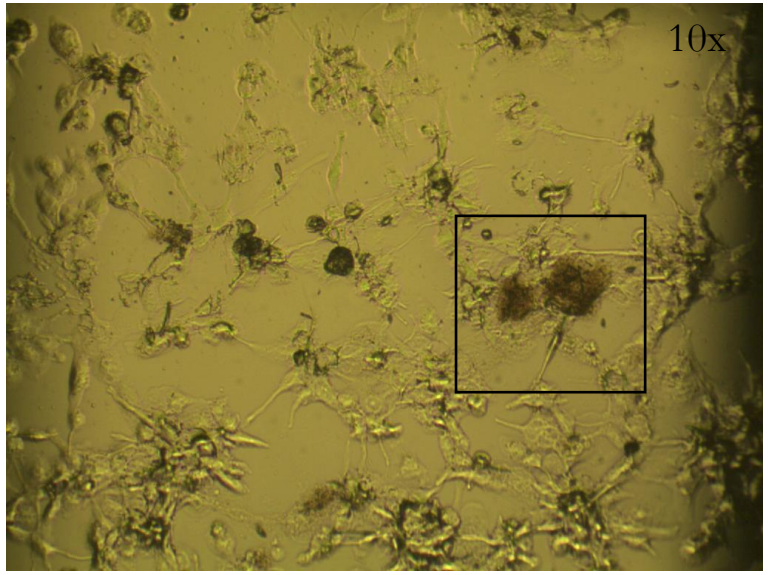
Clusters of agglomerated materials: organic and inorganic signals

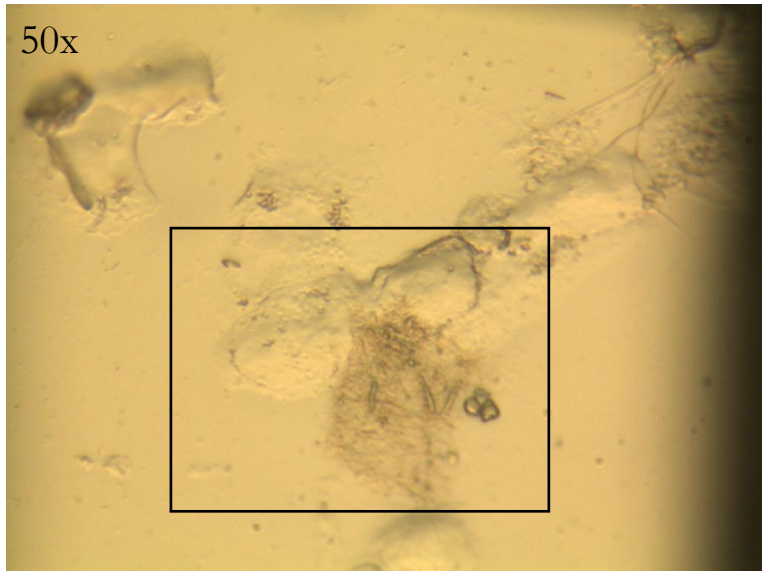
- Not found in erionite neither crocidolite systems
- Found in all differentiation (M0, M1, M2)
- Found also in not differentiated THP1
- Increasing size and concentrarion of the clusters with increasing treatment time

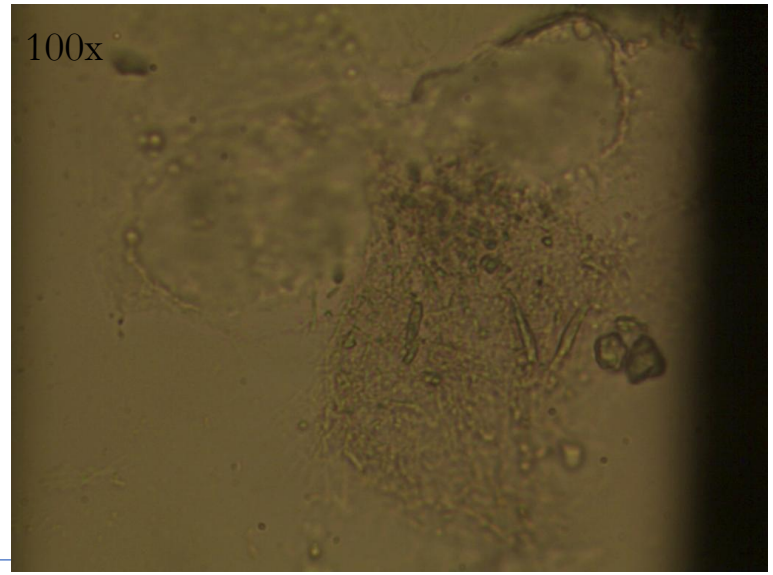
THP1-Untreated 10x



THP1-Ctl

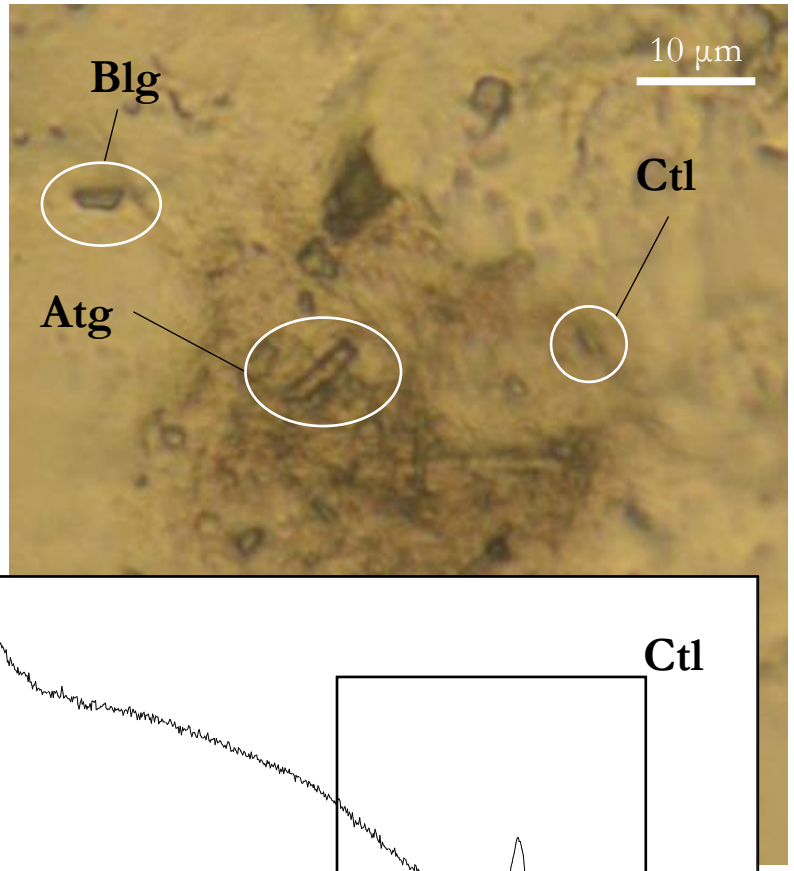


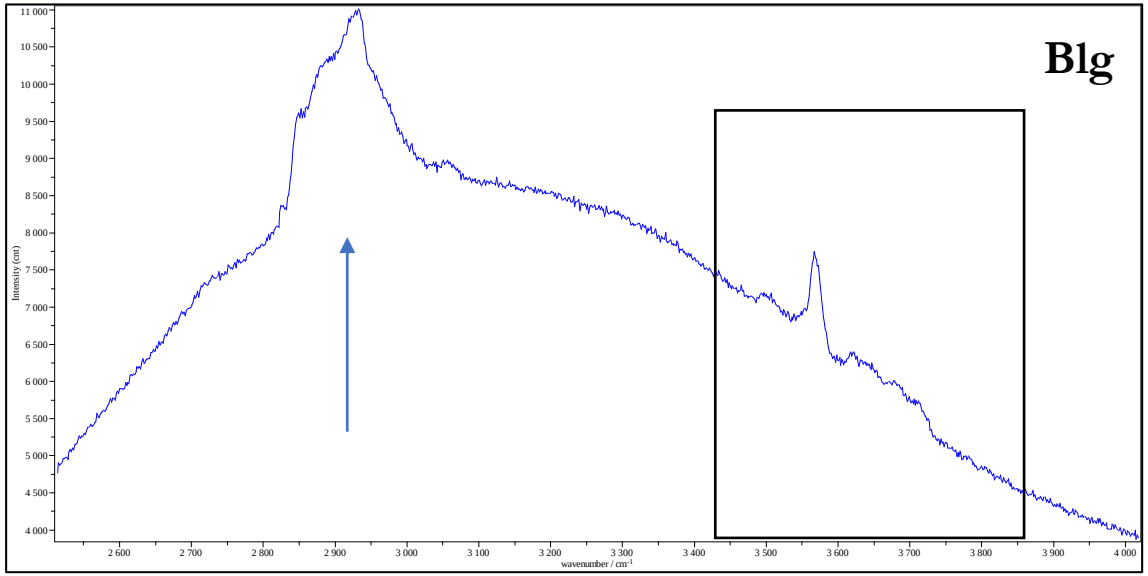


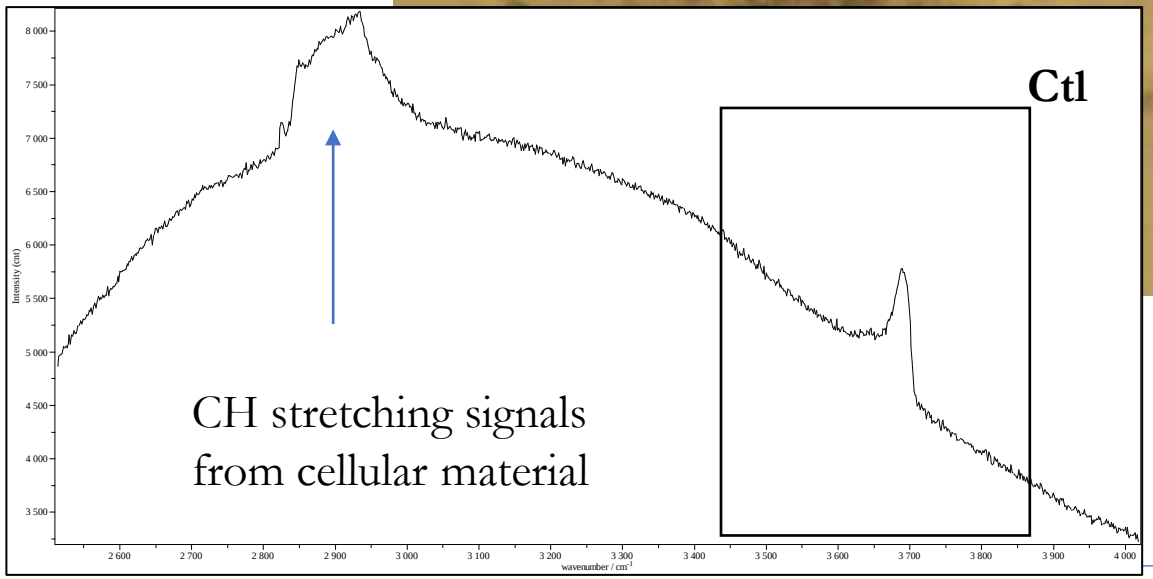


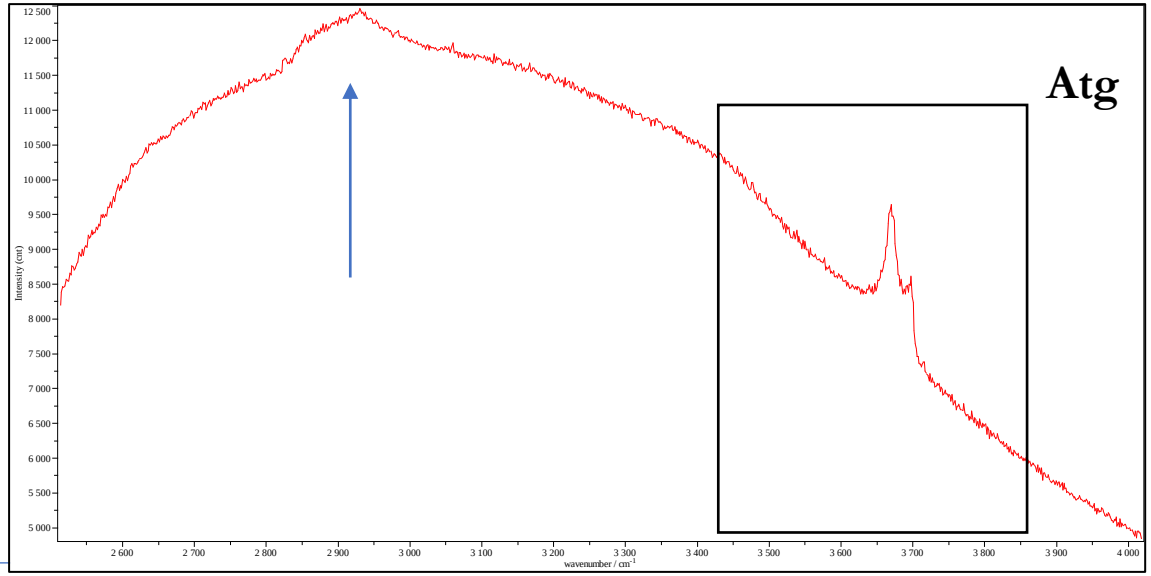
- Fibres and (probable) fibres fragments: **Ctl, Atg, Blg**
- **Cellular** signals
- Several dark coloured micrometric crystals: **magnetite and sulphides** mainly
- Reddish micrometric crystals: not complete identification
- **Iron** compounds: iron dissolution in the clusters?
- Formation of new compounds after THP1 interactions?

Chrysotile, Antigorite, Balangeroite fibres found in the clusters



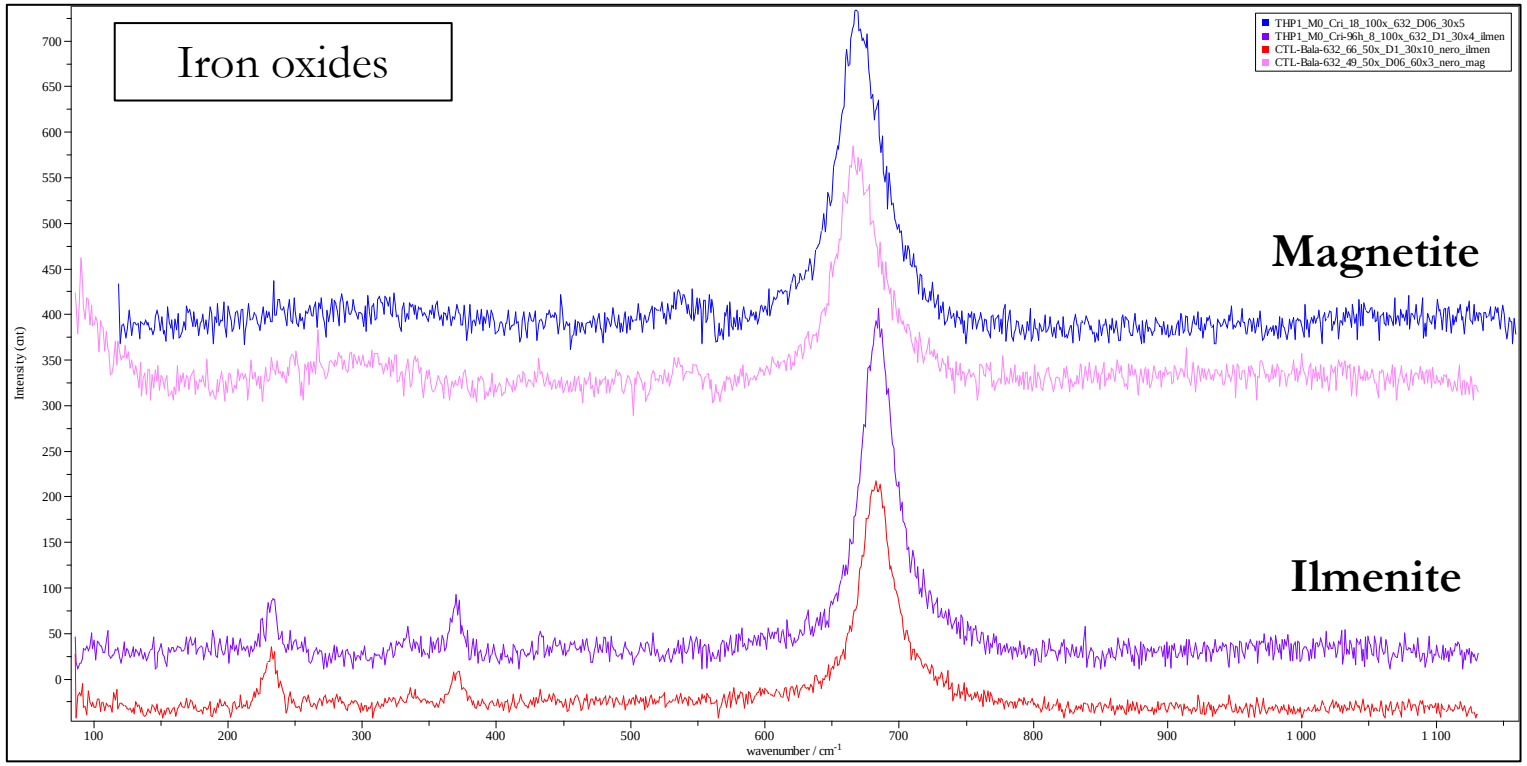


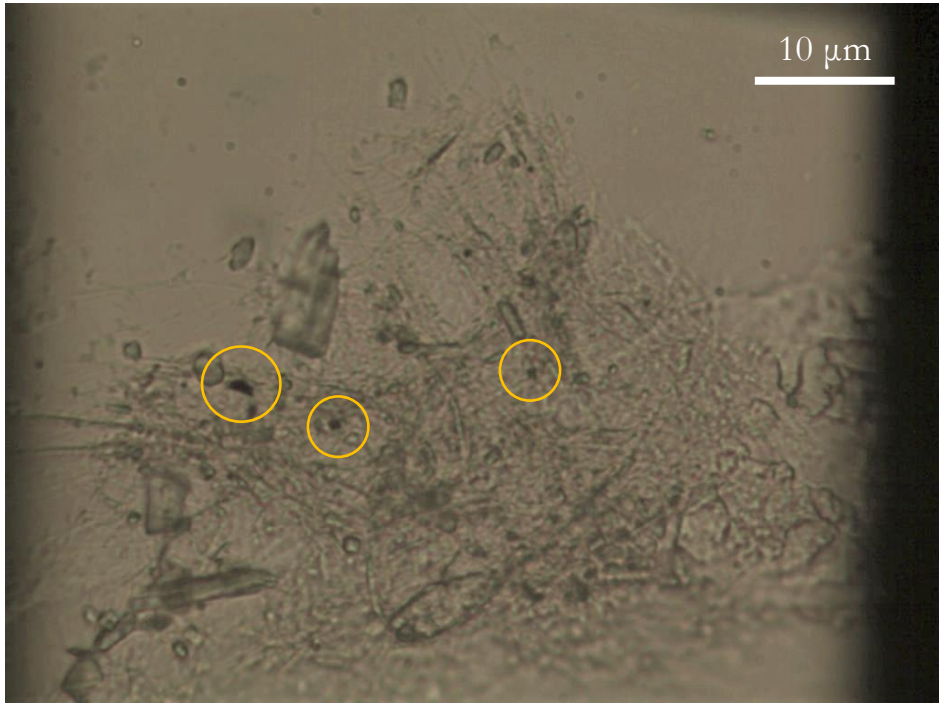




Iron compounds in the clusters: oxides

- Iron oxides: magnetite mainly, rare ilmenite and hematite.
- Similar compounds found also in Ctl from Balangero without cells



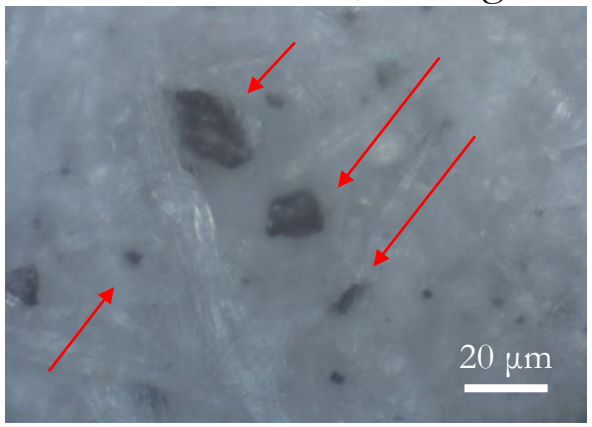


THP1-Ctl

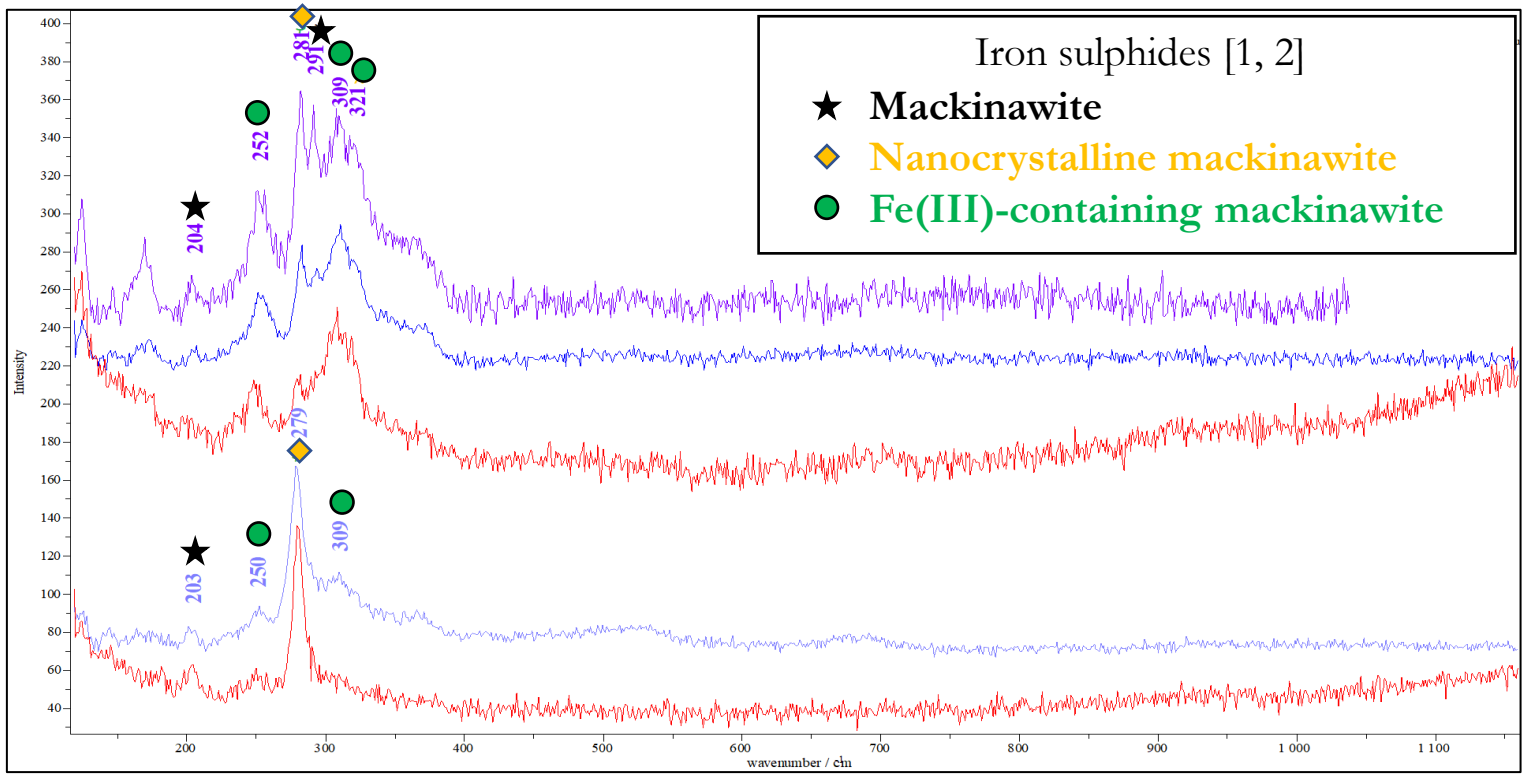
Ctl, Balangero

THP1-Ctl

Ctl, Balangero



Iron compounds in the clusters: sulphides

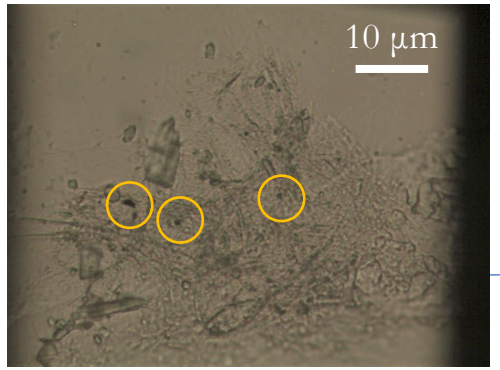


THP1-Ctl

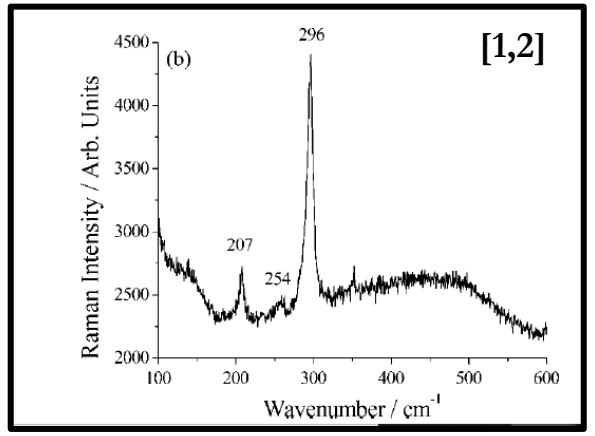
Ctl, Balangero

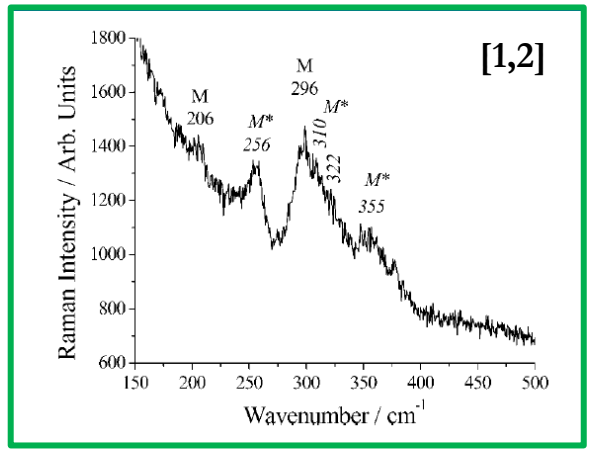
THP1-Ctl

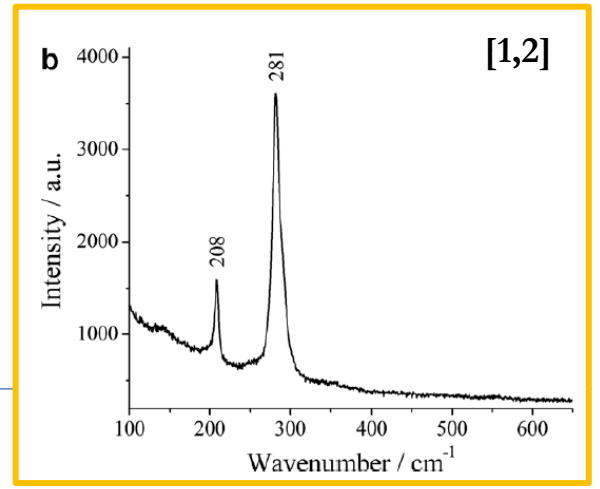
Ctl, Balangero



- Iron sulphides: mackinawite ($Fe^{II}S$) mainly
- Mackinawite in different forms: nano-mackinawite and partially oxidized mackinawite (Fe(III)-containing mackinawite)
- Similar compounds found also in Ctl from Balangero without cells





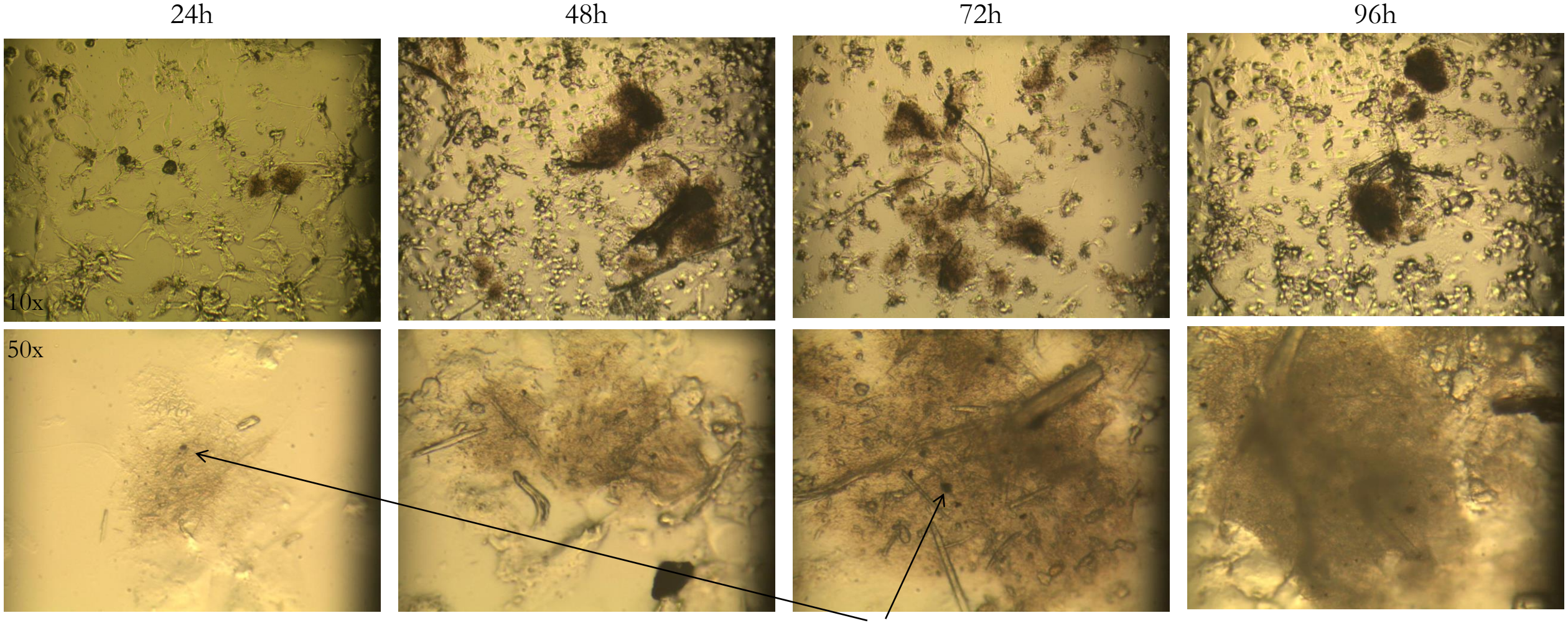


[1] Bourdoiseau J.-A. et al., *J. Raman Spectrosc.* 42 (2011) 496–504

[2] Bourdoiseau J.-A. et al., *Corrosion Science* 50 (2008) 3247–3255

Larger clusters as treatment time increases

THP1-M0
Ctl



- **Clusters size and concentration** increase as treatment time increases
- **Iron** compounds in clusters at different treatment time

Treatment time

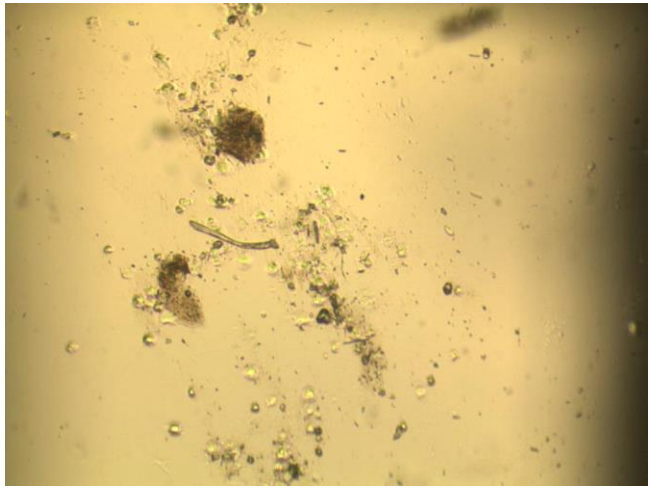
Presence of clusters in not differentiated THP1

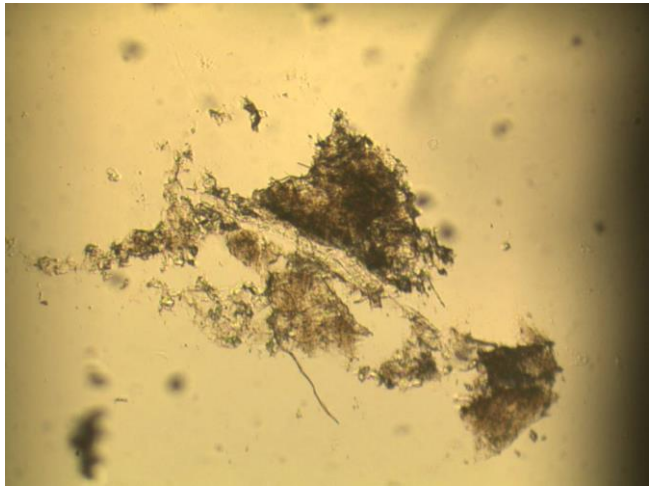
No-differentiation THP1
Ctl

24h

72h

10x

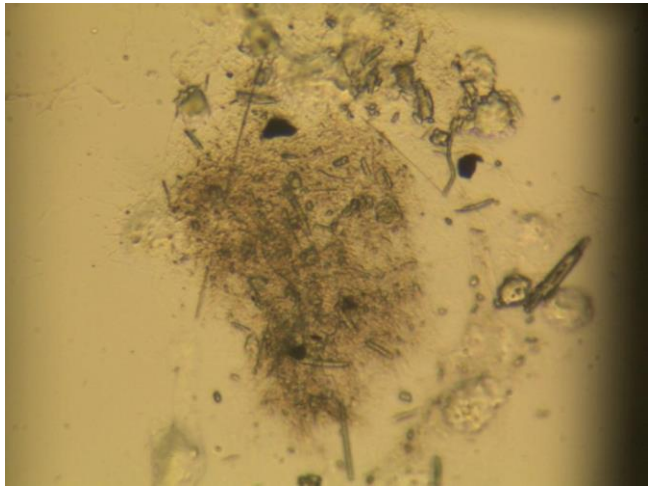


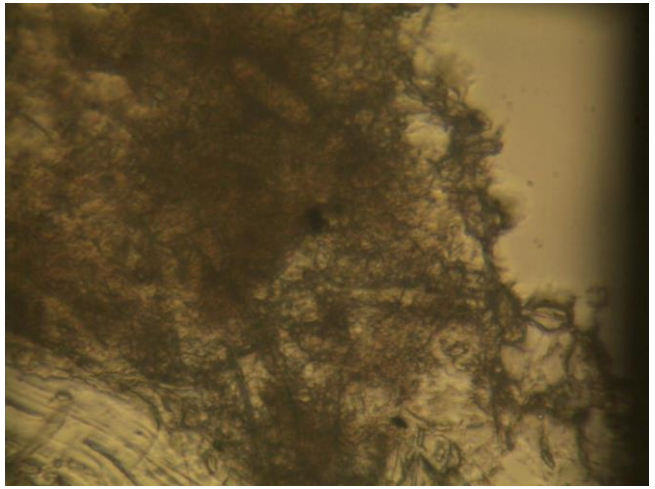


As observed in THP1 systems:

- Clusters not observed in untreated cells
- Clusters size and concentration increase as treatment time increases
- Iron compounds found in clusters at different treatment times

50x

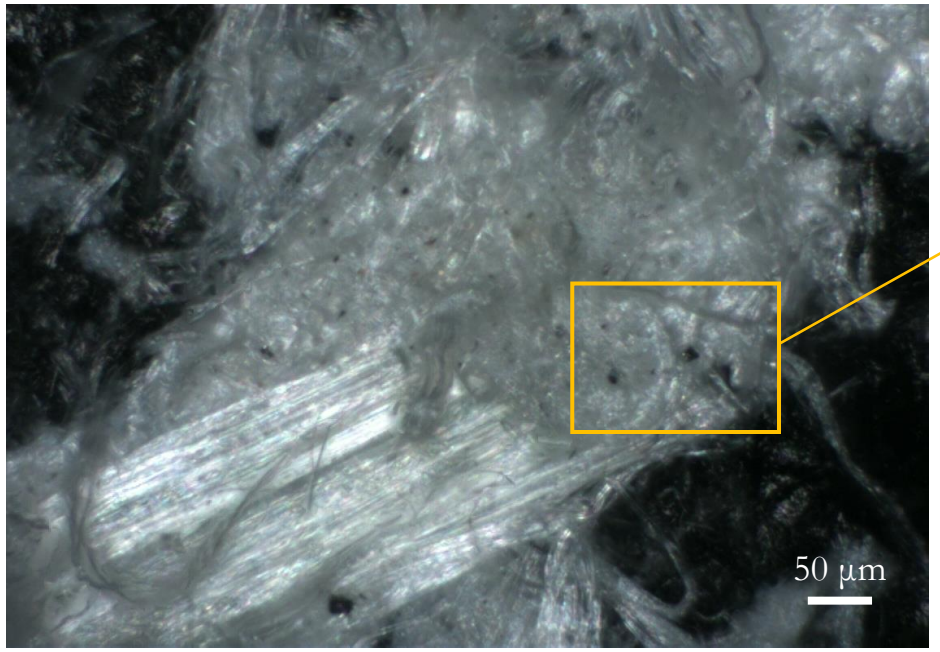


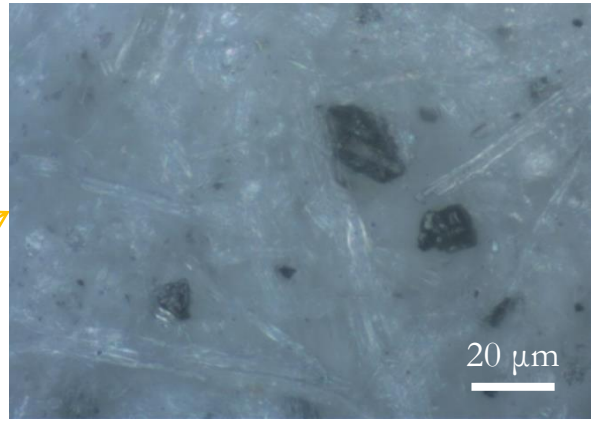


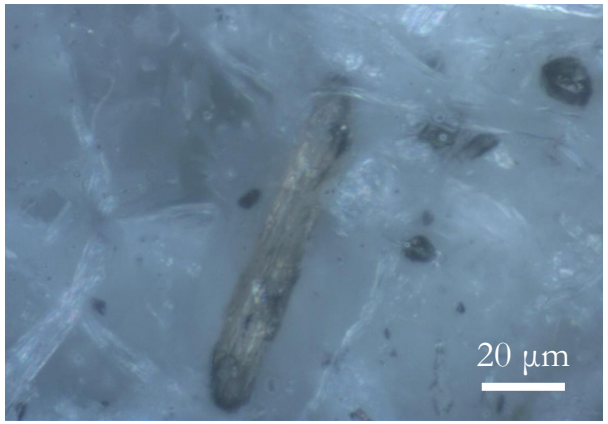
Incorporation of materials starts before differentiation

Treatment time

Iron compounds in Chrysotile from Balangero: a micro-Raman identification







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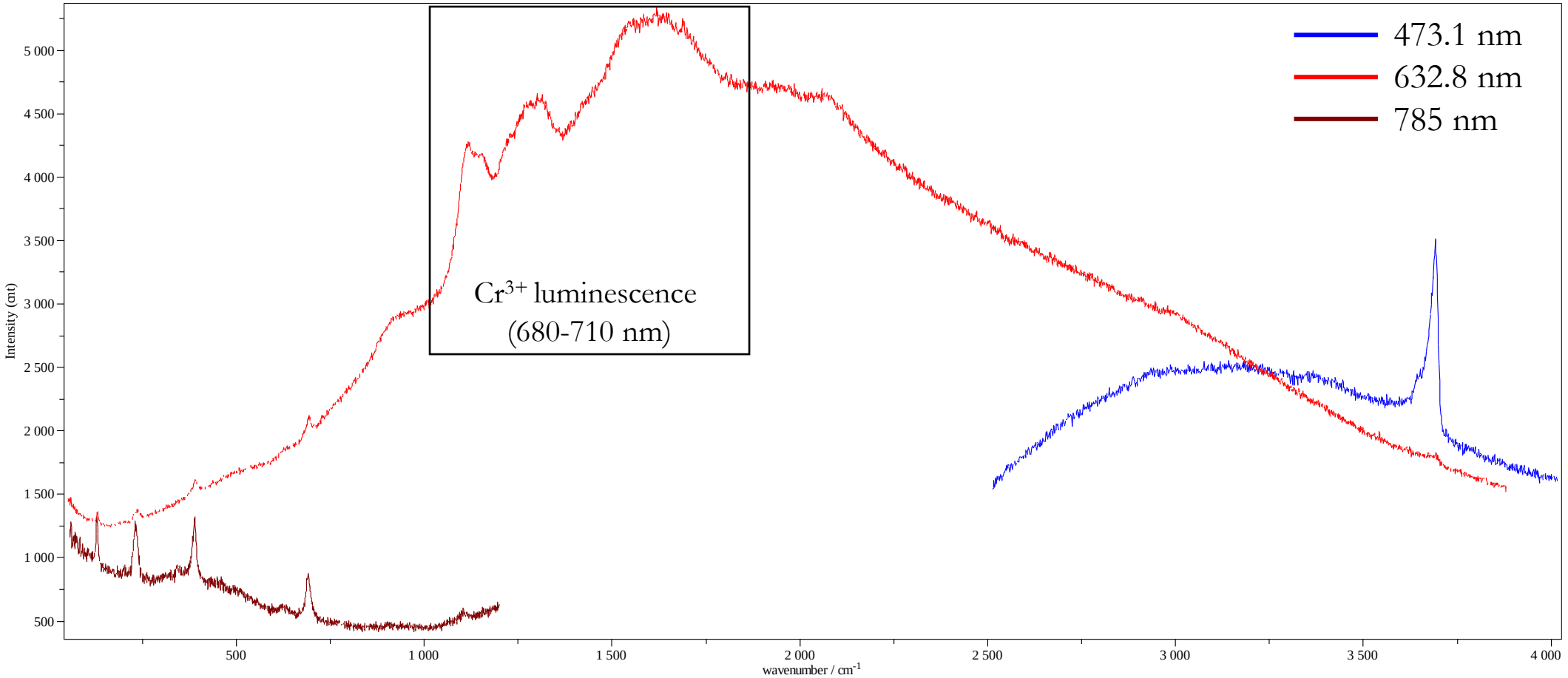
Abstract submitted to EMC2020 – 3rd European Mineralogical Conference (29/08 – 02/09/2021)

T5. Environmental mineralogy and low T geochemistry > T5-S2. Iron oxides and oxyhydroxides: petrology, environmental relevance and industrial applications

emc2020
3rd European Mineralogical Conference Cracow Poland
29 August - 2 September 2021

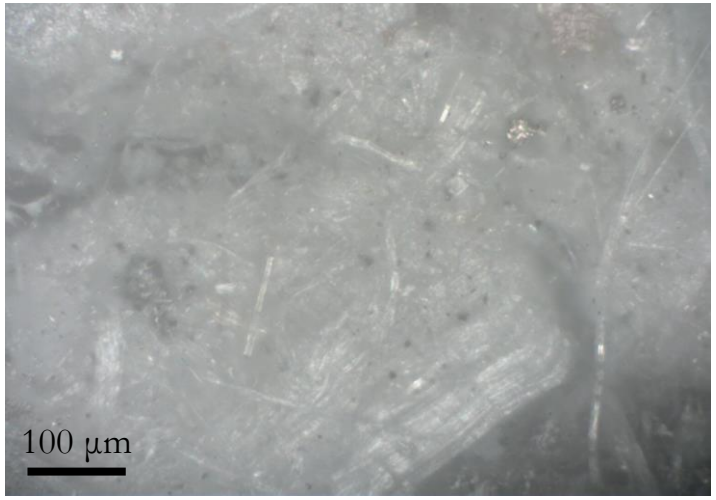
L. Fornasini, S. Raneri, D. Bersani, L. Mantovani, A. F. Gualtieri, *Manuscript to be submitted*

Chrysotile from Balangero: fibres and Cr^{3+} luminescence

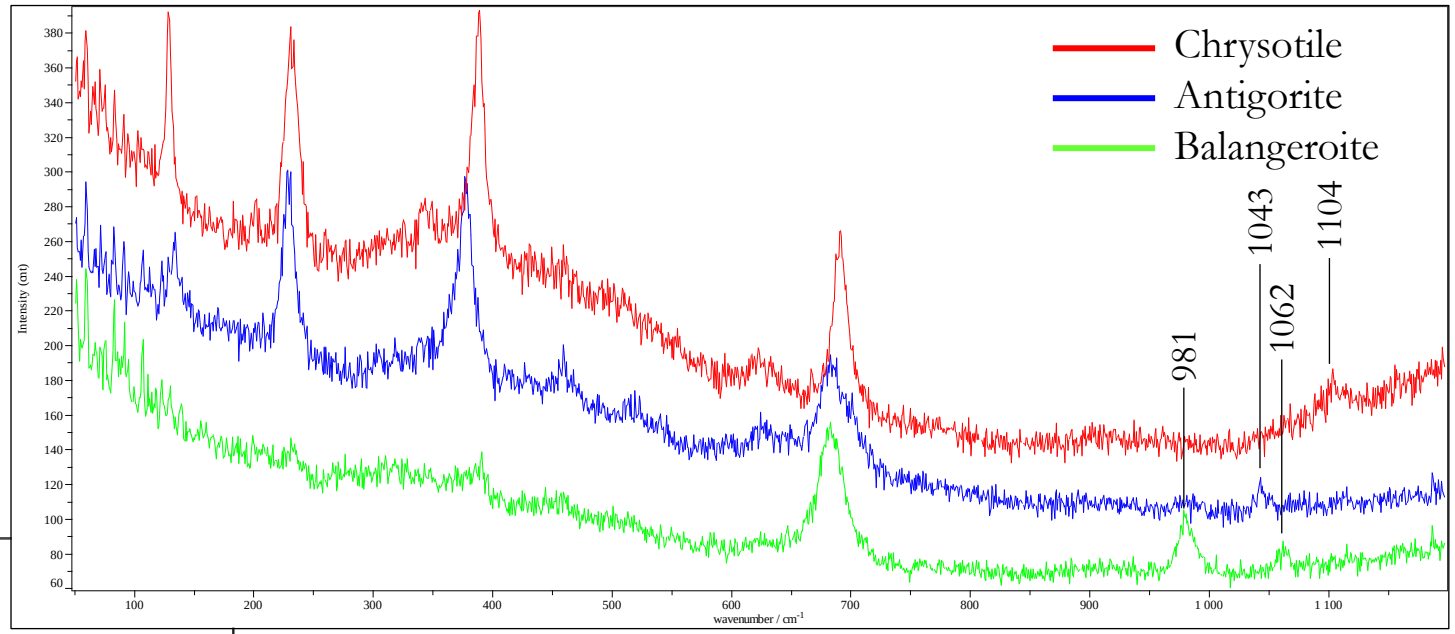


- Cr^{3+} luminescence between 680-710 nm (632.8 nm excitation)
- Low-wavenumber range signals in absence of luminescence contribution (785 nm excitation)
- Univocal OH stretching vibration modes of Ctl fibres (473.1 nm excitation)

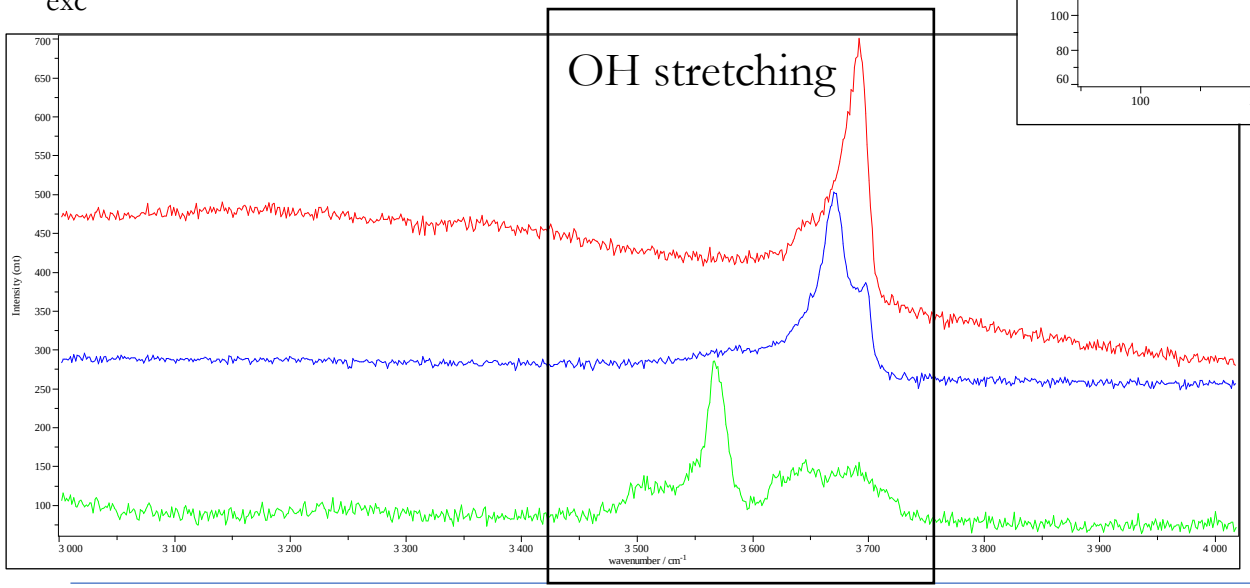
Fibrous phases: chrysotile, antigorite and balangeroite



λ_{exc}=785 nm

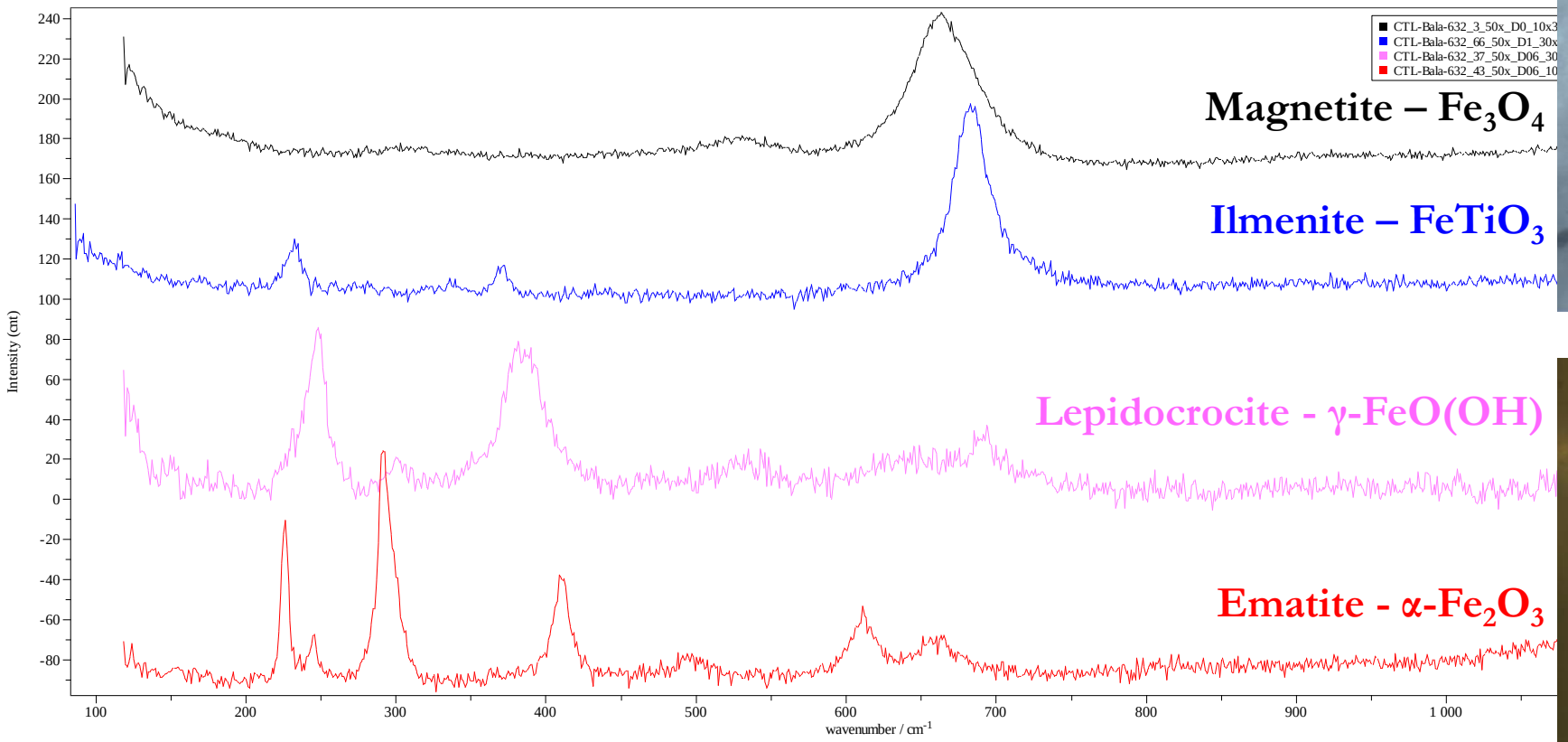


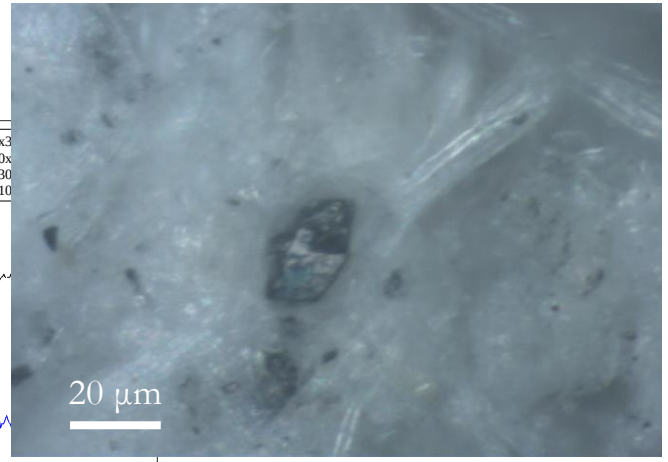
λ_{exc}=473.1 nm

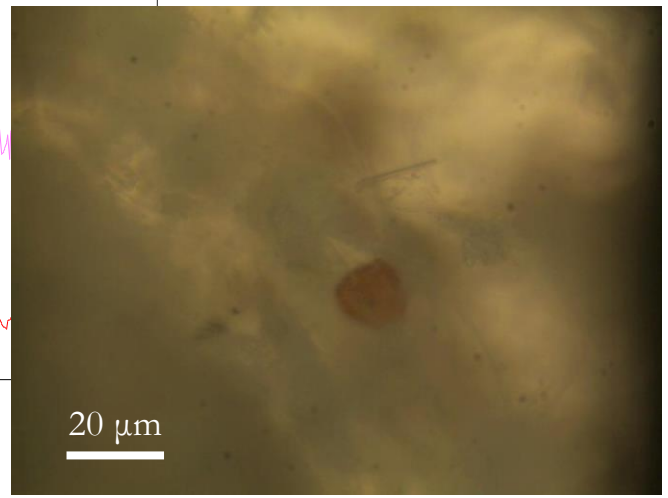


- Discrimination among chrysotile, antigorite and balangeroite signals
- Low-wavenumber range with slight shift positions, differences in the region around 1000-1100 cm^{-1}
- Univocal OH stretching vibration modes for the three different fibrous phases

Iron compounds in Chrysotile from Balangero: oxides and oxyhydroxides

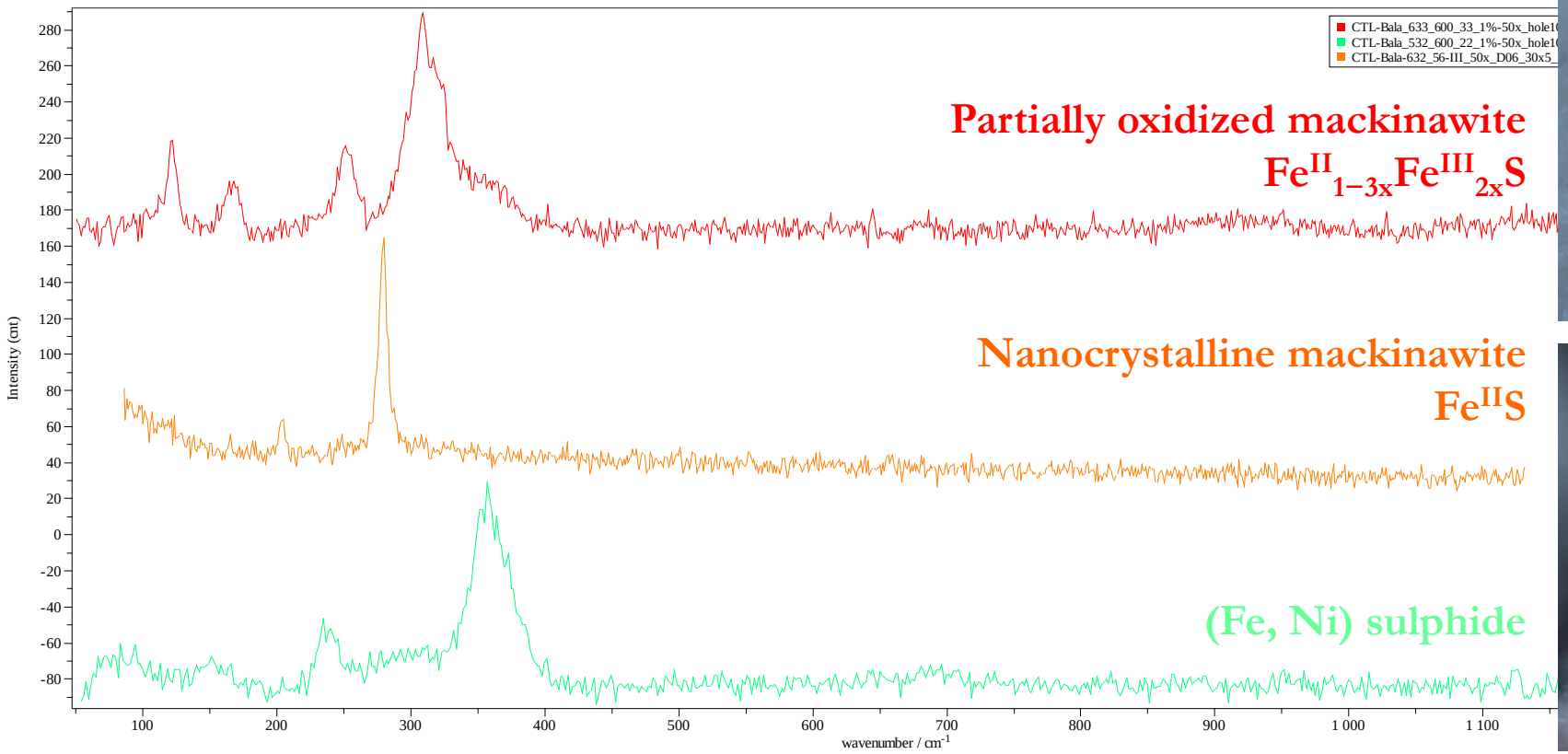


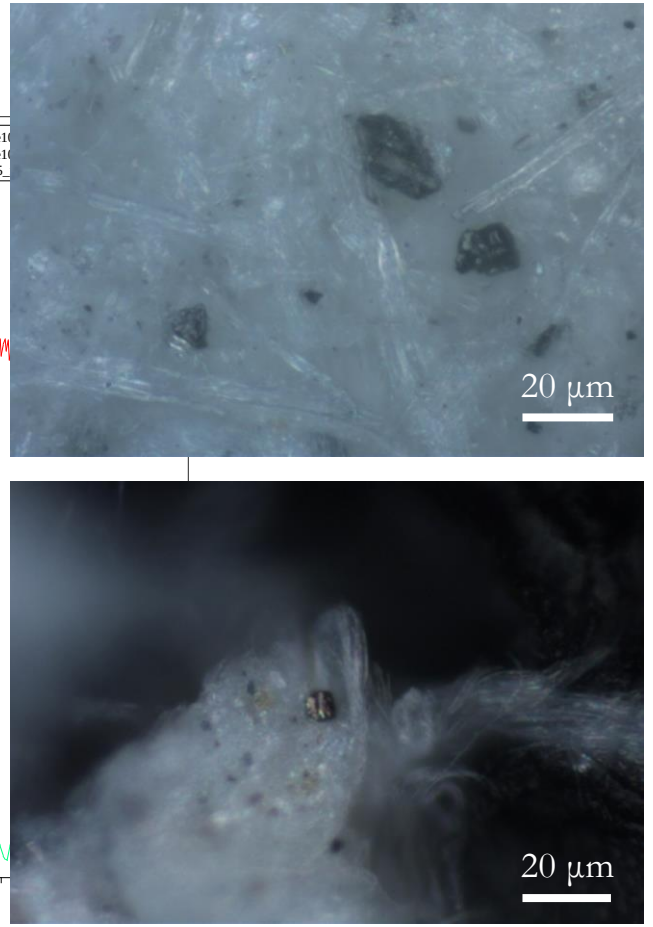




- Micrometric crystals (usually <10 µm) with reddish and blackish colours
- Identification of iron oxides as magnetite, ilmenite and hematite (rare) and iron oxyhydroxides as lepidocrocite (rare)
- Fe(II) and Fe(III) presence in iron oxides and oxyhydroxides

Iron compounds in Chrysotile from Balangero: sulphides



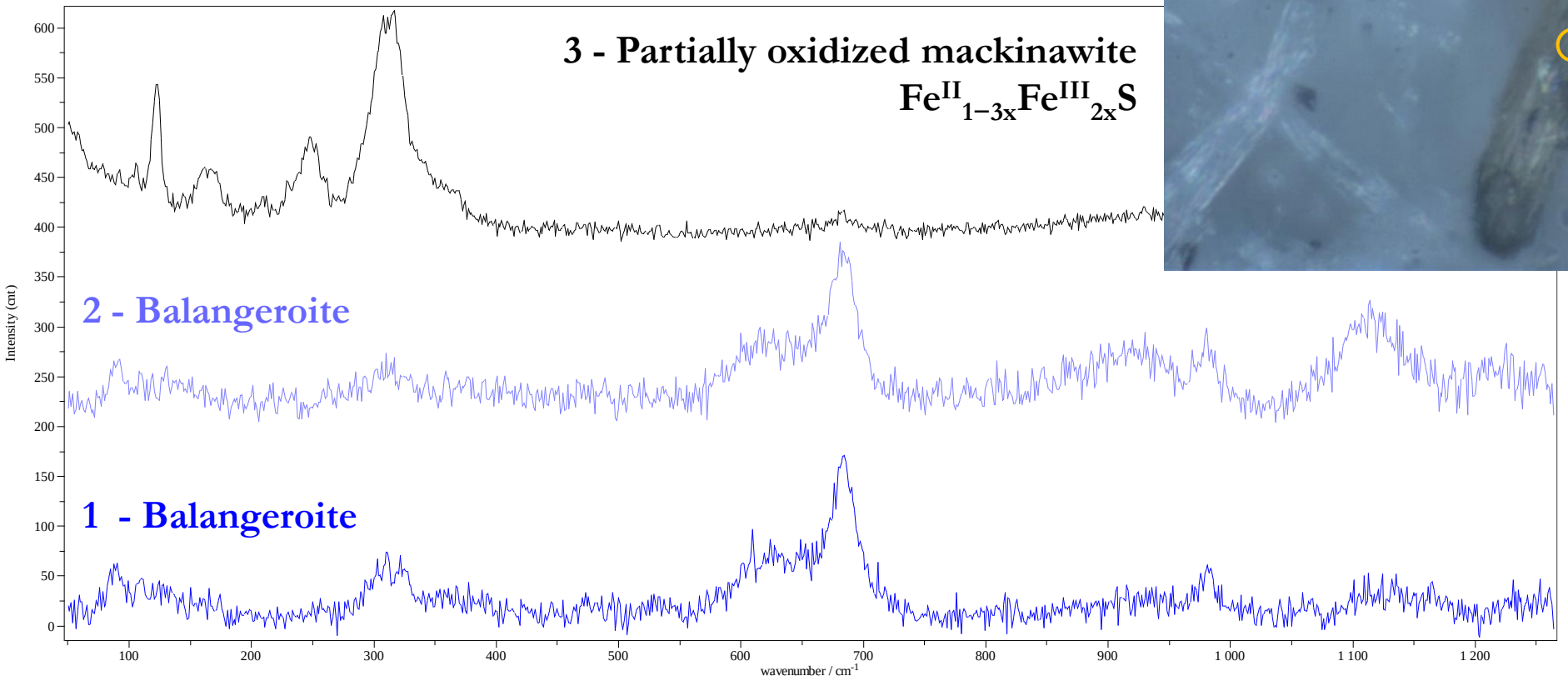


[1] Bourdoiseau J.-A. et al., *J. Raman Spectrosc.* 42 (2011) 496–504
[2] Bourdoiseau J.-A. et al., *Corrosion Science* 50 (2008) 3247–3255

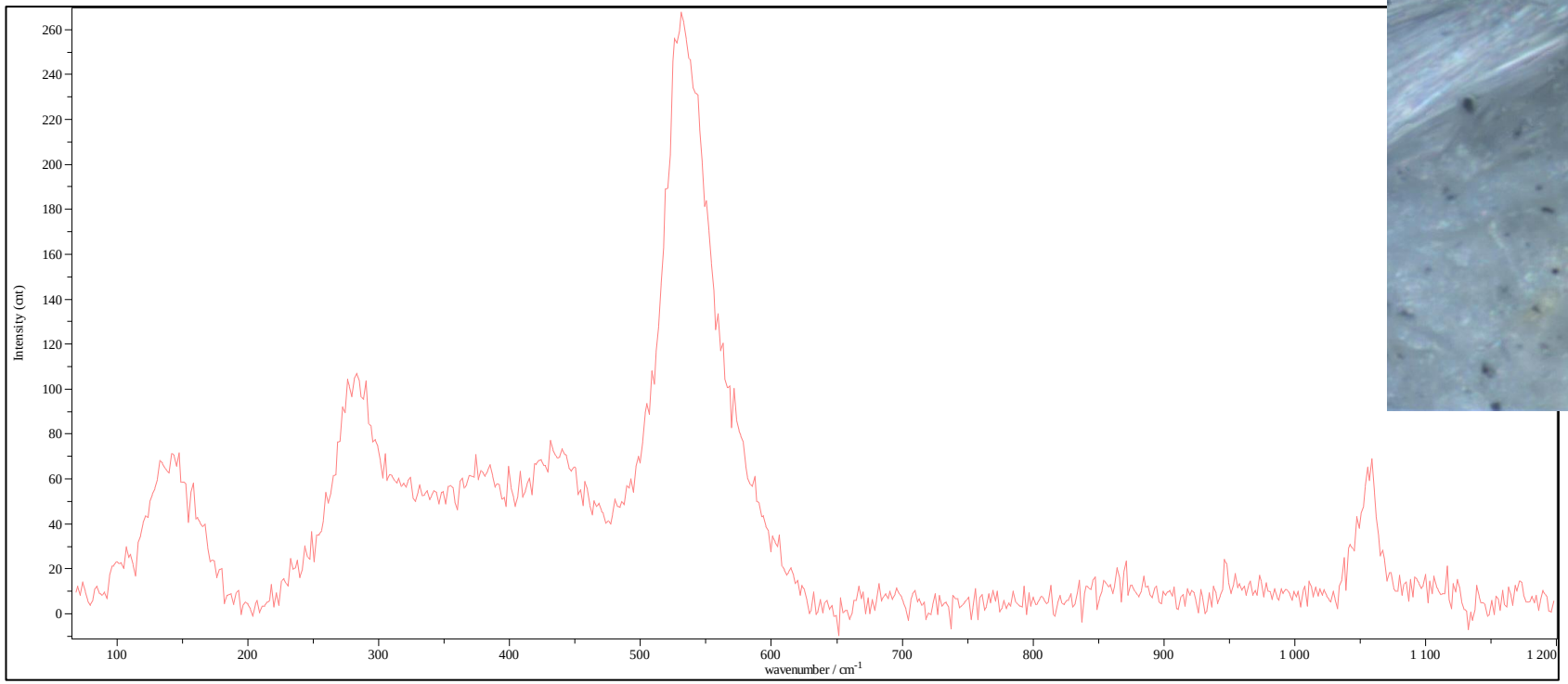
- Micrometric crystals (usually <10 µm) with blackish colour
- Identification of iron sulphides as mackinawite [1,2] and Fe-Ni sulphides (rare): S, Fe and Ni detected by SEM-EDS
- Mackinawite in different forms as nanocrystalline mackinawite and partially oxidized mackinawite [1,2]
- Fe(II) and Fe(III) presence in iron sulphides

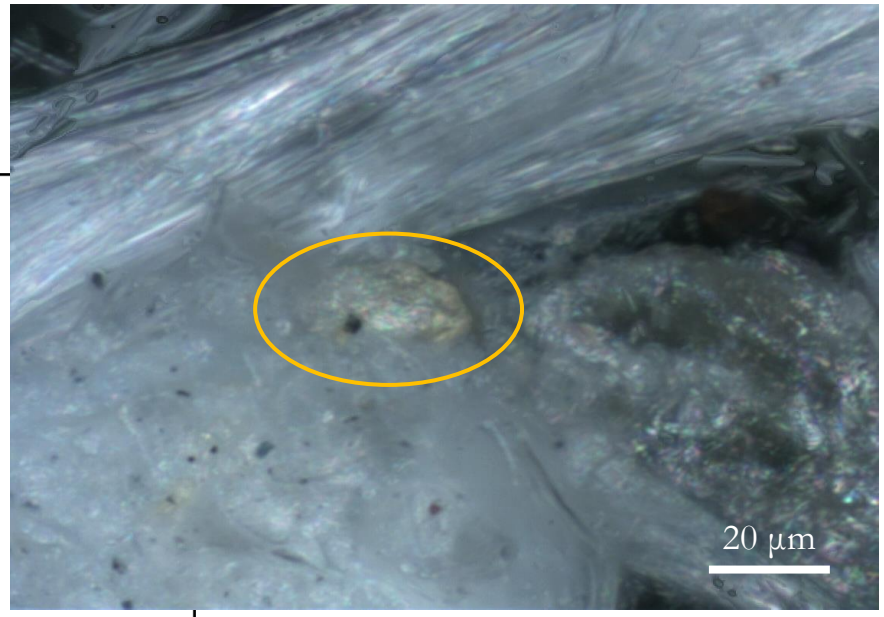
Iron compounds: sulphides mixed with fibres

- Identification of iron compounds also mixed with fibres, as shown for balangeroite and partially oxidized mackinawite



Iron compounds: carbonates





- Micrometric yellow crystals
- Probable carbonates containing Fe and Mg detected by SEM-EDS

As of today conclusions

Fibres-cell systems

- Fibres **phagocytosis** in THP1, not in A549
- Different **morphologies** among the 3 investigated fibres
- Presence of 3 fibrous phases in chrysotile systems: **chrysotile, antigorite and balangeroite**
- Accessory minerals in chrysotile systems in coloured micro-crystals: **iron oxides** and **sulphides**
- **Clusters of agglomerated materials** containing both fibres and cellular material, including dark coloured crystals
- Larger and denser clusters as treatment time increases
- Presence of clusters in not differentiated THP1: **materials is incorporated before the differentiation**

Iron compounds in Balangero chrysotile

- Fibres identification in chrysotile from Balangero: **chrysotile, antigorite and balangeroite**
- **Cr^{3+} luminescence** detected within the Raman spectra on the fibres
- **Micrometric crystals of iron compounds:** iron **oxides** and **oxyhydroxides** as magnetite, ilmenite, hematite and lepidocrocite; iron **sulphides** as mackinawite and (Fe, Ni) sulphide; iron **carbonates** containing Fe and Mg
- Fe(II) and Fe(III) presence in iron compounds: metals release to be considered in the reactivity and dissolution of asbestos fibres in the lungs.

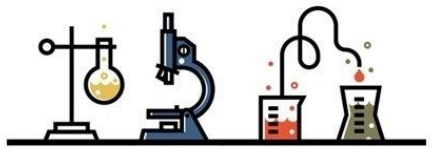
Work-in-progress and future analyses

- Iron compounds in chrysotile from Balangero: paper submission
- Investigation of changes in fibres at different treatment time of fibres-cells systems: analyses supporting the unit form University of Genova
- Iron distribution in clusters of fibres-cells systems through synchrotron analyses: next proposal for TwinMic beamline at Elettra - Trieste

Conferences partecipation

emc2020
3rd European Mineralogical Conference Cracow Poland
29 August - 2 September 2021

- L. Fornasini, D. Bersani, S. Raneri, A. F. Gualtieri, *Iron compounds identification by micro-Raman spectroscopy in chrysotile asbestos from Balangero,* abstract submitted to **EMC2020 - 3rd European Mineralogical Conference** (29/08 – 02/09/2021) – Online – T5. Environmental mineralogy and low T geochemistry > T5-S2. Iron oxides and oxyhydroxides: petrology, environmental relevance and industrial applications



Acknowledgements

Simona Raneri, Istituto di Chimica dei Composti OrganoMetallici, CNR-ICCOM Pisa
Danilo Bersani, Dipartimento di Scienze Matematiche, Fisiche e Informatiche - UNIPR
Anna Maria Bassi, Dipartimento di Medicina Sperimentale - UNIGE
Sonia Scarfì, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita - UNIGE
Vanessa Almonti, Dipartimento di Medicina Sperimentale - UNIGE
Serena Mirata, Dipartimento di Scienze della Terra, dell'Ambiente e della Vita – UNIGE
Barbara Marengo, Dipartimento di Medicina Sperimentale – UNIGE
Alessandro Francesco Gualtieri, Dipartimento di Scienze Chimiche e Geologiche - UNIMORE
Dario Di Giuseppe, Dipartimento di Scienze Chimiche e Geologiche - UNIMORE
Luciana Mantovani, Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale – UNIPR
Matteo Masino, Dipartimento di Scienze Chimiche, della Vita e della Sostenibilità Ambientale – UNIPR

Thank you for the attention