

# PRIN: PROGETTI DI RICERCA DI RILEVANTE INTERESSE NAZIONALE

Bando 2017 - Prot. 20173X8WA4

FIBRES: a multidisciplinary mineralogical, crystal-chemical and biological project to amend the paradigm of toxicity and cancerogenicity of mineral fibres



1506  
UNIVERSITÀ  
DEGLI STUDI  
DI URBINO  
CARLO BO

Riunione del 29 giugno 2021  
Unità di Urbino



## Contributo al progetto generale

Caratterizzazione chimico-fisica della fibra selezionata (crisotilo russo) per la raccolta dei parametri per il modello FPTI e classificazione: **analisi EPR**

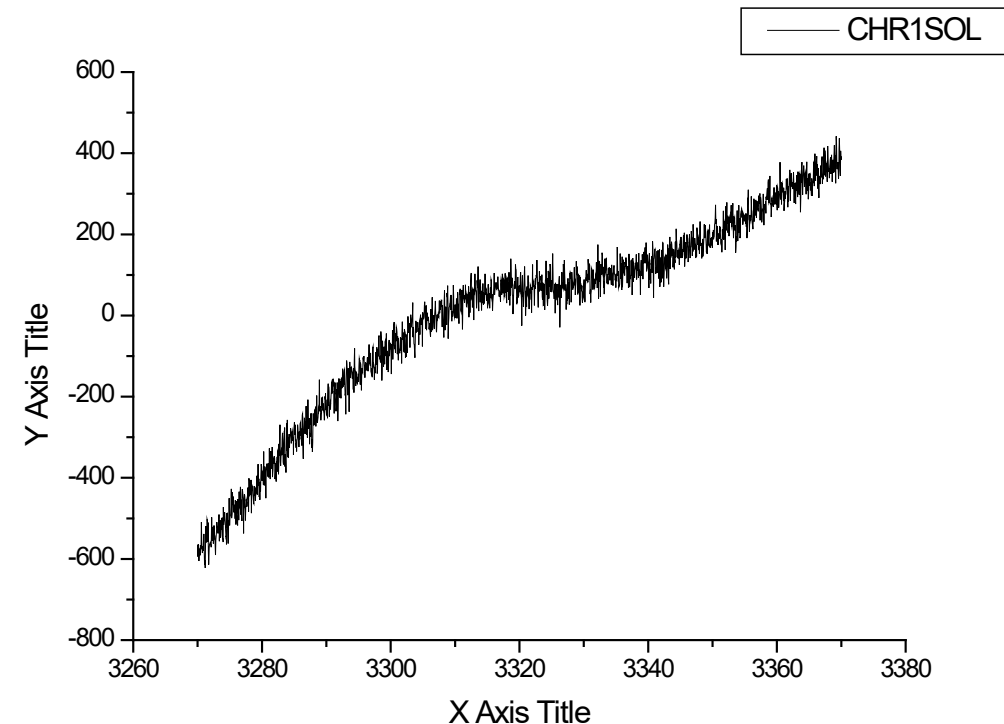
Le analisi EPR condotte per il campione di crisotilo russo (CHR1) sono state effettuate seguendo le procedure di interazione con sonde nitrossido già impiegate in studi precedenti sulle zeoliti fibrose (Mattioli et al., 2016 JHM; Gualtieri et al., 2018 AM MIN)

- interazione del solido previo trattamento di riduzione con soluzioni acquose 1mM di sonde (CAT1, CAT8, TOH) per 24h sotto agitazione meccanica
- campione suddiviso in surnatante e solido asciugato su carta filtro
- analisi in EPR

## Contributo al progetto generale

Caratterizzazione chimico-fisica della fibra selezionata (crisotilo russo) per la raccolta dei parametri per il modello FPTI e classificazione: **analisi EPR**

Purtroppo gli spettri dei solidi non presentano alcun segnale riconducibile a specie nitrossido, probabilmente a causa di un segnale preponderante relativo a impurità del campione (ossidi di ferro?) che copre il segnale della sonda, come si può evincere dallo spettro a fianco.



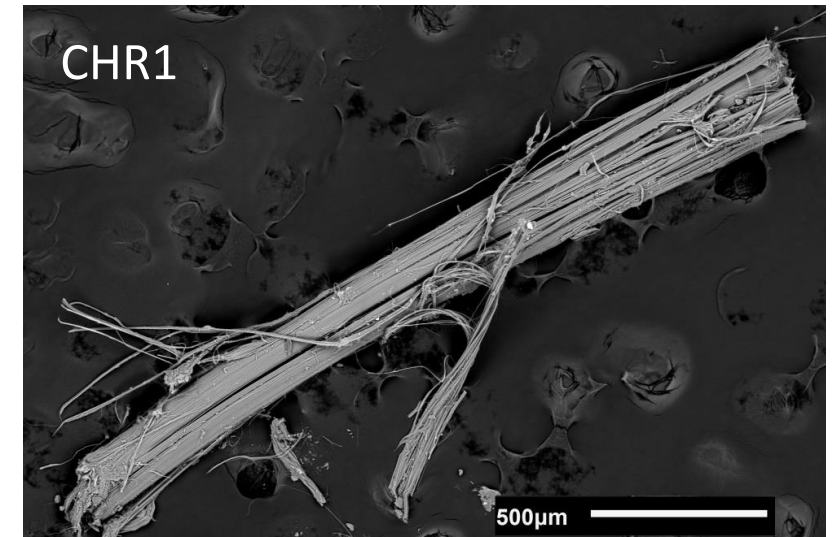
## Contributo al progetto generale

### Caratterizzazione chimico-fisica della fibra selezionata (crisotilo russo) per la raccolta dei parametri per il modello FPTI e classificazione: analisi EPR

Non è stato possibile prelevare la soluzione surnatante in quanto il campione adsorbe l'intero quantitativo di soluzione rigonfiandosi.

Sono in corso valutazioni e ulteriori prove sperimentali con altre sonde paramagnetiche idrofobe e solventi non acquosi, e prove di cinetica in funzione della concentrazione delle specie paramagnetiche.

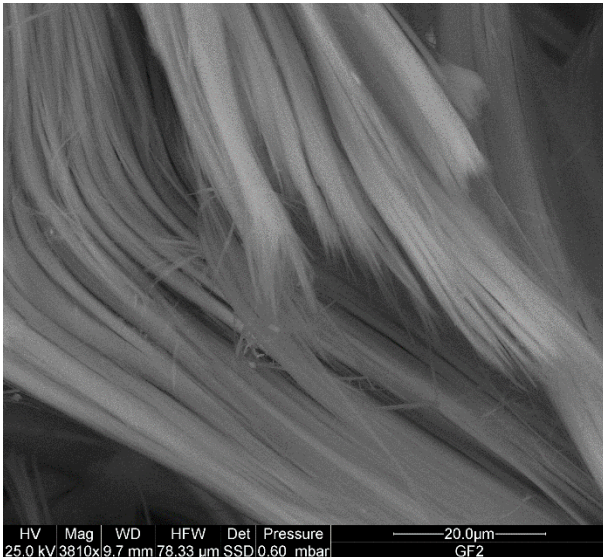
Non disperiamo ancora...



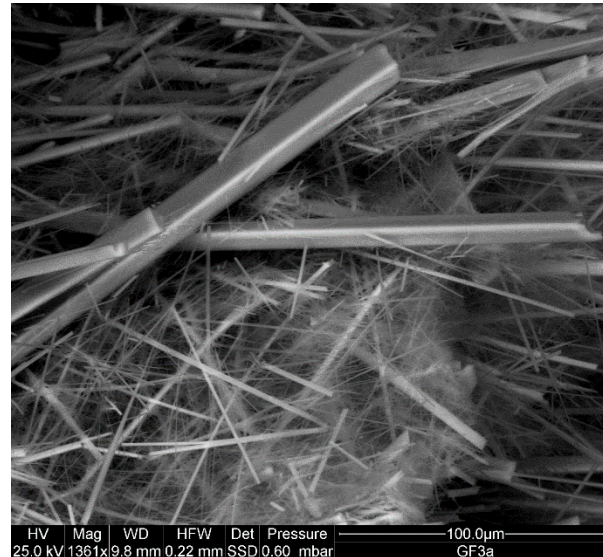
## Sottoprogetti unità locale

### 1. Caratterizzazione chimico-fisica-mineralogica di zeoliti fibrose: mesolite-thomsonite-erionite

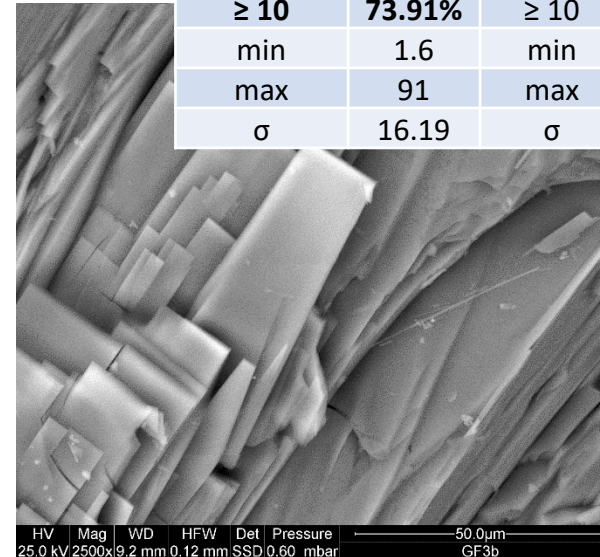
#### *Morfologia e morfometria*



GF2 - Erionite



GF3a - Mesolite



GF3b - Thomsonite

Erionite (GF2)		Mesolite (GF3a)		Thomsonite (GF3b)	
Width (µm)		Width (µm)		Width (µm)	
≤0.5	80.44%	≤0.5	88.40%	≤0.5	1.49%
0.6-1.0	13.91%	0.6-1.0	10.20%	0.6-1.0	5.95%
> 1.1	5.65%	> 1.1	1.40%	> 1.1	92.57%
min	0.1	min	0.1	min	0.4
max	2.7	max	1.3	max	17
σ	0.35	σ	0.21	σ	3.73
Lenght (µm)		Lenght (µm)		Lenght (µm)	
≤ 4.9	5.22%	≤ 4.9	49.80%	≤ 4.9	7.43%
5 - 9.9	20.87%	5 - 9.9	41.20%	5 - 9.9	25.28%
≥ 10	73.91%	≥ 10	9%	≥ 10	67.29%
min	1.6	min	1.4	min	2
max	91	max	22	max	80
σ	16.19	σ	3.78	σ	21.56

$D_{ae} = 0.82 \mu\text{m}$   
GF3a (mesolite)

## Sottoprogetti unità locale

**1. Caratterizzazione  
chimico-fisica-mineralogica di zeoliti  
fibrose: mesolite-thomsonite-erionite**

*Composizione chimica  
EMPA e SEM  
(in collaborazione con  
Paolo Ballirano UniRoma1)*

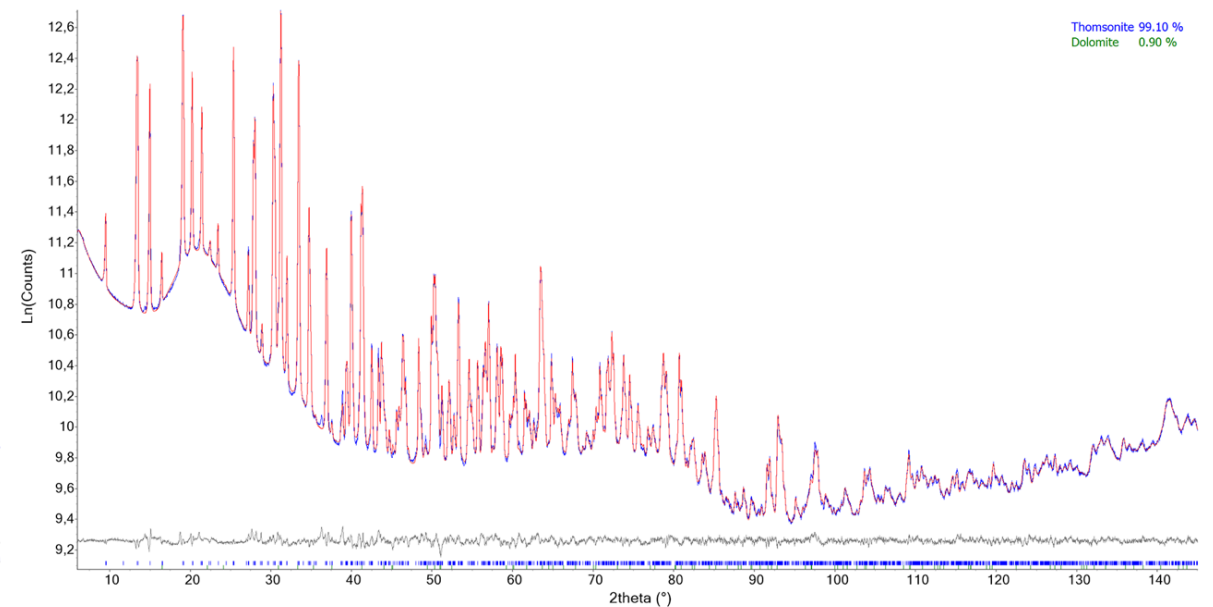
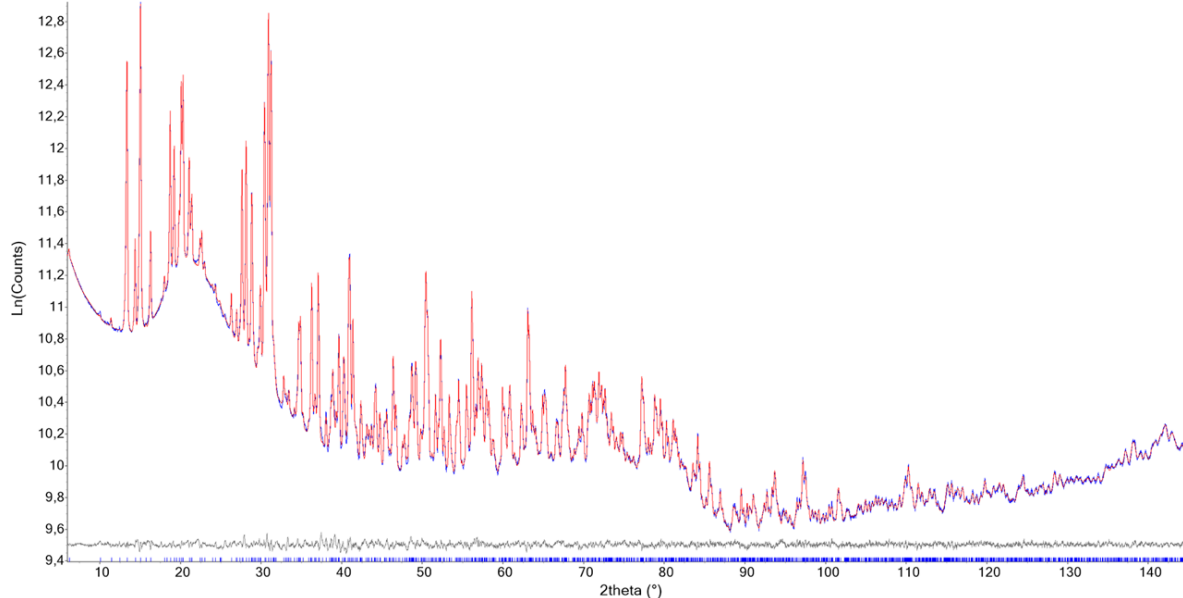
	Mesolite		Thomsonite		Erionite	
	EMPA	SEM	EMPA	SEM	EMPA	SEM
SiO <sub>2</sub>	46.29(32)	45.30(51)	40.95(61)	39.94(76)	59.55(82)	58.57(15)
Al <sub>2</sub> O <sub>3</sub>	25.20(22)	26.23(34)	28.28(39)	29.53(47)	16.79(28)	17.86(10)
CaO	9.68(12)	11.17(15)	11.47(32)	12.71(218)	3.45(12)	3.10(5)
MgO	0	0	0	0	1.73(4)	1.71(11)
K <sub>2</sub> O	0	0	0	0	3.43(5)	3.46(5)
Na <sub>2</sub> O	5.11(9)	3.23(74)	5.14(22)	3.37(152)	1.28(39)	1.13(4)
H <sub>2</sub> O*	14.06(50)	14.06(0)	14.45(69)	14.45(0)	14.15(82)	14.15(0)
Total	100.34	100.00	100.29	100.00	100.38	100.00
Si	73.08(24)	71.28(12)	22.04(24)	21.36(26)	27.01(7)	26.47
Al	46.92(24)	48.72(12)	17.96(24)	18.64(26)	8.99(7)	9.53
Ca	16.40(16)	18.88(21)	6.62(20)	7.30(132)	1.68(4)	1.50
Mg	0	0	0	0	1.17(3)	1.16
K	0	0	0	0	1.99(2)	2.00
Na	15.64(28)	9.88(22)	5.36(20)	3.48(154)	1.14(36)	0.99
H <sub>2</sub> O	74.2(31)	73.96(88)	26.00(146)	25.84(32)	21.47(156)	21.37
O	240.76(12)	239.44(43)	80.32(6)	79.72(62)	71.91(17)	71.39
R	0.609(2)	0.594(1)	0.551(6)	0.534(6)	0.750(2)	0.735
M/(M+D)	0.489(6)	0.34(7)	0.448(16)	0.32(13)	0.52(3)	0.53
E%	-3.10	2.70	-3.48	3.40	2.07	14.6



## Sottoprogetti unità locale

### 1. Caratterizzazione chimico-fisica-mineralogica di zeoliti fibrose: mesolite-thomsonite-erionite

*XRPD e raffinamento strutturale (in collaborazione con Paolo Ballirano UniRoma1)*



## Sottoprogetti unità locale

### 1. Caratterizzazione chimico-fisica-mineralogica di zeoliti fibrose: mesolite-thomsonite-erionite

*XRPD e raffinamento strutturale (in collaborazione con Paolo Ballirano UniRoma1)*

	Mesolite	Thomsonite	Erionite
R <sub>Bragg</sub> (%)	0.44	1.15	1.03
R <sub>p</sub> (%)	1.38	1.95	2.20
R <sub>WP</sub> (%)	1.85	2.60	3.23
Space group	Fdd2	Pcnn	P6 <sub>3</sub> /mmc
a (Å)	18.41604(16)	13.06918(15)	13.2792(3)
b (Å)	56.6812(5)	13.08398(15)	= a
c (Å)	6.54882(6)	13.19143(12)	15.0798(4)
Vol. (Å <sup>3</sup> )	6835.94(11)	2255.69(4)	2302.87(11)

Mesolite			
	s.s. from ref.	partition from ref.	EF cations EMPA
Na1	182.6(13)	Ca <sub>0.736</sub> Na <sub>15.264</sub>	
Ca1	294.1(11)	Ca <sub>13.088</sub> Na <sub>2.912</sub>	
Tot.	477(2)	Ca <sub>13.824</sub> Na <sub>18.176</sub>	Ca <sub>16.40(16)</sub> Na <sub>15.64(28)</sub>
Thomsonite			
	s.s. from ref.	partition from ref.	EF cations EMPA
Na1	113.3(4)	Ca <sub>2.808</sub> Na <sub>5.192</sub>	
Ca1	77.4(3)	Ca <sub>3.708</sub> Na <sub>0.292</sub>	
Tot.	190.7(7)	Ca <sub>6.516</sub> Na <sub>5.484</sub>	Ca <sub>6.62(20)</sub> Na <sub>5.36(20)</sub>
Erionite			
	s.s. from ref.	partition from ref.	EF cations EMPA
Ca1	38.3(15)	Mg <sub>1.170</sub> Na <sub>2.205</sub>	
Ca2	19.7(10)	Ca <sub>0.645</sub> Na <sub>0.618</sub>	
Ca3	20.7(14)	Ca <sub>1.035</sub>	
K1	38.0(0)	K <sub>2.00</sub>	
Tot.	117(4)	Ca <sub>1.680</sub> Mg <sub>1.170</sub> K <sub>2.000</sub> Na <sub>2.823</sub>	Ca <sub>1.68(4)</sub> Mg <sub>1.17(3)</sub> K <sub>1.99(2)</sub> Na <sub>1.14(36)</sub>

## Sottoprogetti unità locale

### 1. Caratterizzazione chimico-fisica-mineralogica di zeoliti fibrose: mesolite-thomsonite-erionite

*Dati BET* (surface area, pore volume and pore size)  
(in collaborazione con Dario Di Giuseppe, Valentina Scognamiglio, Miriam Hanuskova, Alessandro F. Gualtieri - UniMore)

BET surface area decreases in the following order:  
**erionite > mesolite > thomsonite.**

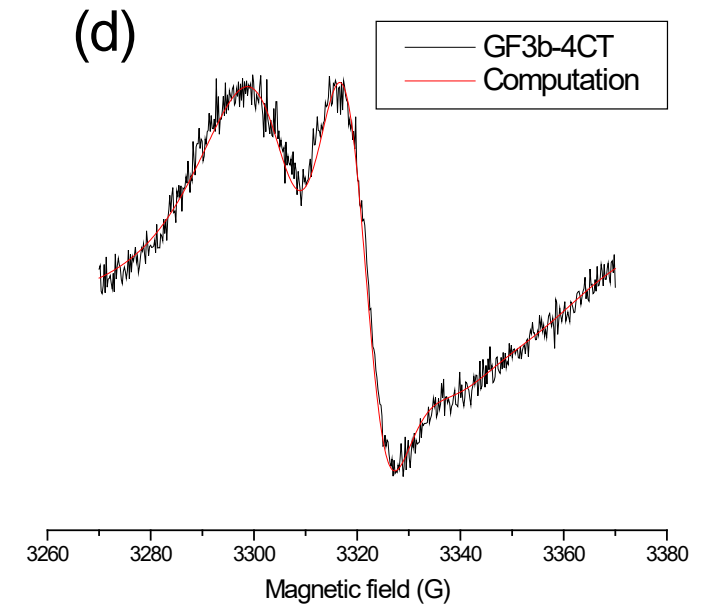
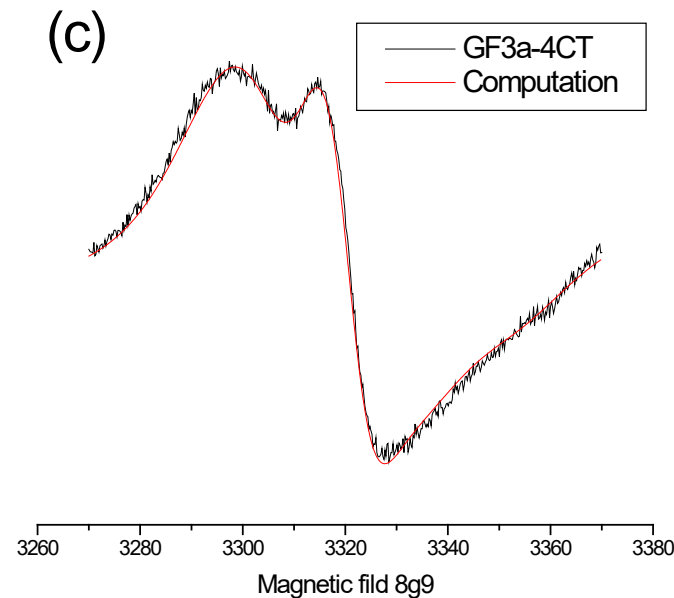
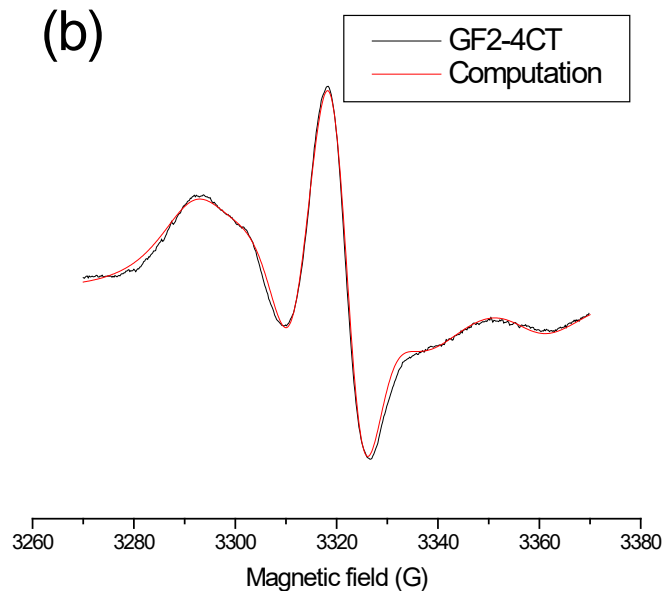
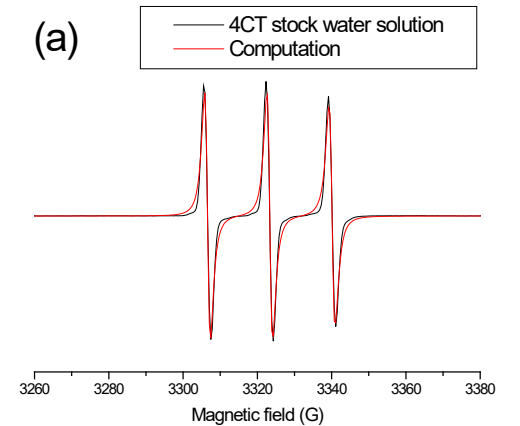
Conversely, the pore volume and pore size decrease in the following order:  
**mesolite > erionite > thomsonite**

	ERIONITE (GF2)	MESOLITE (GF3a)	THOMSONITE (GF3b)
<b>SURFACE AREA</b>			
BET Surface Area (m <sup>2</sup> /g)	<b>8.1439</b>	1.5519	0.3841
t-plot External Surface Area (m <sup>2</sup> /g)	<b>9.1885</b>	1.999	0.4984
Single point surface area at p/p° (m <sup>2</sup> /g)	<b>7.7073</b>	1.4051	0.3478
<b>PORE VOLUME</b>			
Single point adsorption total pore volume of pores (cm <sup>3</sup> /g)	0.053949	0.517325	0.001036
t-plot micropore volume (cm <sup>3</sup> /g)	-0.000658	-0.000279	-0.000068
<b>PORE SIZE</b>			
Adsorption average pore width (4V/A by BET) (Å)	264.9796	313.2088*	107.9395
BJH Adsorption average pore width (4 V/A) (Å)	233.029	299.249	109.047

## Sottoprogetti unità locale

### 1. Caratterizzazione chimico-fisica-mineralogica di zeoliti fibrose: mesolite-thomsonite-erionite

*Dati EPR* (4CT probe in water solution (a) and adsorbed in different zeolites (b, c, d))

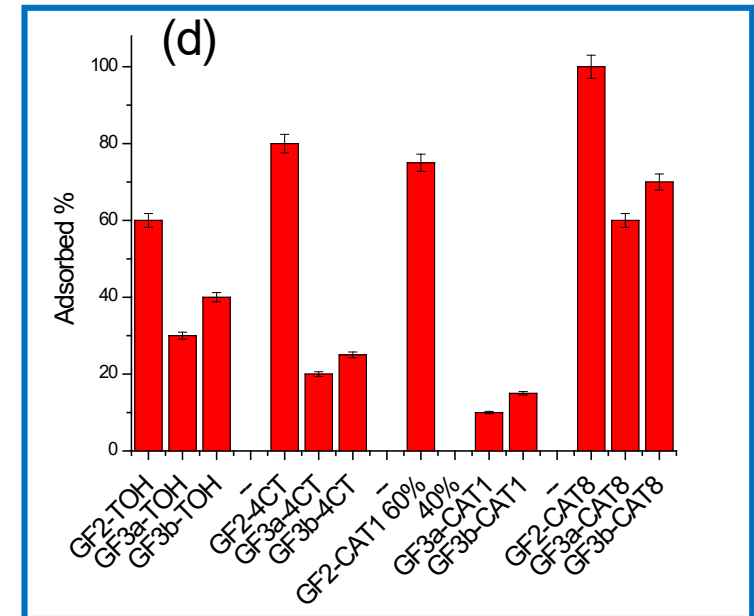
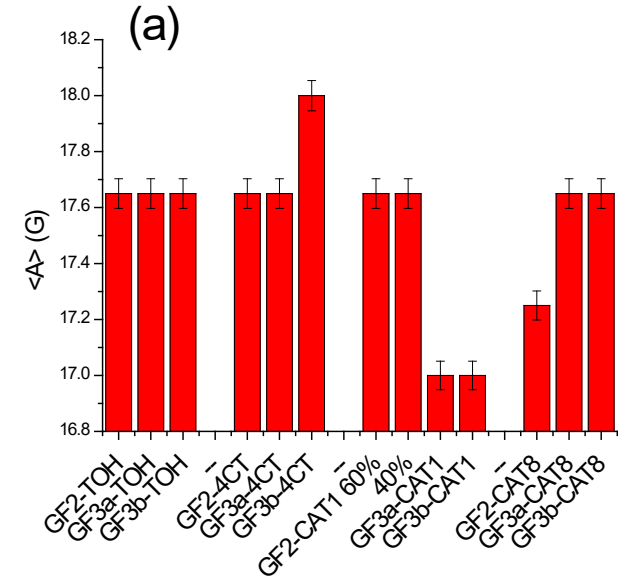
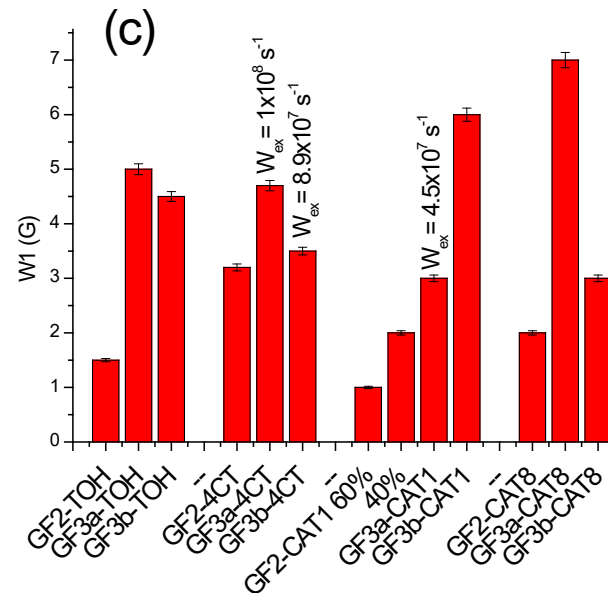
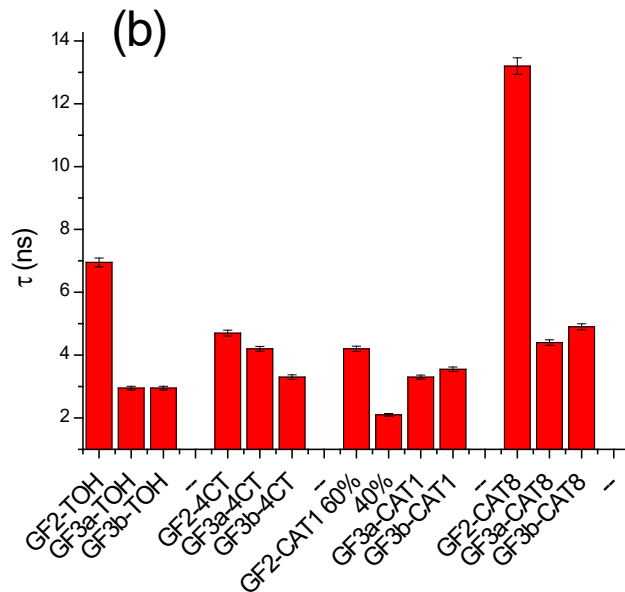




## Sottoprogetti unità locale

### 1. Caratterizzazione chimico-fisica-mineralogica di zeoliti fibrose: mesolite-thomsonite-erionite

*Dati EPR* (Histograms comparing the polarity parameter)



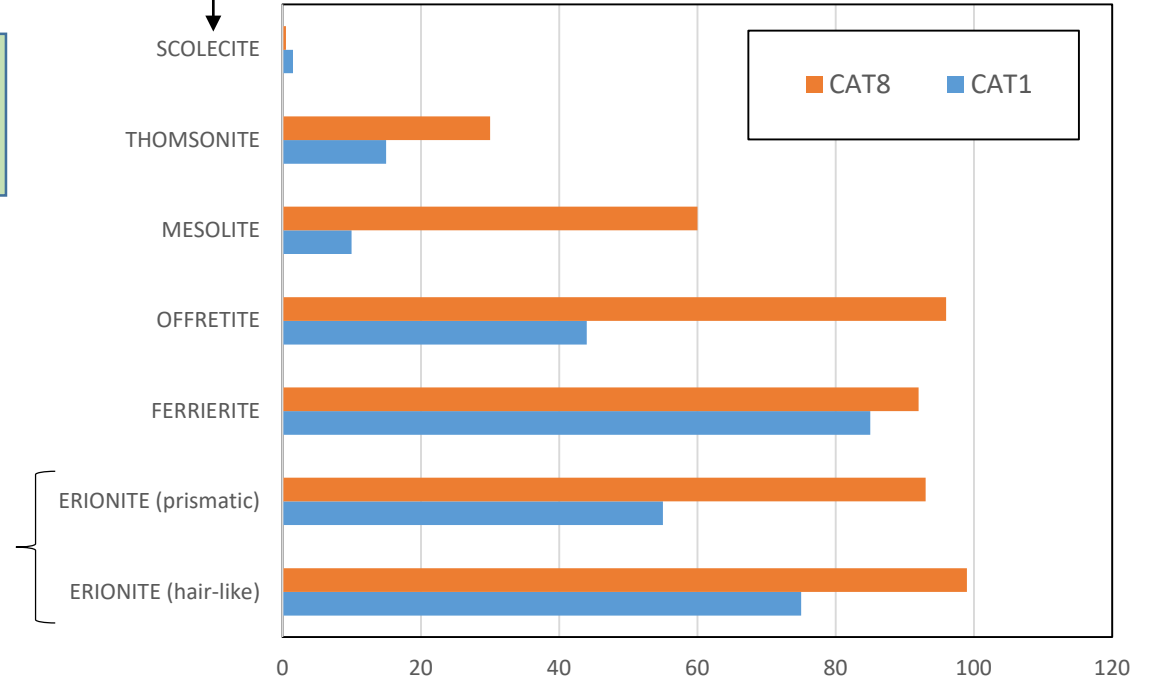
## Sottoprogetti unità locale

### 1. Caratterizzazione chimico-fisica-mineralogica di zeoliti fibrose: mesolite-thomsonite-erionite

% di sonda adsorbita: confronto con altre zeoliti fibrose (dati da Mattioli et al., 2016; Gualtieri et al., 2018)

«positive» carcinogenic erionite

«negative» carcinogenic scolecite



*Manoscritto pronto per la sottomissione*

## Characterization, interaction capability and potential toxicity of fibrous zeolites erionite, mesolite and thomsonite

Matteo Giordani<sup>a</sup>, Michele Mattioli<sup>a</sup>, Michela Cangiotti<sup>a</sup>, Alberto Fattori<sup>a</sup>, Maria Francesca Ottaviani<sup>a</sup>, Michele Betti<sup>b</sup>, Paolo Ballirano<sup>c</sup>, Alessandro Pacella<sup>c</sup>, Dario Di Giuseppe<sup>d</sup>, Valentina Scognamiglio<sup>d</sup>, Miriam Hanuskova<sup>e</sup>, Alessandro F. Gualtieri<sup>d</sup>

## Sottoprogetti unità locale

### 2. Effetti di cito-tossicità in vitro di zeoliti fibrose: mesolite-thomsonite-erionite

Suspension & Adherent Cell Culture (Jurkat and HT-22)

**Jurkat cells** are an immortalized line of human T lymphocyte cells. Their primary use is to determine the mechanism of differential susceptibility of cancers to drugs and radiation. Round cells growing singly or in clumps in suspension. Doubling time is about 25-35 hours

**HT-22** is an immortalized mouse hippocampal cell line and their primary use is a valuable cell model for studies of toxicity in neuronal cells. Adherent cells growing singly. Doubling time is about 22 hours.

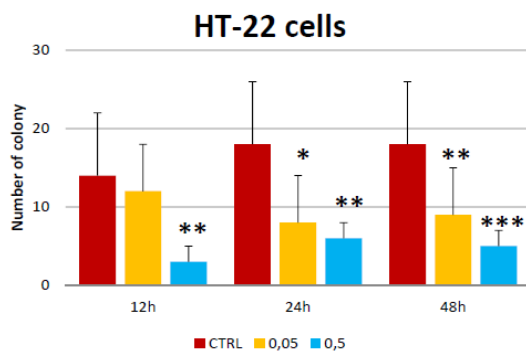
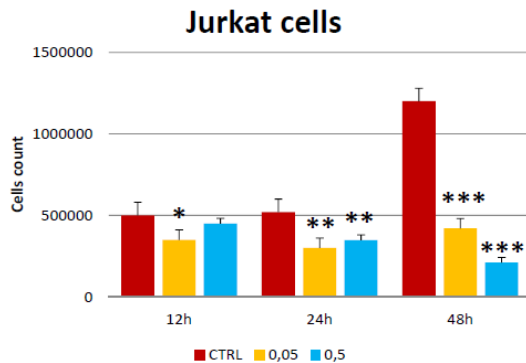
Cells treatment was carried out using 3 different concentrations (5, 0,5 and 0,05 mg/mL) for 3 different incubation times (12, 24 and 48h), according to literature.



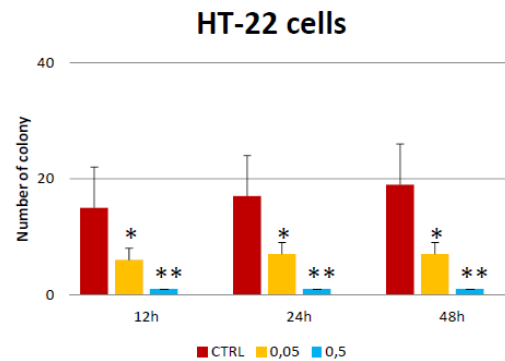
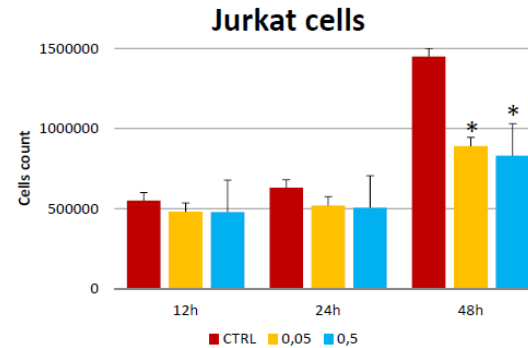
# Sottoprogetti unità locale

## 2. Effetti di cito-tossicità in vitro di zeoliti fibrose: mesolite-thomsonite-erionite

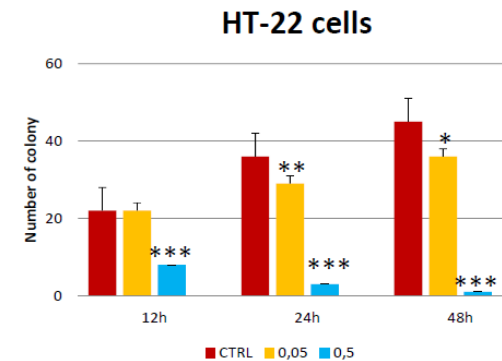
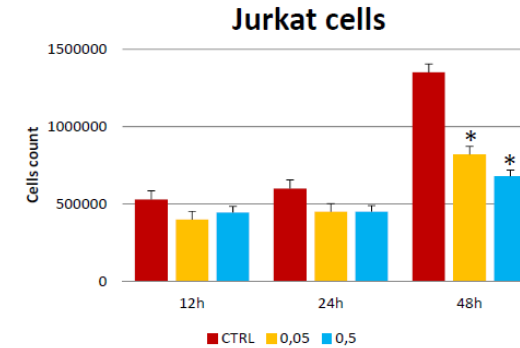
### Fibrous erionite (GF2)



### Mesolite (GF3A)



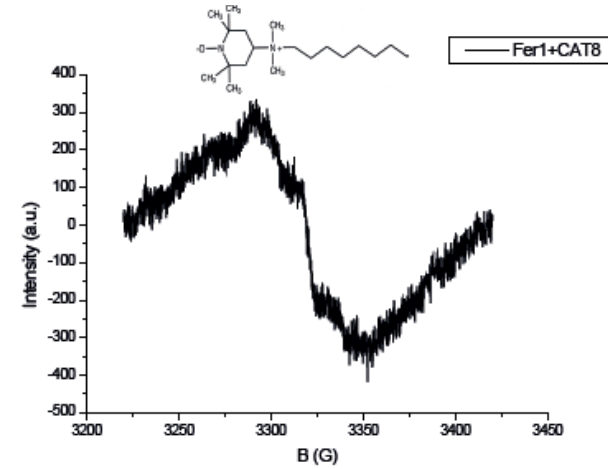
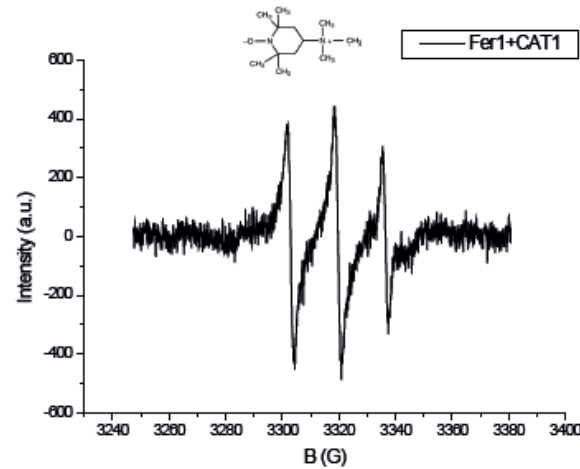
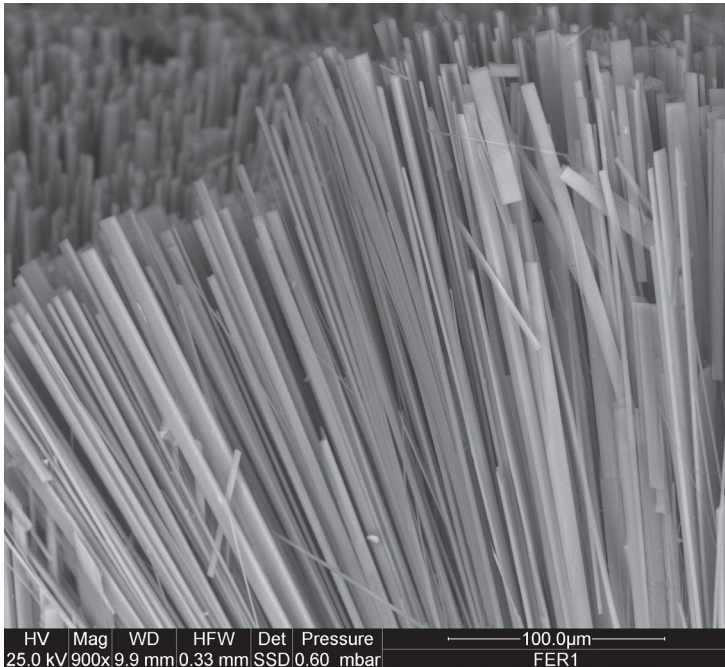
### Thomsonite (GF3B)





## Sottoprogetti unità locale

### 3. Caratterizzazione di nuovi campioni di zeoliti fibrose: Mg-ferrierite (Lessini)



SiO <sub>2</sub>	66,81
Al <sub>2</sub> O <sub>3</sub>	11,98
FeO	1,68
MgO	2,73
CaO	1,08
K <sub>2</sub> O	2,13
H <sub>2</sub> O	13,6

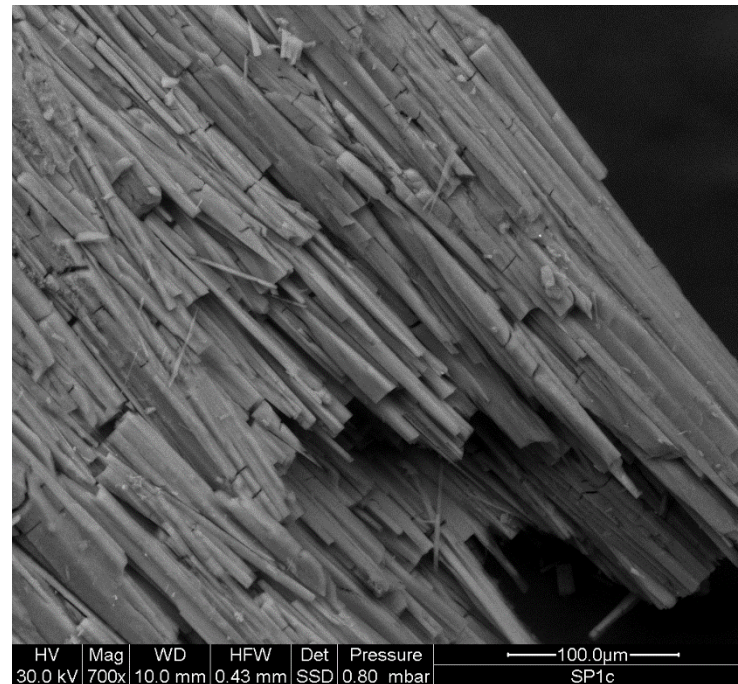
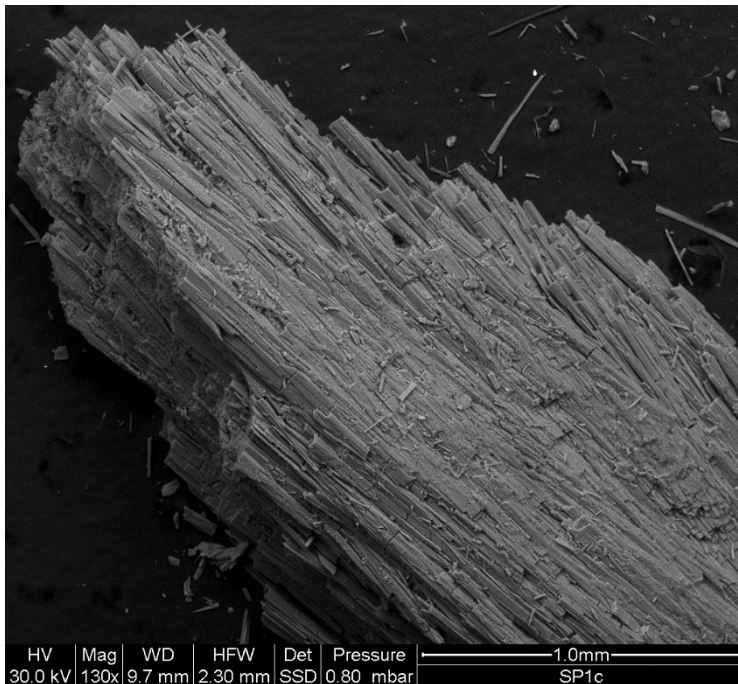
EPR spectra of the solid particles after adsorption of CAT1 and CAT8 probes

Major elements concentration (wt%) by EMPA

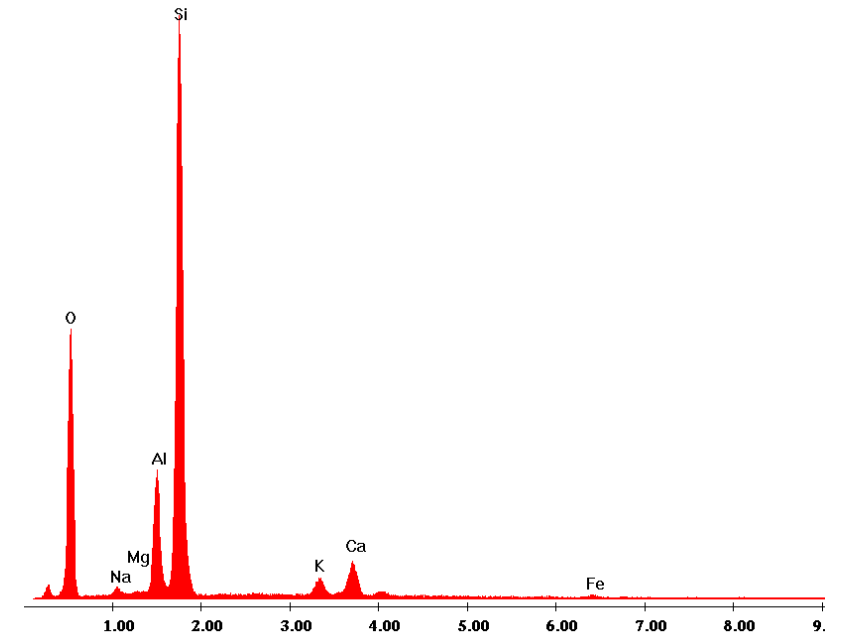


## Sottoprogetti unità locale

### 3. Caratterizzazione di nuovi campioni di zeoliti fibrose: mordenite (Lessini)



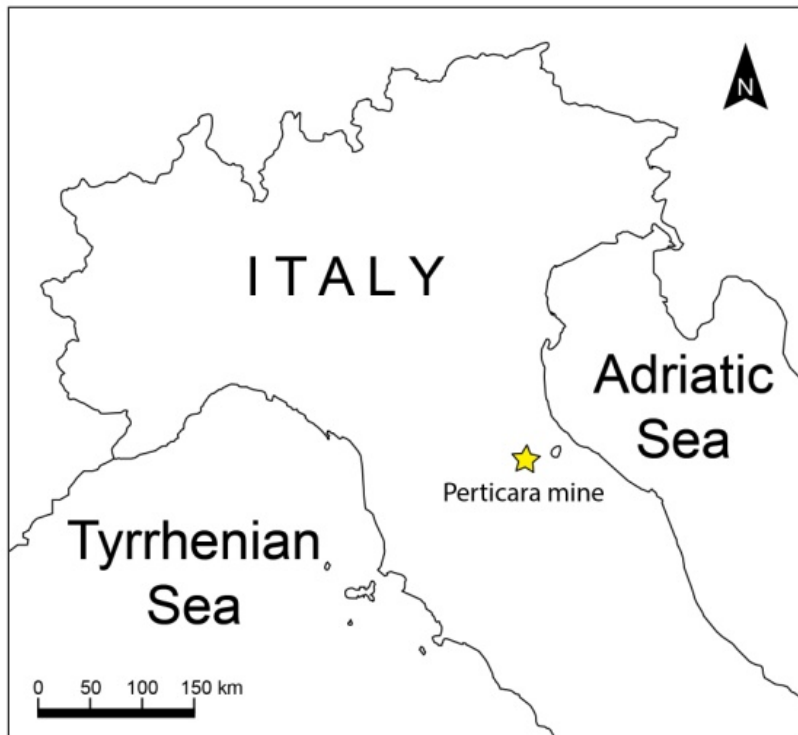
Label A: SP1c





## Sottoprogetti unità locale

### 4. Caratterizzazione e implicazioni tossicologiche di un minerale fibroso fortemente solubile: epsomite

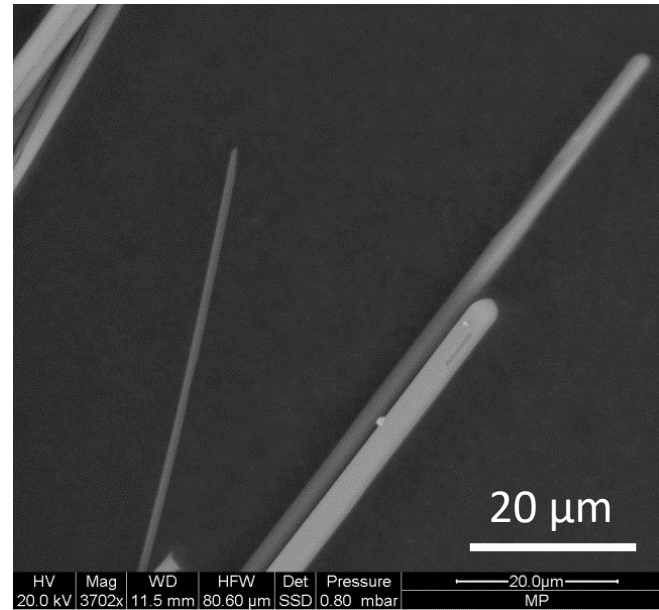
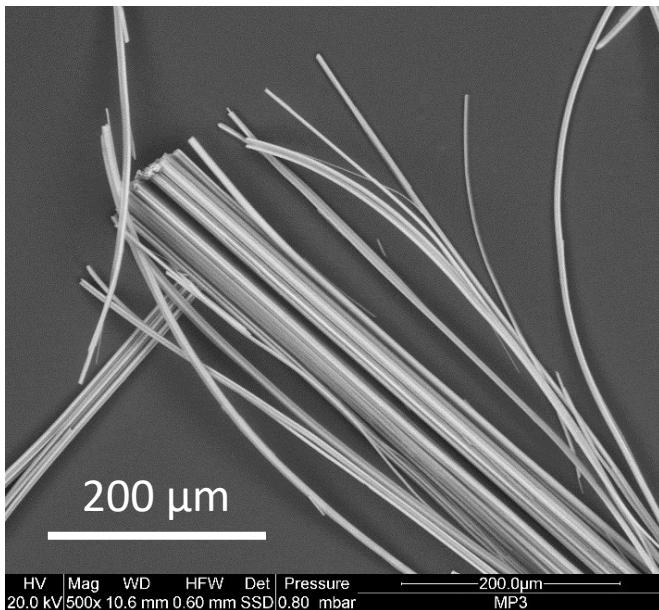


**Epsomite fibrosa**  
 $\text{Mg}(\text{SO}_4) \cdot 7\text{H}_2\text{O}$

Data by SEM-EDS, XRPD, ICP-AES and Alpha Spectrometry measurements were combined and integrated to characterize morphology, crystal chemistry, mineralogy and radiological characteristics of epsomite.

## Sottoprogetti unità locale

### 4. Caratterizzazione e implicazioni tossicologiche di un minerale fibroso fortemente solubile: epsomite



Epsomite (MP)	Po-210 Bq g <sup>-1</sup>	U-238 Bq g <sup>-1</sup>	Th-232 Bq g <sup>-1</sup>	Th-228 Bq g <sup>-1</sup>
1	5.82 ± 0.87	-	-	0.134 ± 0.020
2	6.41 ± 0.96	-	-	0.128 ± 0.019
3	3.97 ± 0.60	-	-	0.110 ± 0.017
4	6.15 ± 0.92	-	-	-
<b>Average</b>	<b>5.59</b>	< 1.0 10 <sup>-2</sup>	< 1.0 10 <sup>-3</sup>	<b>0.124</b>
St. dev.	1.11	-	-	0.012

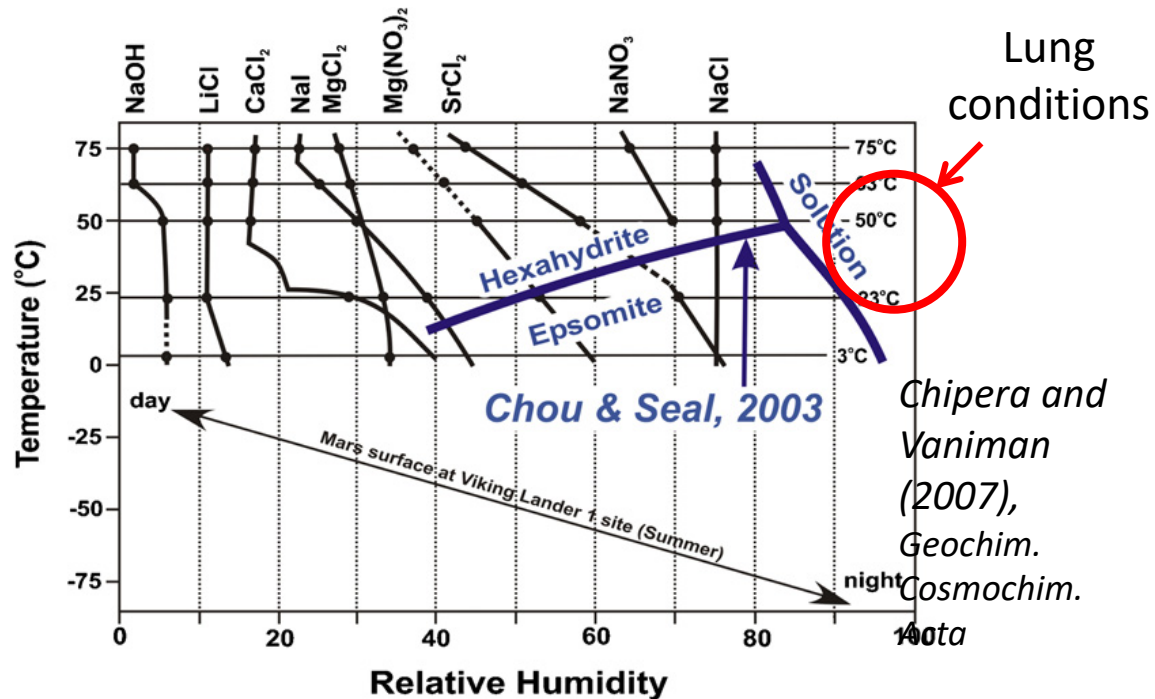
D<sub>ae</sub> (MP) epsomite: **5.1**



D<sub>ae</sub> < 10 μm (pass the larynx, thoracic fraction)

## Sottoprogetti unità locale

### 4. Caratterizzazione e implicazioni tossicologiche di un minerale fibroso fortemente solubile: epsomite



### Epsomite: effects after inhalation?

- 1- Chemicals originating after dissolution in the lungs
- 2- “Trojan horse” effect of toxic metals
- 3- Effect of radiogenic elements



# Sottoprogetti unità locale

## 4. Caratterizzazione e implicazioni tossicologiche di un minerale fibroso fortemente solubile: epsomite

Register Program by Theme Exhibitors & Sponsors My Goldschmidt

12bO2 - Inorganic particles and elongate mineral particles (EMP), interaction with the biosphere, and risk assessment

Monday, 5 July 2021  
17:45 - 19:00  
Online - Room 11

[Could soluble minerals be dangerous for human health? The epsomite case study](#)  
**Matteo Giordani<sup>1</sup>, Michele Mattioli<sup>1</sup>, Maria Assunta Meli<sup>1</sup>, Carla Roselli<sup>1</sup>, Ivan Fagiolino<sup>2</sup>, Laura Valentini<sup>1</sup>, Fabio Peruzzi<sup>3</sup> and Michele Betti<sup>1</sup>,**  
 (1)University of Urbino Carlo Bo, (2)Gruppo C.S.A. spa, (3)Speleological Federation of the Emilia-Romagna Region  
 Online - Room 11  
[PDF/PPT e-presentation available](#)

*Manoscritto pronto per la sottomissione*

### Could soluble minerals be dangerous for human health? The epsomite case study

Matteo Giordani<sup>1</sup>, Maria Assunta Meli<sup>2</sup>, Carla Roselli<sup>2</sup>, Michele Betti<sup>2</sup>, Fabio Peruzzi<sup>3</sup>, Marco Taussi<sup>1</sup>, Laura Valentini<sup>2</sup>, Ivan Fagiolino<sup>4</sup>, Michele Mattioli<sup>1</sup>



1506  
UNIVERSITÀ  
DEGLI STUDI  
DI URBINO  
CARLO BO

# FIBRES: a multidisciplinary mineralogical, crystal-chemical and biological project to amend the paradigm of toxicity and cancerogenicity of mineral fibres



*minerals*

an Open Access Journal by MDPI

IMPACT  
FACTOR  
2.380

CITESCORE  
2.6  
SCOPUS

## Elongated Mineral Particles and Health

### Guest Editors

Dr. Matteo Giordani, Dr. Michele Mattioli

### Deadline

17 December 2021

[mdpi.com/si/83172](https://mdpi.com/si/83172)

**Special** Issue

Invitation to submit

### Already published:

Rinaudo et al. "Asbestos Fibers and Ferruginous Bodies Detected by VP-SEM/EDS in Colon Tissues of a Patient Affected by Colon-Rectum Cancer: A Case Study"

### In prep:

UniRoma1 (Ballirano group), UniMore (Gualtieri group), UniUrb (Mattioli-Giordani)



*minerals*

an Open Access Journal by MDPI

IMPACT  
FACTOR  
2.380

CITESCORE  
2.6  
SCOPUS

### Elongated Mineral Particles and Health

#### Guest Editors:

**Dr. Matteo Giordani**  
Department of Pure and Applied  
Sciences, University of Urbino  
Carlo Bo, 61029 Urbino, Italy  
[matteo.giordani@uniurb.it](mailto:matteo.giordani@uniurb.it)

**Dr. Michele Mattioli**  
Department of Pure and Applied  
Sciences, University of Urbino  
Carlo Bo, 61029 Urbino, Italy  
[michele.mattioli@uniurb.it](mailto:michele.mattioli@uniurb.it)

Deadline for  
manuscript submissions:  
**17 December 2021**

#### Message from the Guest Editors

The attention of scientists to mineral particles and fibers of inhalable size has increased significantly recently, due to their potential hazard for humans. Asbestos minerals (chrysotile, amosite, crocidolite, tremolite, actinolite, anthophyllite), fibrous antigorite and balangeroite, the amphiboles winchite, richterite, and fluoro-edenite, the zeolites erionite, offretite, ferrierite, and mordenite, and also talc and clay minerals such as sepiolite and palygorskite are of strong interest to the scientific community. Many factors play roles in their toxicity, but the most important are the particle size (length, diameter, relative ratio, and aerodynamic equivalent diameter) and their chemical composition.

This Special Issue aims to collect a broad overview of the research taking place on elongated minerals. A wide range of contributions is welcome: (i) Field sampling and geological survey of mineral particles and fibers, as well as rock containing such materials; (ii) mineralogical, chemical, and physical characterization; (iii) determination of surface properties; (iv) experimental determination of thermodynamic and kinetic parameters; (v) molecular and geochemical modeling; (vi) understanding and quantification of dissolution and growth mechanisms, both in water and in specific media (e.g., biological fluids); (vii) technological applications, with a special focus on the capability of mineral fibers to act as substrates for environmental remediation processes.



[mdpi.com/si/83172](https://mdpi.com/si/83172)

**Special** Issue