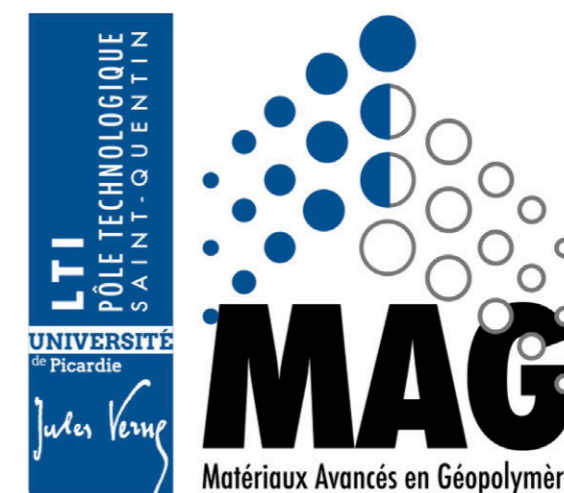




16th GP-Camp



Saint-Quentin (France)

July 8-10, 2024



State of the Geopolymer R&D 2024

Joseph Davidovits

Geopolymer research 1988

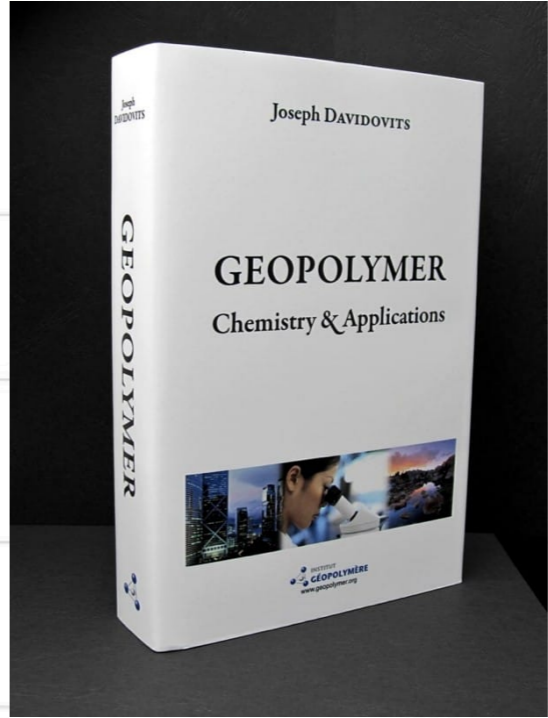
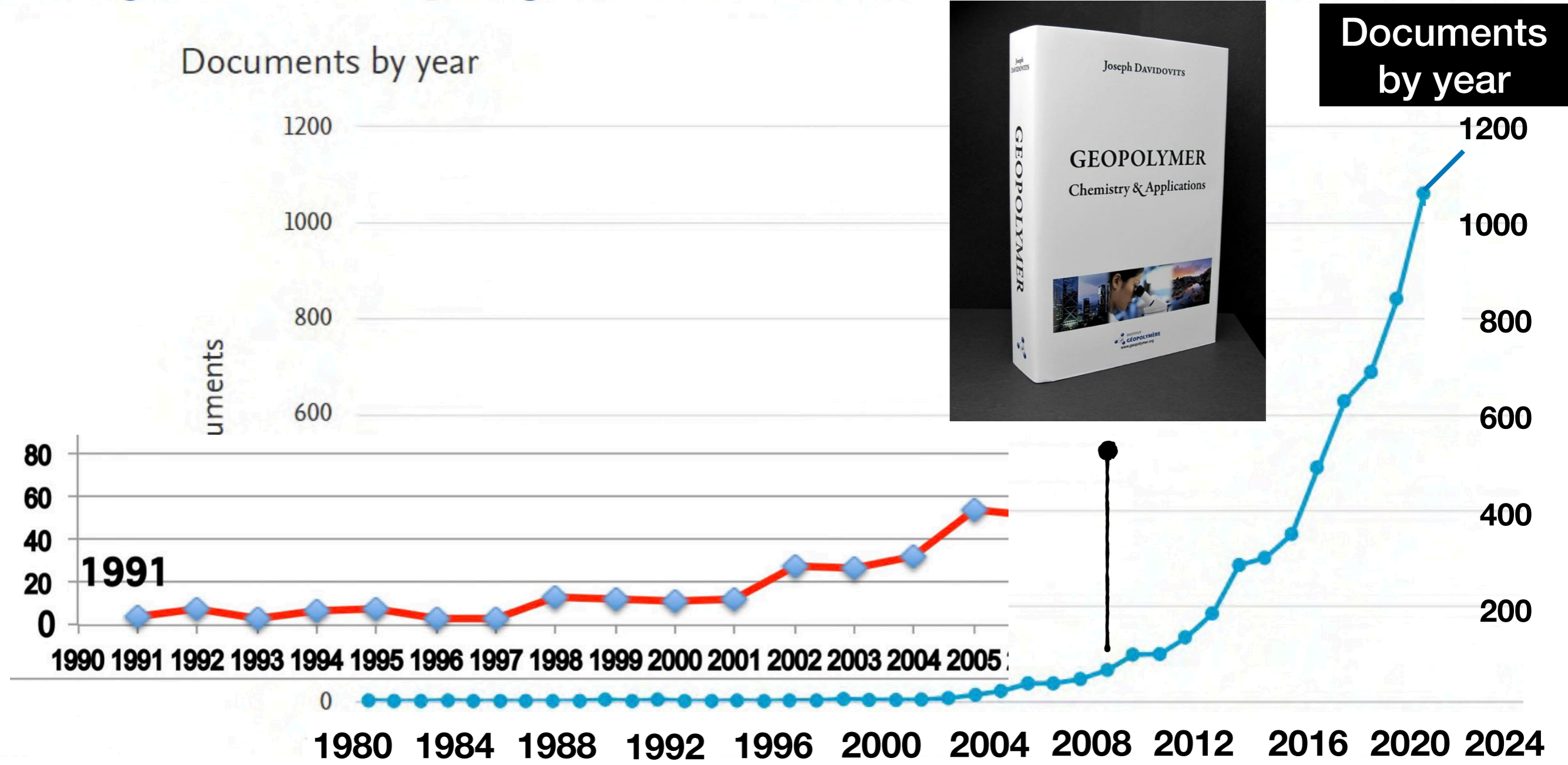
1st Geopolymer conference



Geopolymer research 2018



Subject „Geopolymer“ in Scientific Publications



Literature Search: Statistical data of SCOPUS database ^F

State of the Geopolymer R&D 2024

Geopolymer science.

From primary to quaternary structures

1975-1976: mineral polymer

1978-1979: geopolymers

2 systems:

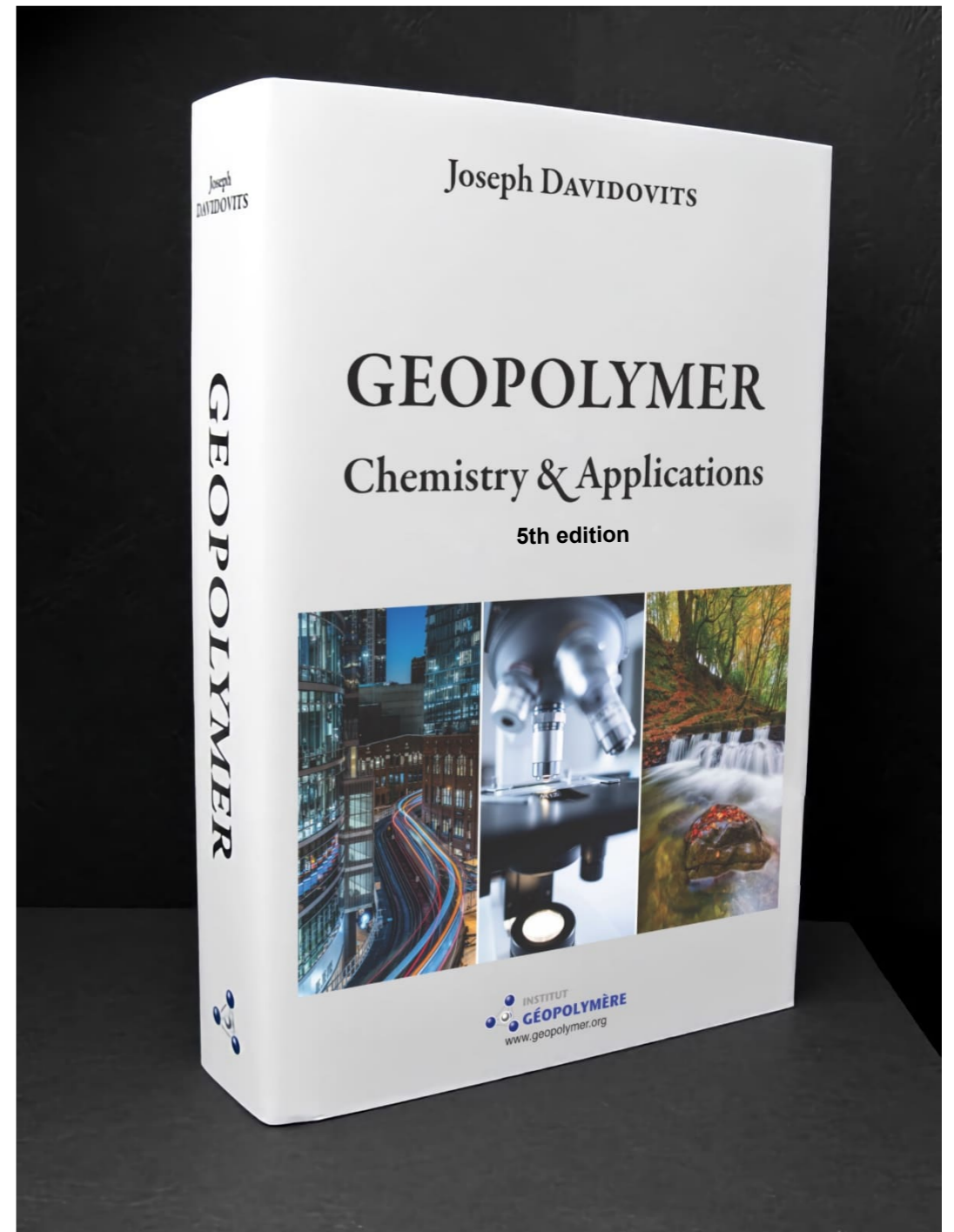
- poly(sialate)-alkaline-based GP

Na-based and K-based

- alumoxy-acid-based GP

phosphoric-based

and organic-based



***a) Poly(sialate)-based
Geopolymerization***

a) Poly(sialate)-based Geopolymerization

1. Alkalinization ~~*alkali-activation*~~
2. Depolymerization of silicates
3. Gel formation of oligo-sialates
4. Polycondensation
5. Reticulation, networking
6. Geopolymer solidification

From primary to quaternary structures

Alkalinization *and* Depolymerization of silicates:

primary structure

Gel formation of oligo-sialates:

secondary structure

Polycondensation:

tertiary structure

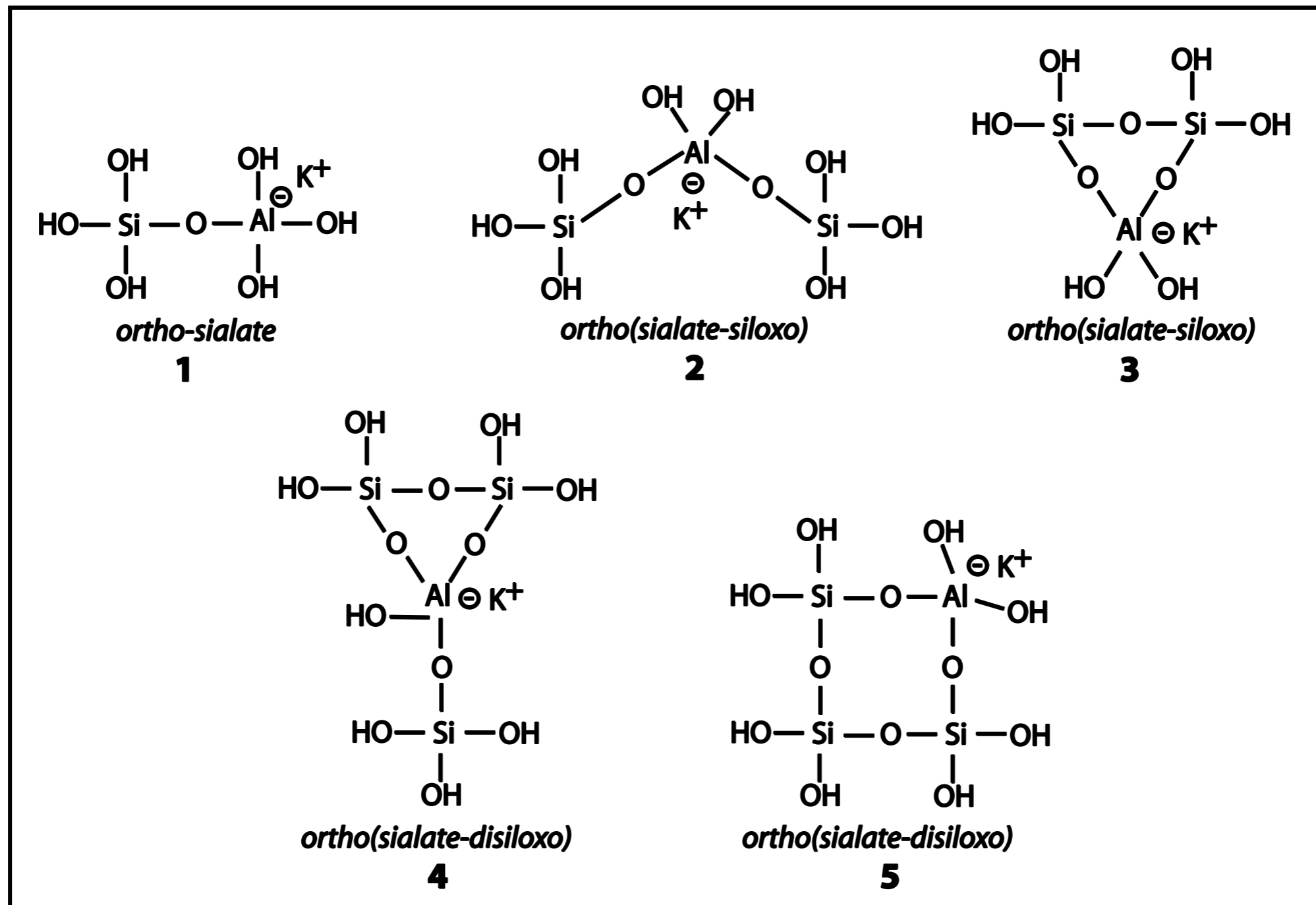
Reticulation, networking + GP solidification:

quaternary structure

From primary to quaternary structures

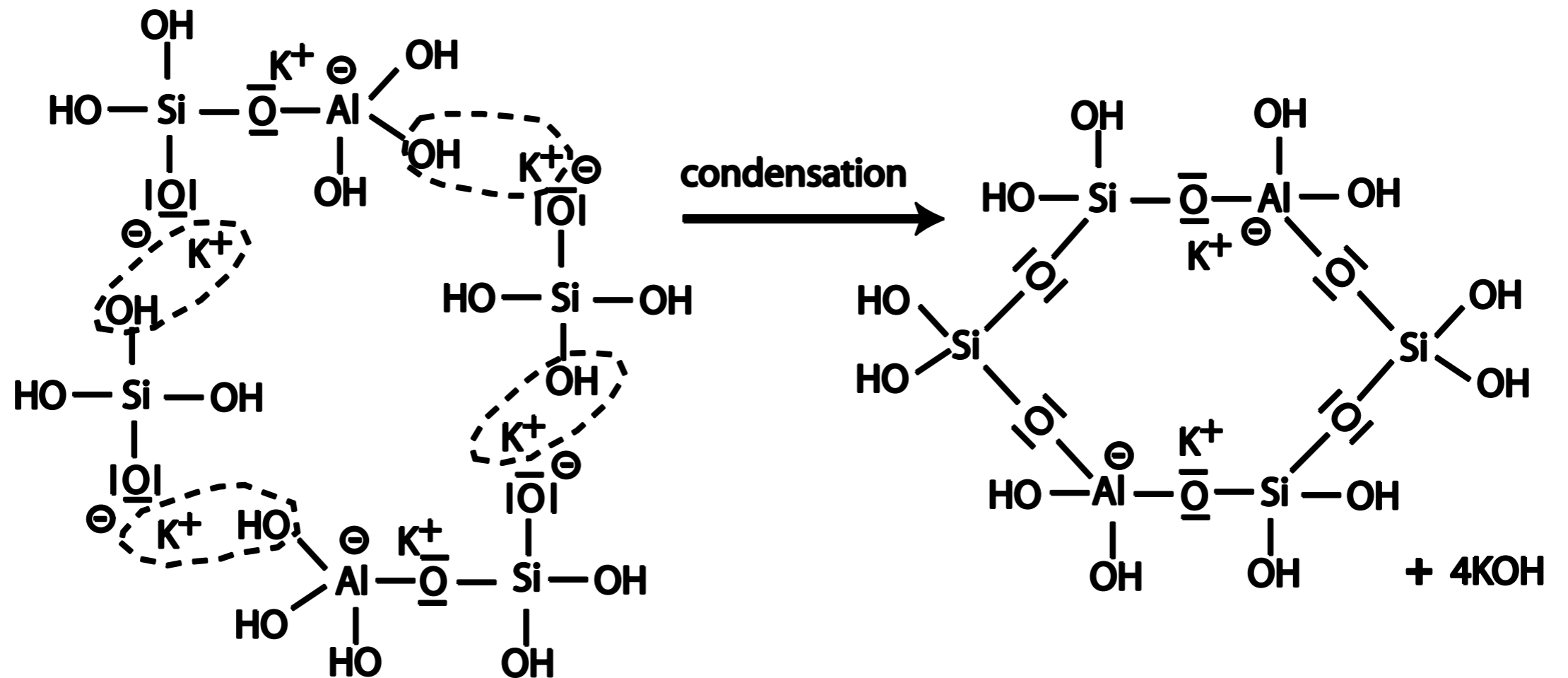
Alkalinization *and* Depolymerization of silicates:

primary structure



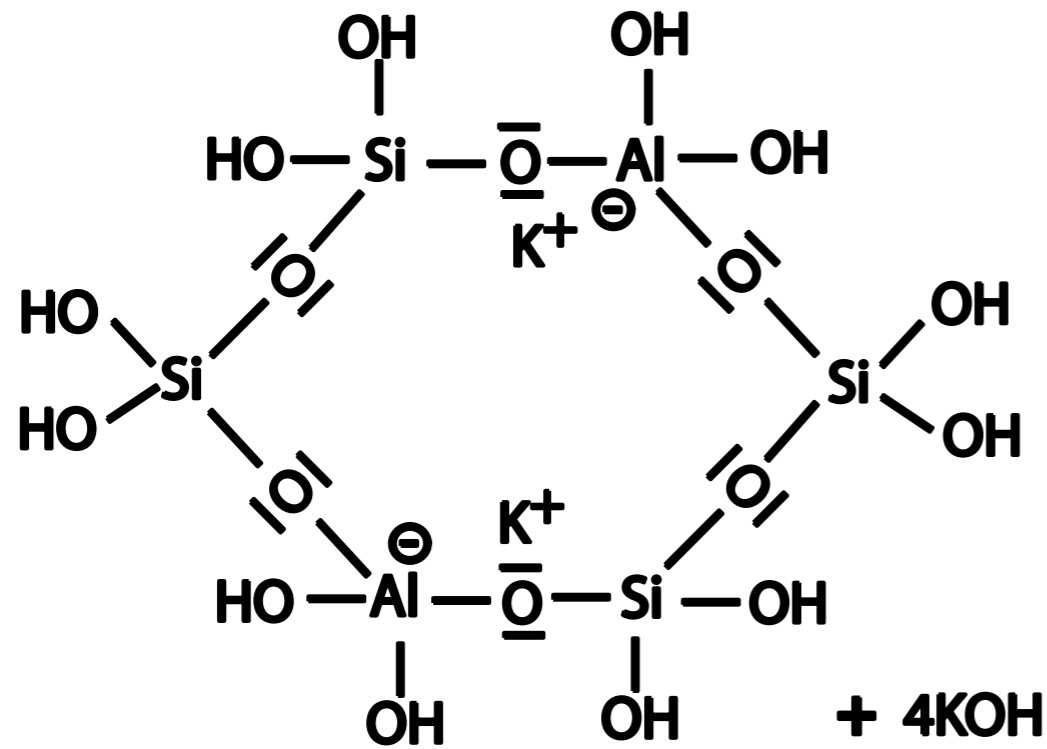
Gel formation of K-oligo(sialate-siloxo)

secondary structure



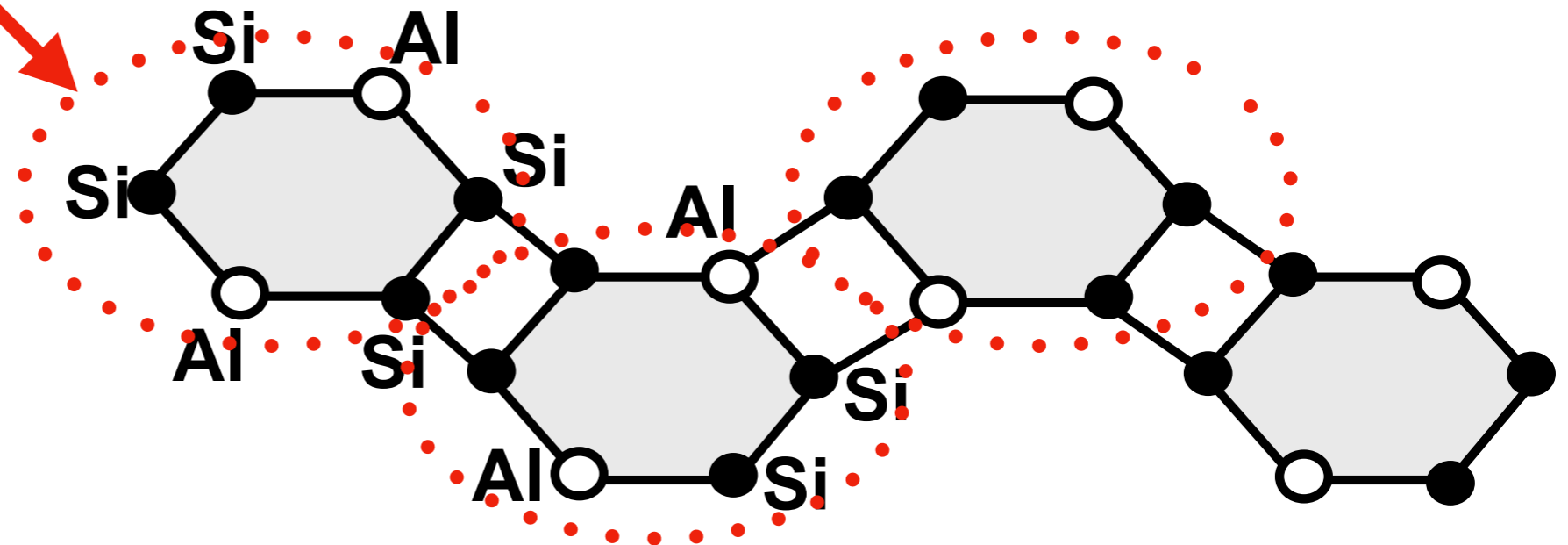
Polycondensation of K-poly(sialate-siloxo)

tertiary structure



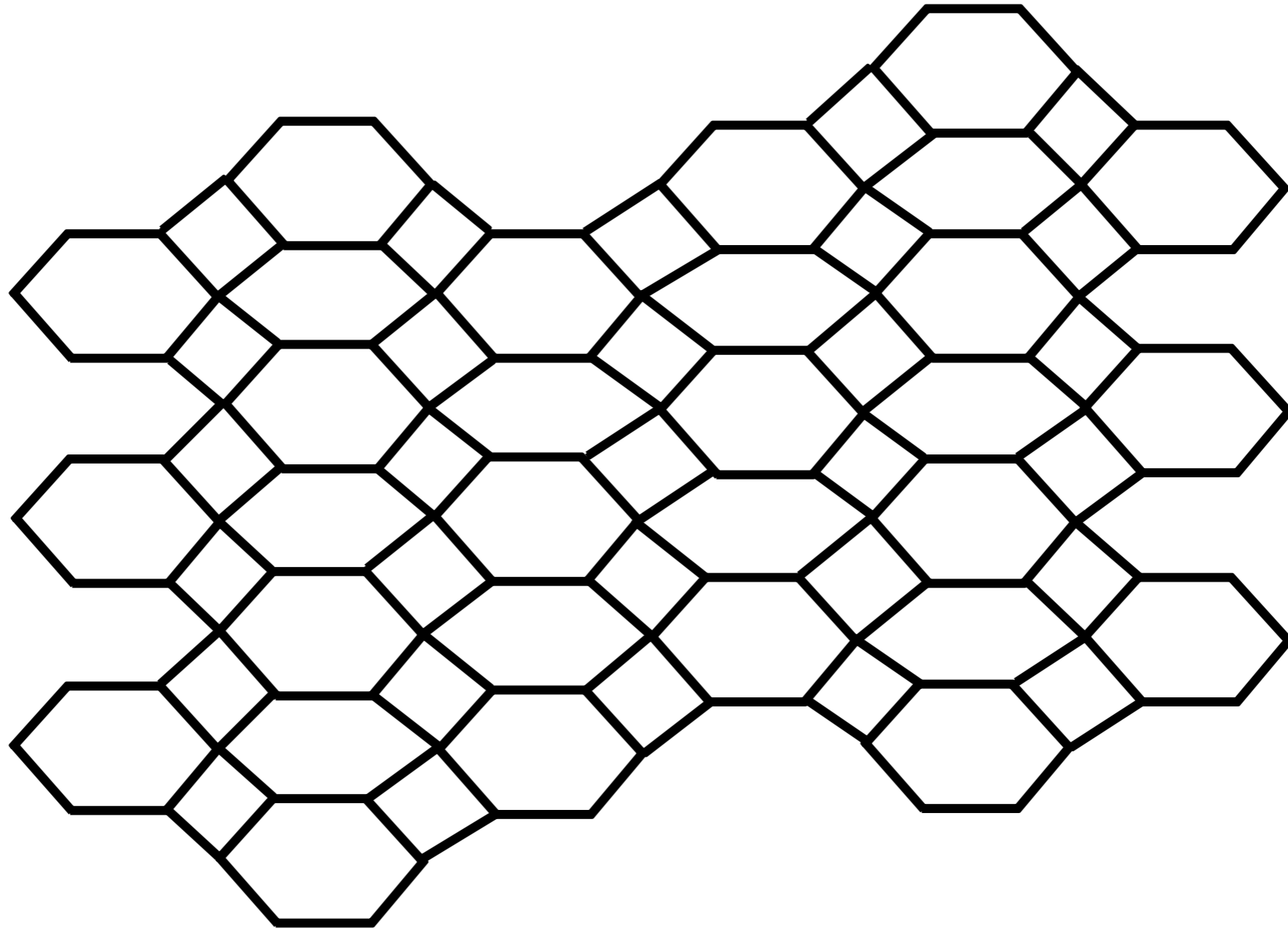
K-oligo(sialate-siloxo)

K-Poly(sialate-siloxo)

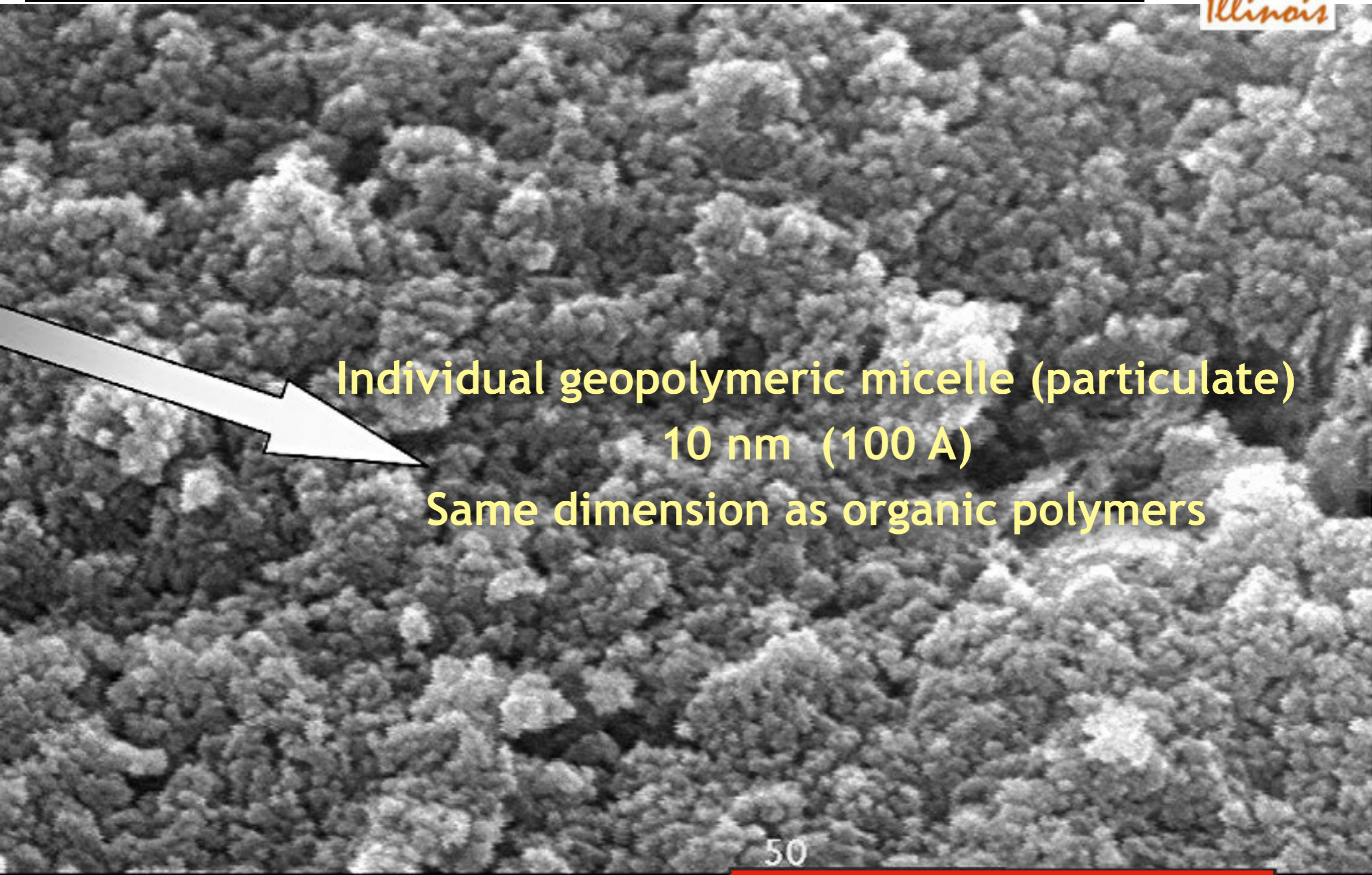


Reticulation, networking of K-poly(sialate-siloxo)

quaternary structure



Leucite framework KSi_2AlO_6

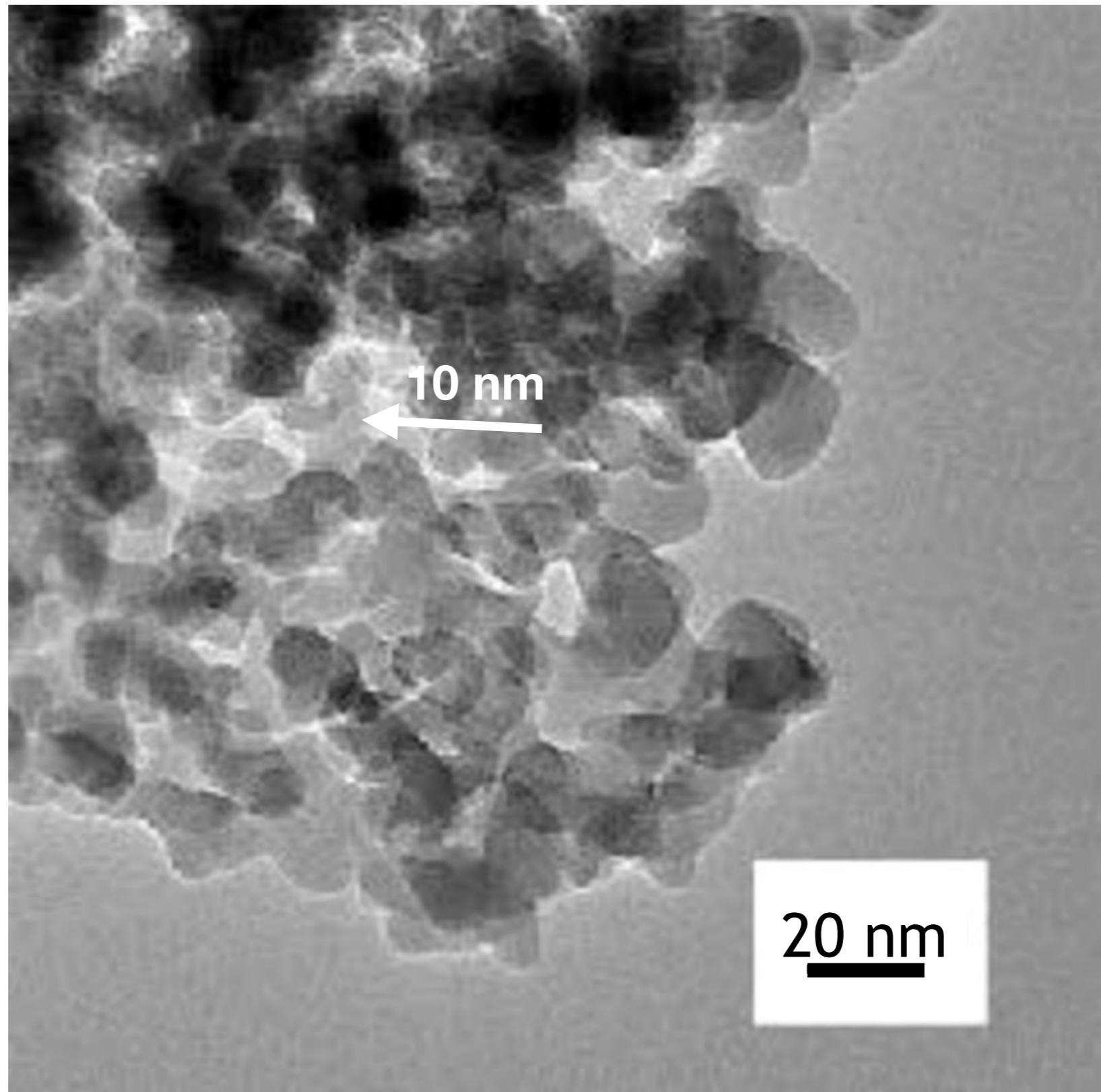


Individual geopolymeric micelle (particulate)
10 nm (100 Å)
Same dimension as organic polymers

50

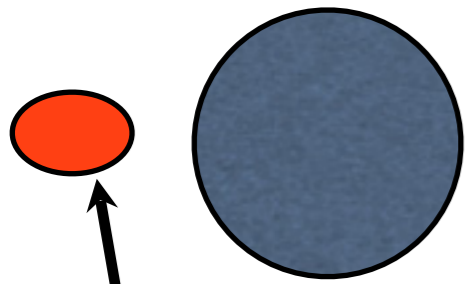
Step 5
reticulation

*quaternary
structure*



2012 Prof. Dong-Kyun (Don) Seo's team
School of Molecular Sciences, Arizona State University, Tempe, USA

Colloidal
silica
30-40 nm



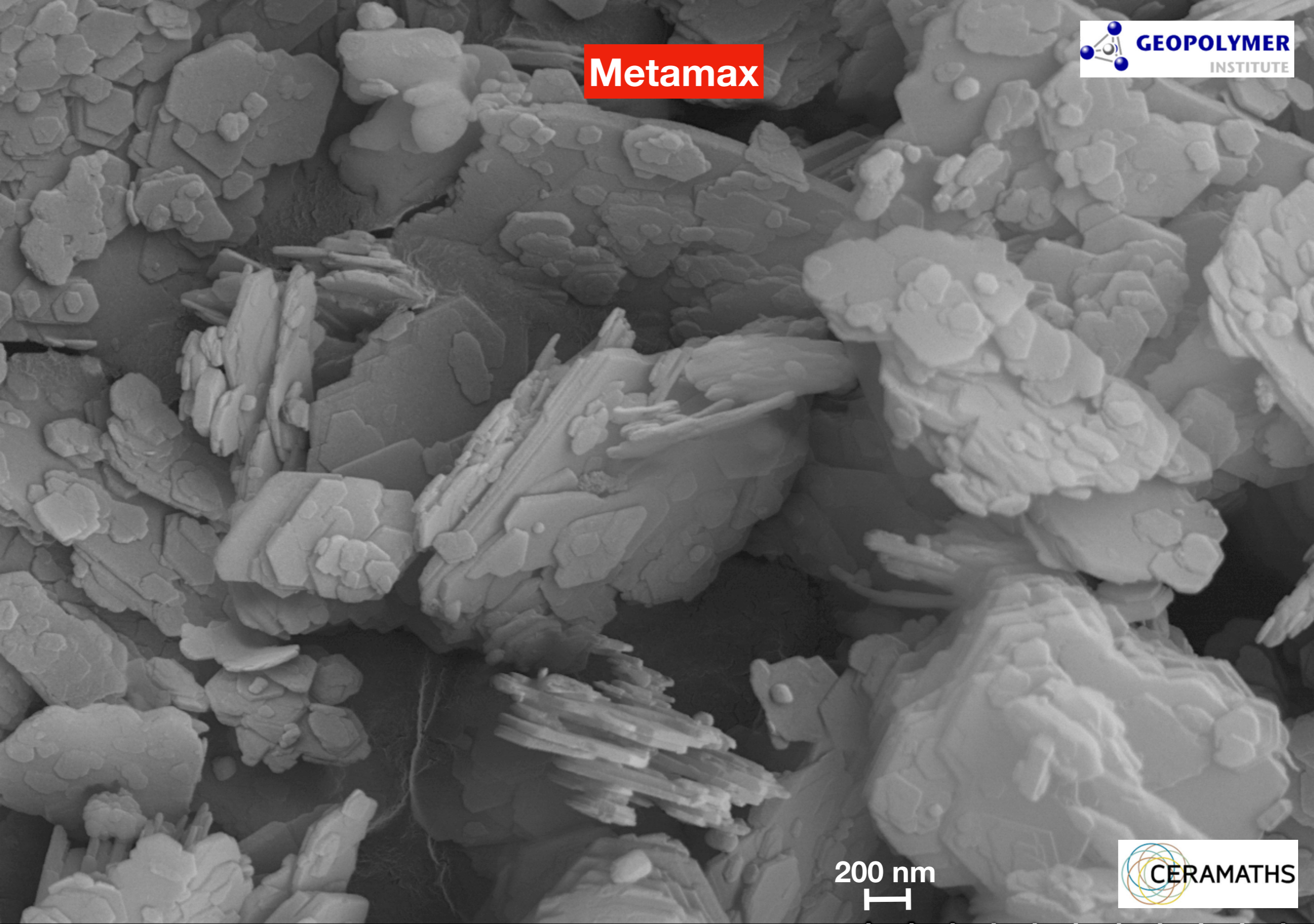
GP-micelle
10-20 nm

Silica Fume
200-300 nm

Fly ash
3-15 μ

Poly(sialate) Geopolymer = nano material
not unknown « Gel » or « Hydrate »

Metamax



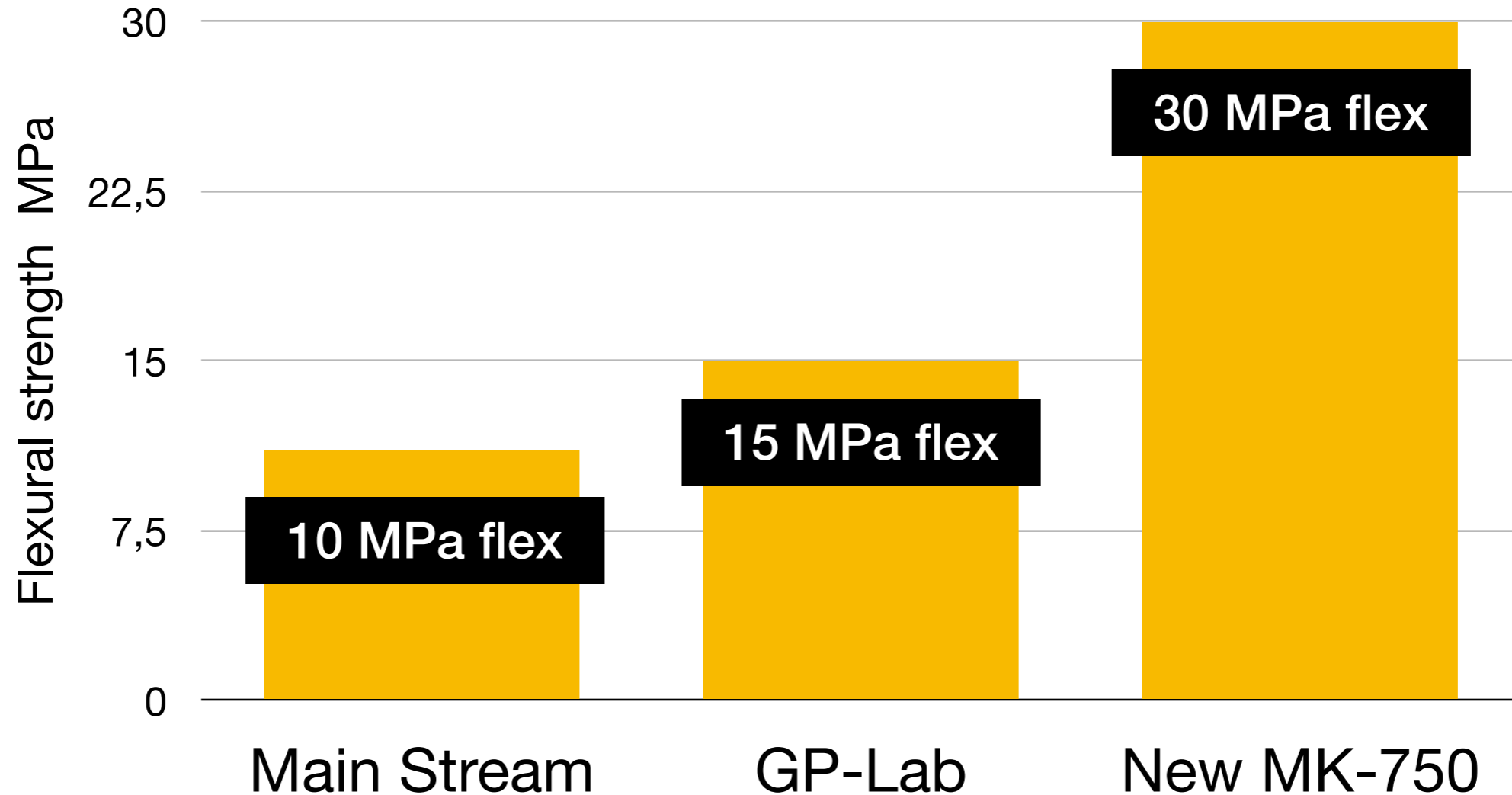
200 nm




SU5000 15.0kV x20.0k BSE-ALL

2.00µm

High-strength MK



Flexural strength 25-30 MPa

Compressive strength 180 MPa

with mineral filler: feldspar

Kaolin clay

C90F

halloysite

halloysite

kaolinite

200 nm

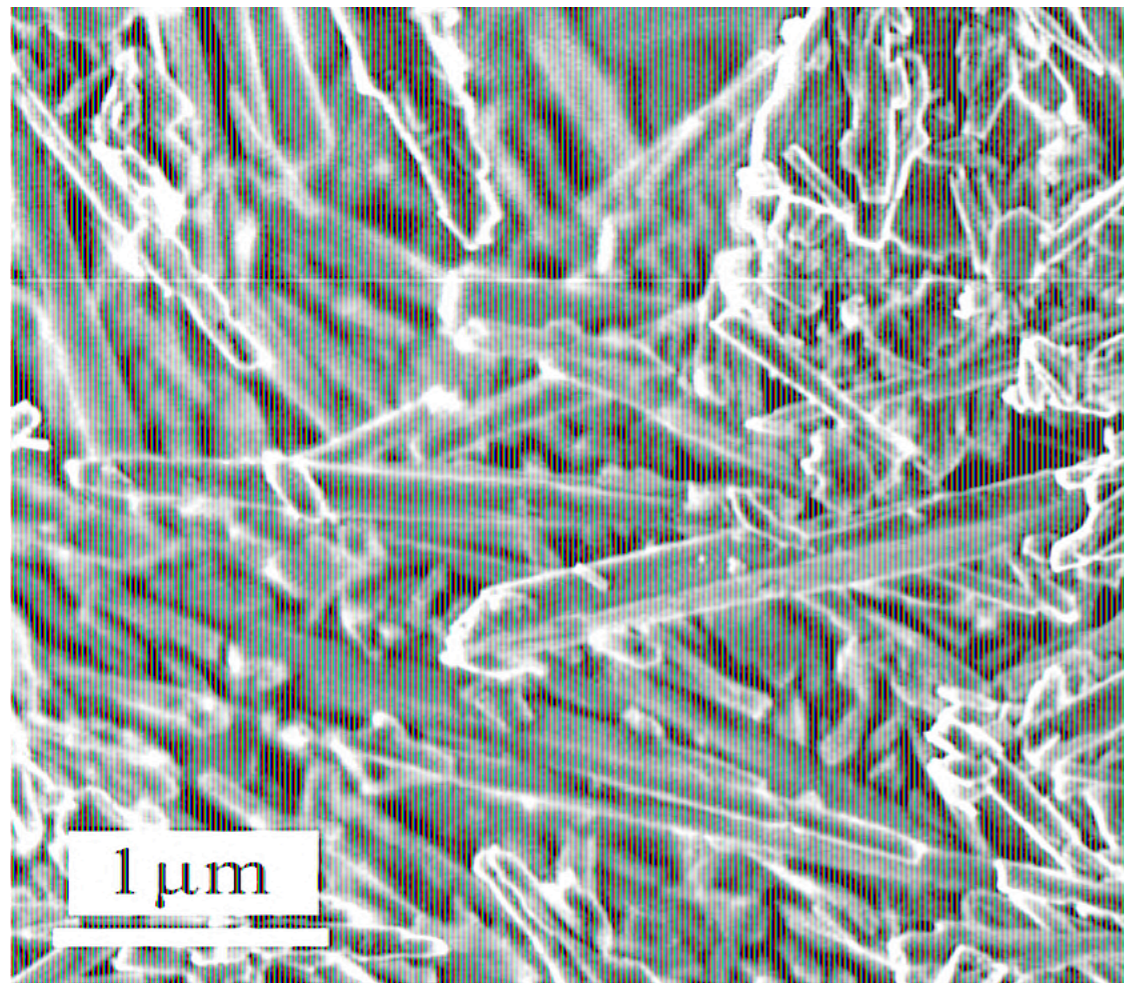


Article *Minerals* **2019**, *9*, 670; doi:10.3390/min9110670

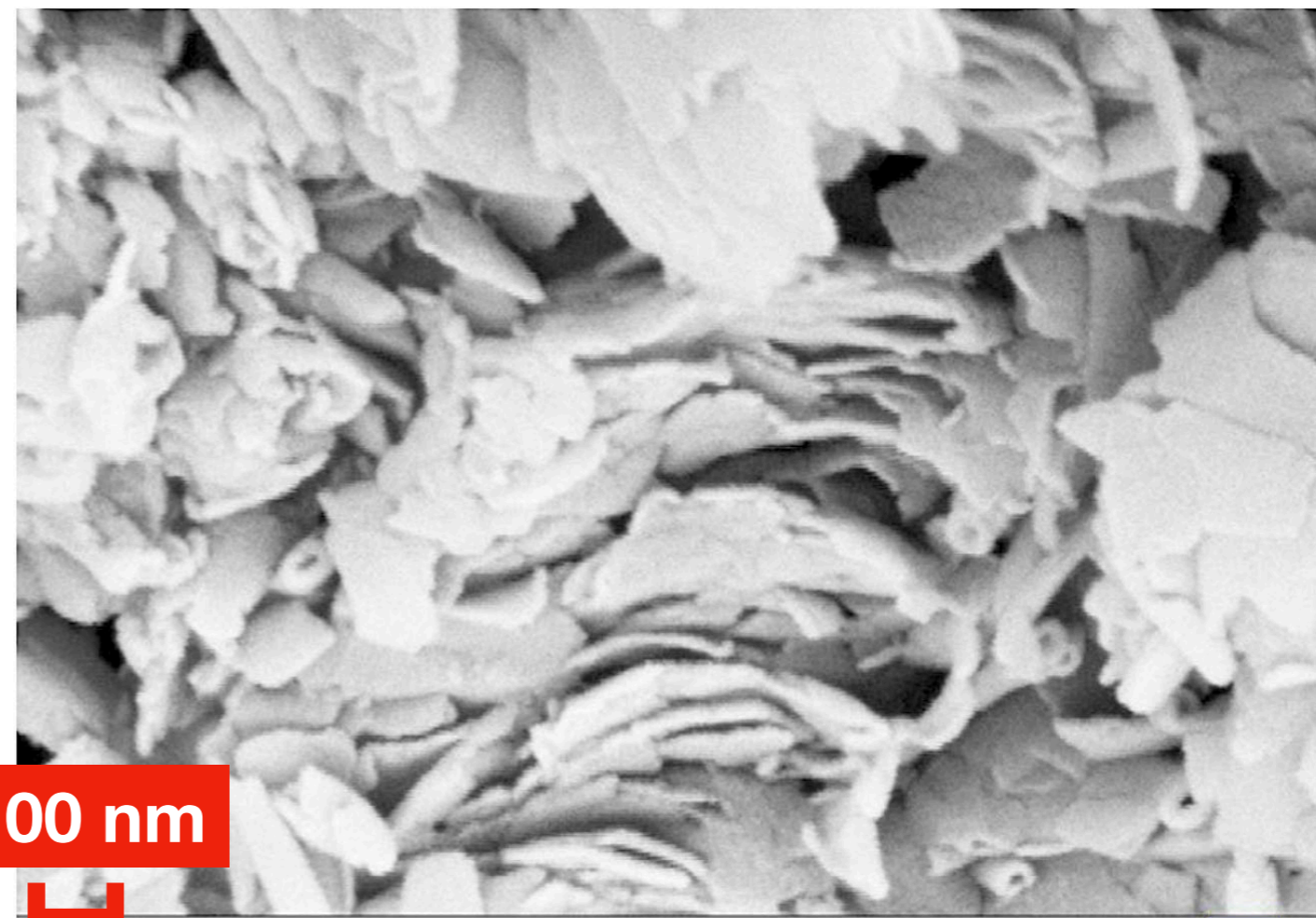
Characterization of Diatomaceous Earth and Halloysite Resources of Poland

Marcin Lutyn'ski, **Piotr Sakiewicz** and **Sylwia Lutynska**, Silesian University of Technology, Gliwice, Poland.

Halloysite nanotubes



Halloysite nanoplates



100 nm

Tempoz C90F



meta-kaolinite

meta-halloysite

200 nm



2.00µm

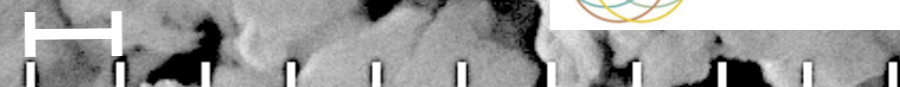
SU5000 15.0kV x20.0k BSE-ALL

Tempoz M88

meta-kaolinite

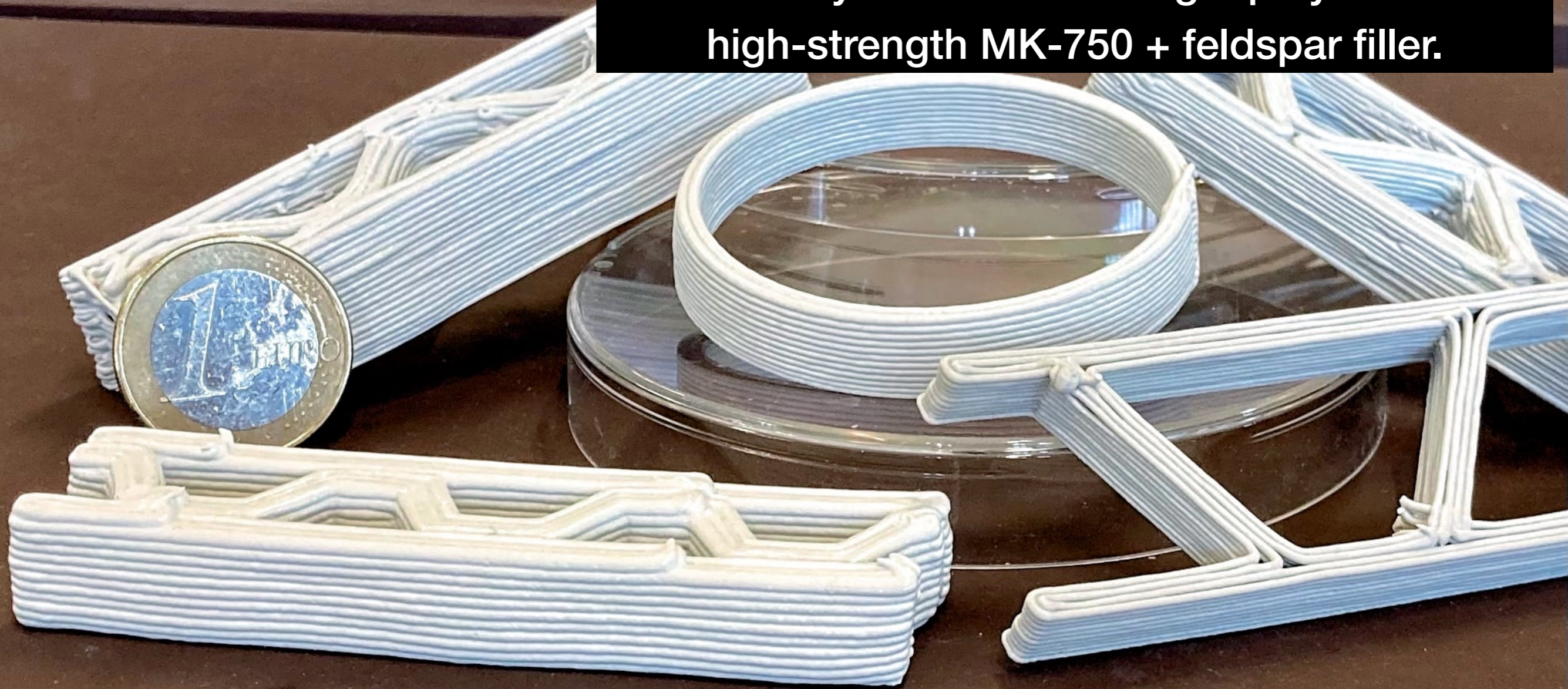
meta-halloysite

200 nm



3D printing ceramic-type geopolymer

High-Strength 3D-Printed Geopolymer Ceramic
0.7 mm to 1mm thread
Chemically stable K-based geopolymer with
high-strength MK-750 + feldspar filler.



meta-kaolinite

Geopolymer-micelles

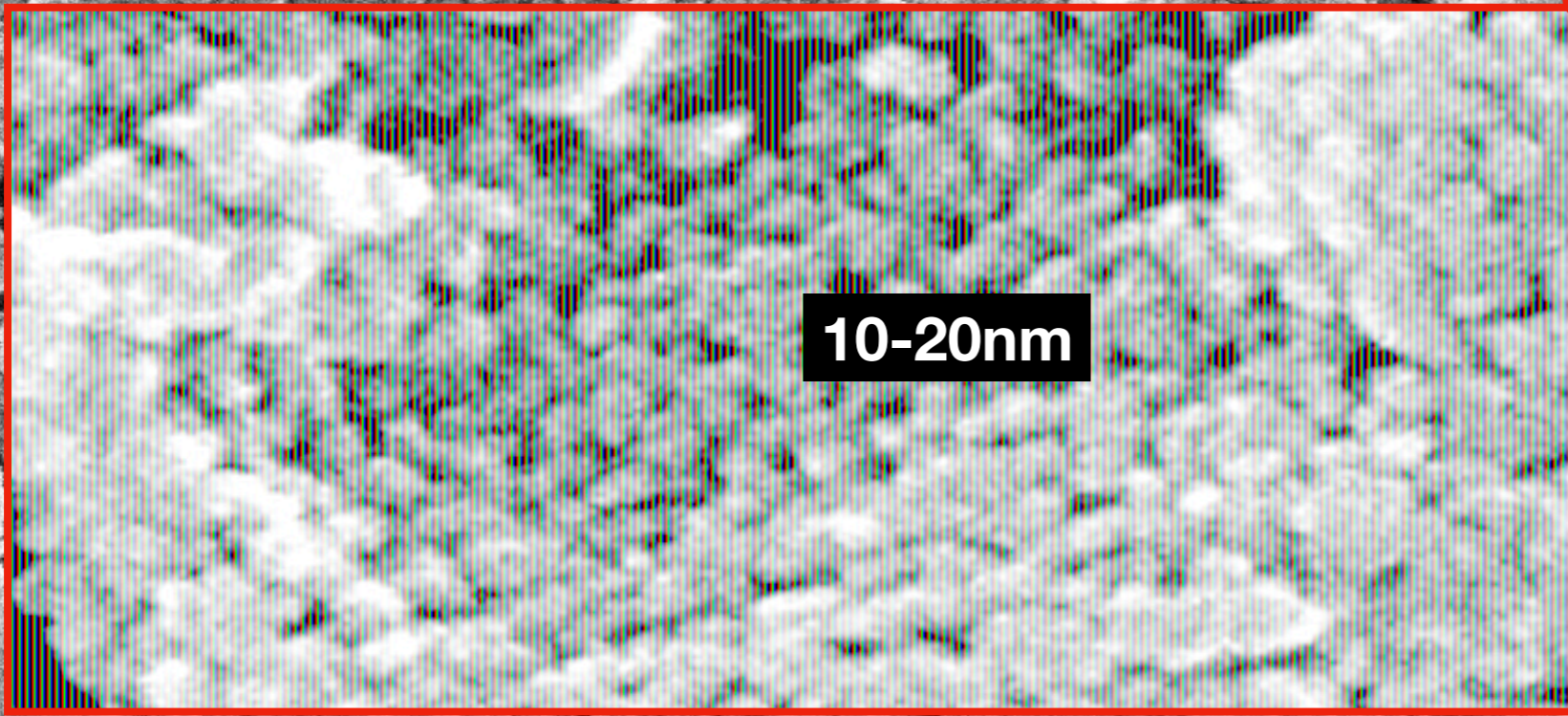
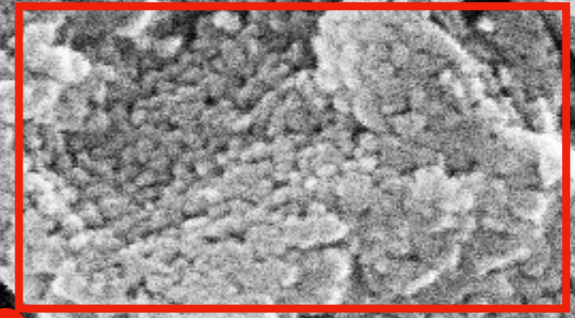
100 nm

Geopolymer-micelles

100 nm



Geopolymer-micelles



10-20nm

100 nm

The conclusion of this study is that we have demonstrated that the quaternary structure of metakaolin-based geopolymer is a well-defined 3D polymeric network in the form of individual particles called *geopolymer micelles*, with overall dimensions in the range of 10 to 20 nm.

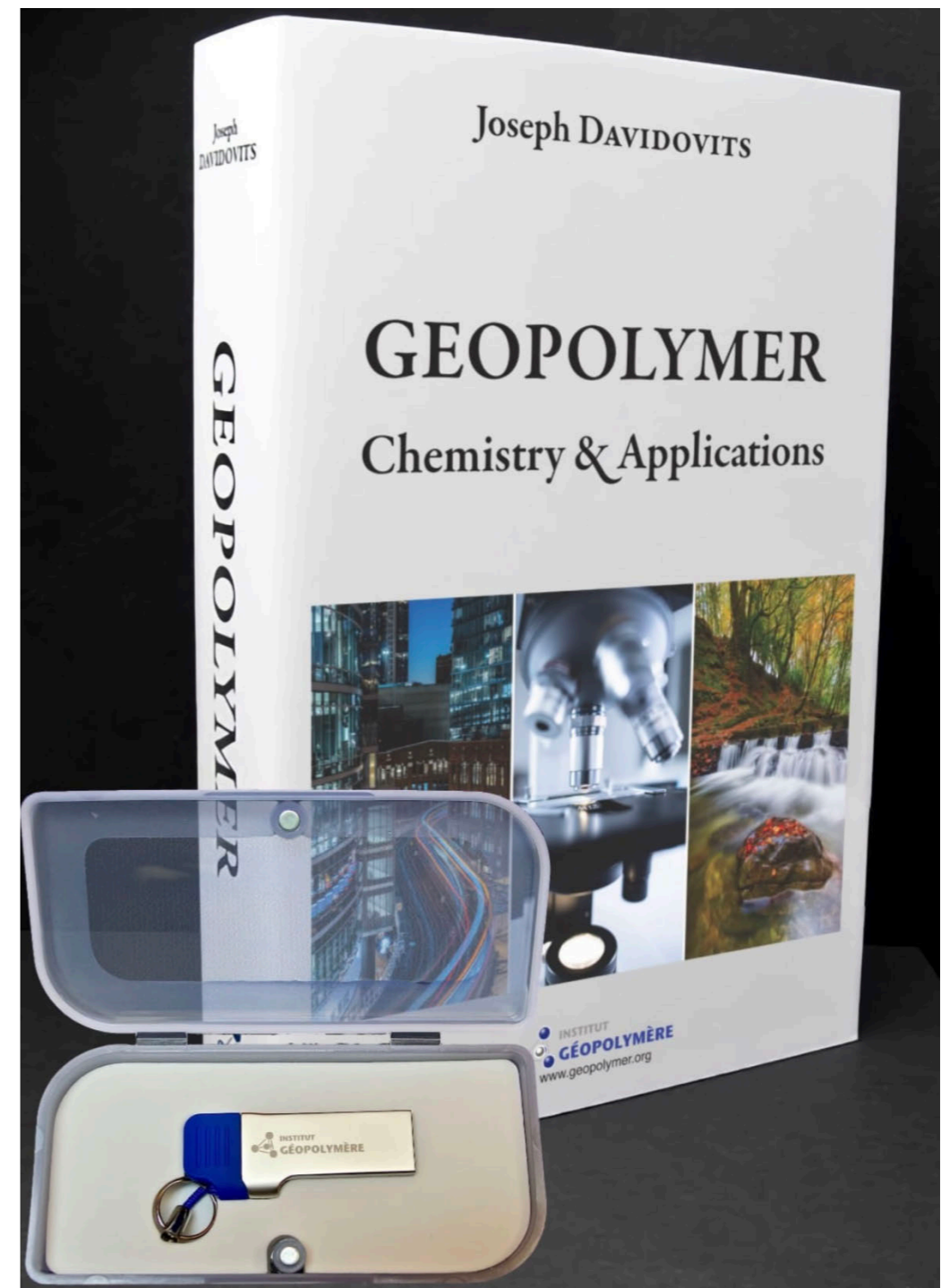
The quaternary structure of the nano-sized K-based geopolymer micelle retains the same shape when heated up to 1000°C. Its microstructure also remains X-ray amorphous. At higher temperatures it crystallizes into the mineral leucite with a melting point above 1400°C.

This explains its unique structural properties, for example:

- ◆ excellent thermal shock resistance at high or very low temperatures,
- ◆ resistance to very high vacuum,
- ◆ making it the ideal material for lunar, space and extraterrestrial applications.

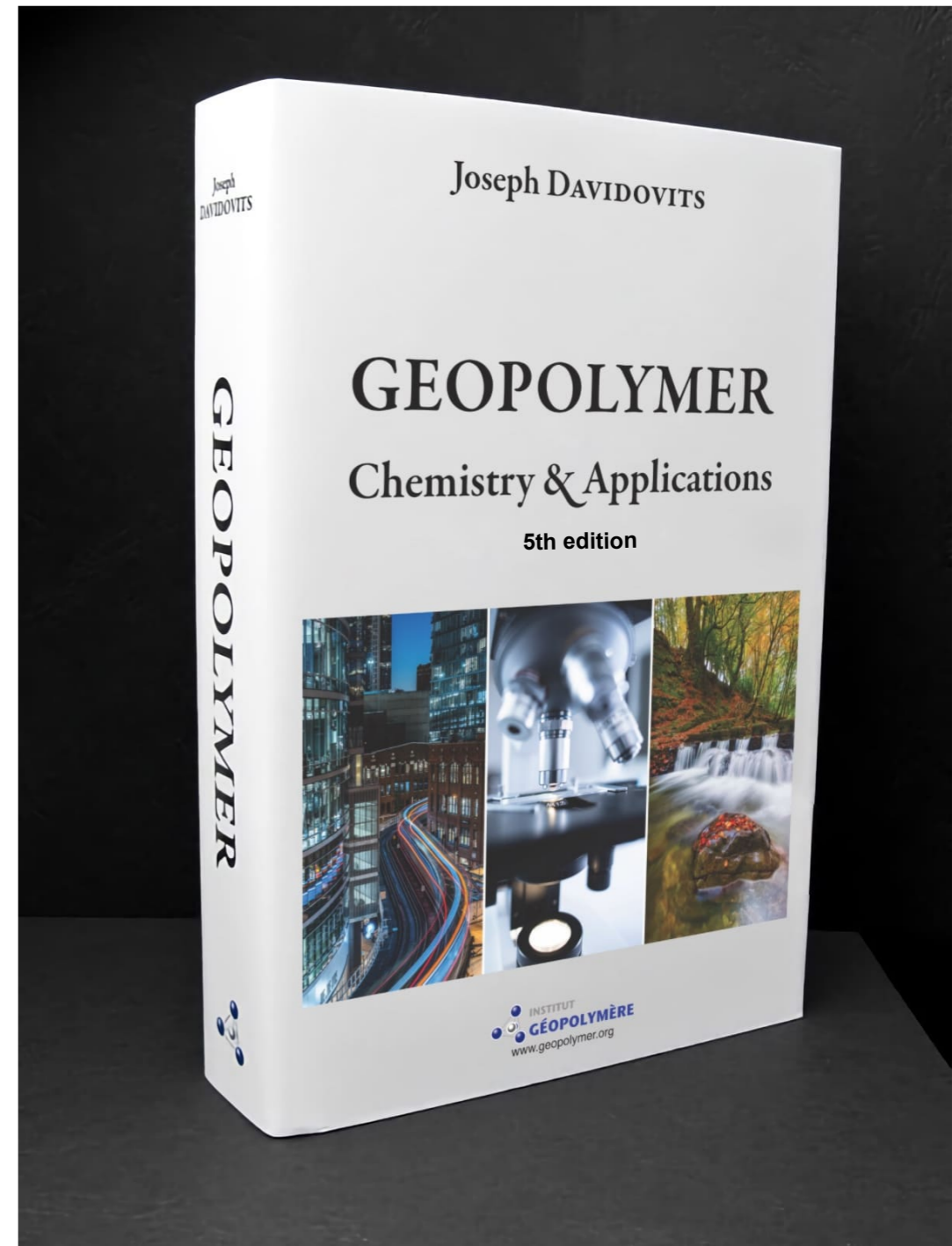
Cement scientists who promote the misconception that the result of geopolymerization is a NASH or KASH type hydrate are mistaken. Alkali activated materials are not geopolymers.

They can purchase the *Geopolymer Bundle* book and learn how to produce true Geopolymers.



***b) Alumoxy-based
Geopolymerization
Al-O-X***

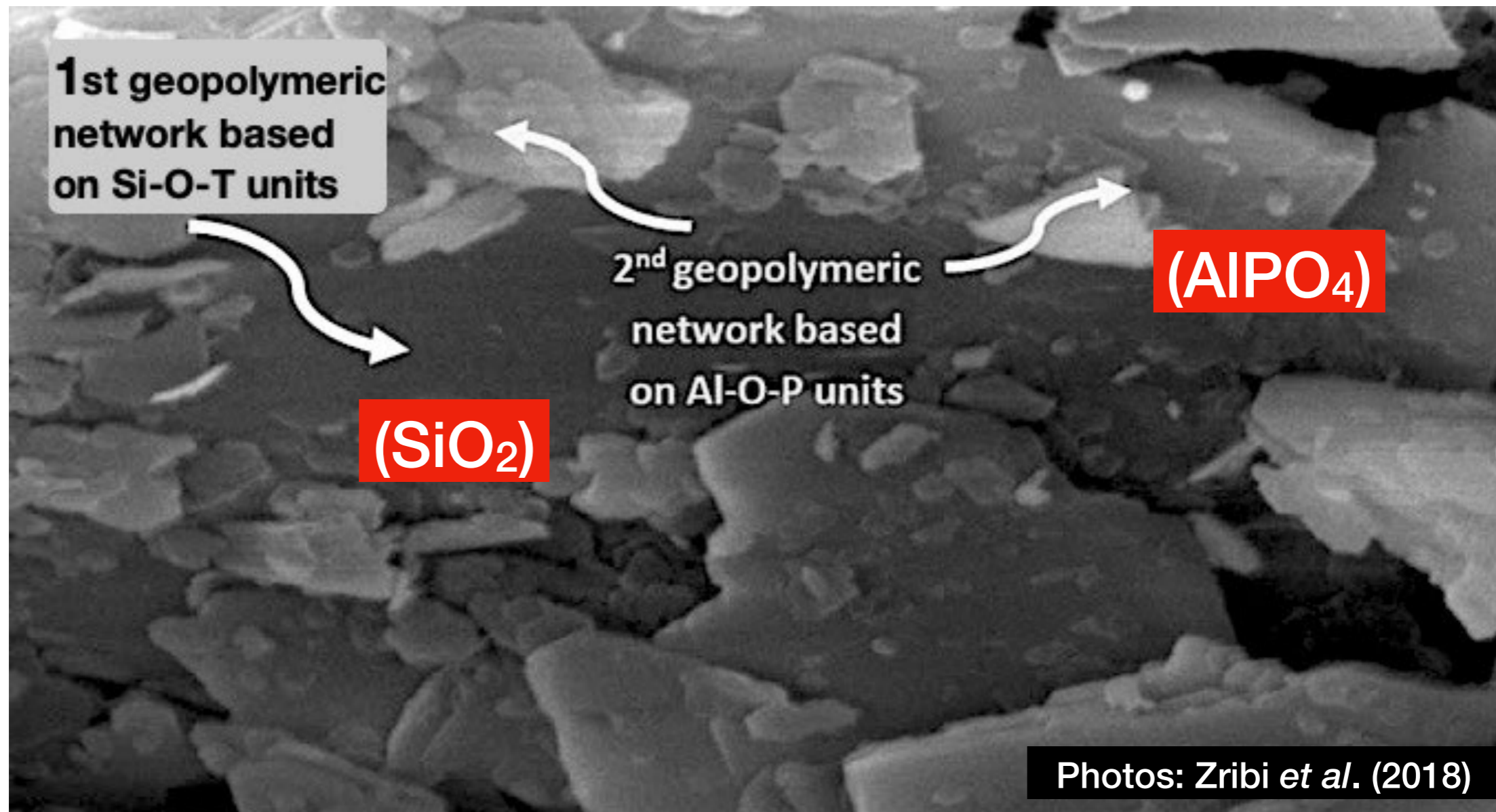
*phosphoric acid-based
organic acids-based*



**Chapter 14
Phosphate based-GP**

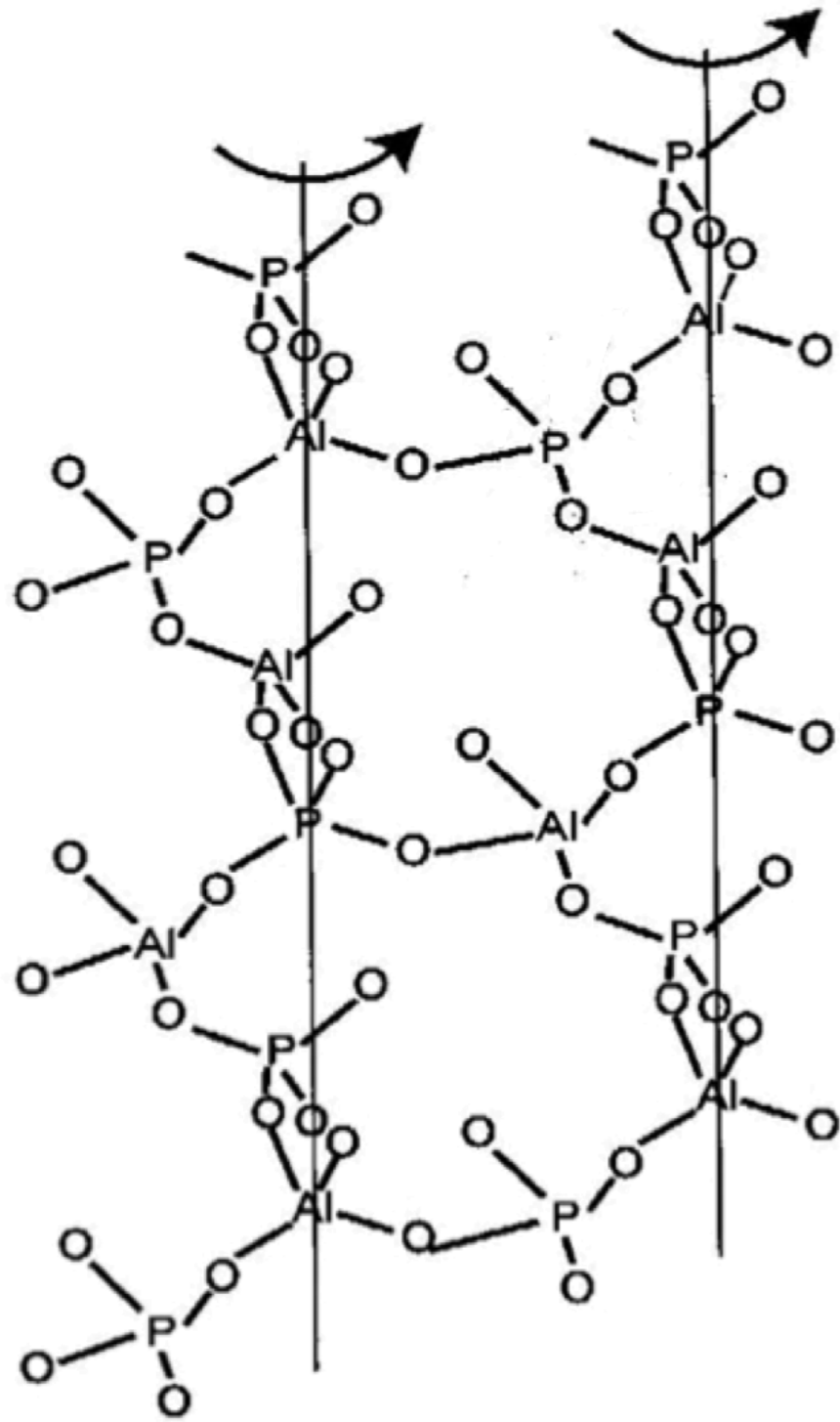
Alumoxy-based Geopolymerization Al-O-X

Phosphoric acid + MK-750

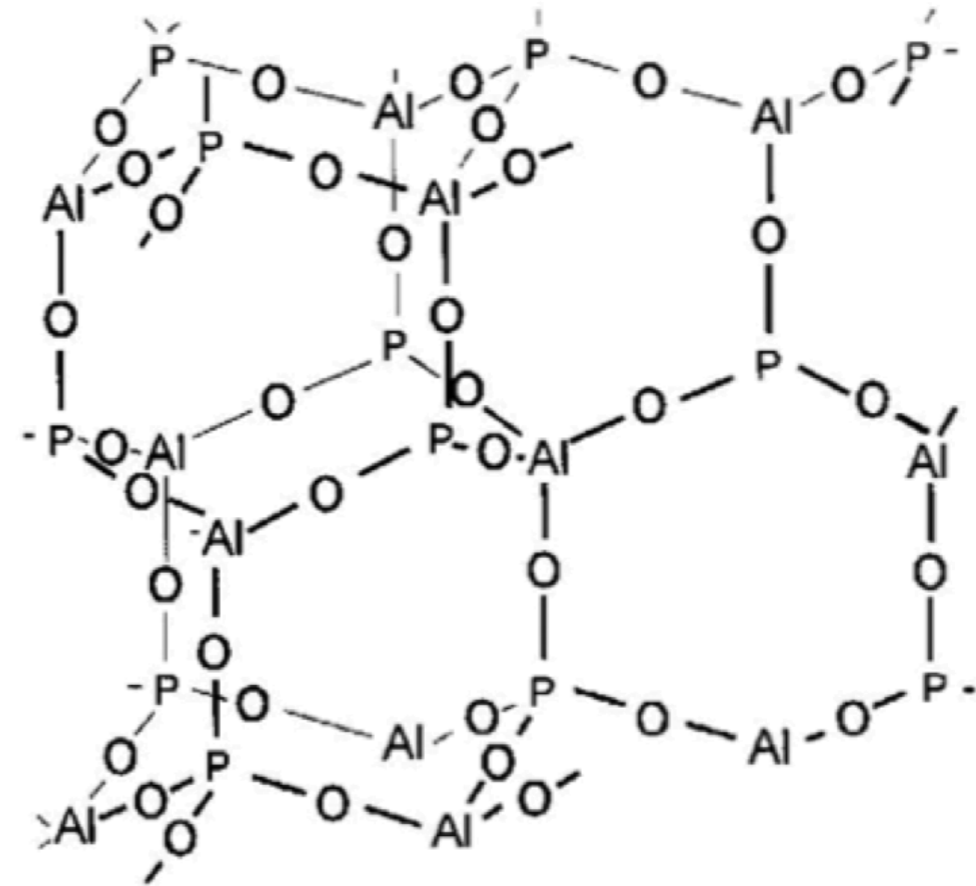


Polymeric structures of AlPO_4 -Geopolymers

Cross linked $(\text{Al-O-P-O})_n$
poly(alumoxy-phospho) chains



AlPO_4 -berlinite (isostructural to quartz)



AlPO_4 -tridymite/cristobalite

Alumoxy-based Geopolymerization Al-O-X

organic acids-based

We believe we have now found the principles of the *alumoxy-based geopolymerization Al-O-X*.

They are no longer alkaline-based (Na,K)Si-O-Al (Na,K)-sialate. It was not easy because we had to take a new approach.

But thanks to the perseverance of my son, Ralph Davidovits, we succeeded.

One of our breakthroughs is the ability to replicate famous ancient artifacts such as the ancient hard stone vases from the early dynasties (2500 BC) in Egypt.

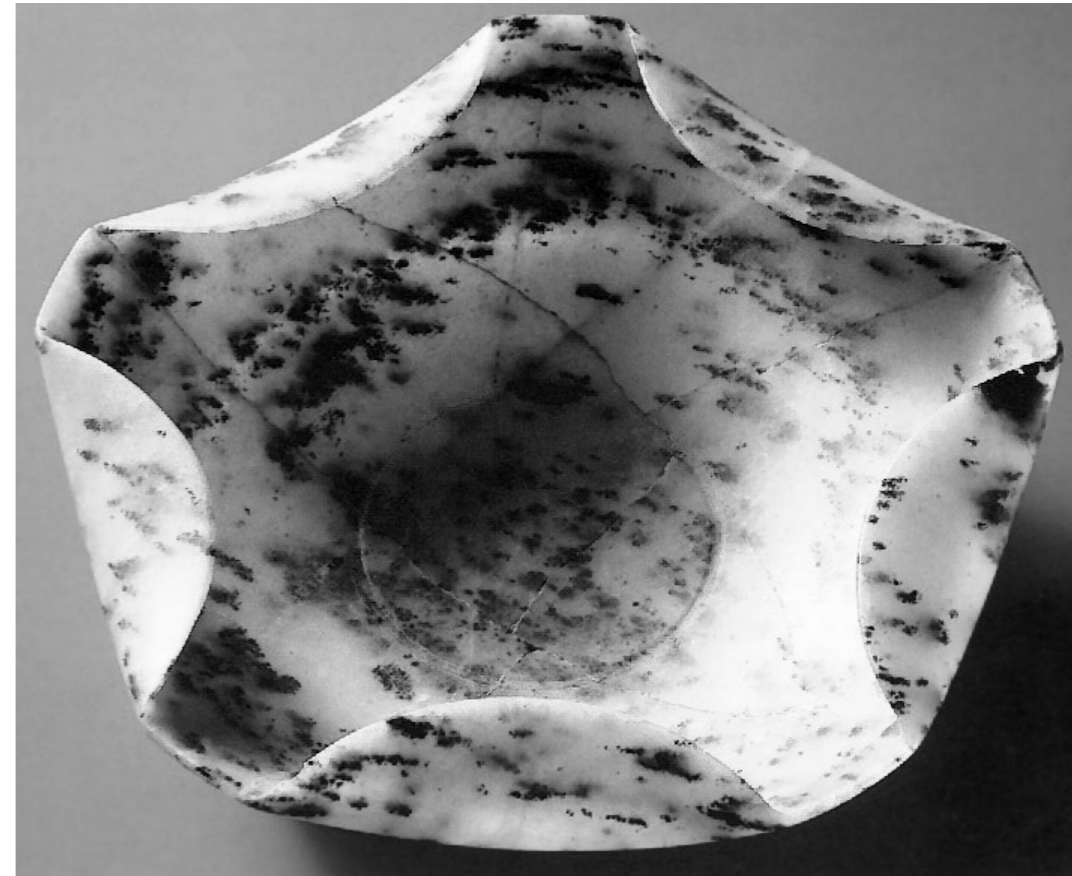
Alumoxy-based Geopolymerization Al-O-X

organic acids-based

These vases are thought to have been made from geological hard stones. An impossible carving task indeed.

We believe that these ancient artefacts were made using artificial stones.

I have always maintained that these vases were made of a moldable stone paste, similar to clay and ceramics.



Berkeley, Phoebe Hearst M. (USA)



Boston, Museum of Fine Arts (USA)

Alumoxy-based Geopolymerization

organic acids-based

Indeed they were made using a method very similar to that developed at Tiwanaku/Pumapunku in Bolivia, South America for the andesite volcanic monuments.

See the articles and videos at the Geopolymer Institute web-site, at :

www.geopolymer.org/archaeology/

Book : “*Ancient Geopolymers in South America and Easter Island*” is planned for Nov. 2024, by Springer-Nature.





State of the Geopolymer R&D 2024

Joseph Davidovits