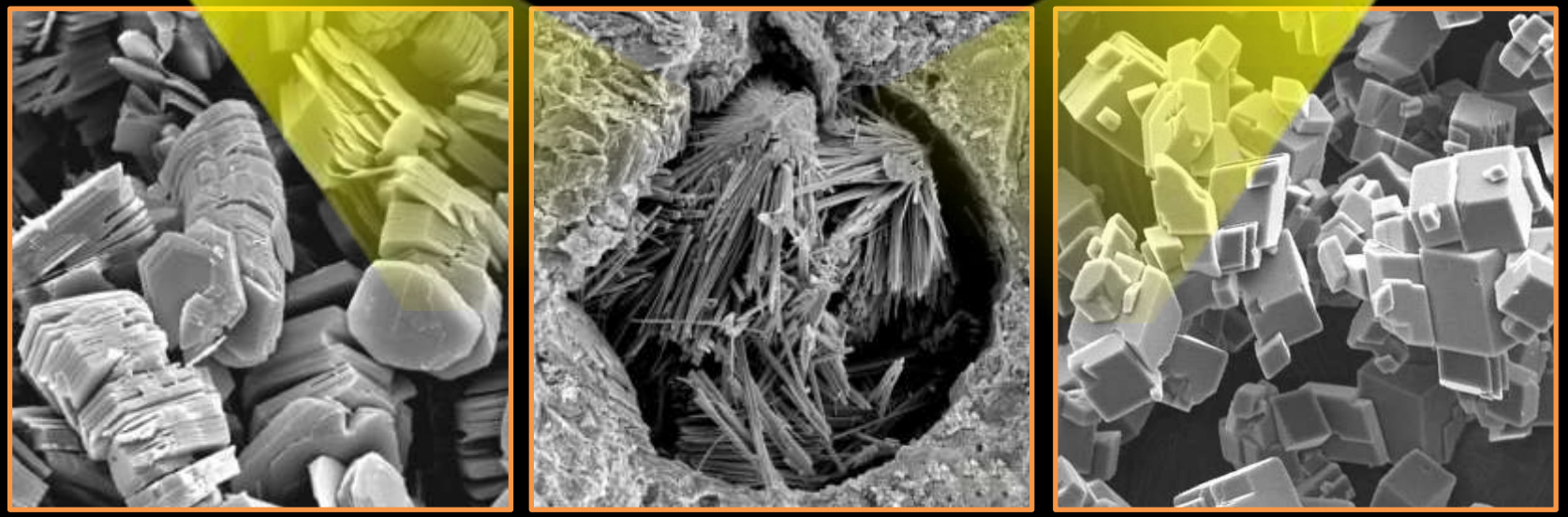
Industrial minerals in the spotlight:

optimizing their environmental performance for sustainable development

Luca Valentini

Università di Padova

GNM school "physical properties of minerals"
Bressanone/Brixen, 12-15 Feb 2018



SOME DEFINITIONS...

MINERAL

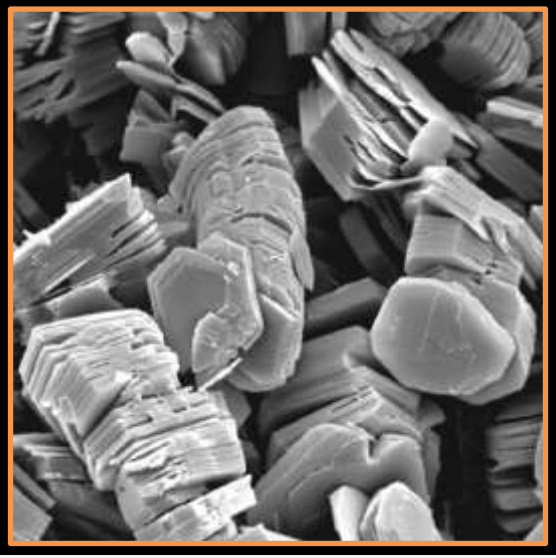
A mineral substance is defined as a naturally occurring,

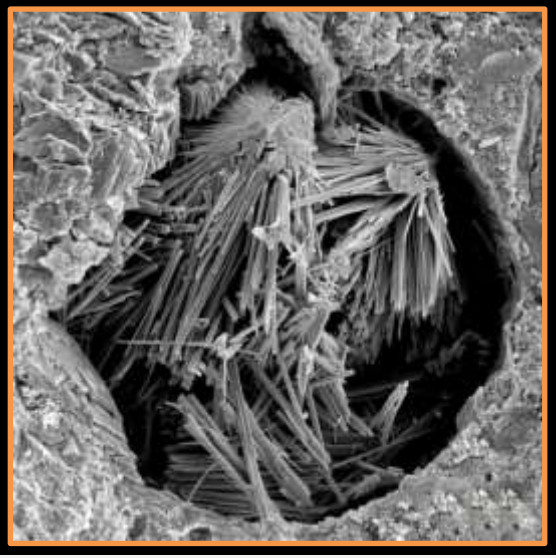
homogeneous solid, inorganically formed,

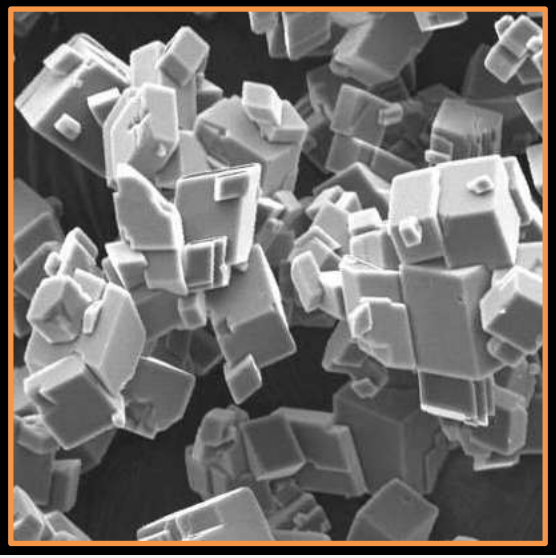
with a well defined chemical composition (or range of compositions),

and an ordered atomic arrangement, that has been formed by geological processes,

either on Earth or in extraterrestrial bodies (*Mineralogical Society of America*)







SOME DEFINITIONS...

NATURAL vs. ...NON-NATURAL, SYNTHETIC, MAN-MADE (WHAT ELSE?)

Cambridge Dictionary

Make your words meaningful

natural

adjective · UK /ˈnætʃ.ᵊr.ᵊl/ US /ˈnætʃ.ɚ.ᵊl/

natural *adjective* **(NOT ARTIFICIAL)**

B1 **as found in nature and not involving anything made or done by people:**

a natural substance

People say that breast-feeding is better than bottle-feeding because it's more natural.

*He died from natural **causes** (= because he was old or ill).*

*Floods and earthquakes are natural **disasters**.*

Natural food or drink is pure and has no chemical substances added to it and is therefore thought to be healthy:

natural mineral water

natural ingredients

SOME DEFINITIONS...

NATURAL vs. ...NON-NATURAL, SYNTHETIC, MAN-MADE (WHAT ELSE?)

- not involving anything made or done by people

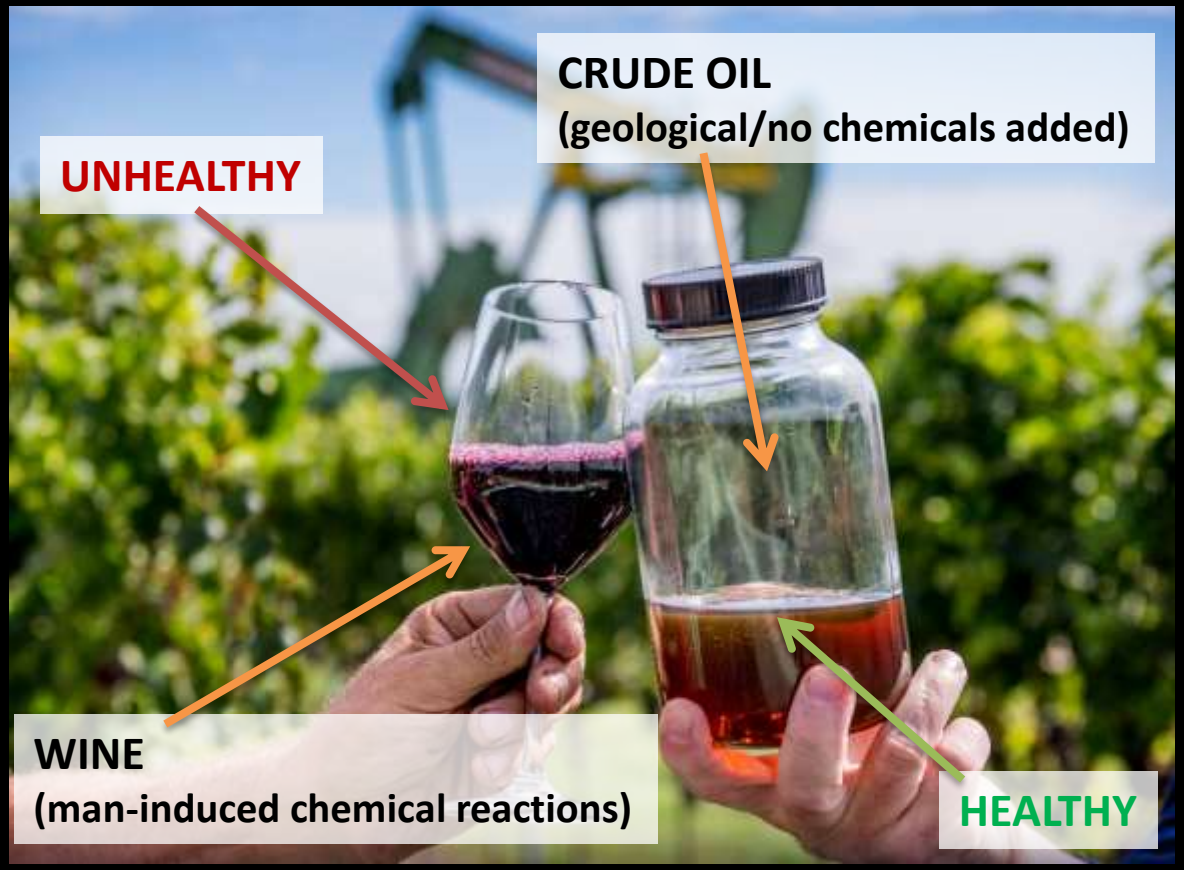
Grown vs Mined

Diamonds	Grown	Mined
Chemical Composition	C	C
Crystalline Structure	Cubic	Cubic
Refractive Index	2.42	2.42
Dispersion	0.044	0.044
Hardness	10	10
Density	3.52	3.52

SOME DEFINITIONS...

NATURAL vs. ...NON-NATURAL, SYNTHETIC, MAN-MADE (WHAT ELSE?)

- no chemical substances added and therefore thought to be healthy



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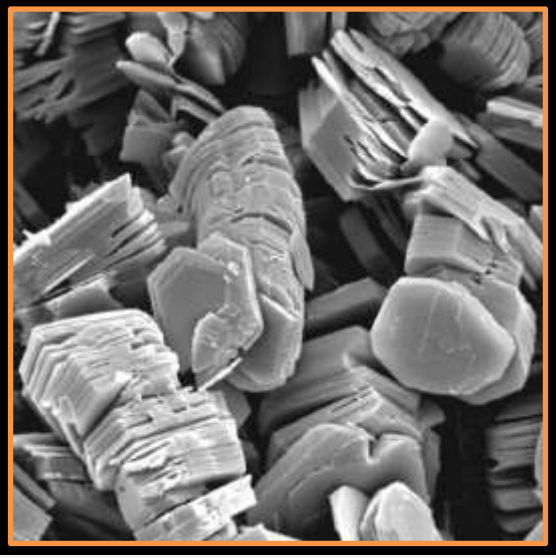
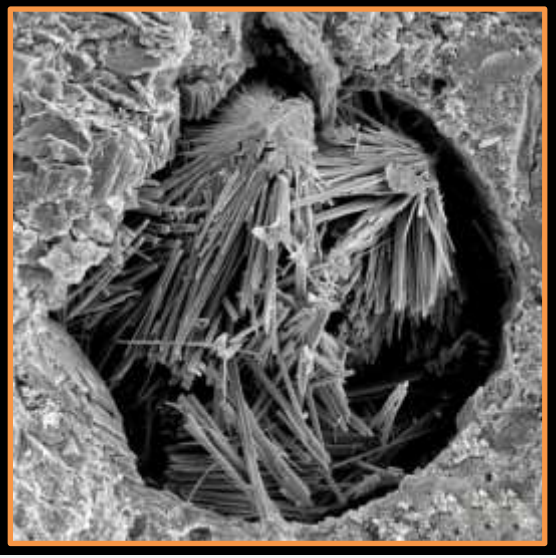
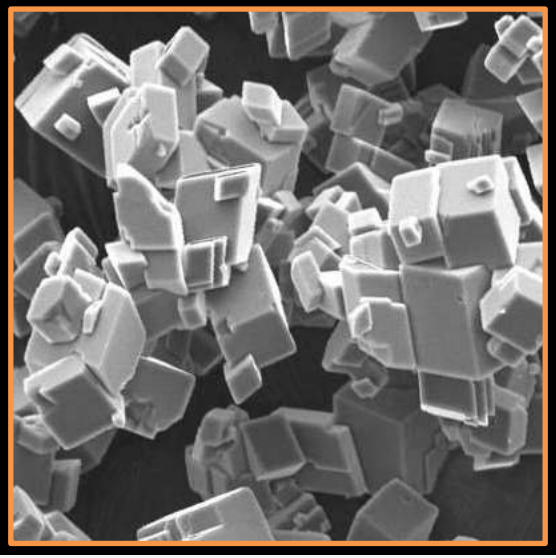






SOME DEFINITIONS...

NATURAL vs. ...NON-NATURAL, SYNTHETIC, MAN-MADE (WHAT ELSE?)

SOME DEFINITIONS…

INDUSTRIAL MINERAL

A geological material obtained by mining (in its broadest sense) which represents a non-metallic, non-fuel raw material of commercial value
(*An Introduction to Industrial Minerals*)

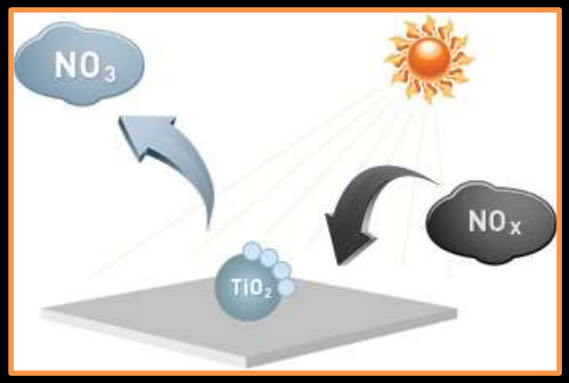
EXAMPLES OF INDUSTRIAL MINERALS

Some metal ores are also used as industrial minerals

Rutile (TiO_2)

Extraction of Ti and use as Ti-oxide

→ **TioCem ®**



Chromite ($FeCr_2O_4$)

Extraction of Cr and use as Cr-oxide

EXAMPLES OF INDUSTRIAL MINERALS

Industrial minerals may be obtained as by-products of ore mining

Galena (PbS)

Baryte ($BaSO_4$)

Sfalerite (ZnS)

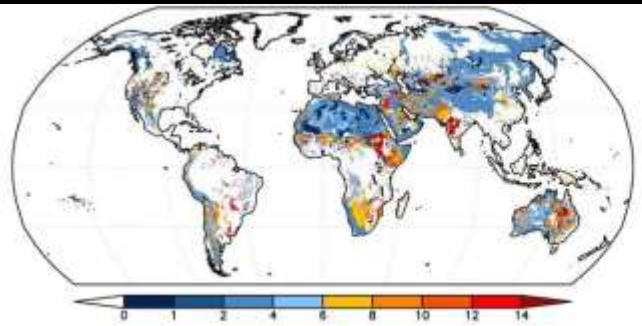
Fluorite (CaF_2)

EXAMPLES OF INDUSTRIAL MINERALS

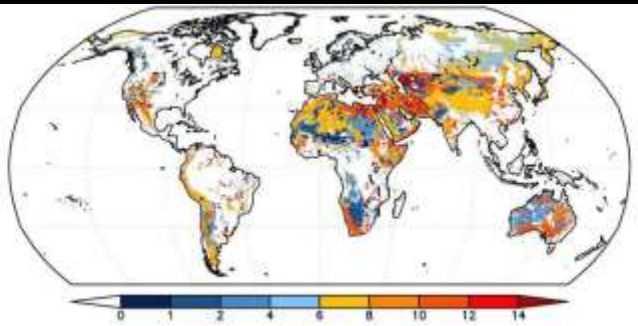
- Asbestos
- Baryte
- Calcite
- Clays
- Corundum
- Diamond
- Dolomite
- Feldspar
- Graphite
- Gypsum
- Magnesite
- Mica
- Quartz
- Talc
- Zeolite
- Zircon

EXAMPLES OF INDUSTRIAL MINERALS

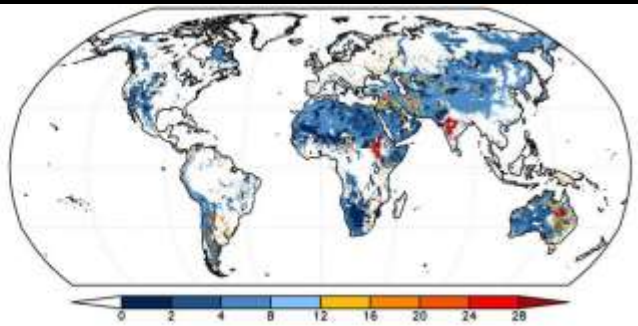
Clay minerals distribution in soils



CAOLINITE



ILLITE

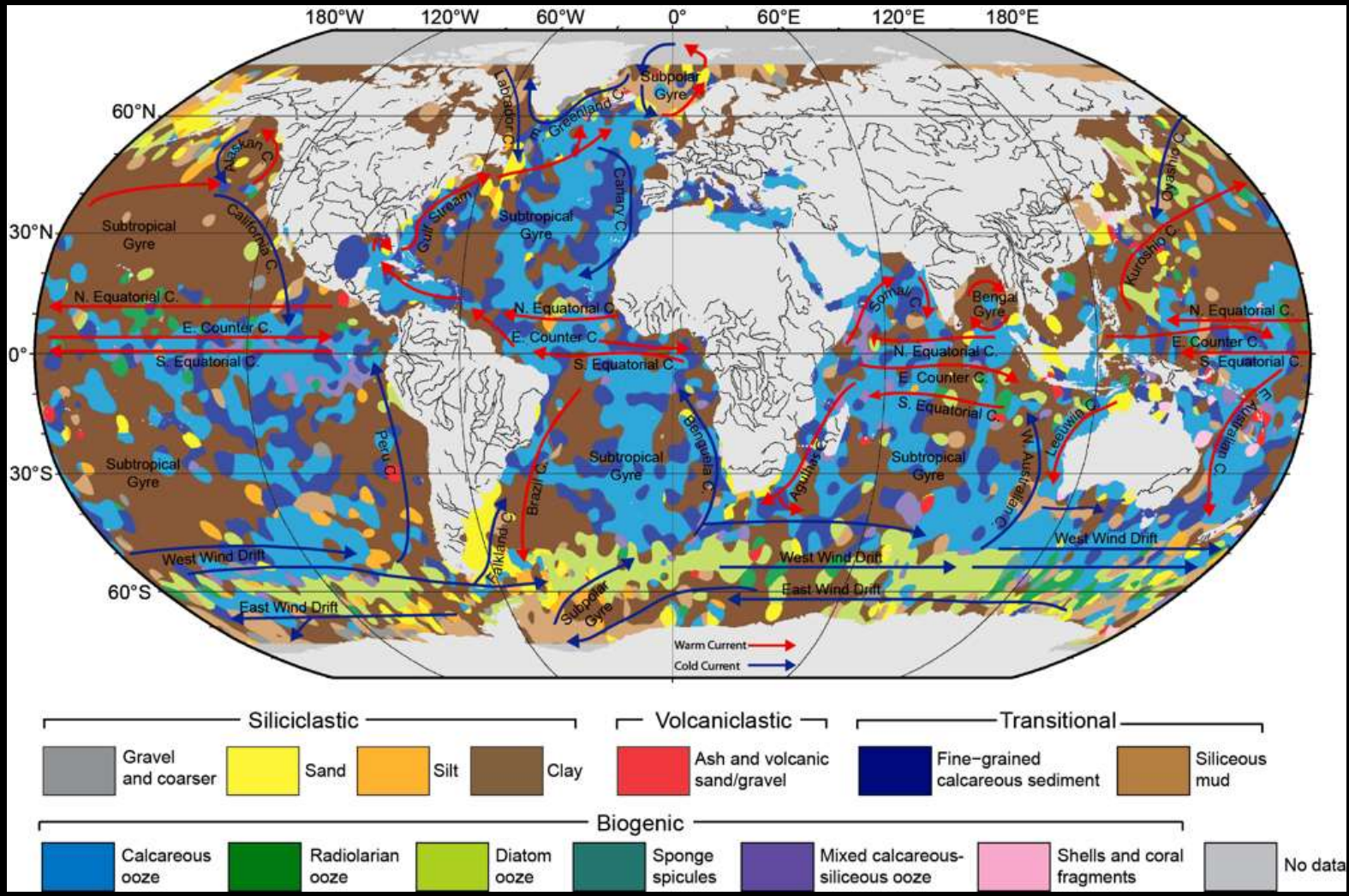


SMECTITE

Worldwide kaolinite production (USGS, 2017) 37,000,000 T

EXAMPLES OF INDUSTRIAL MINERALS

Clay distribution in marine sediments



EXAMPLES OF INDUSTRIAL MINERALS

Worldwide limestone production (USGS, 2017) 350,000,000 T

Properties of materials

made from industrial minerals

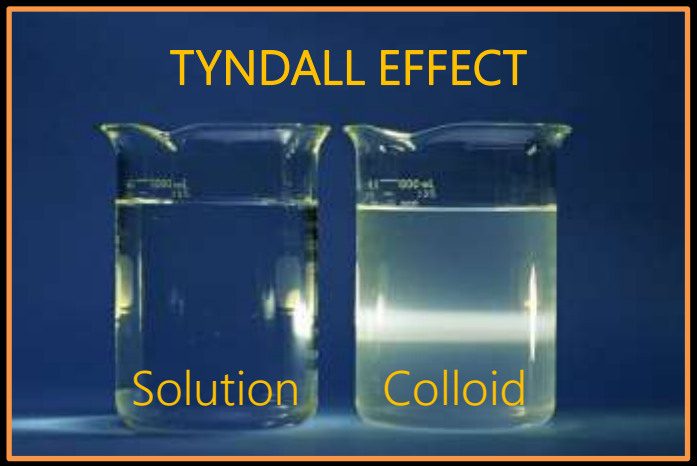
BULK PROPERTIES

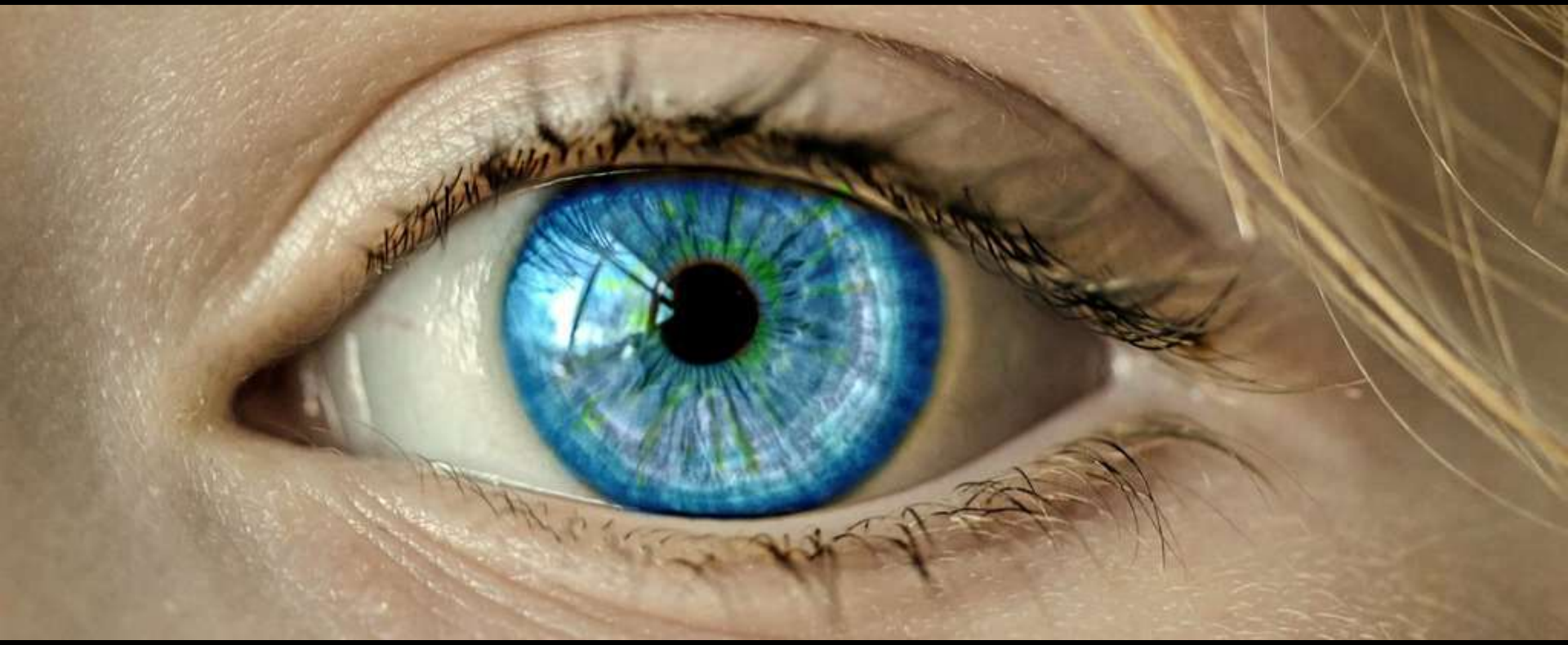
Microstructural features

Microstructure = set of spatial and geometrical relationships among the different phases present in a heterogeneous material

A *heterogeneous material* is made of domains of different phases, or of a single phase in different states of aggregation

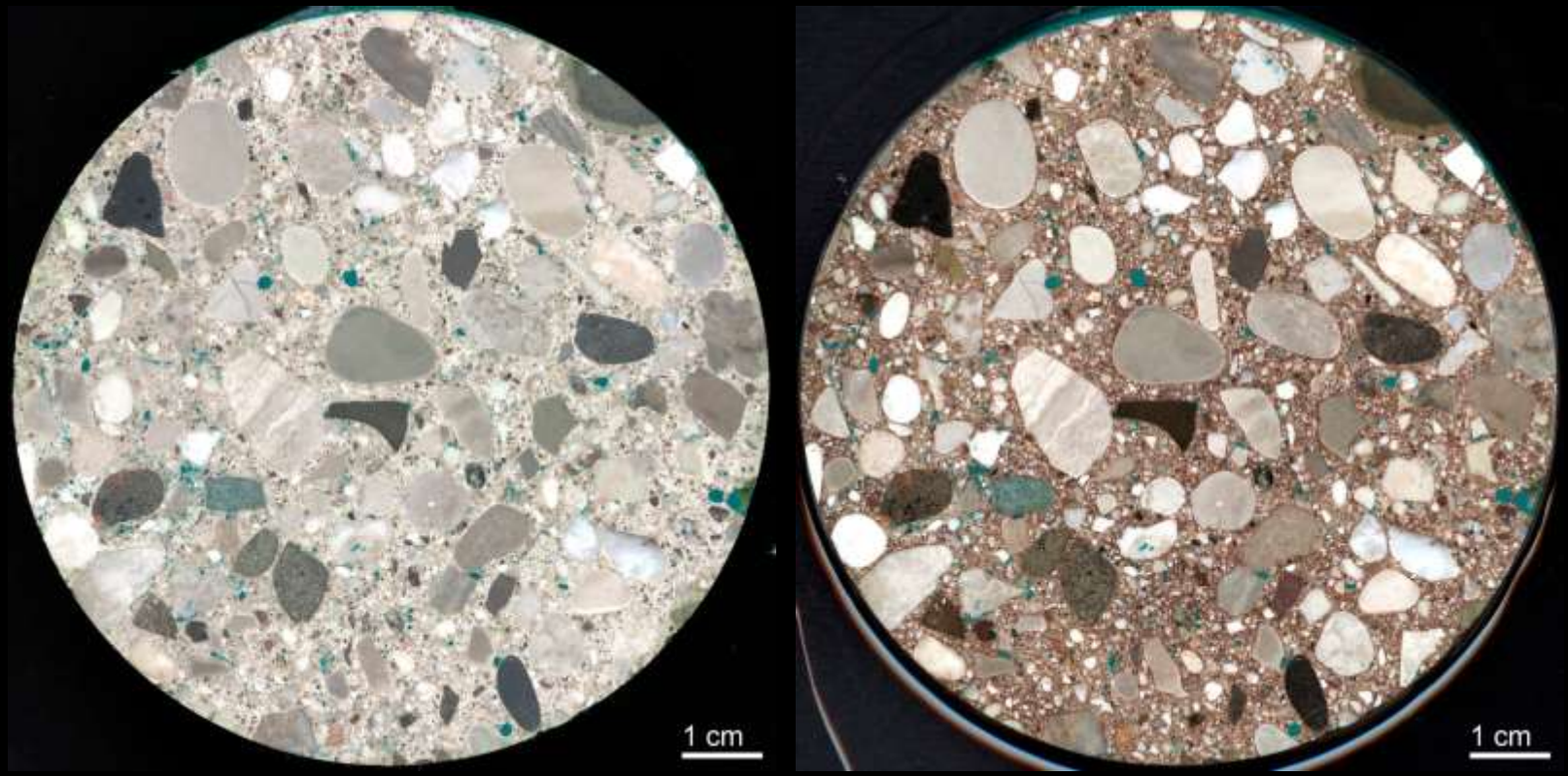
- Colloids
- Gels
- Foams
- Emulsions
- Soils
- Earth's crust
- Bones
- Blood





BULK PROPERTIES

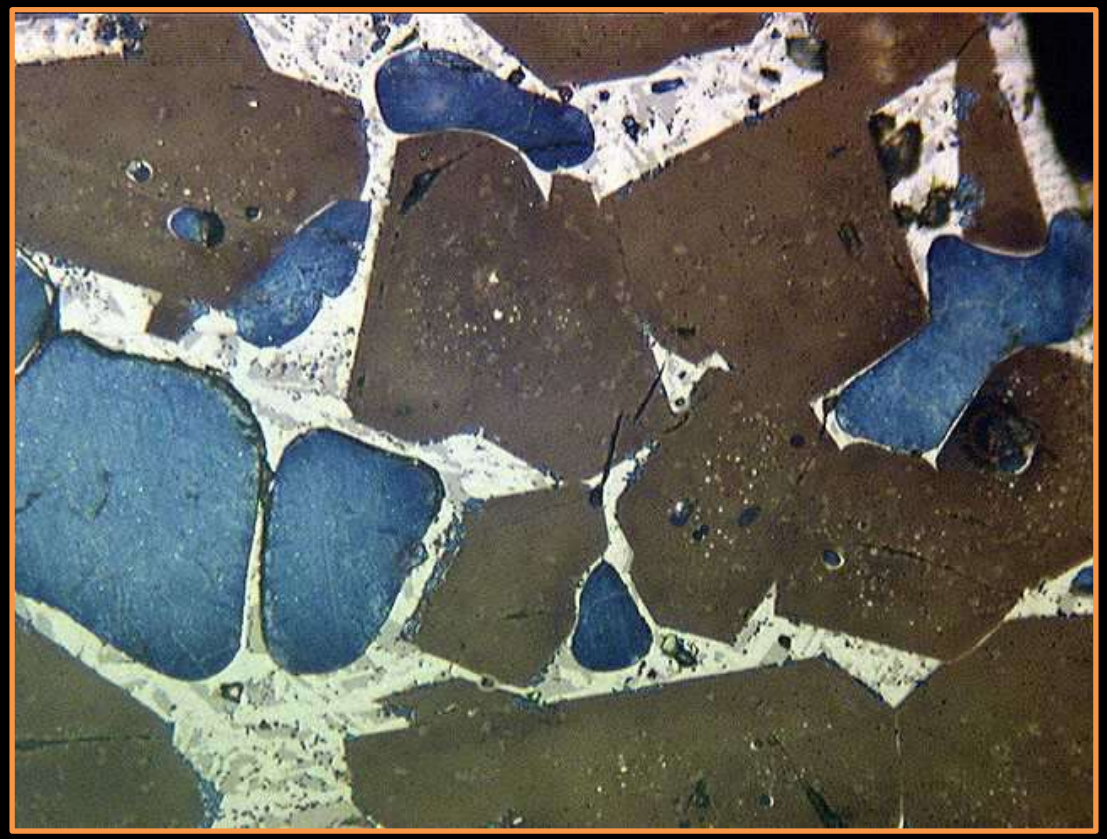
Microstructural features: optical methods



Optical scan of concrete microstructure

BULK PROPERTIES

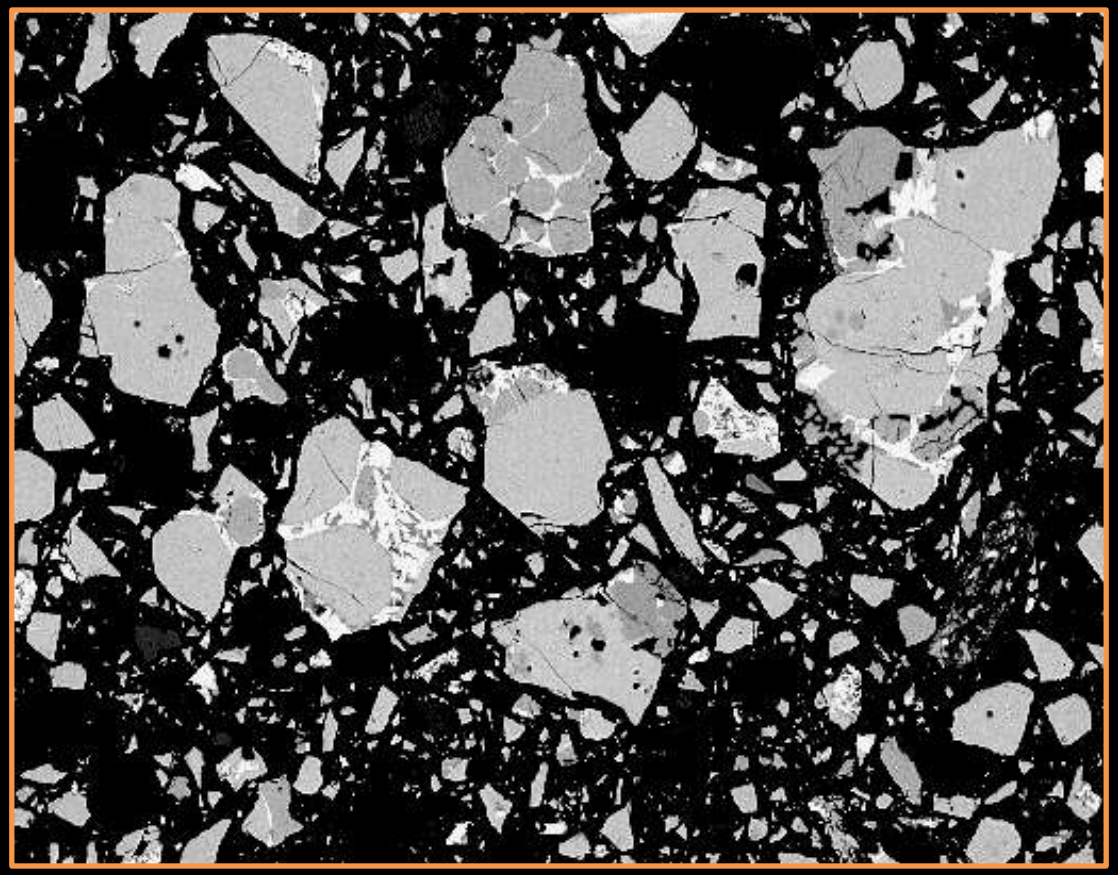
Microstructural features: optical methods



Optical micrograph of clinker microstructure

BULK PROPERTIES

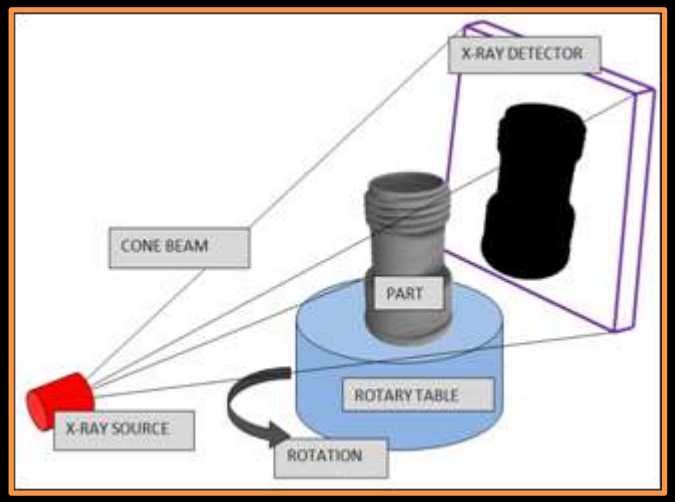
Microstructural features: electron microscopy

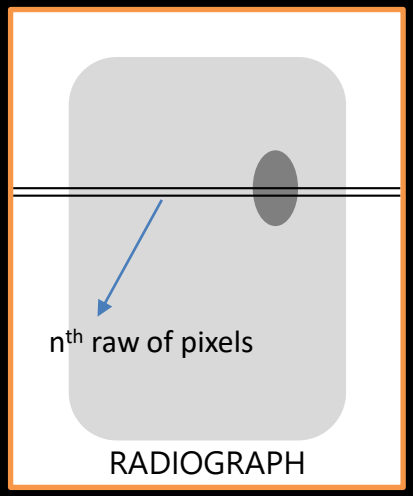


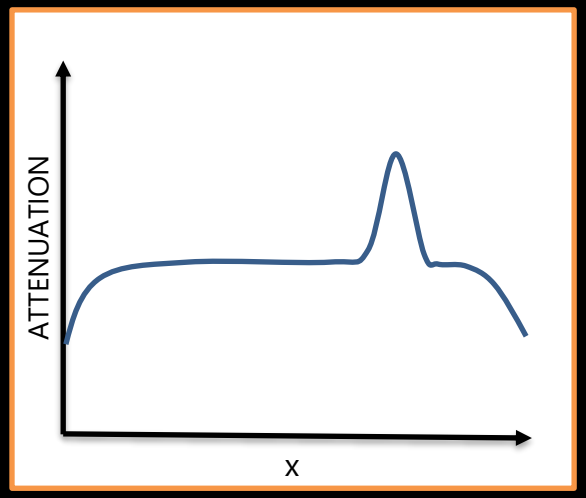
SEM-BSE image of cement powder

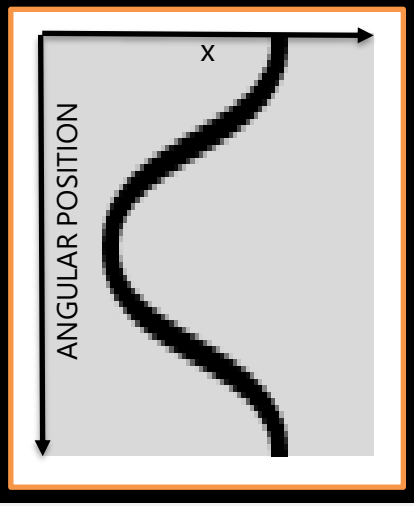
BULK PROPERTIES

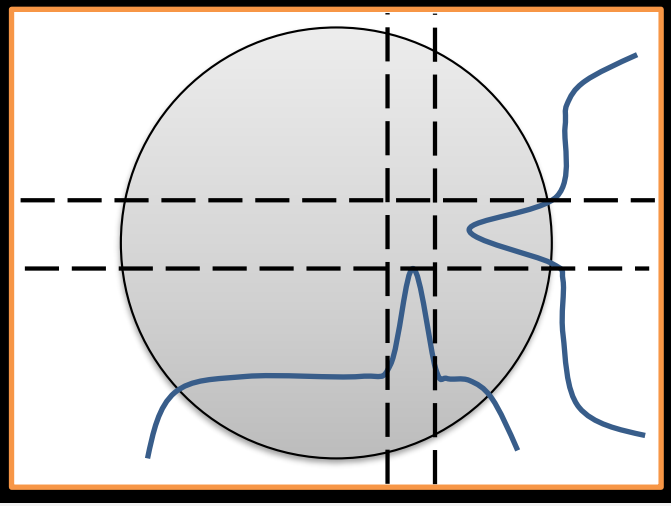
Microstructural features: X-ray tomography

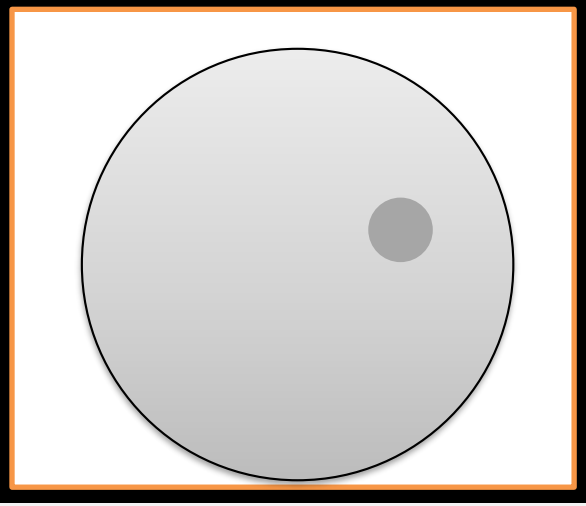












BULK PROPERTIES

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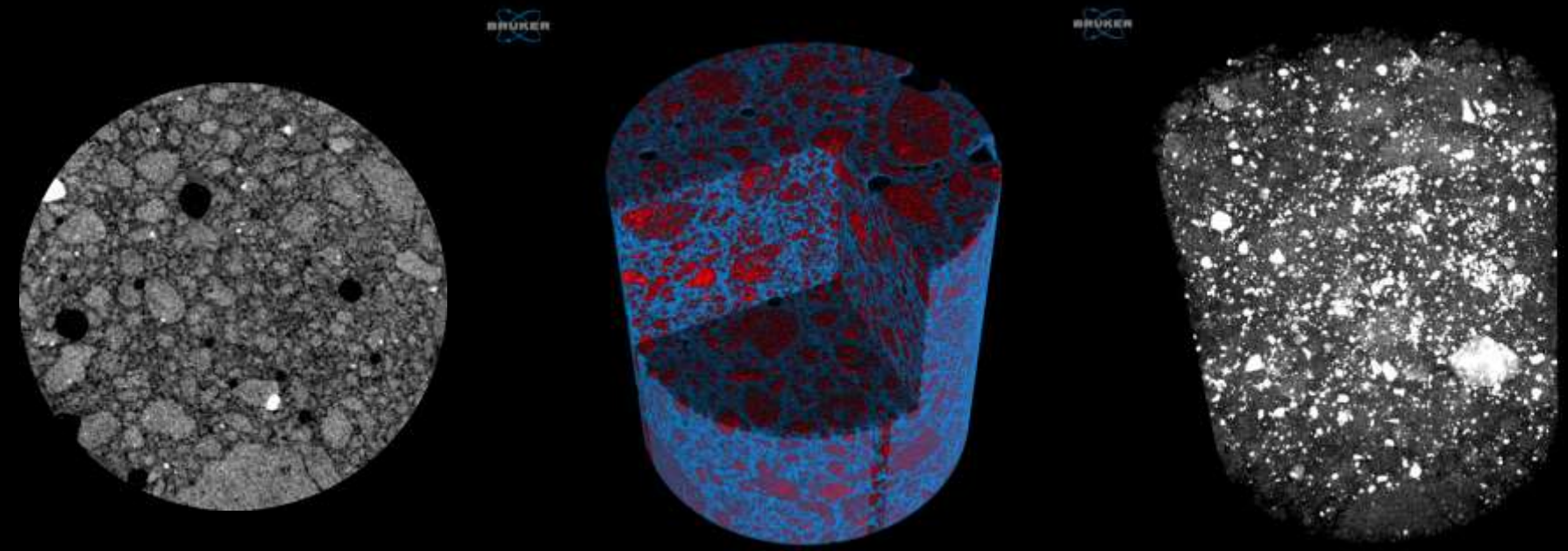
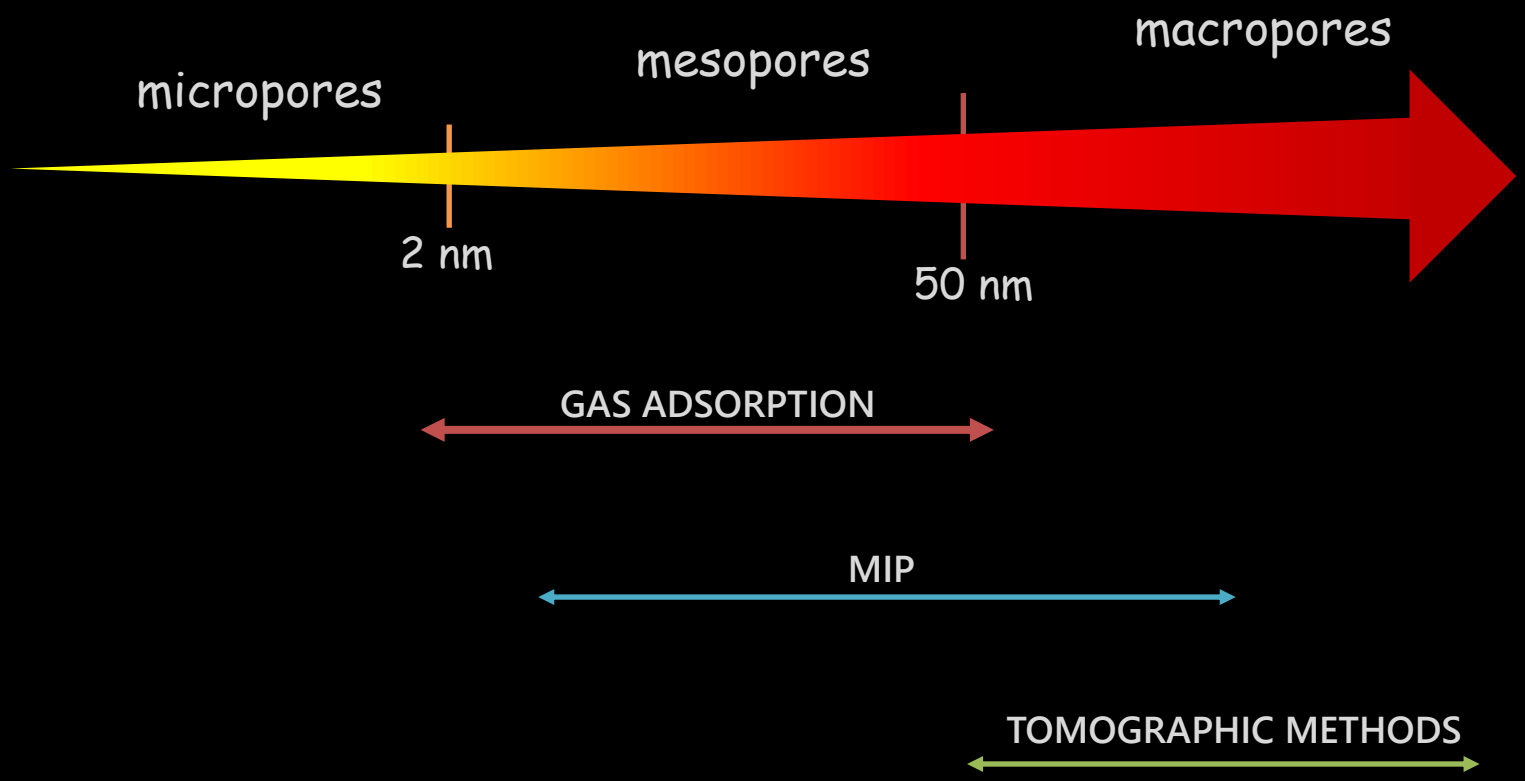


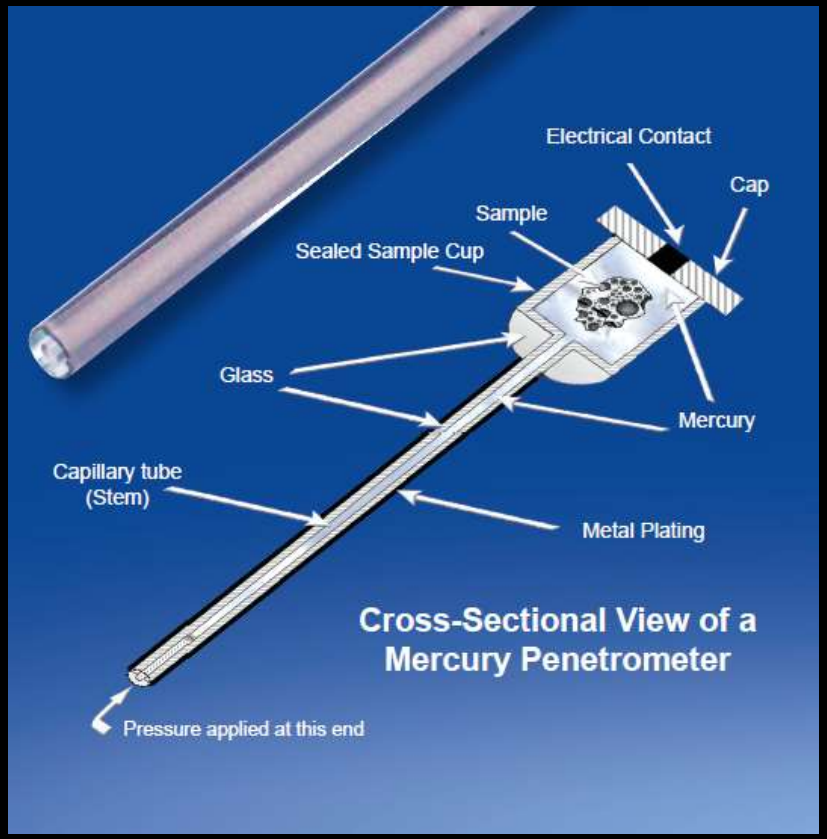
BULK PROPERTIES

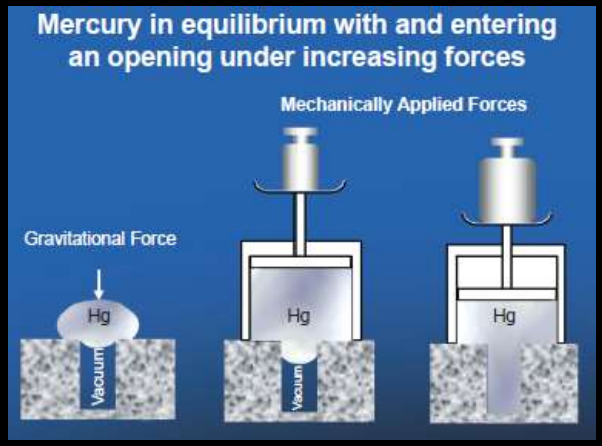
Porosity



BULK PROPERTIES

Porosity: Mercury Intrusion Prorosimetry





$$D = -4\gamma cos\theta / P$$

BULK PROPERTIES

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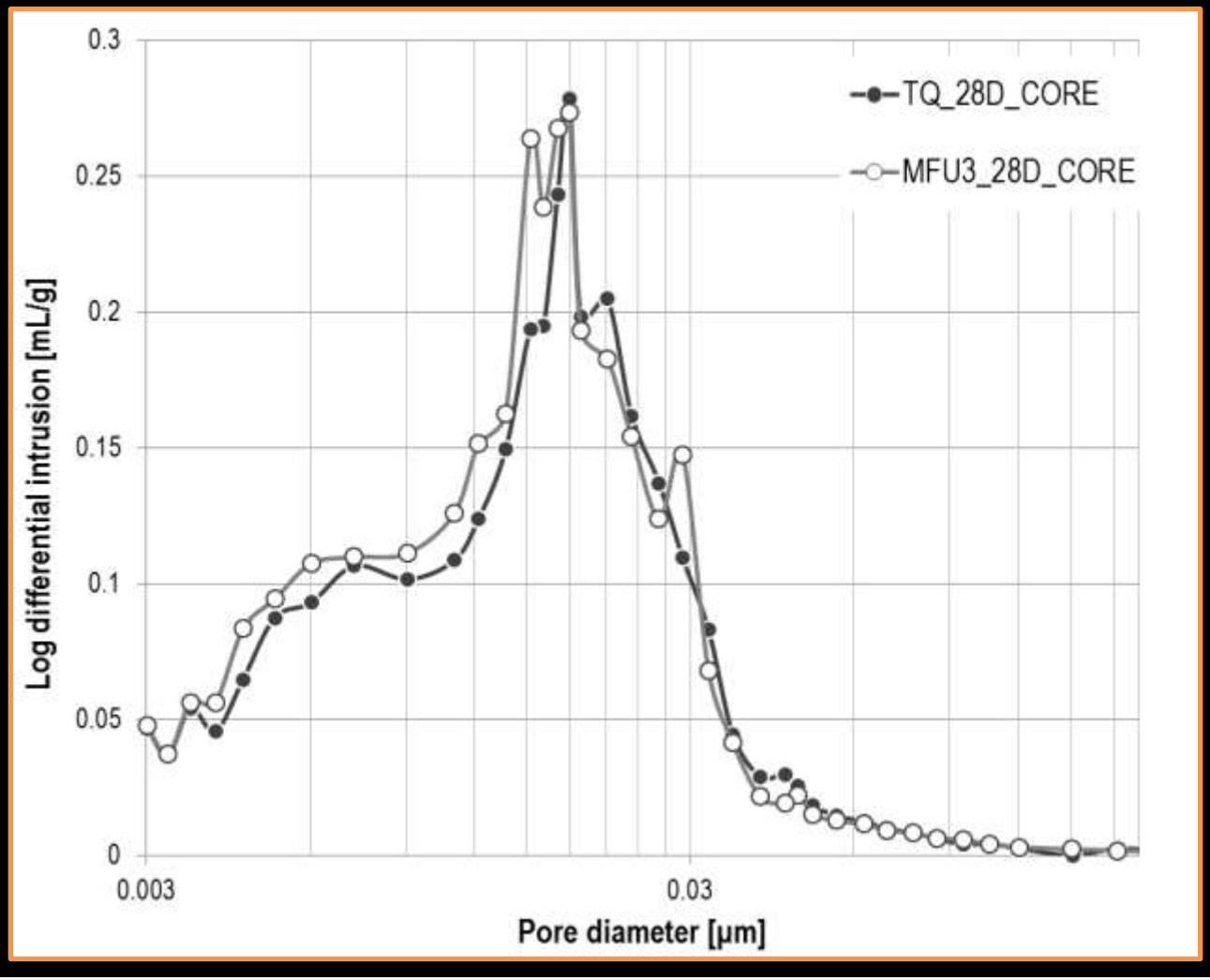
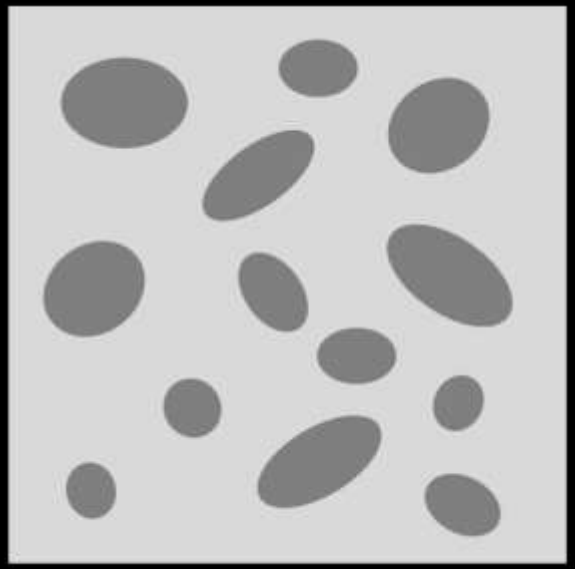
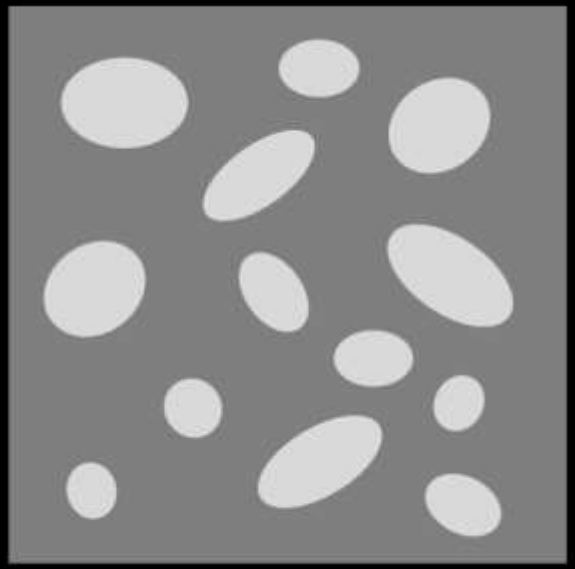


BULK PROPERTIES

Relationship between microstructure and mechanical properties



A percolated



B percolated

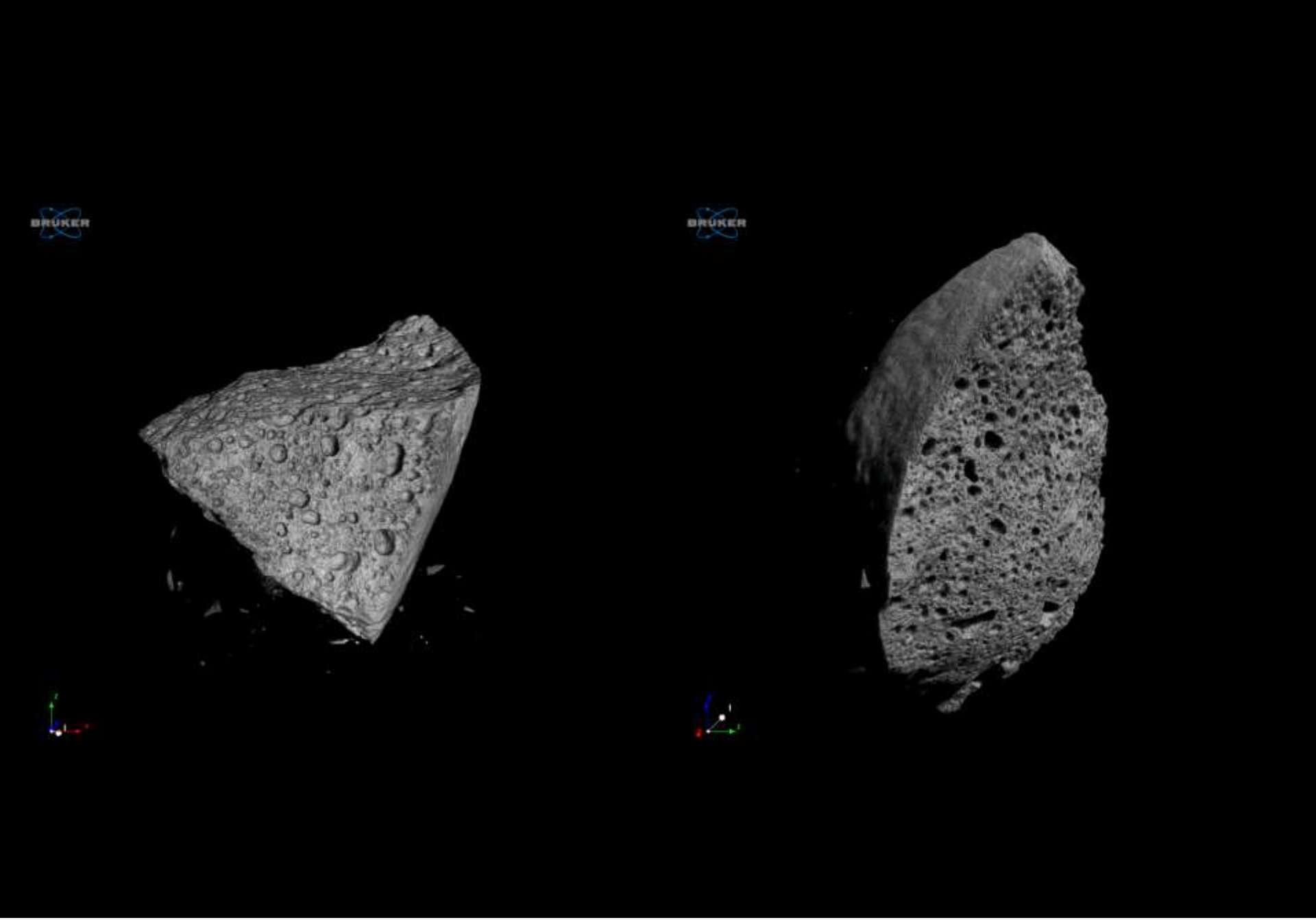
A "soft" phase

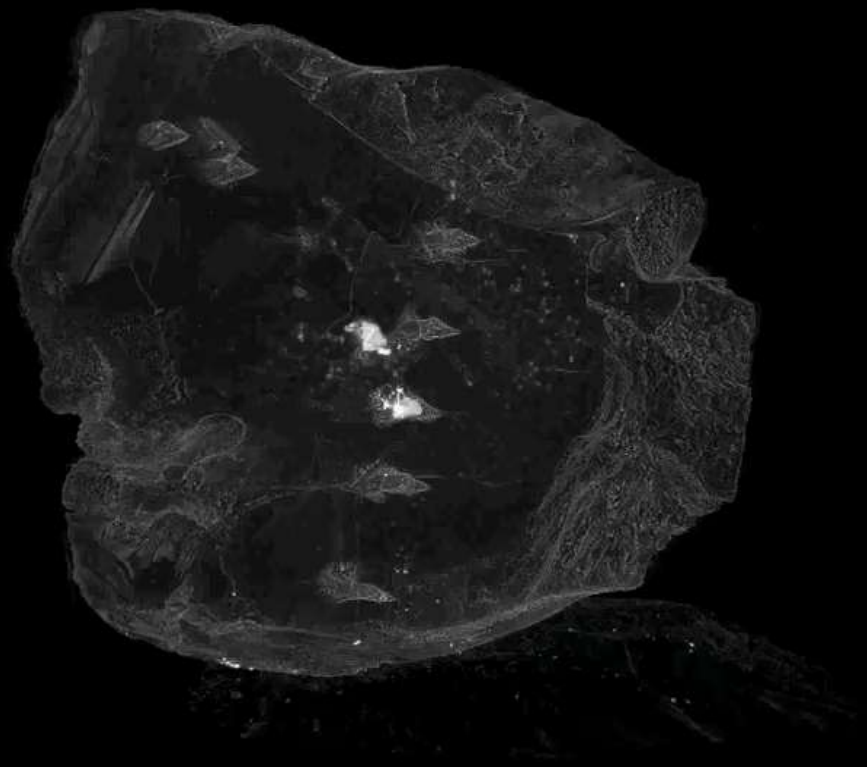
B "hard" phase

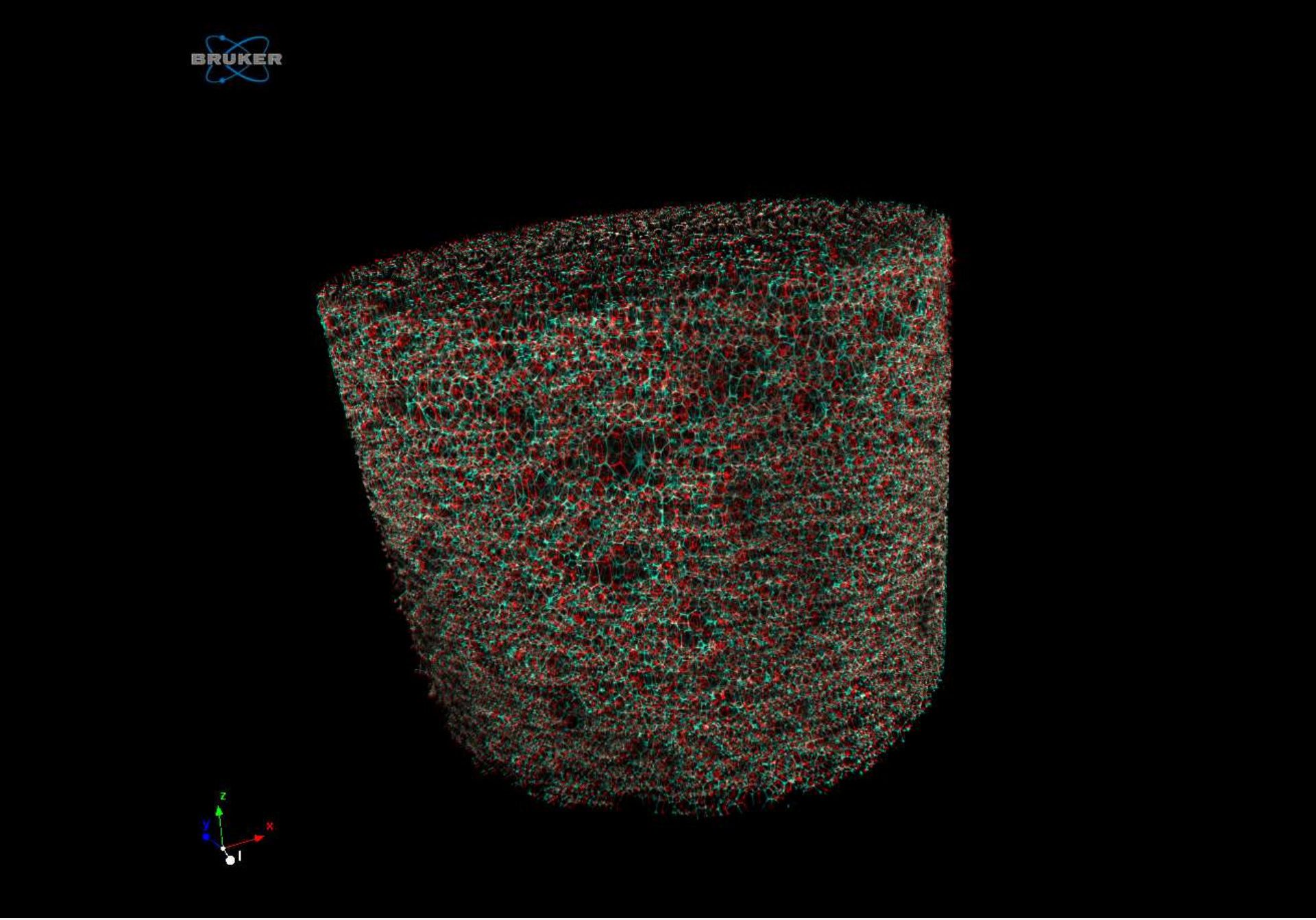
50 % A & 50 % B

Gallery of 3D rendered

Tomographic images


BRUKER
BRUKER

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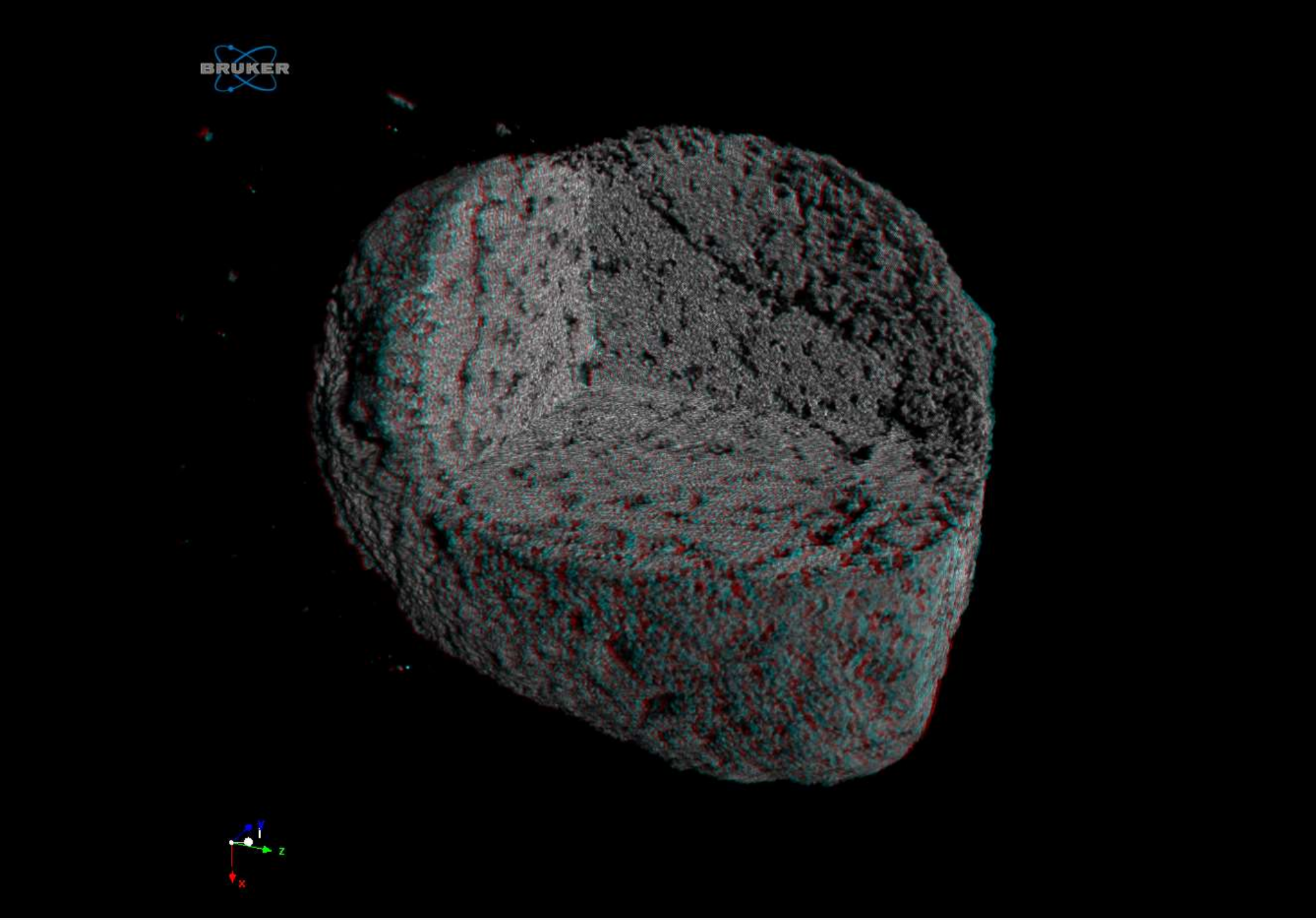
z
y
x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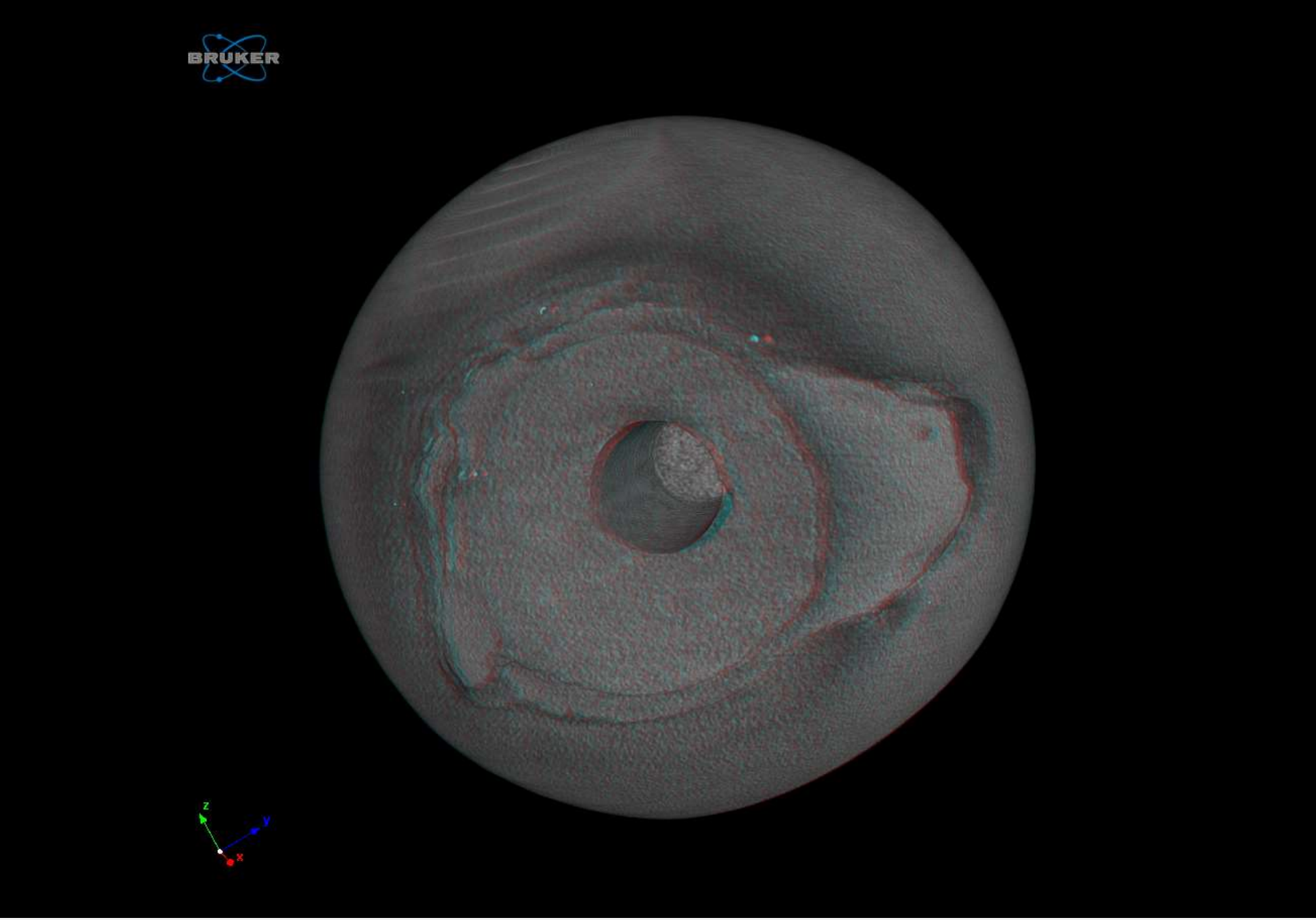
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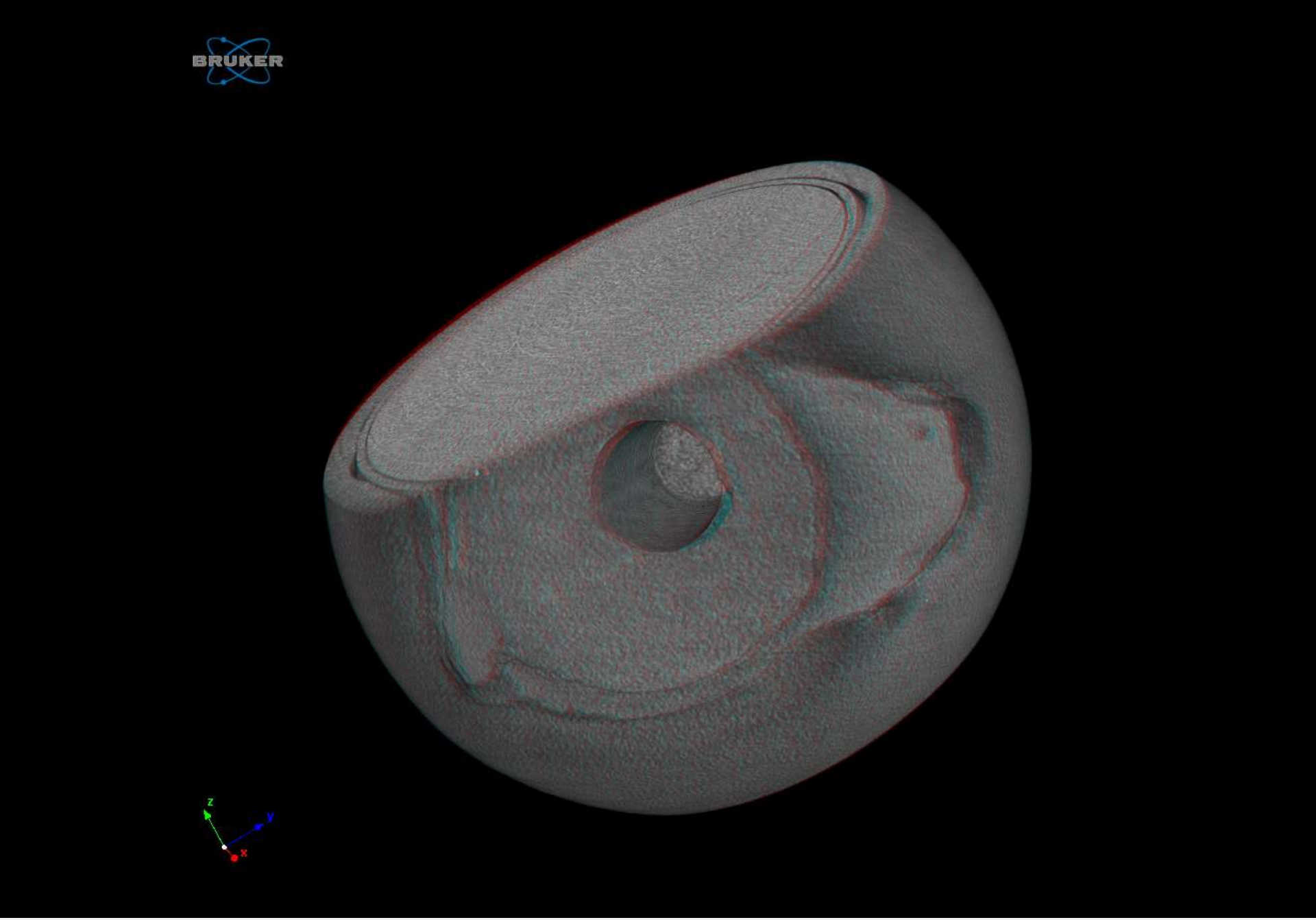
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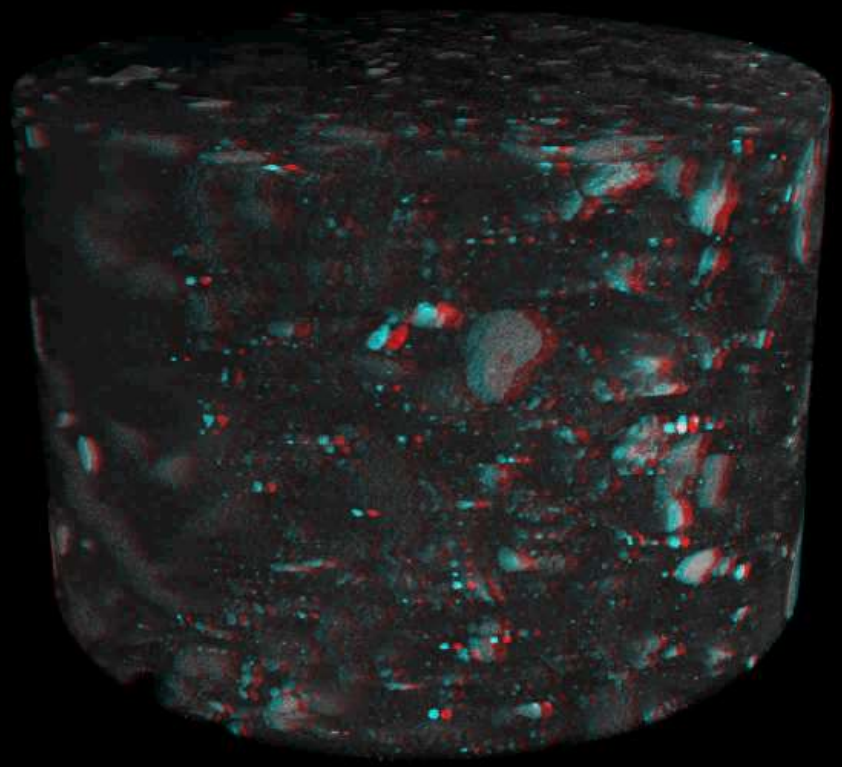
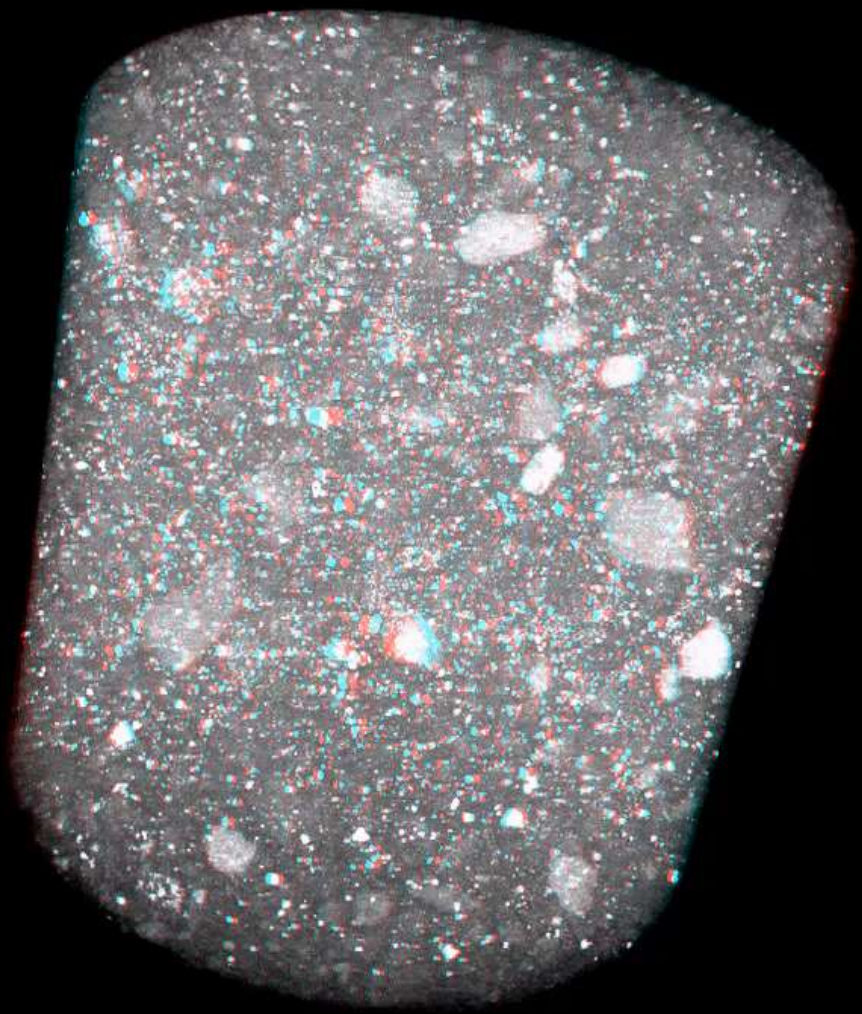
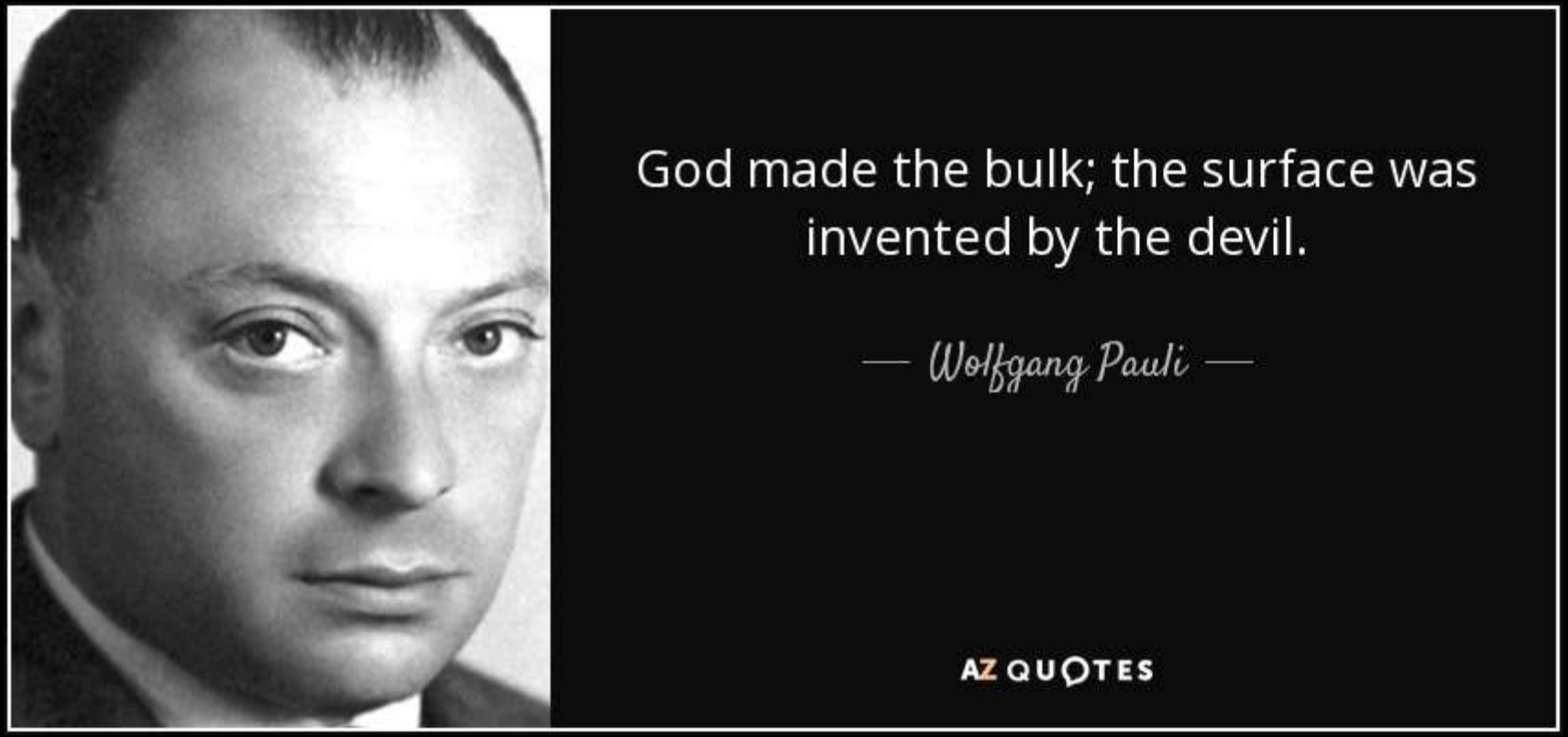




SURFACE PROPERTIES



SURFACE PROPERTIES

SURFACE FREE ENERGY

$$dG = -SdT + VdP + \sum_i \mu_i dn_i + \sum_k \sigma_k dA_k$$

I II

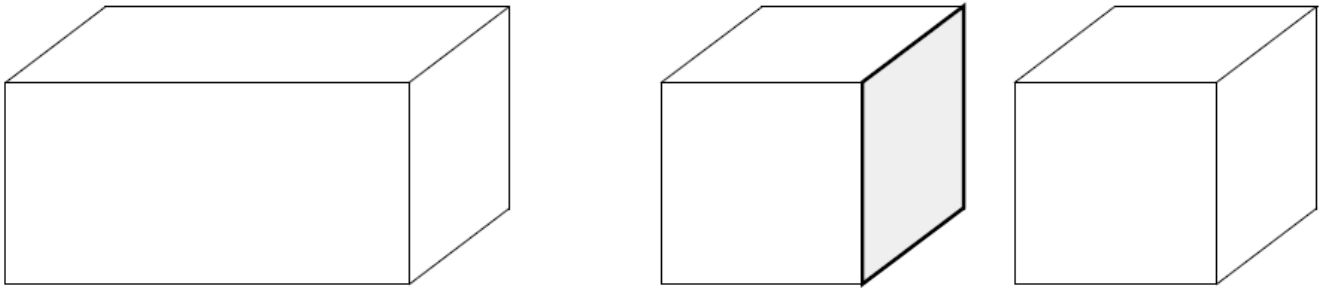


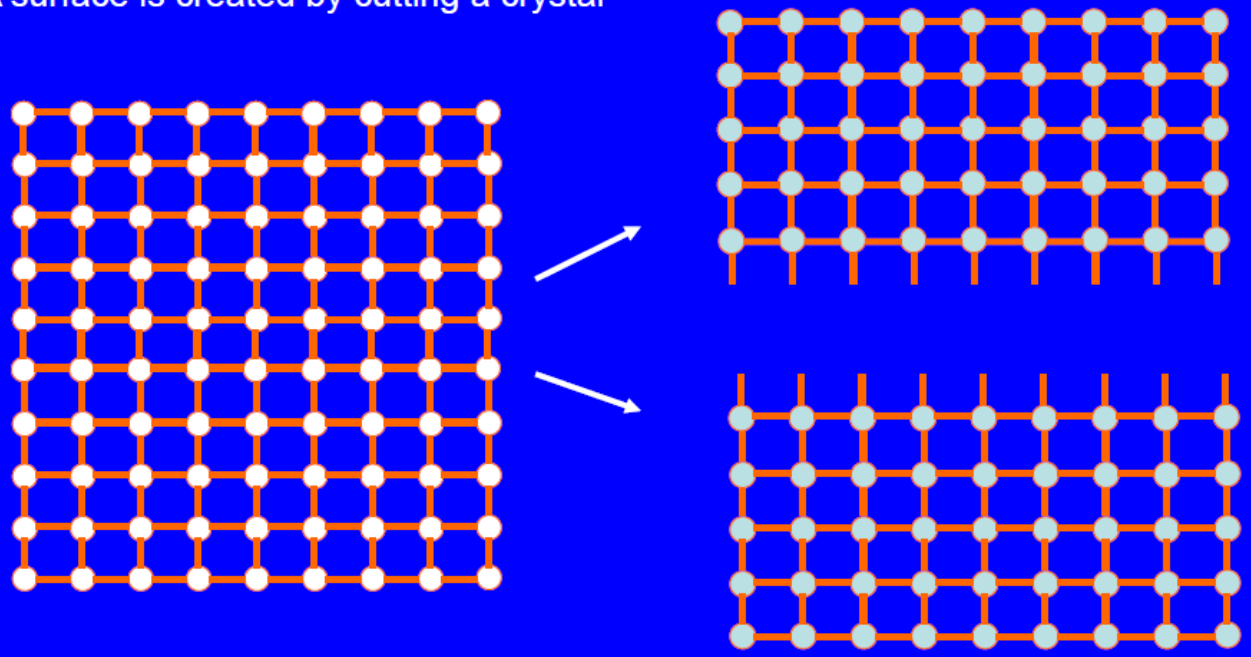
Figure 5.1: Schematic of two configurations of a solid used in defining surface energy.

Surfaces behave differently compared to the bulk!

SURFACE PROPERTIES

Concept of ideal flat surfaces (by cleavage process)

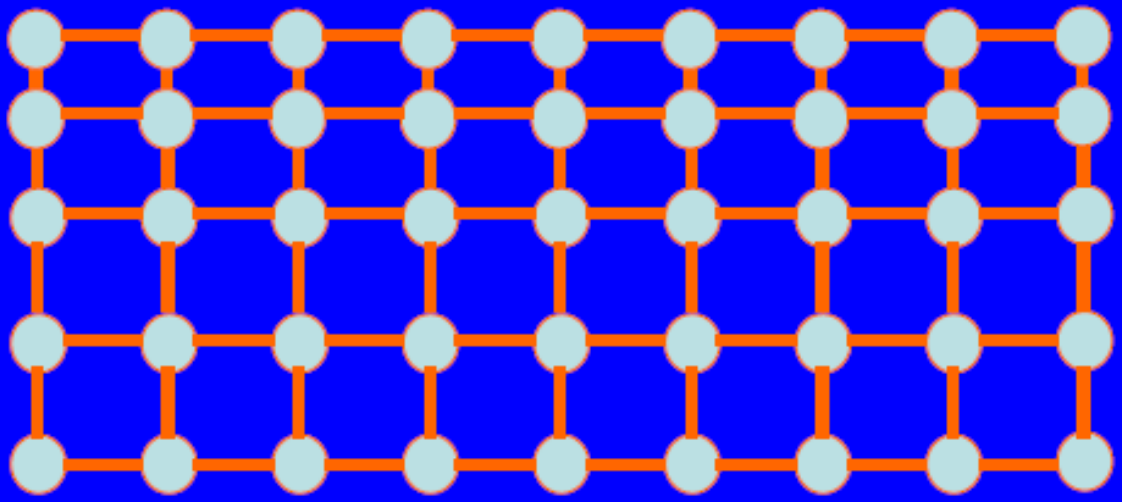
A surface is created by cutting a crystal



But such ideal surfaces are generally unstable

Surfaces behave differently compared to the bulk!

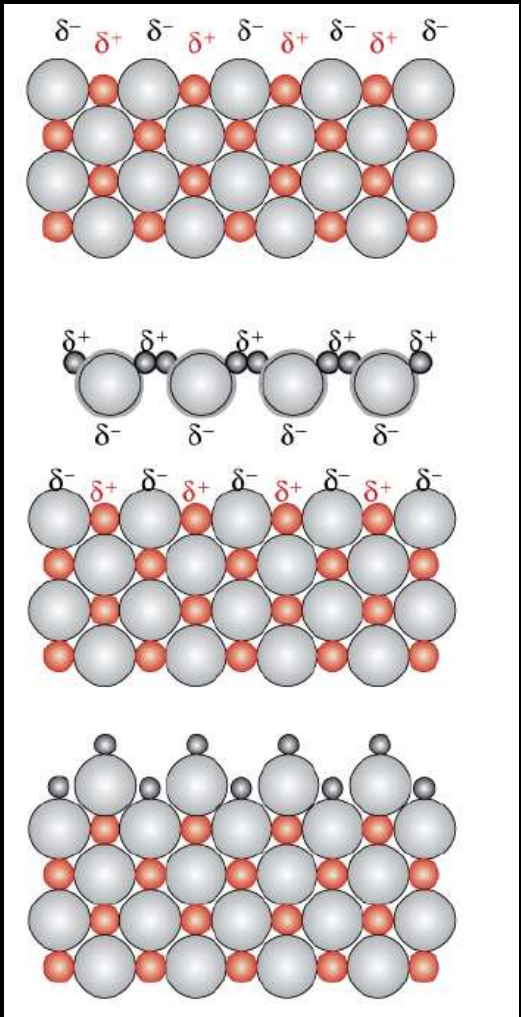
SURFACE PROPERTIES



Surface relaxation:
Modification of the near-surface interplanar distances

Surfaces behave differently compared to the bulk!

SURFACE PROPERTIES



Residual surface charge

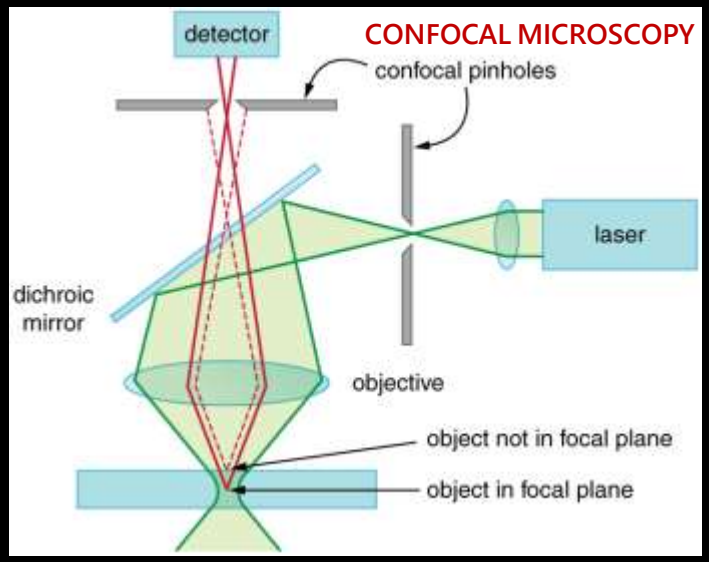
H_2O adsorption (wetting)

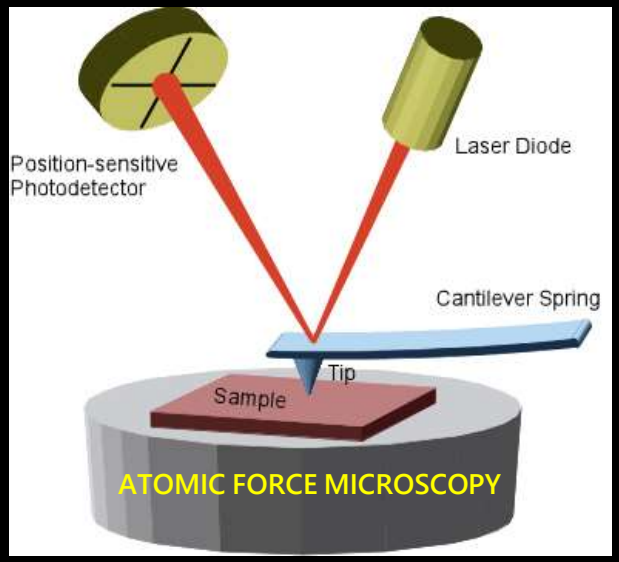
Surface protonation

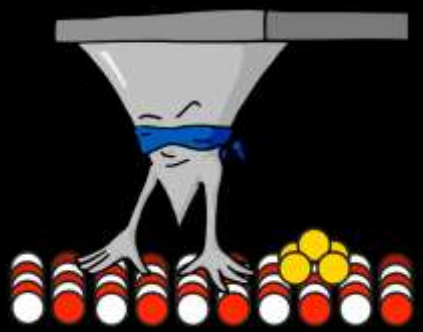
Surfaces behave differently compared to the bulk!

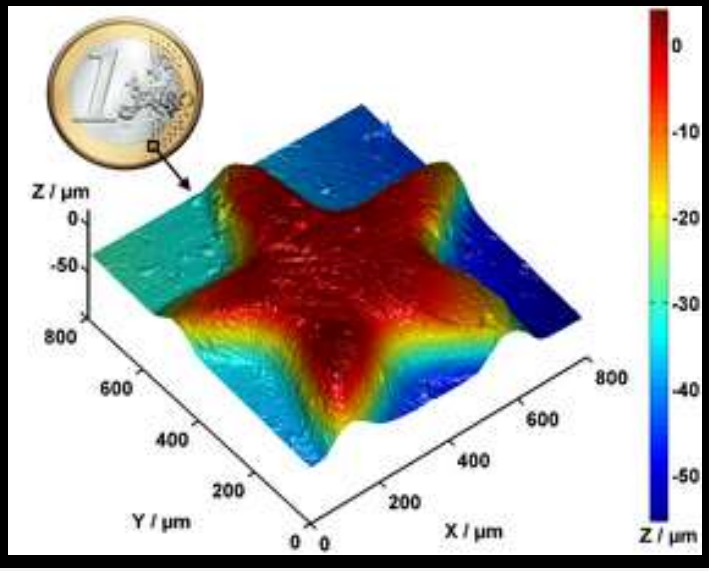
SURFACE PROPERTIES

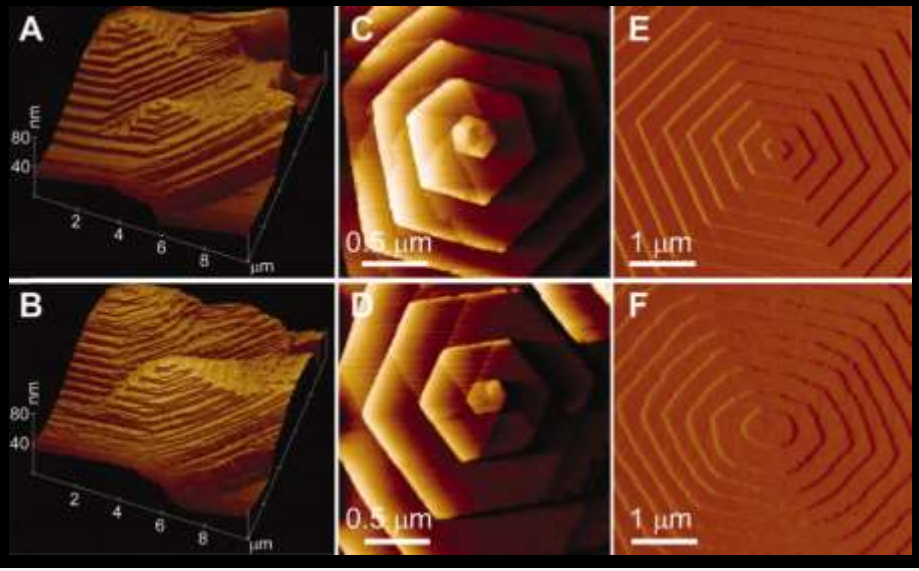
"Observing" surfaces



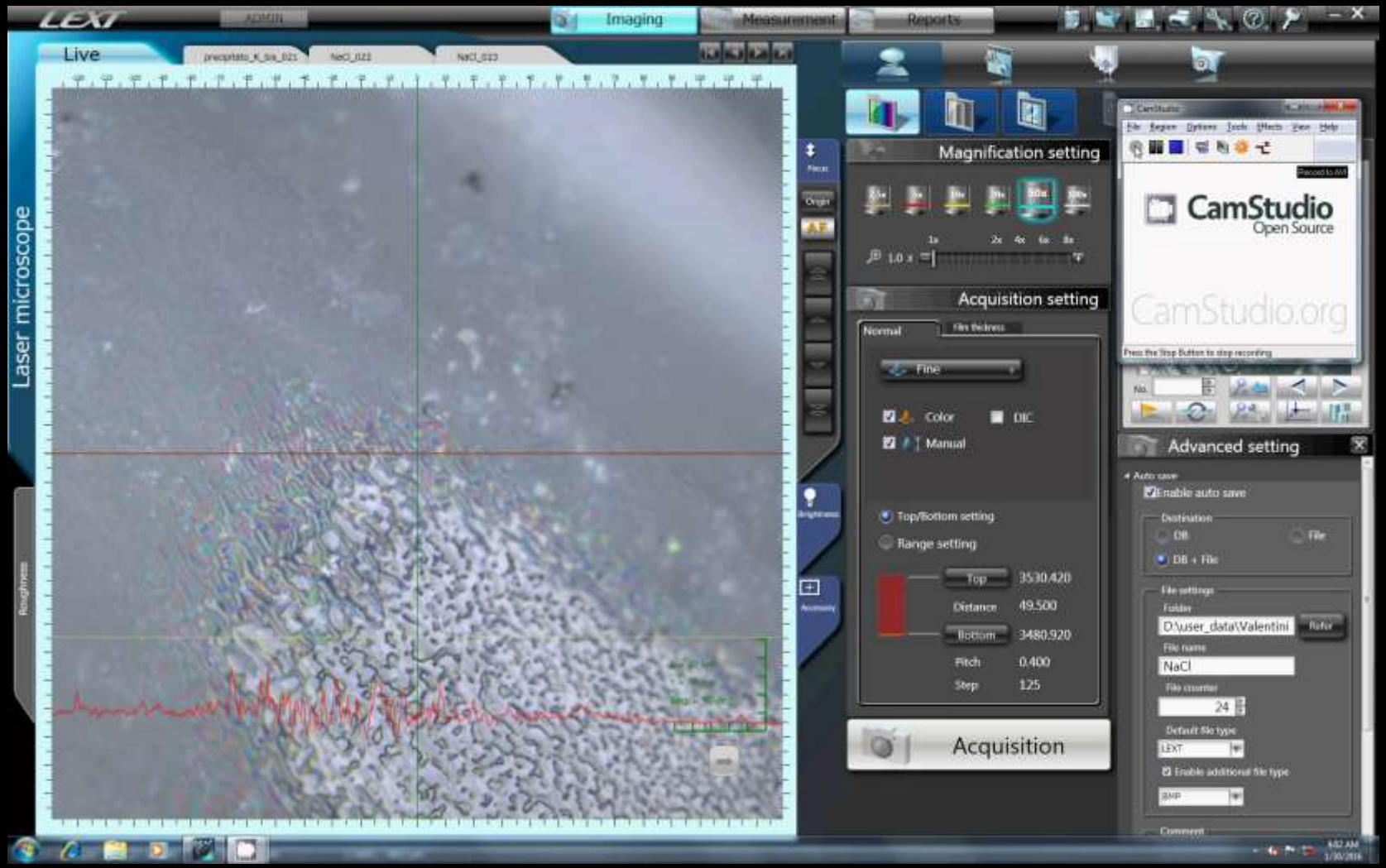






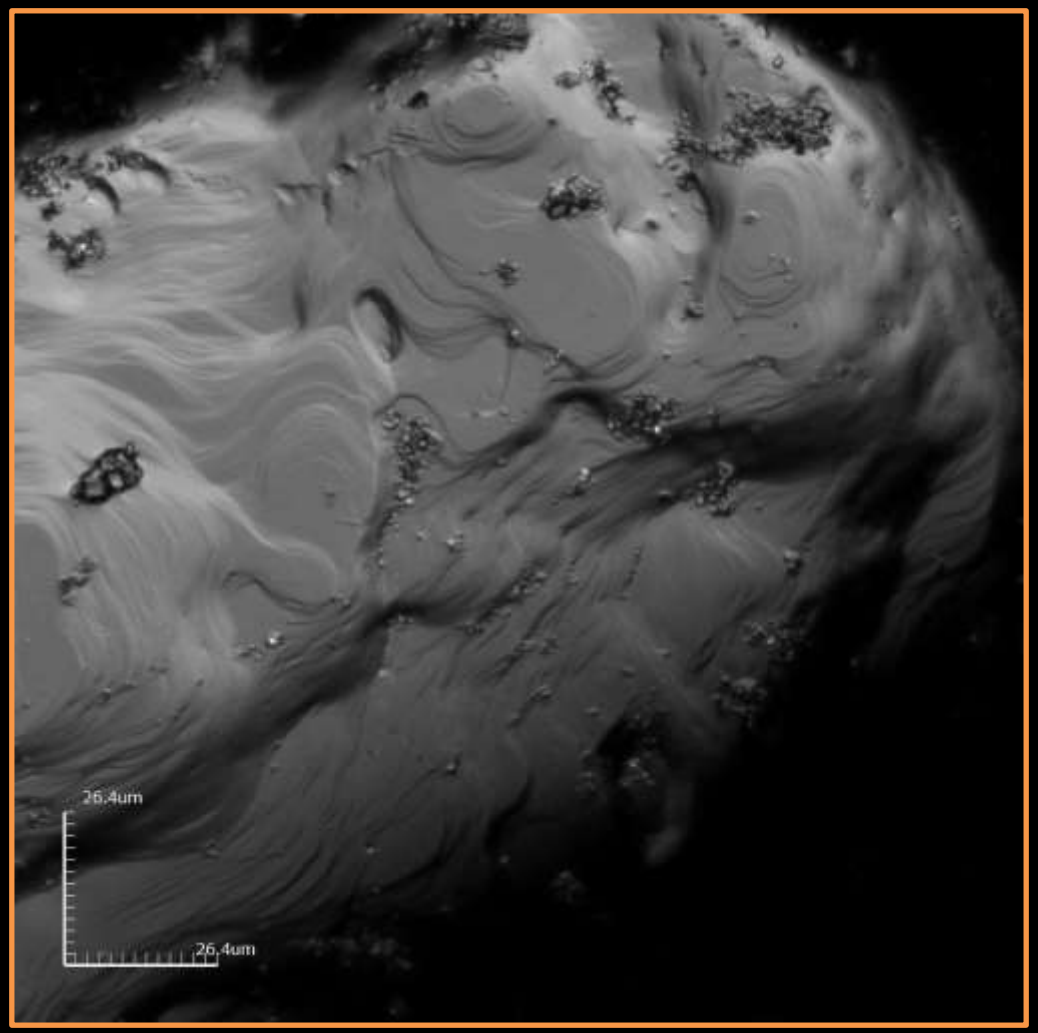


SURFACE PROPERTIES



Surfaces are where things happen

SURFACE PROPERTIES



Surface of NaCl crystal after partial dissolution

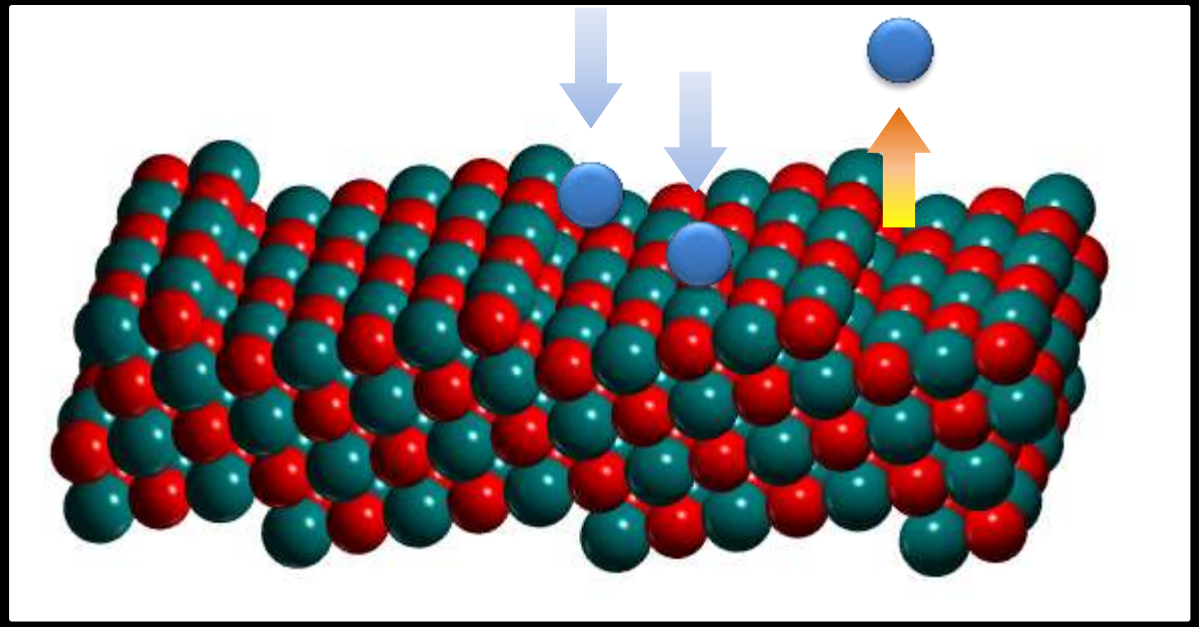
SURFACE PROPERTIES

link to video: https://www.youtube.com/watch?v=8n2AhUYk2WA

Surfaces are where things happen

SURFACE PROPERTIES

Adsorption is the attachment of species in solution at the interface with a pre-existing solid surface, without formation of a new crystal structure

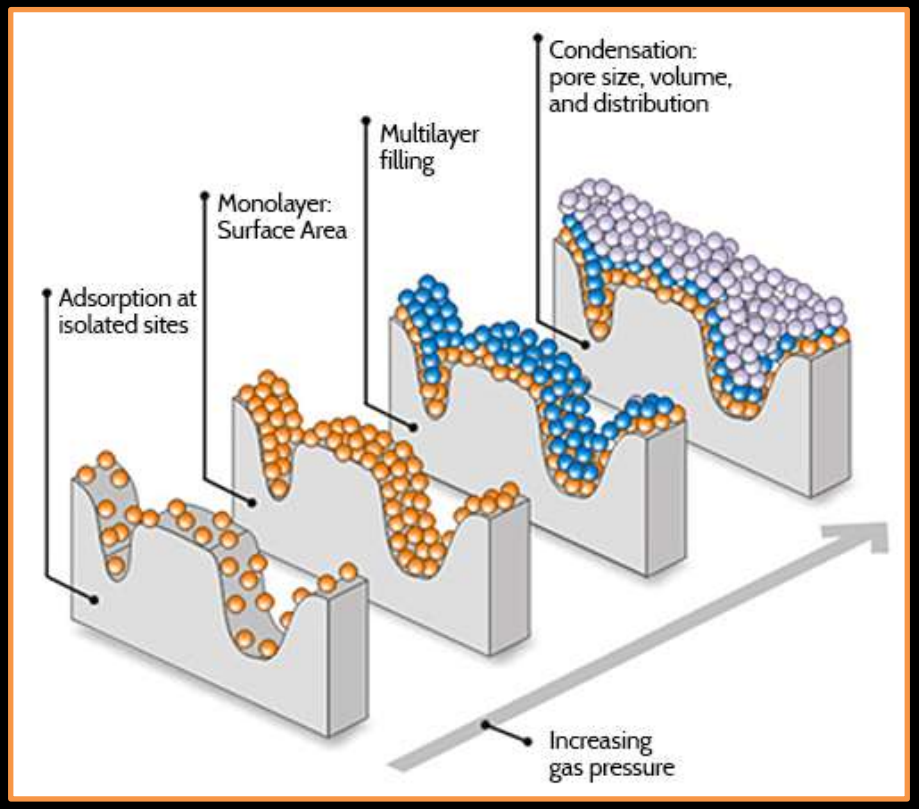


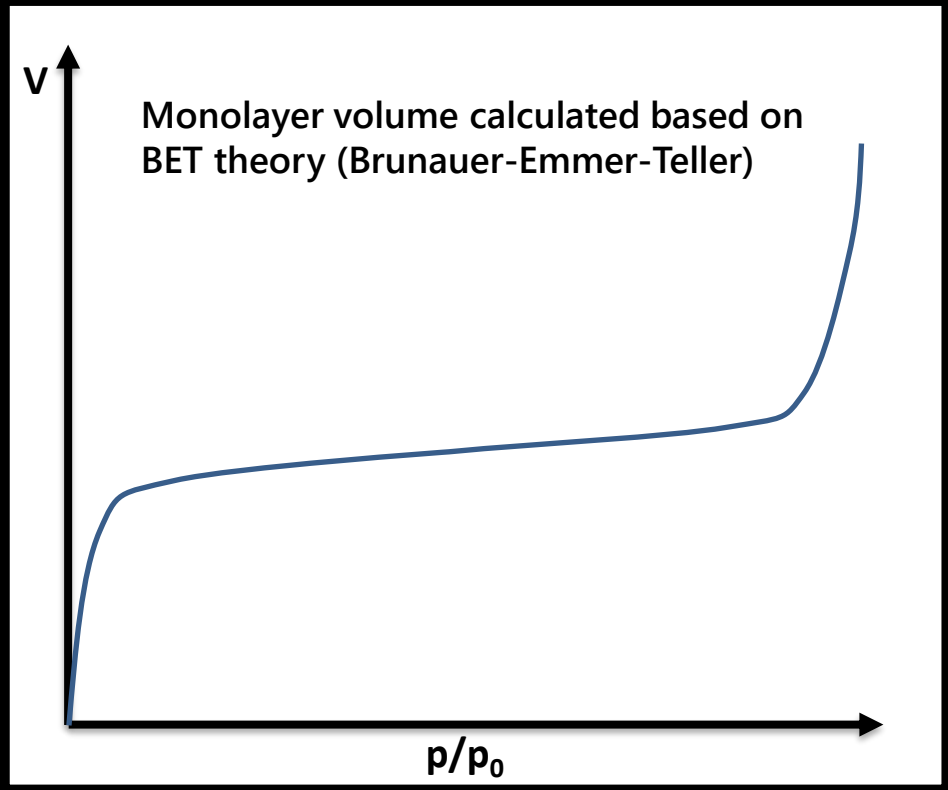
fractional coverage

$$\Theta = \frac{\text{number of occupied adsorption sites}}{\text{number of available adsorption sites}}$$

SURFACE PROPERTIES

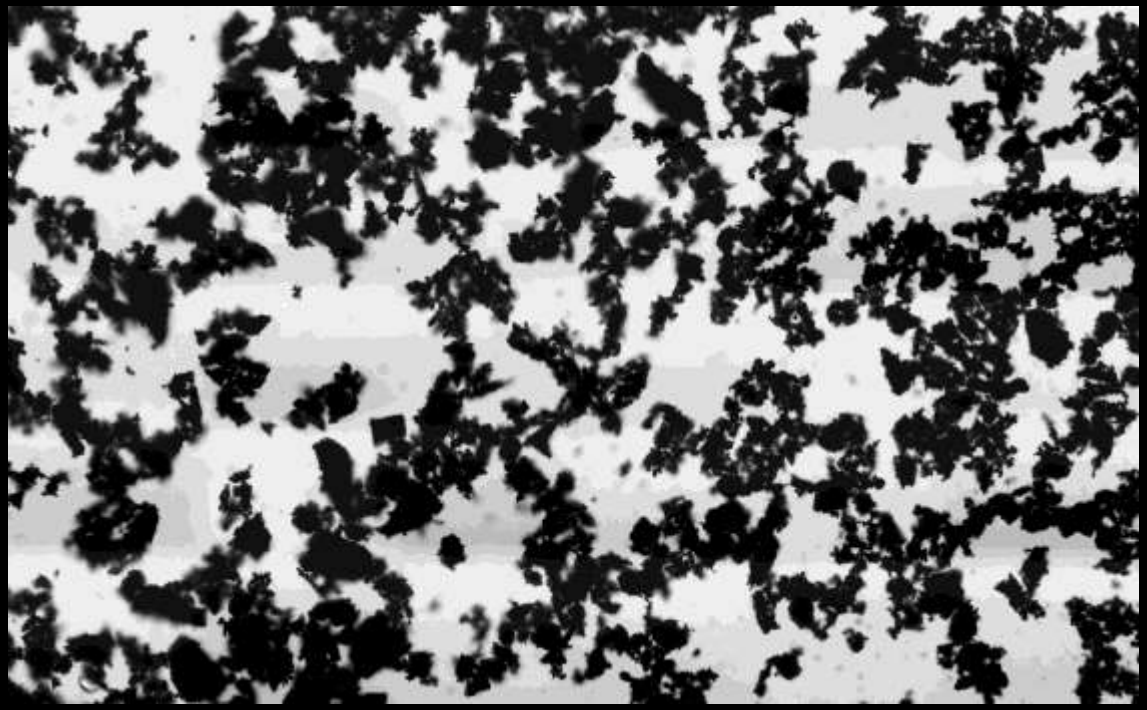
The specific surface area can be measured by controlled adsorption of N_2 (or other gas phases as Ar, Kr, CO_2)



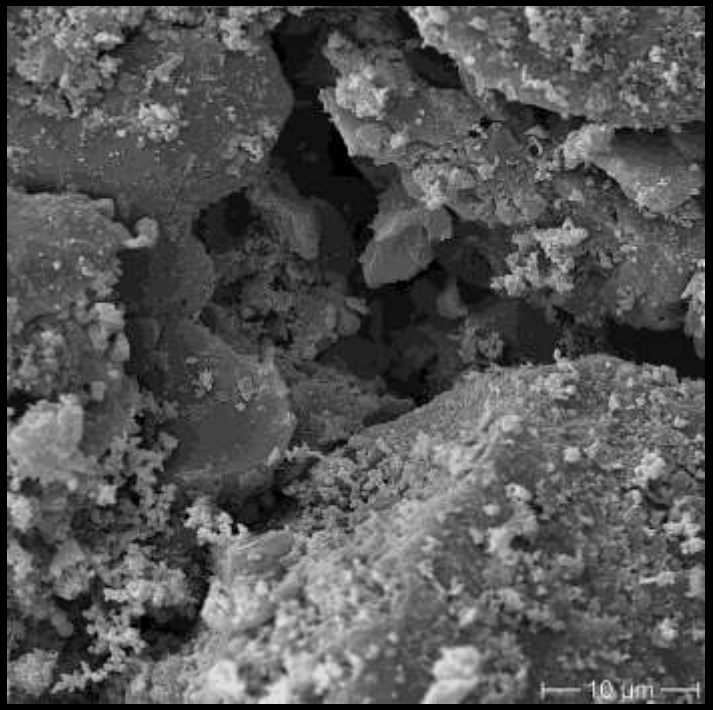


SURFACE PROPERTIES

Activated carbon

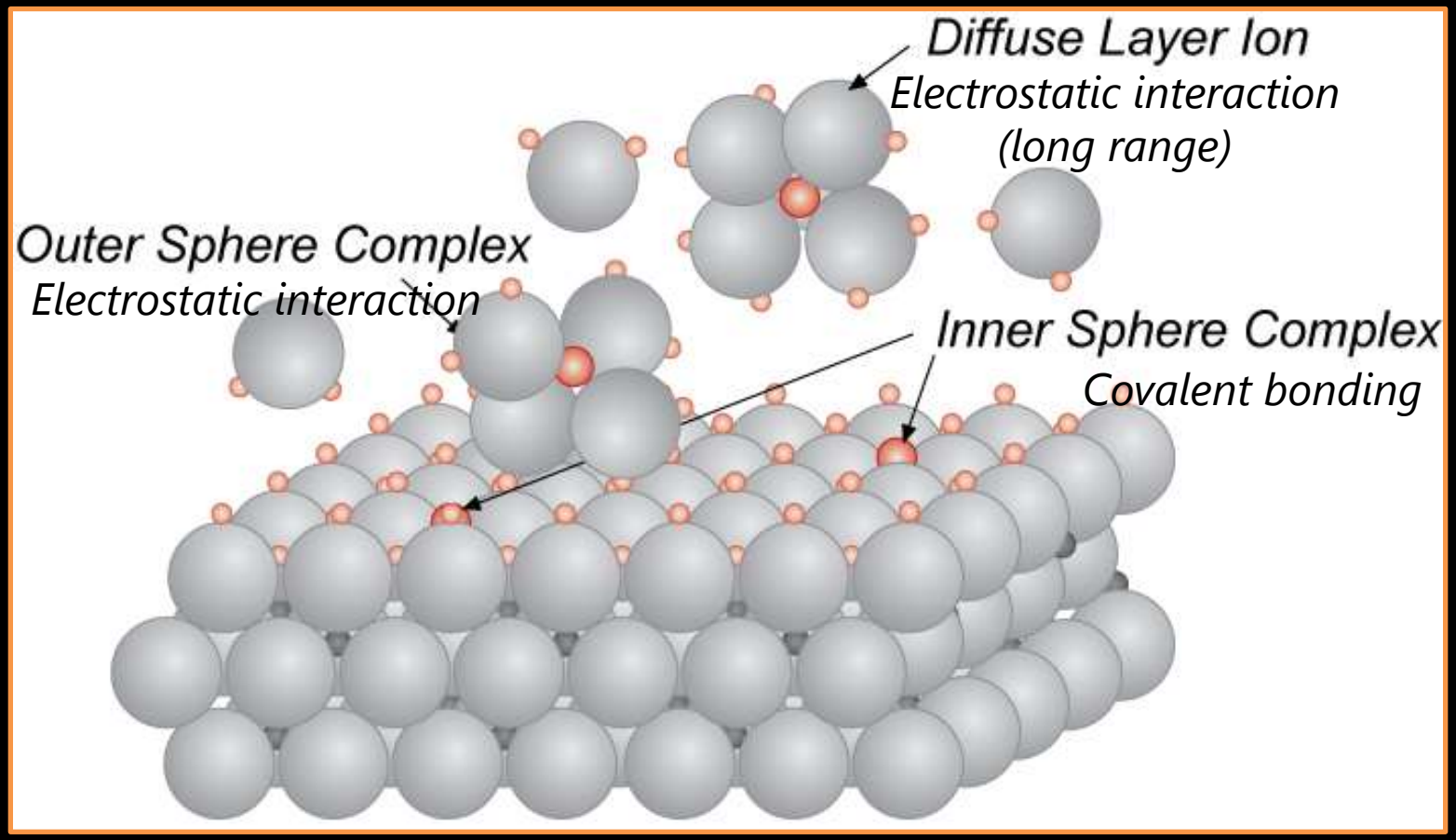


1 mm



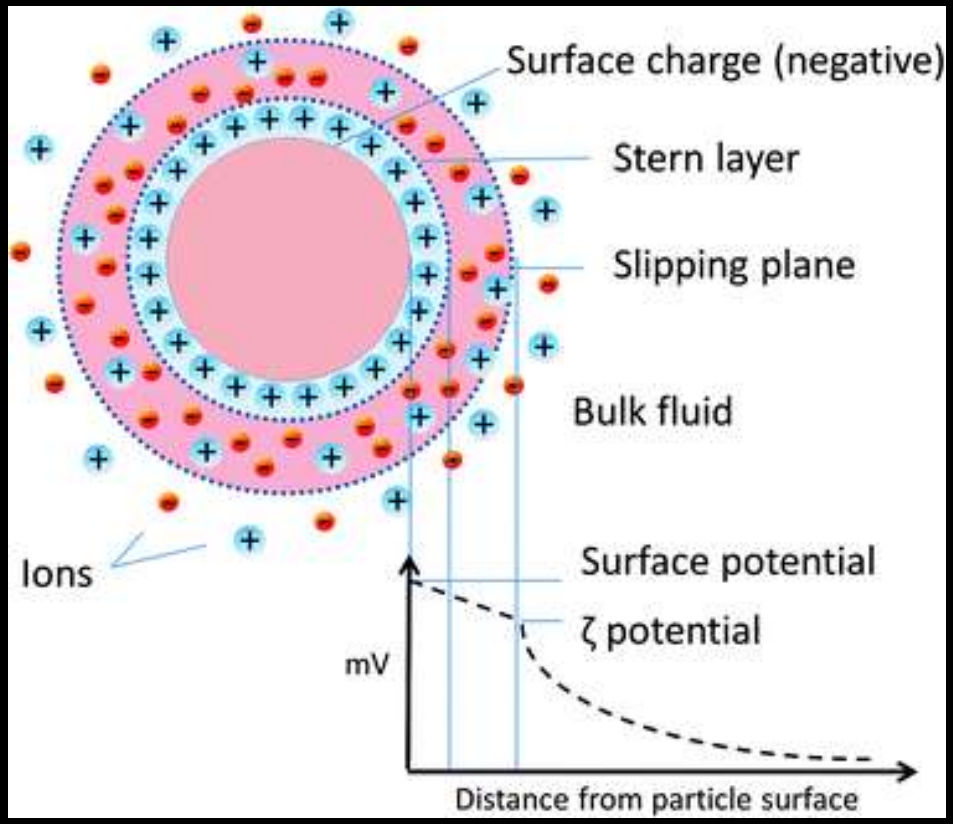
SURFACE PROPERTIES

Electrical double layer



SURFACE PROPERTIES

Electrical double layer



The electric potential of the double layer is defined *zeta potential* (ζ)

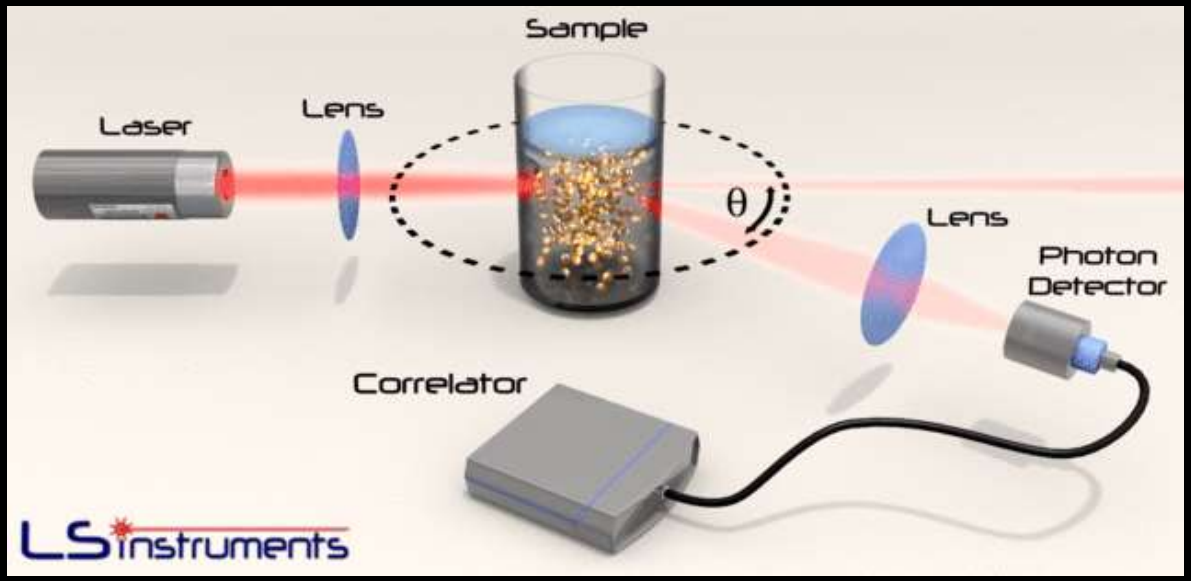
SURFACE PROPERTIES

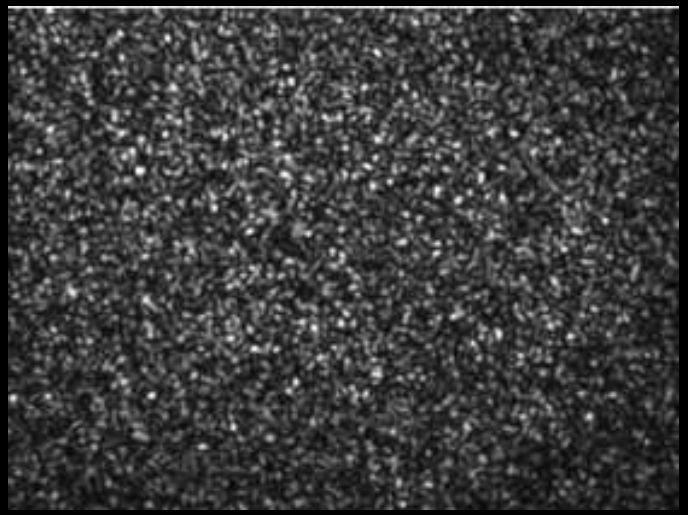
Electrical double layer

ζ potential[mV]	Colloidal stability
0 to ±5	Rapid coagulation or flocculation
±10 to ±30	Incipient instability
±30 to ±40	Moderate stability
±40 to ±60	Good stability
> ±61	Excellent stability

SURFACE PROPERTIES

Zeta-potential measurement: dynamic light scattering





SPECKLE PATTERN

The intensity fluctuation is proportional to the *electrophoretic mobility* within an applied electric field: $\boldsymbol{U = f(\zeta, \epsilon, \eta)}$

Portland cement

and other binders

ORDINARY PORTLAND CEMENT (OPC)

RAW MATERIALS: LIMESTONE + CLAY + GYPSUM

1450 °C

CLINKER MINERALOGY

C_3S	Ca_3SiO_5	**Alite**
C_2S	Ca_2SiO_4	**Belite**
C_3A	$Ca_3Al_2O_6$	**Aluminate**
C_4AF	$Ca_4Al_2Fe_2O_{10}$	**Ferrite**

C = CaO A = Al2O3 F = Fe2O3 S = SiO2 $\overline{S}$ = SO3

PORTLAND CEMENT

CEMENT HYDRATION

MAIN HYDRATION PRODUCTS

C-S-H	$(CaO)_{1.7}(SiO_2)(H_2O)_4$	**Silicato di calcio idrato**
CH	$Ca(OH)_2$	**Portlandite**
C_3ASH_{32}	$Ca_6Al_2(SO_4)_3(OH)_{12}\cdot 26H_2O$	**Ettringite**

C = CaO A = Al2O3 F = Fe2O3 S = SiO2 $\overline{S}$ = SO3

PORTLAND CEMENT

OPC Hydration $Ca_3SiO_5 + 5.3H_2O \rightarrow (CaO)_{1.7}(SiO_2)\cdot 4H_2O + 1.3\ Ca(OH)_2$ Hydraulic binder!

Slaked lime $Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O$ Non-Hydraulic

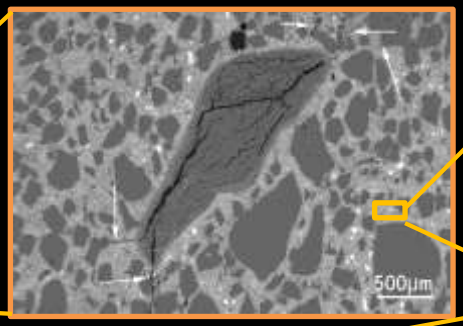
Roman (pozzolanic) cement $x\ Ca(OH)_2 + y\ SiO_{2(am)} + z\ H_2O \rightarrow (CaO)_x(SiO_2)_y \cdot zH_2O$

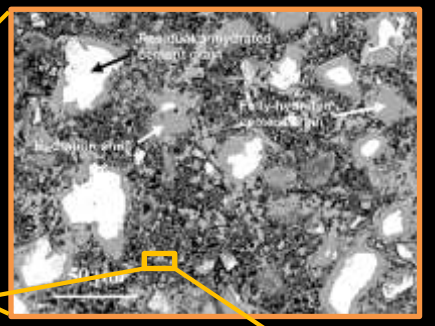
ROMAN CEMENT

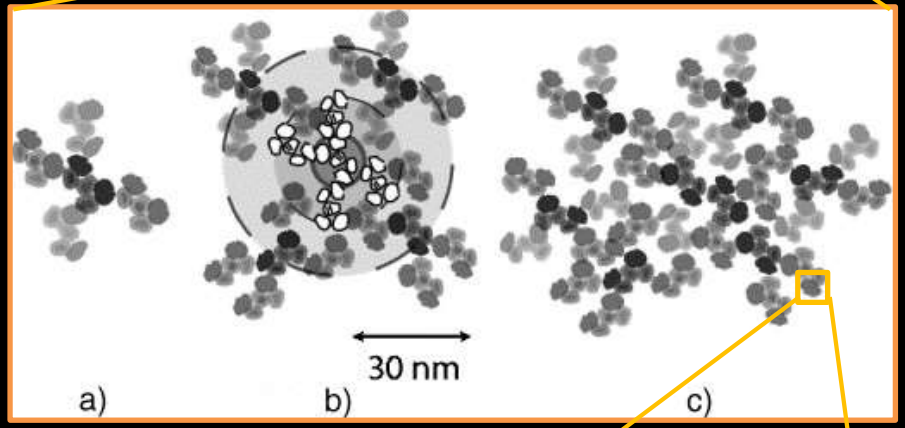
Caesarea Maritima (Israel)

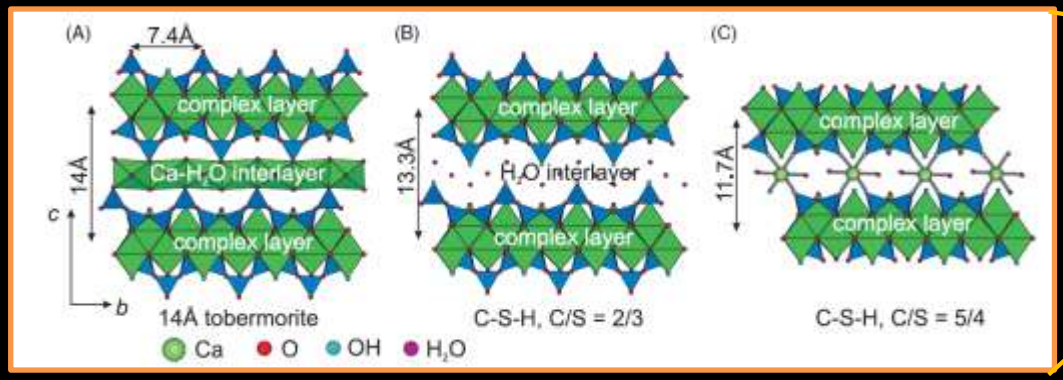
ROMAN CEMENT

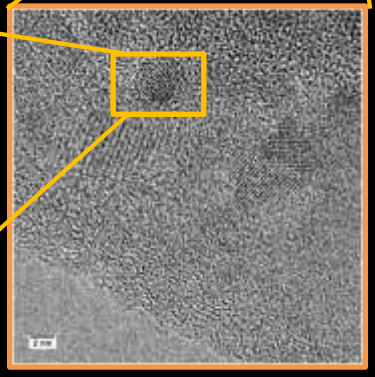
ROMAN CEMENT


500µm



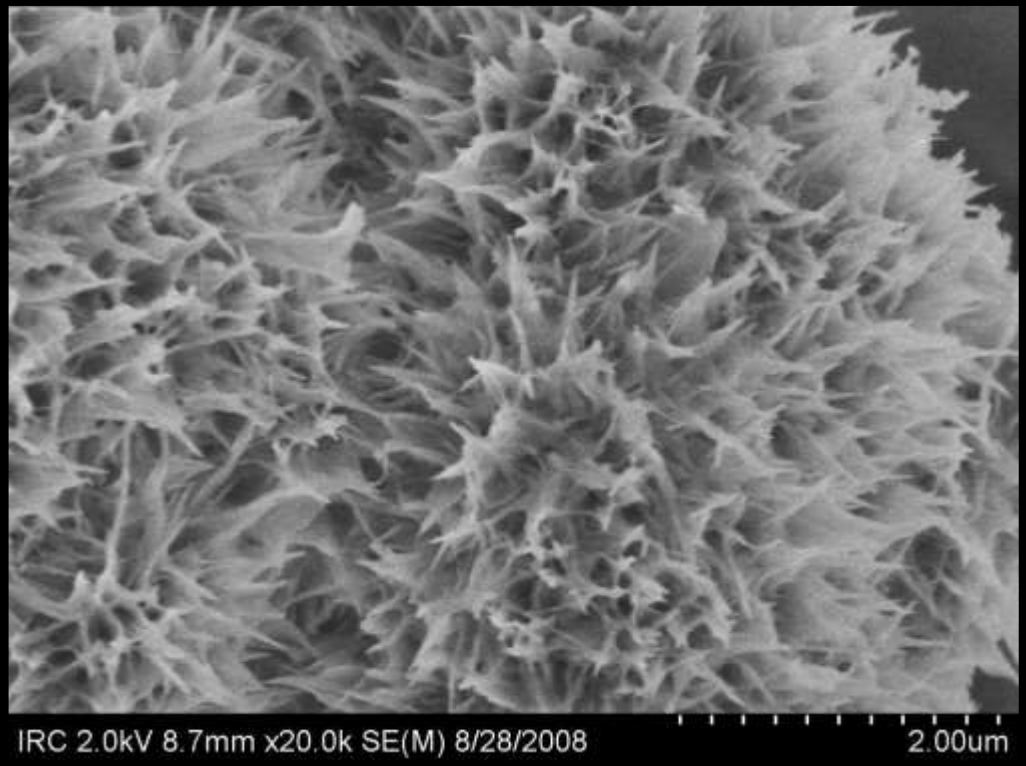

30 nm
a)
b)
c)


(A)
7.4Å
complex layer
14Å
Ca-H2O interlayer
c
complex layer
b
14Å tobermorite
(B)
complex layer
13.3Å
H2O interlayer
complex layer
C-S-H, C/S = 2/3
(C)
complex layer
11.7Å
complex layer
C-S-H, C/S = 5/4
Ca
O
OH
H2O

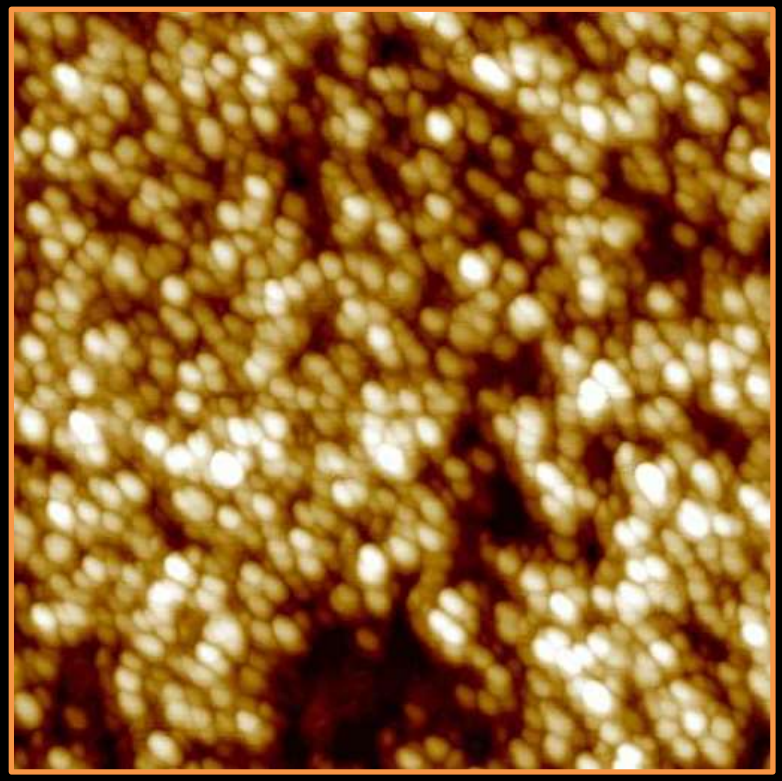


PORTLAND CEMENT

C-S-H: CEMENT HYDRATION PRODUCT



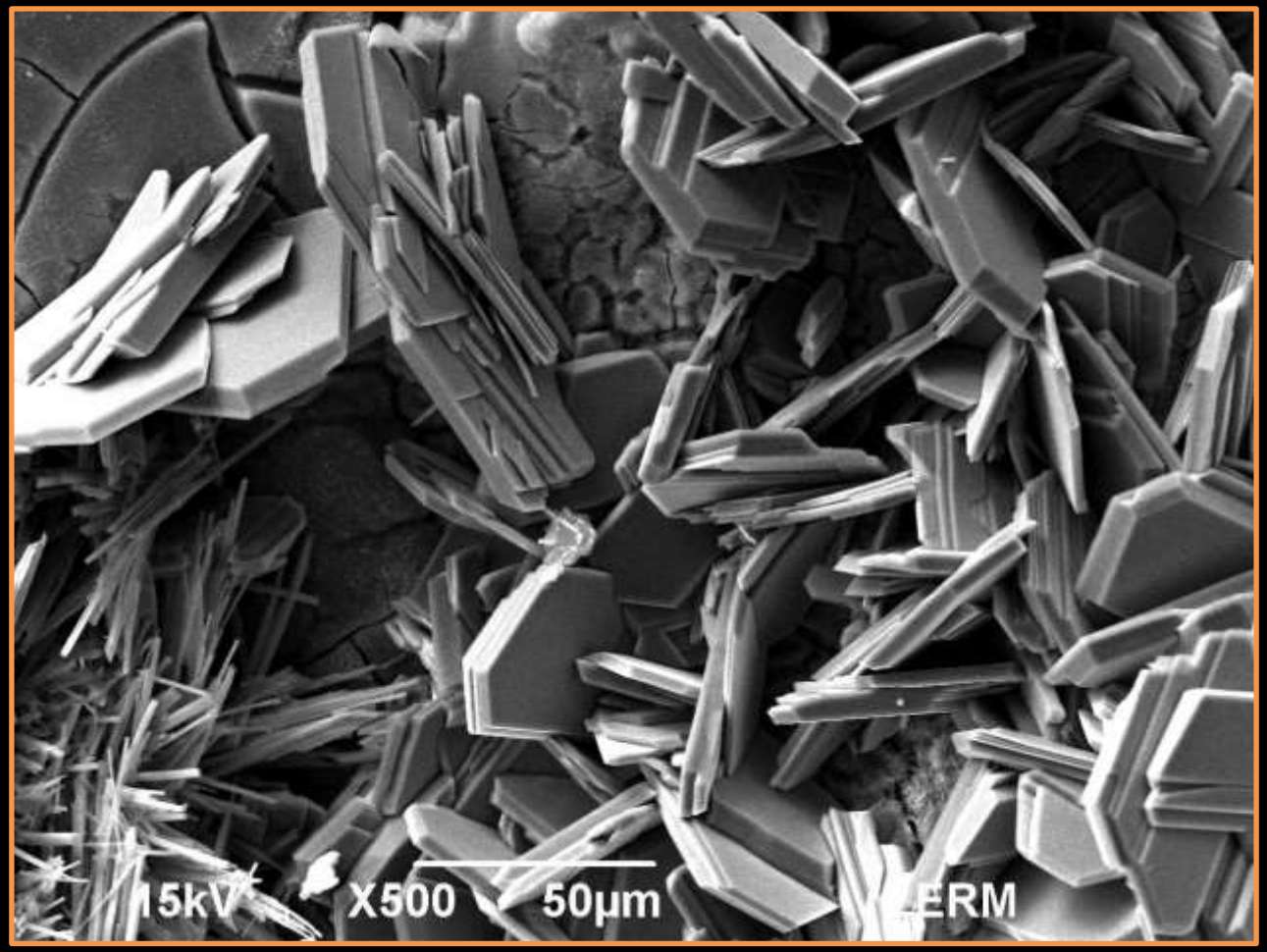
SEM



AFM

PORTLAND CEMENT

CEMENT HYDRATION PRODUCT: PORTLANDITE



PORTLAND CEMENT

CEMENT HYDRATION PRODUCT: ETTRINGITE

CEMENT POROSITY

micropores

mesopores

macropores

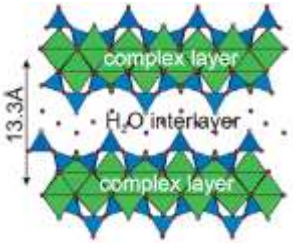
2 nm

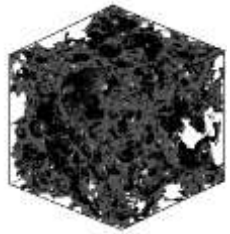
50 nm

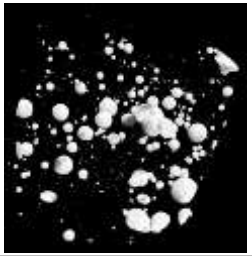
GAS ADSORPTION

MIP

TOMOGRAPHIC METHODS

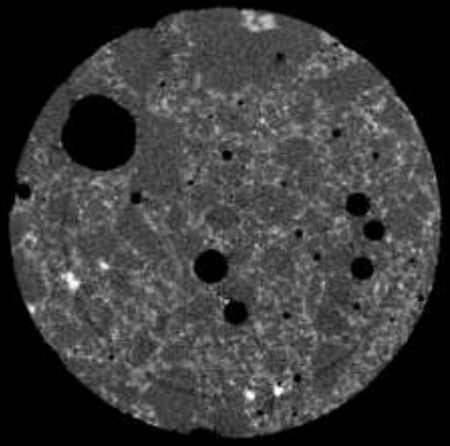


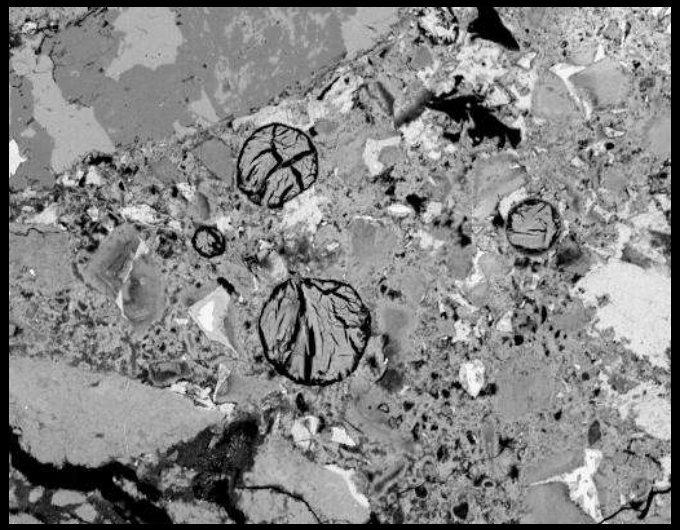


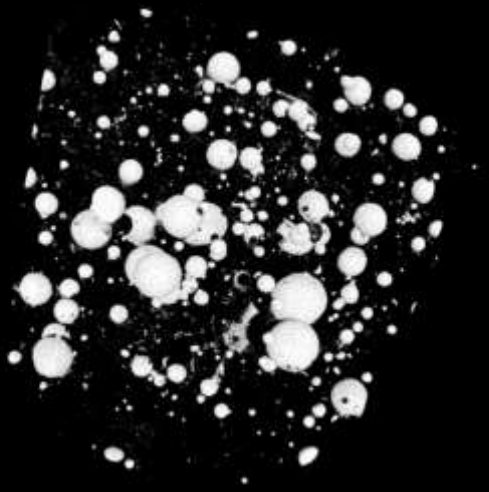


CEMENT POROSITY

Air voids

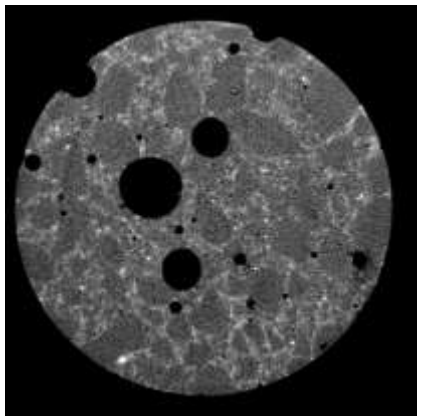


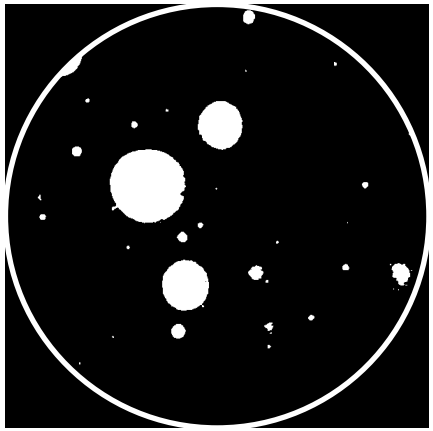


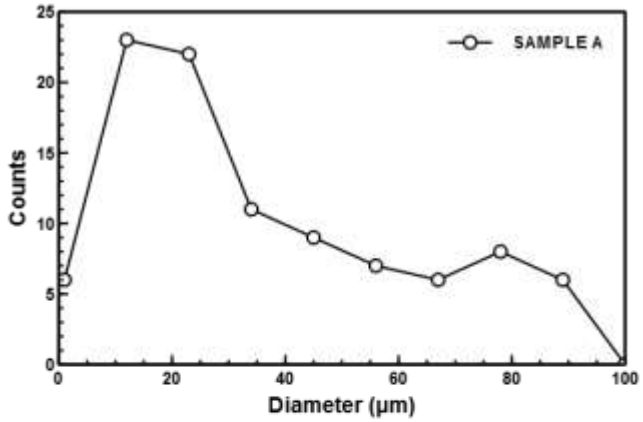


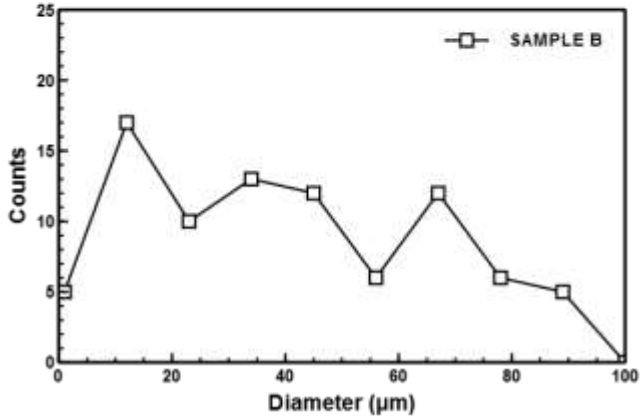
CEMENT POROSITY

Air voids







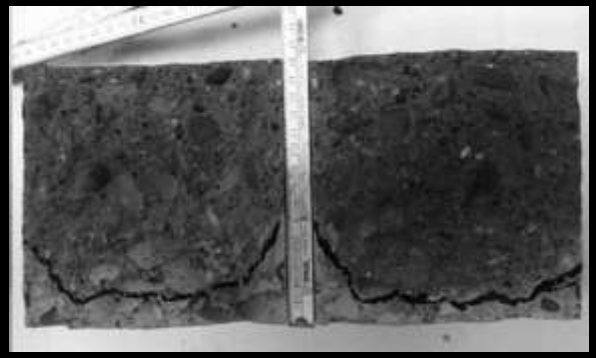


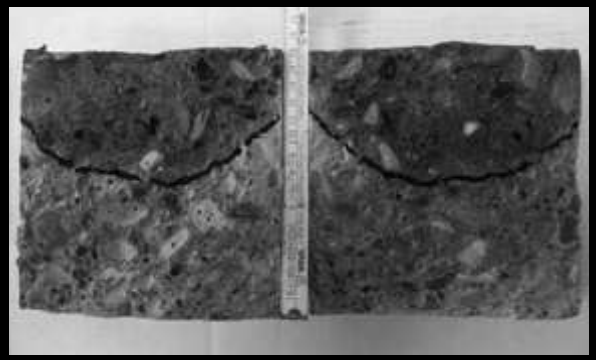
Size distribution by tomographic imaging

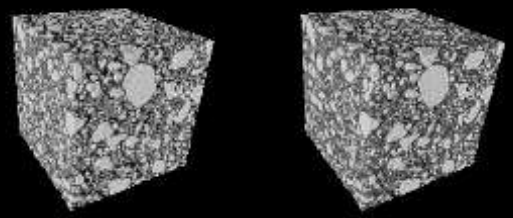
Freeze-thaw degradation

CEMENT POROSITY

Modulating the pore network tortuosity by the use of nano-seeds

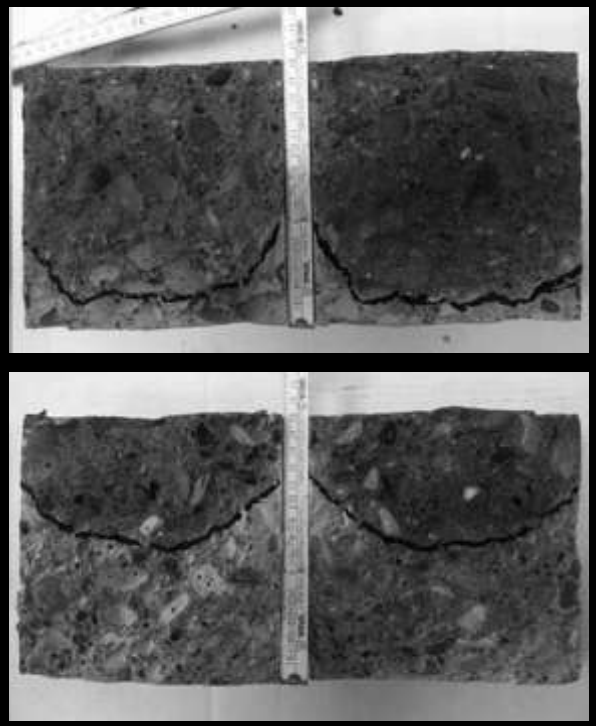


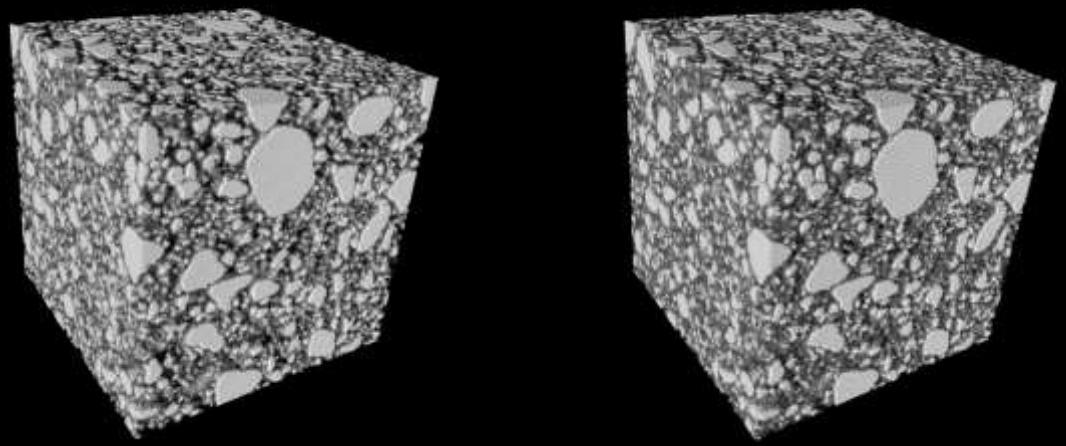




CEMENT POROSITY

Modulating the pore network tortuosity by the use of nano-seeds





CEMENT POROSITY

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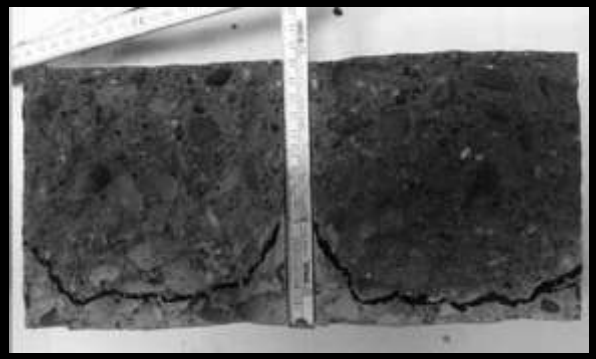
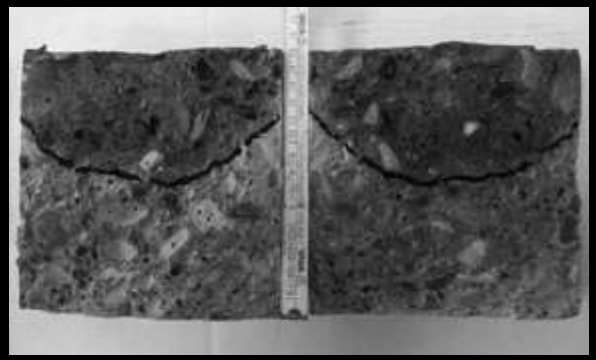
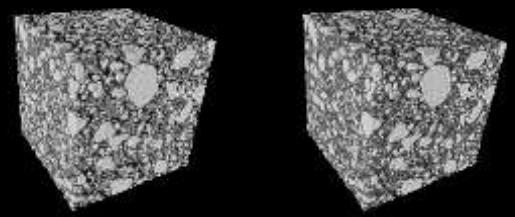
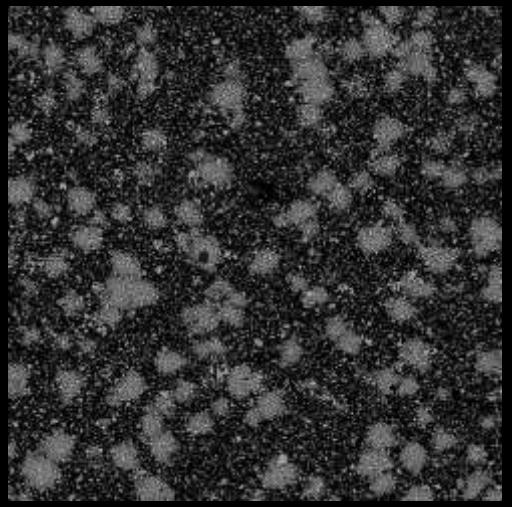
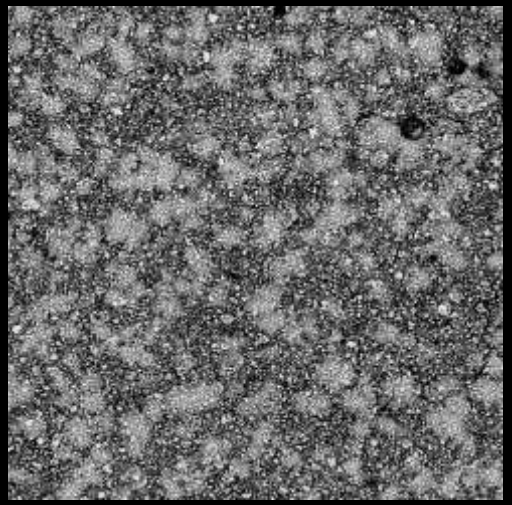
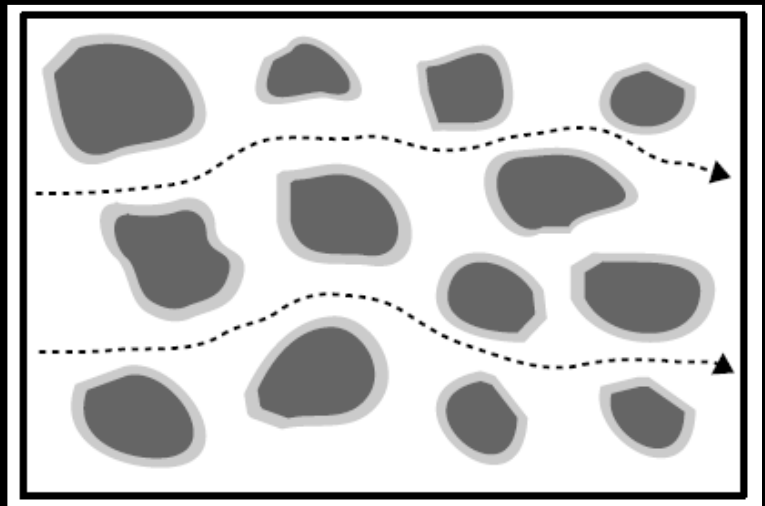


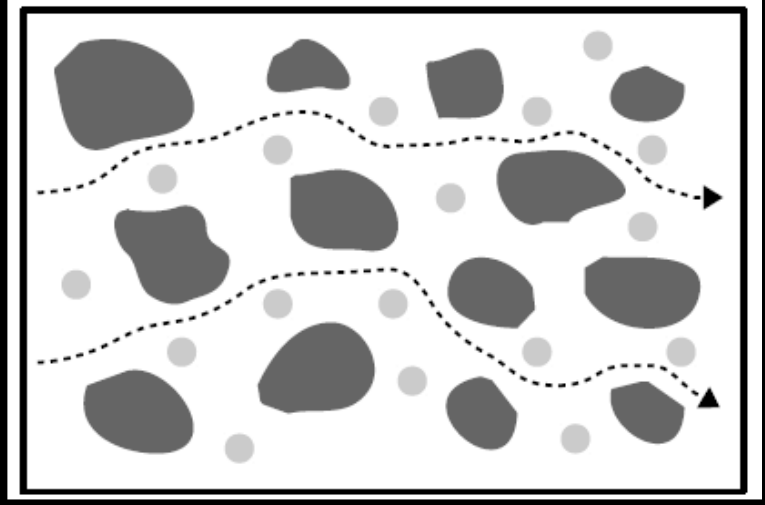






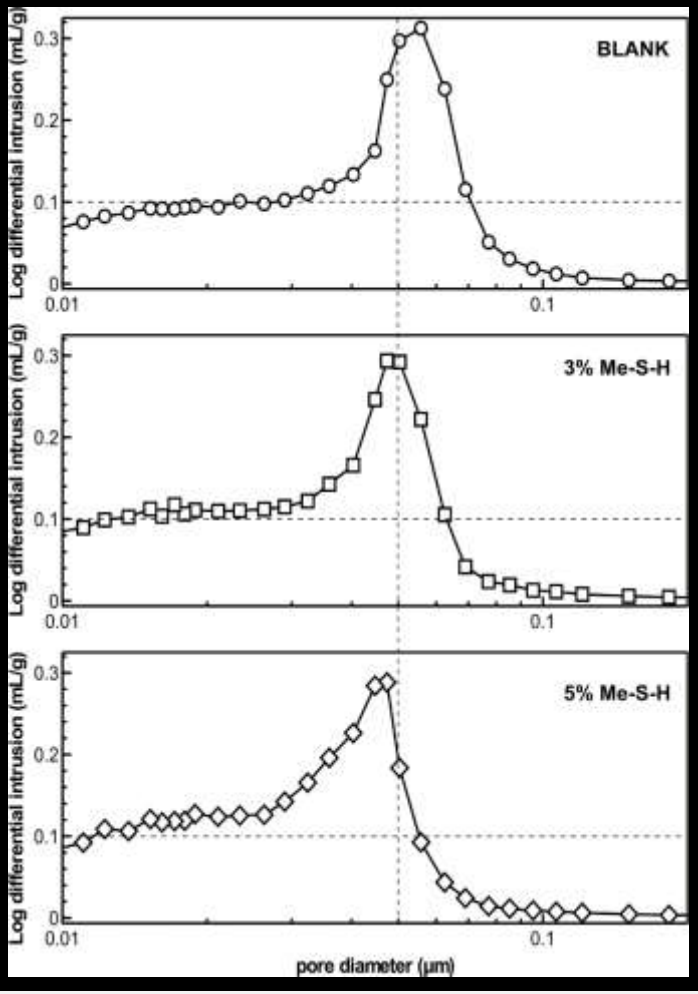


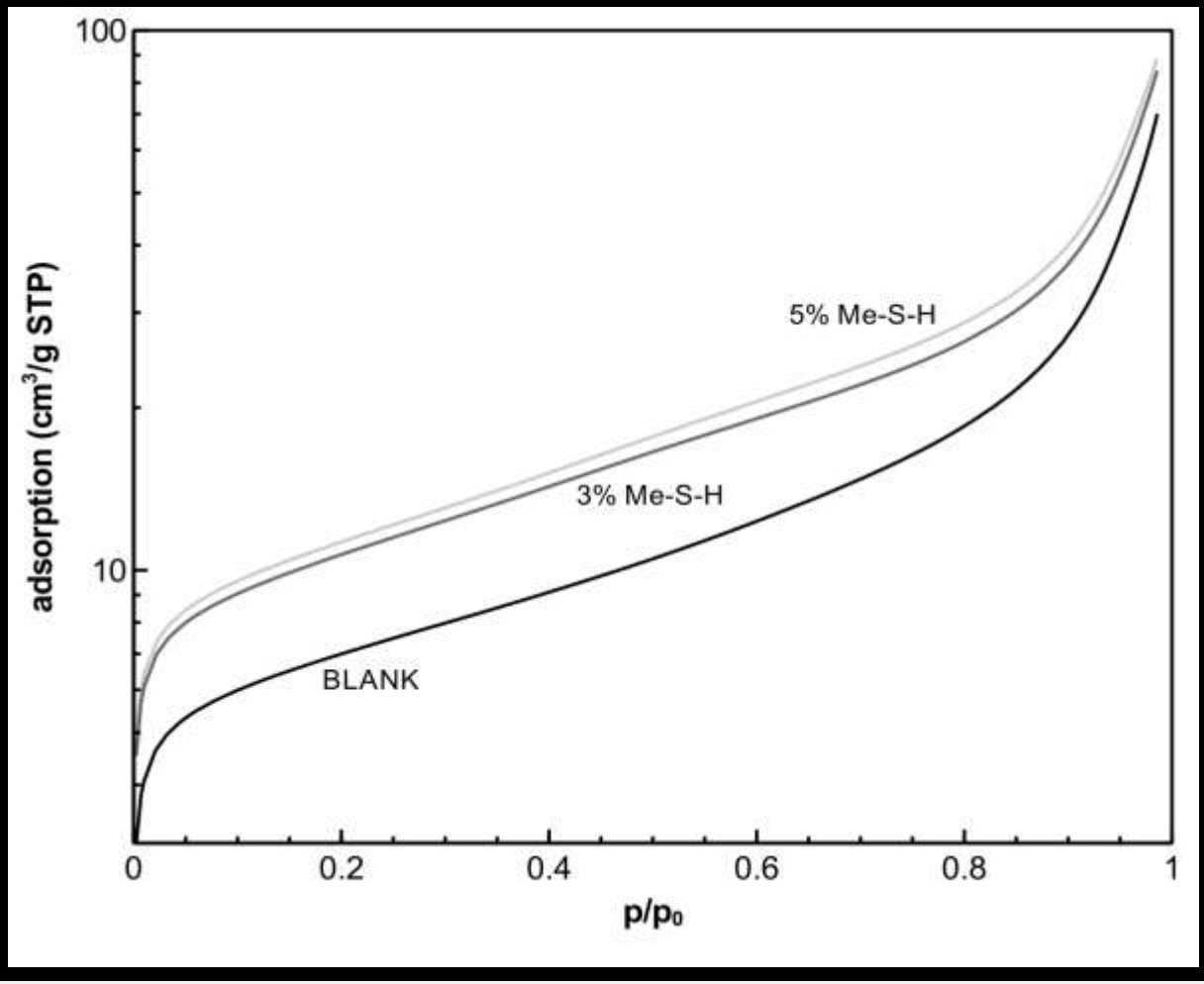




CEMENT POROSITY

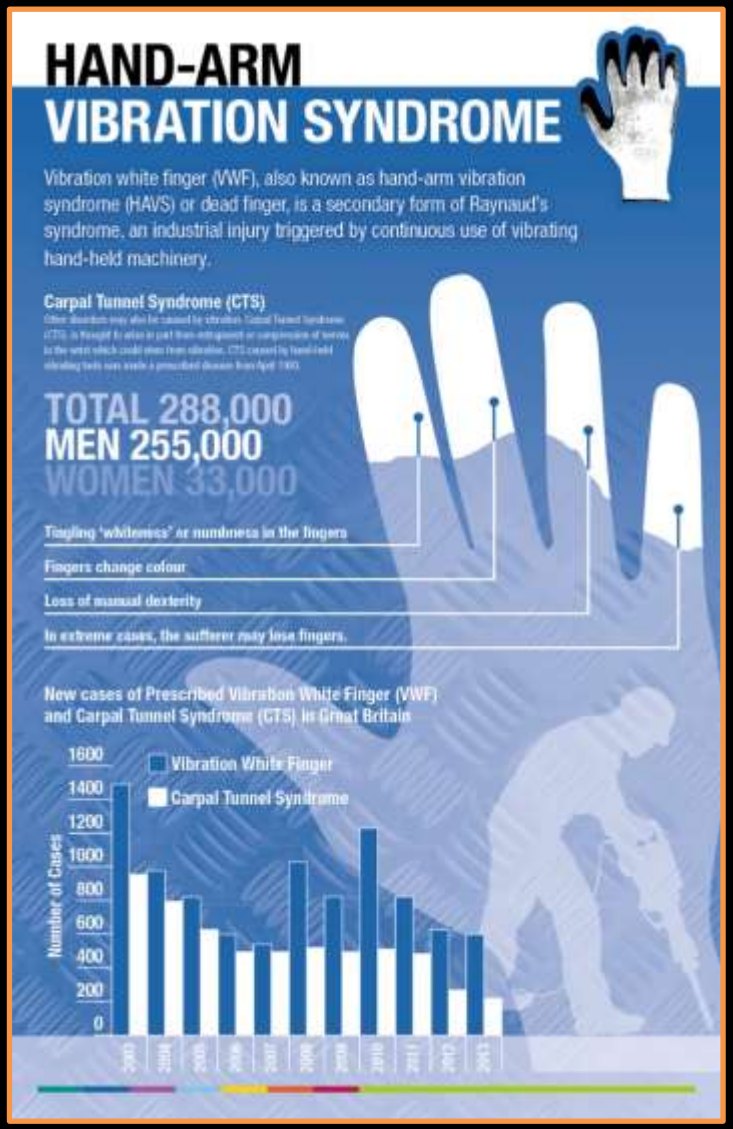
Modulating the pore network tortuosity by the use of nano-seeds





CEMENT WORKABILITY

CEMENT WORKABILITY



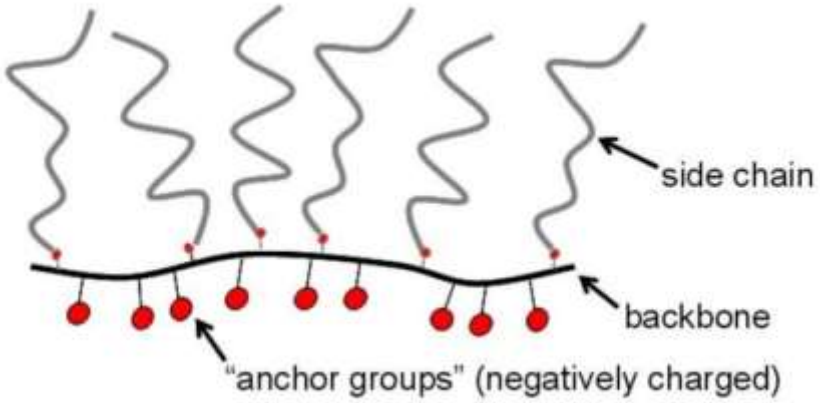
CEMENT WORKABILITY

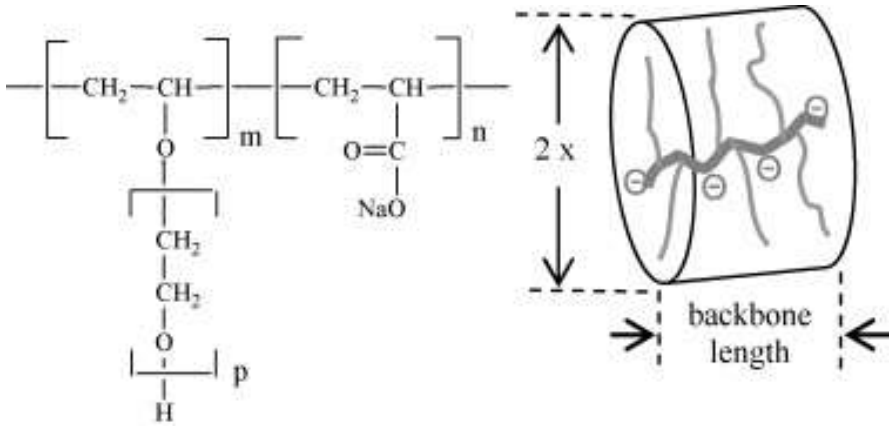
CEMENT WORKABILITY

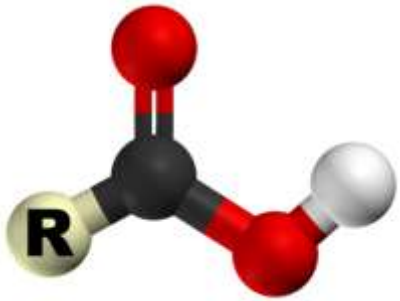
Link to video: https://www.youtube.com/watch?v=QGj-KkjwXJY

CEMENT WORKABILITY

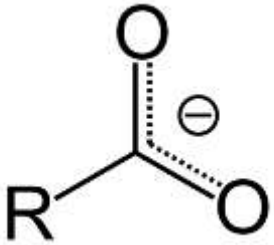
Controlling cement workability by adsorbed organic macromolecules



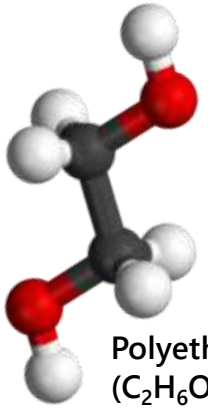




Carboxylic acid (COOH)



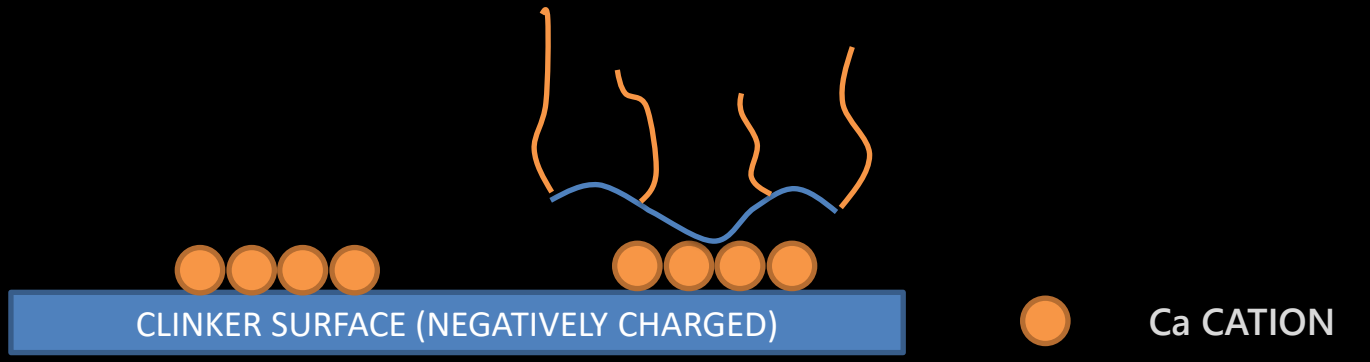
COO-



Polyethylene glycol ($C_2H_6O_2$) PEG

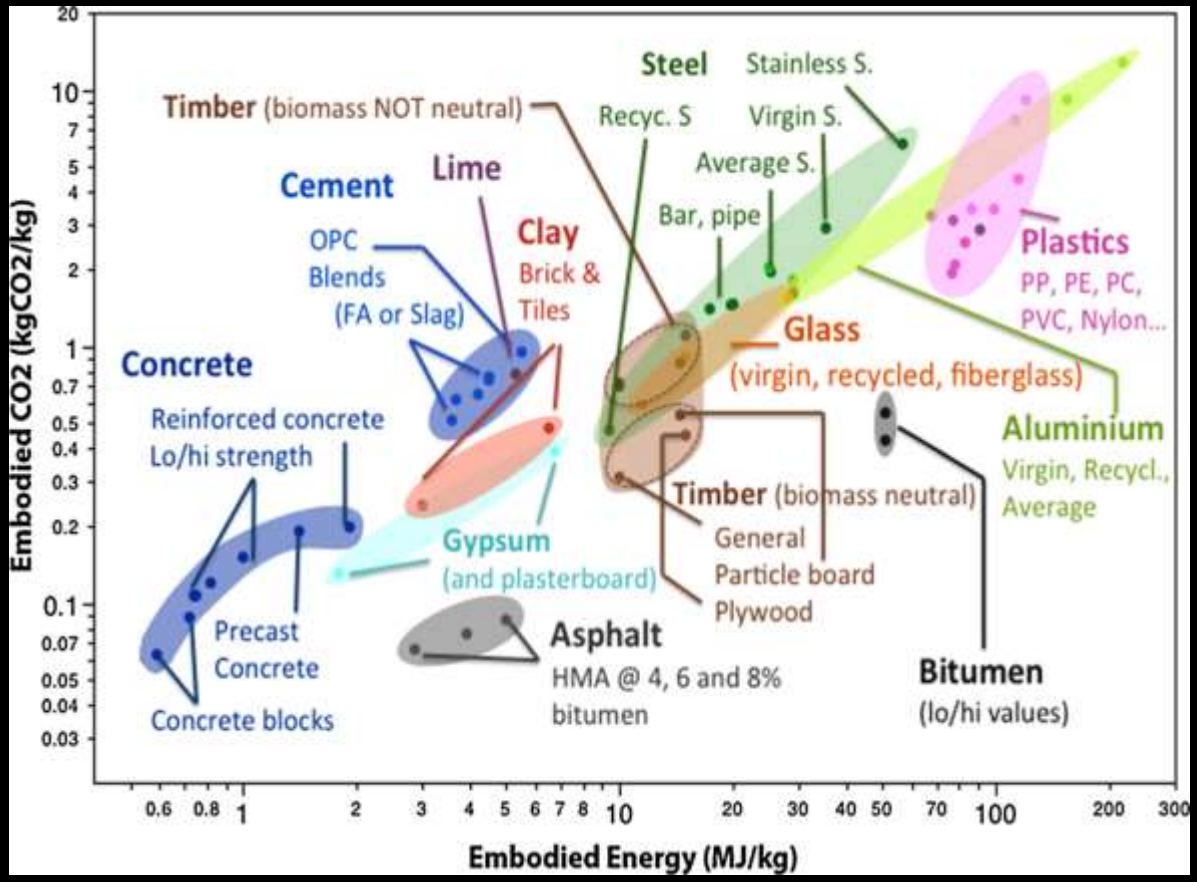
CEMENT WORKABILITY

Controlling cement workability by adsorbed organic macromolecules

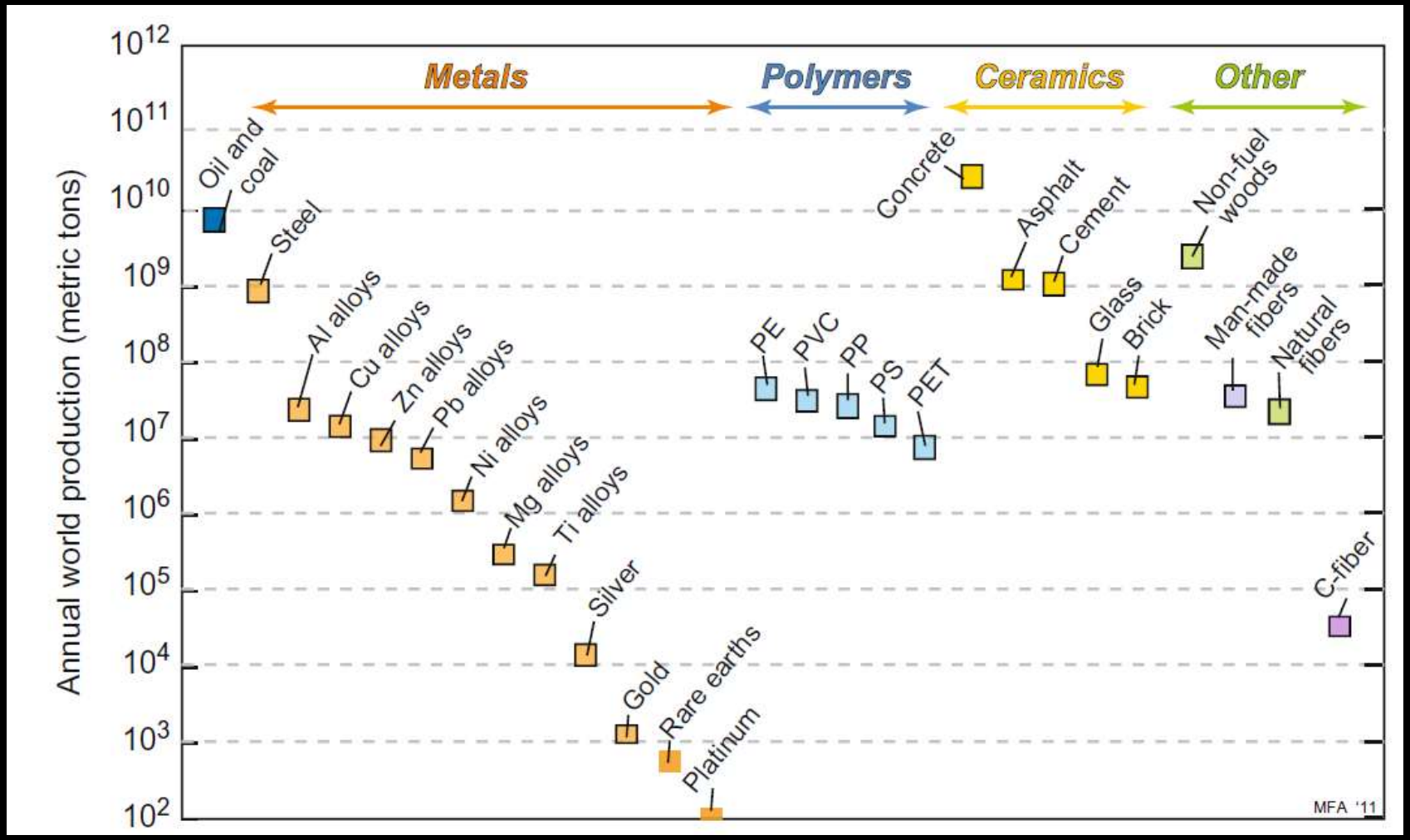


BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

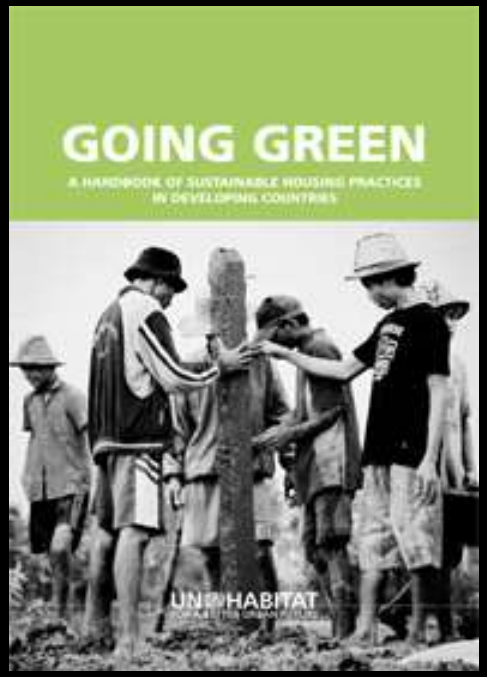
5% – 7%
GLOBAL ANTHROPOGENIC EMISSIONS

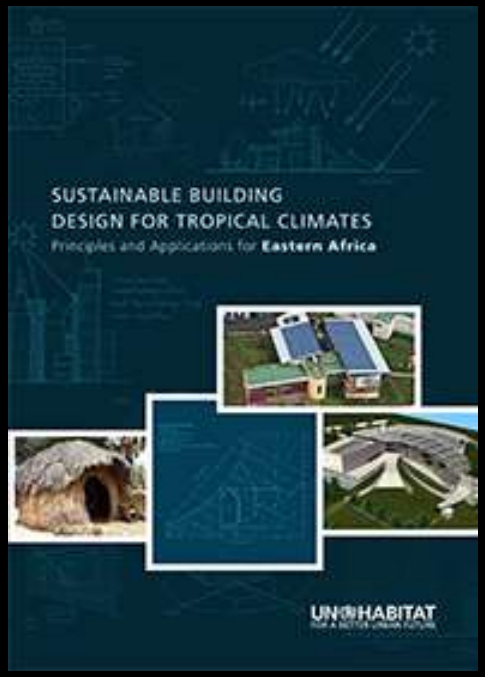


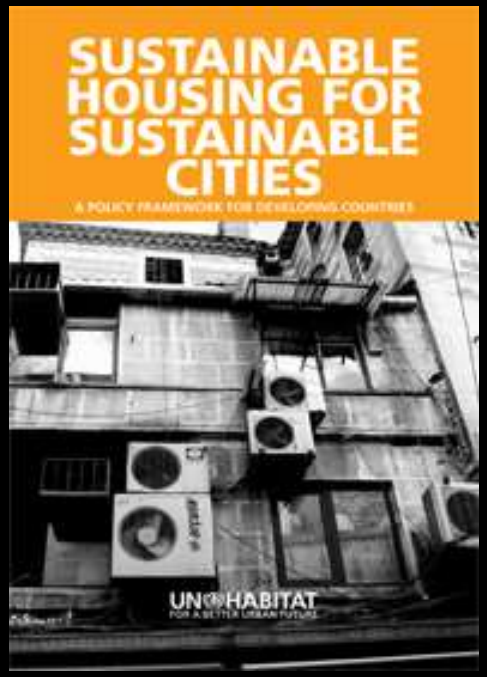
BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT



UN HABITAT
FOR A BETTER URBAN FUTURE

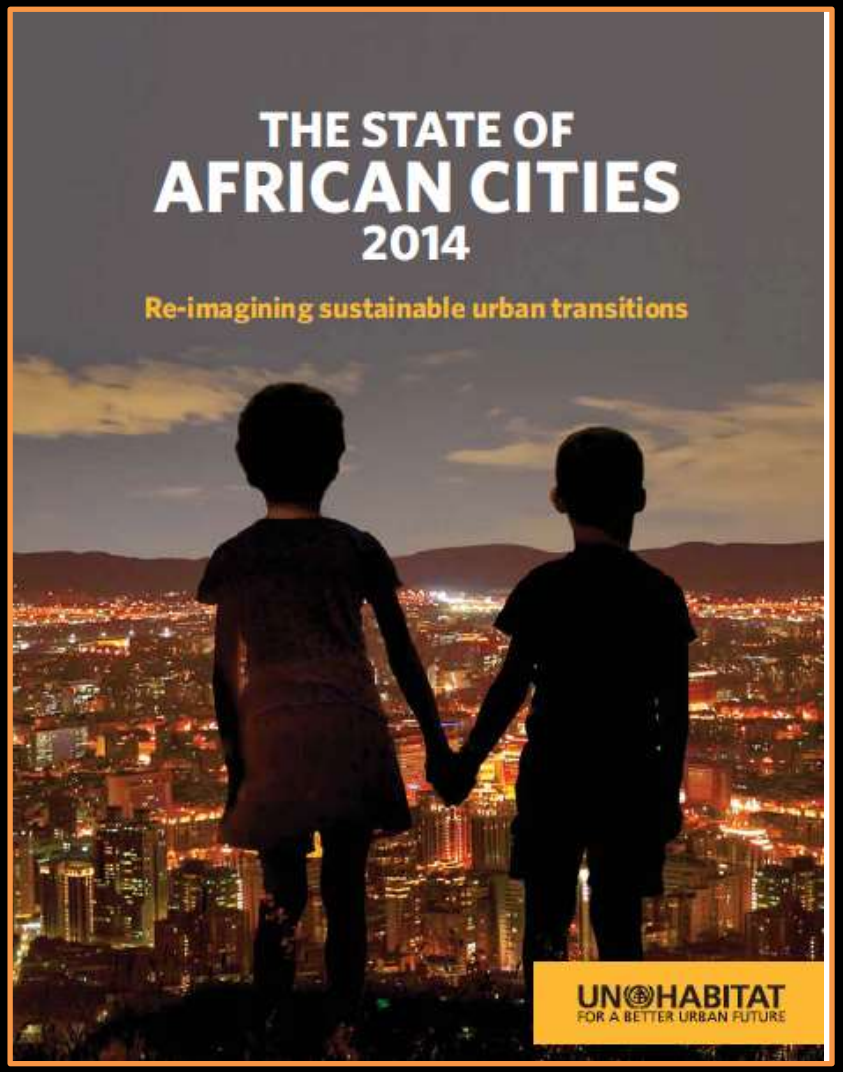


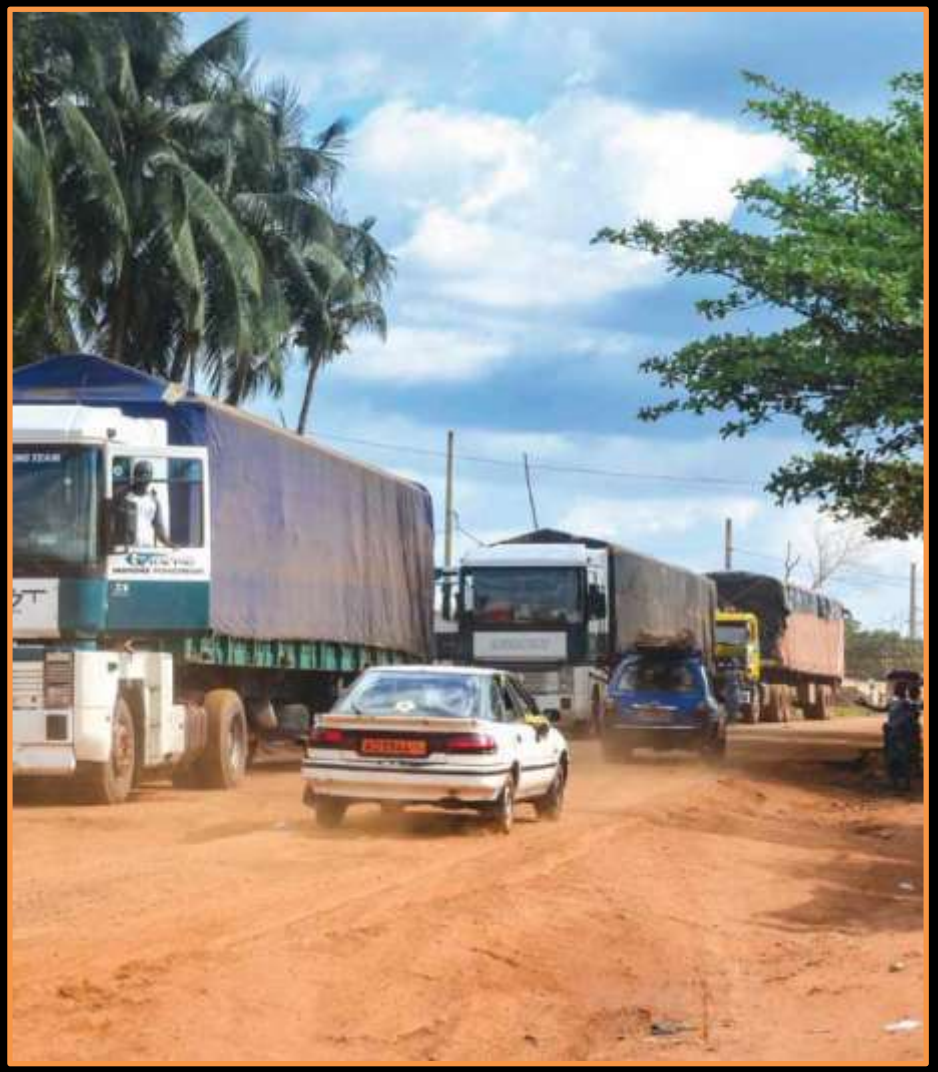




United Nations Human Settlements Programme

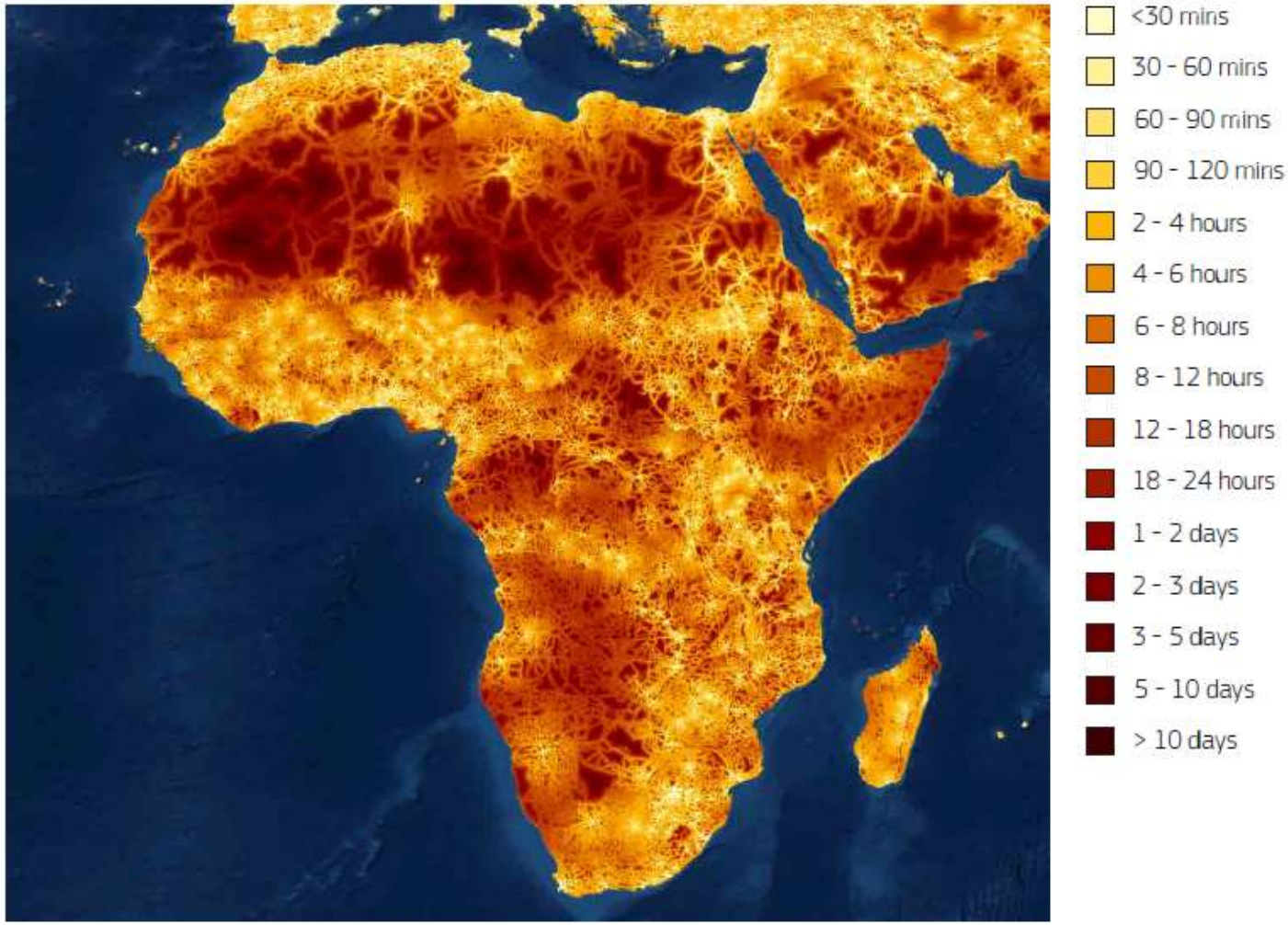
BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT





BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

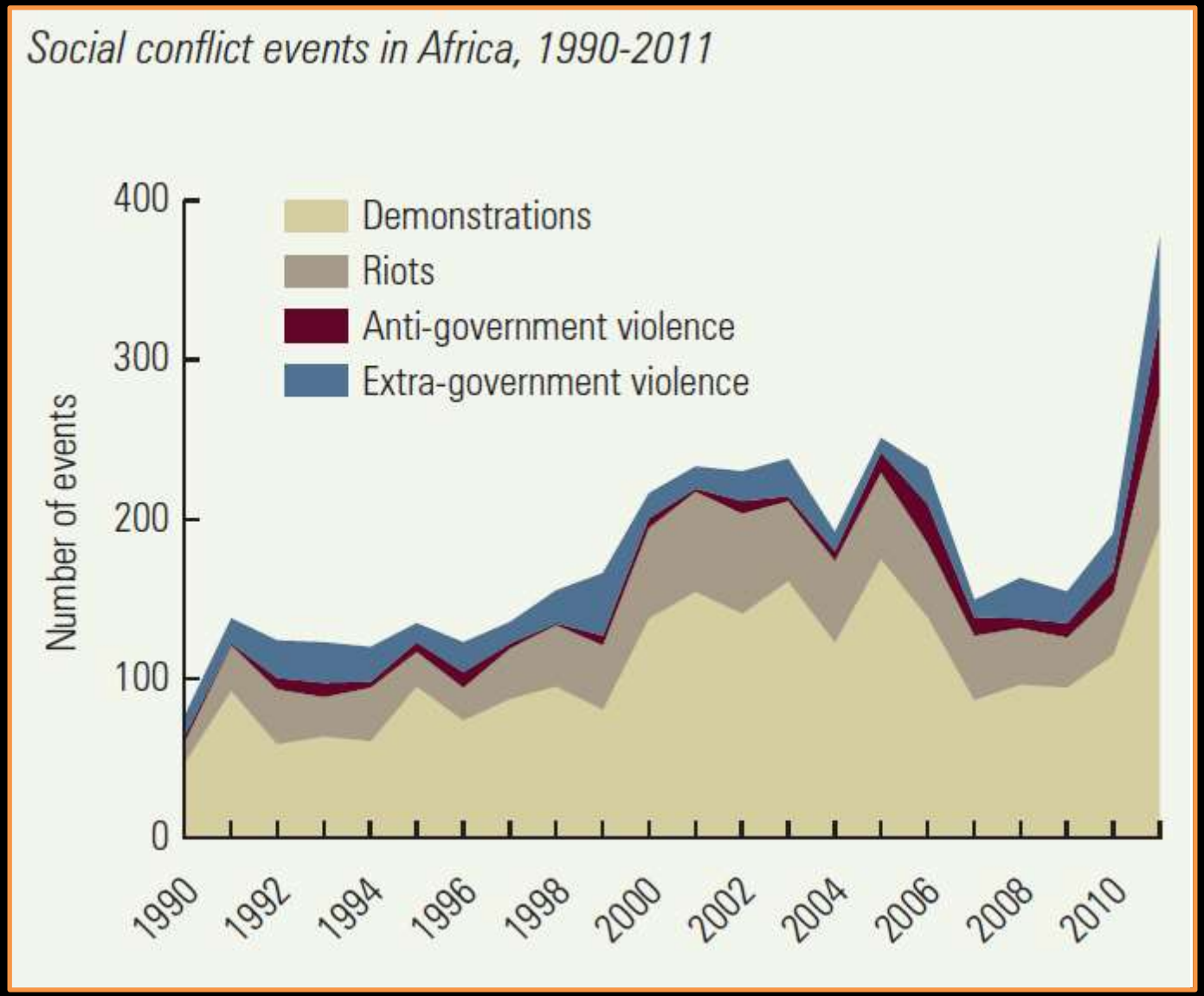
FIGURE 16: Travel time to major cities: the map shows overland travel time to cities with populations of over 50 000; darker colours represent longer travel times *(Source: Nelson et al., 2009)*



BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

Currently one billion people are living in slums

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT



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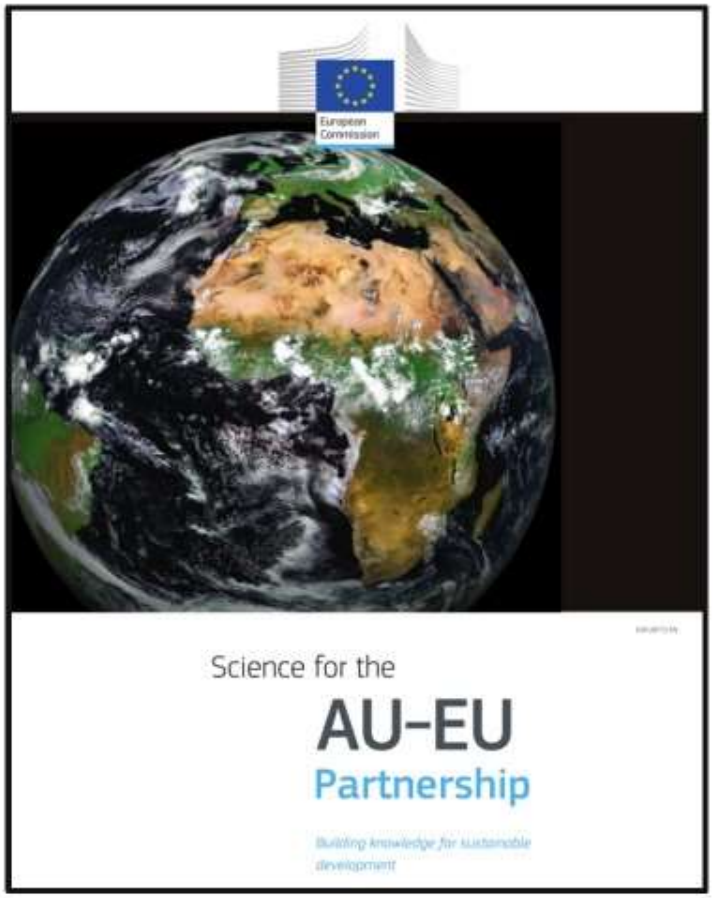

African Union - EU Summit 2017

National Geographic
How Africa's Tech Generation Is Changing the Continent

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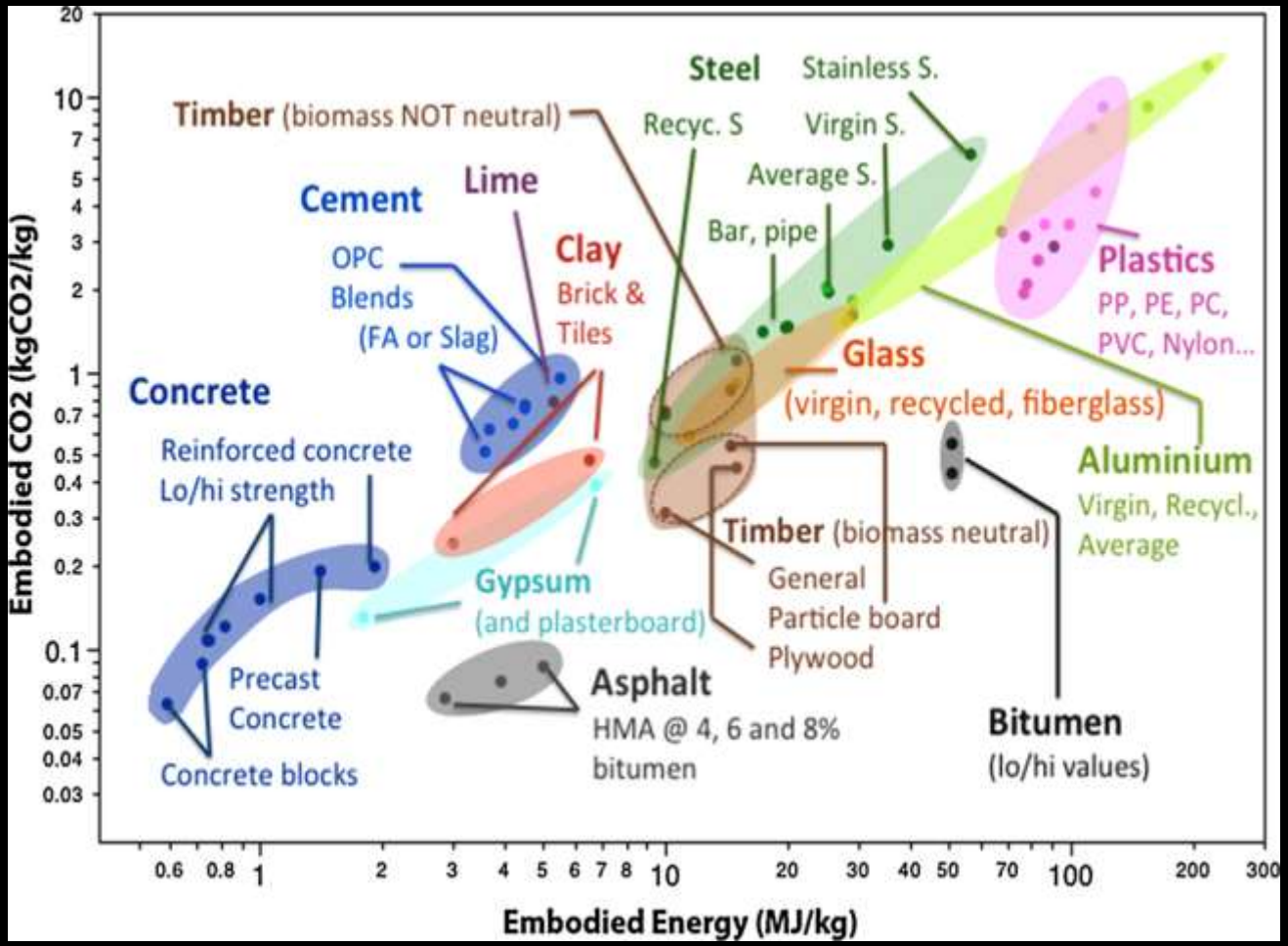
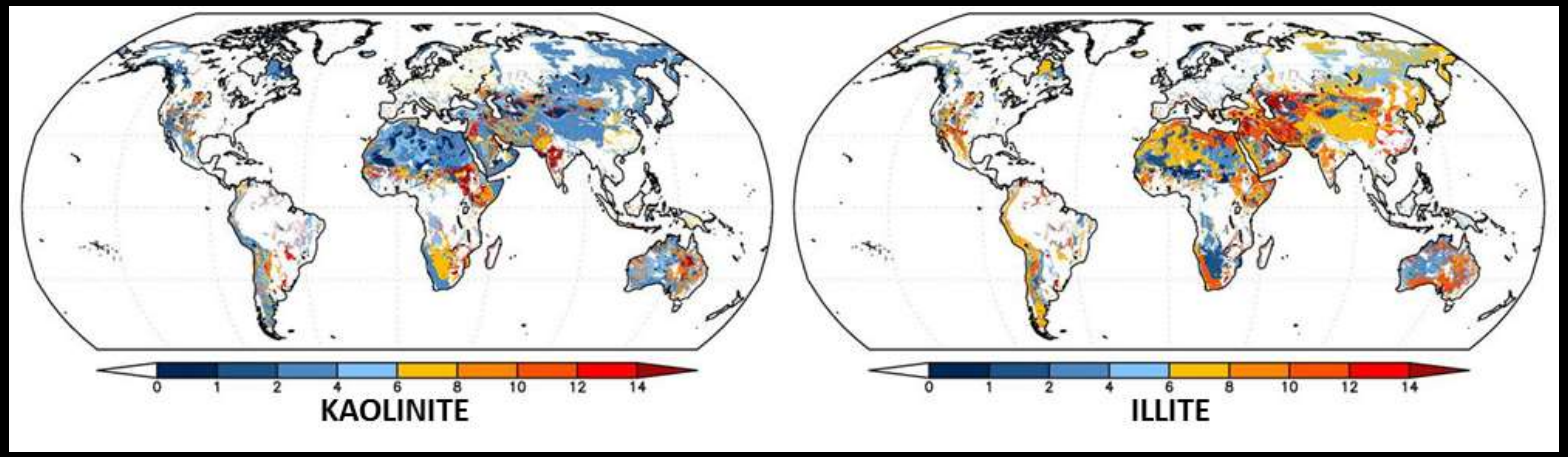


~~$CaCO_3 \rightarrow CaO + CO_2$~~

$Al_2Si_2O_5(OH)_4 \rightarrow Al_2Si_2O_7 + 2H_2O$

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

CLAY MINERALS CONCENTRATION IN SOILS



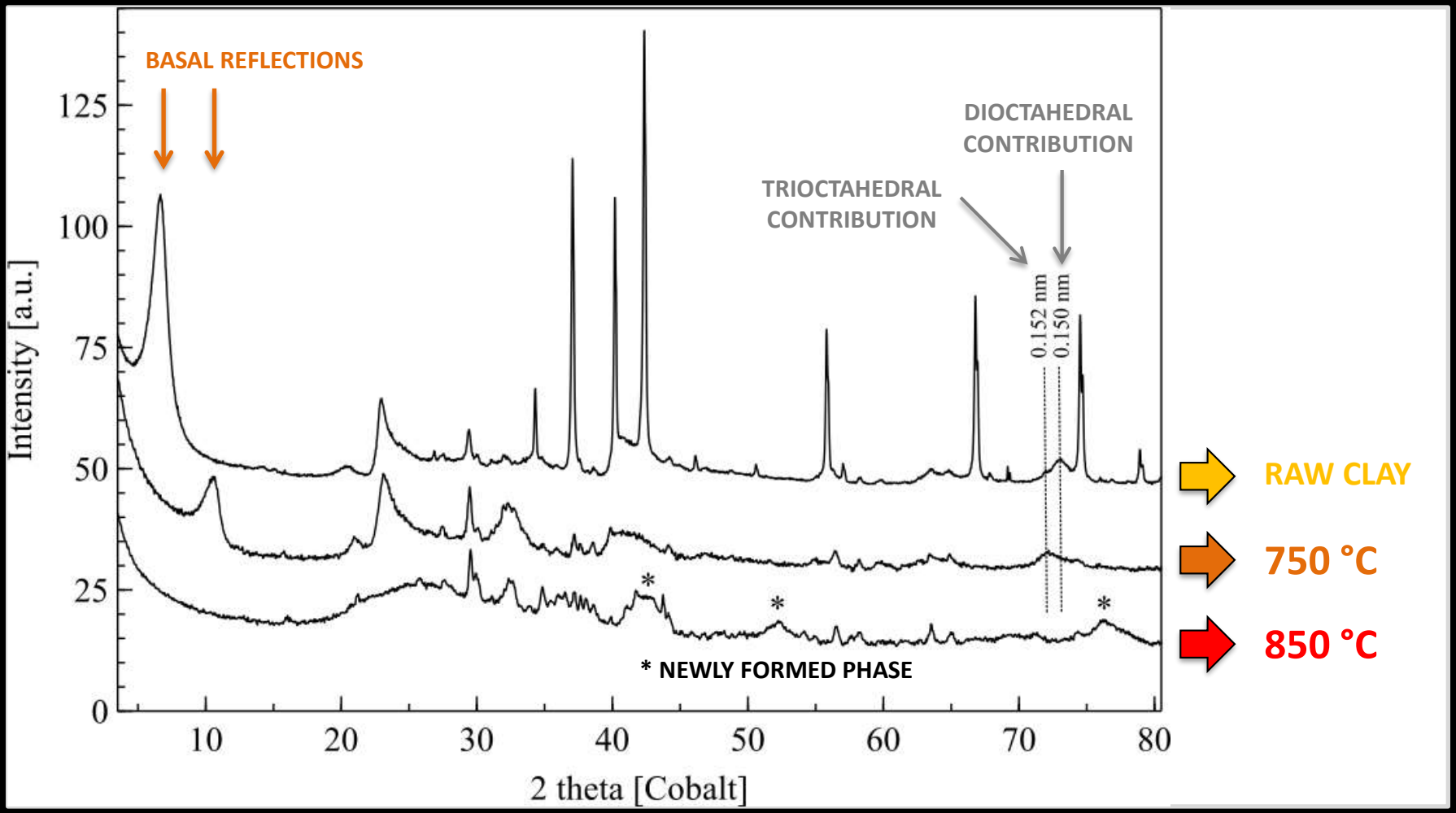
GDP GROWTH (DATA FROM IMF)

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

Thermal activation of smectite clay



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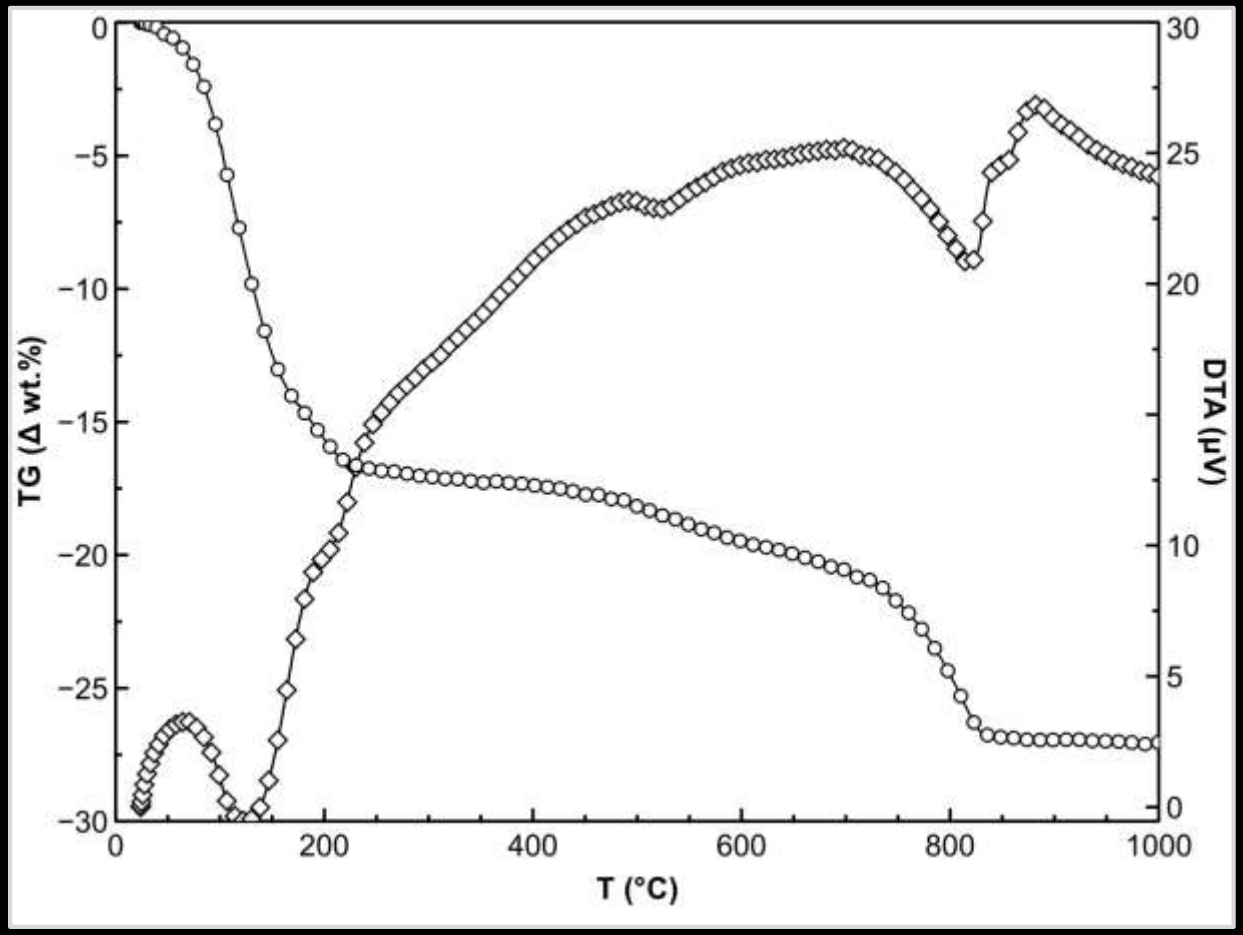
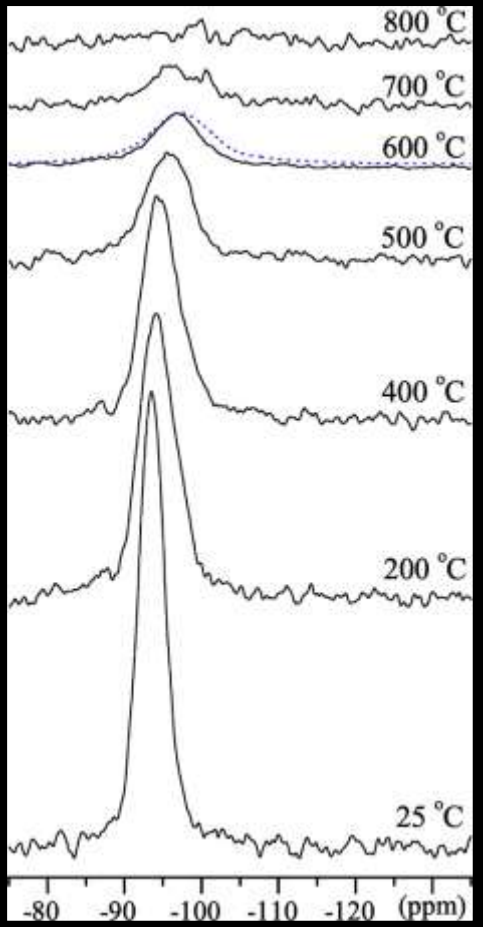
Thermal activation of smectite clay



DTA-TG ANALYSIS



$^{29}Si\{^{1}H\}$ CP/MAS NMR

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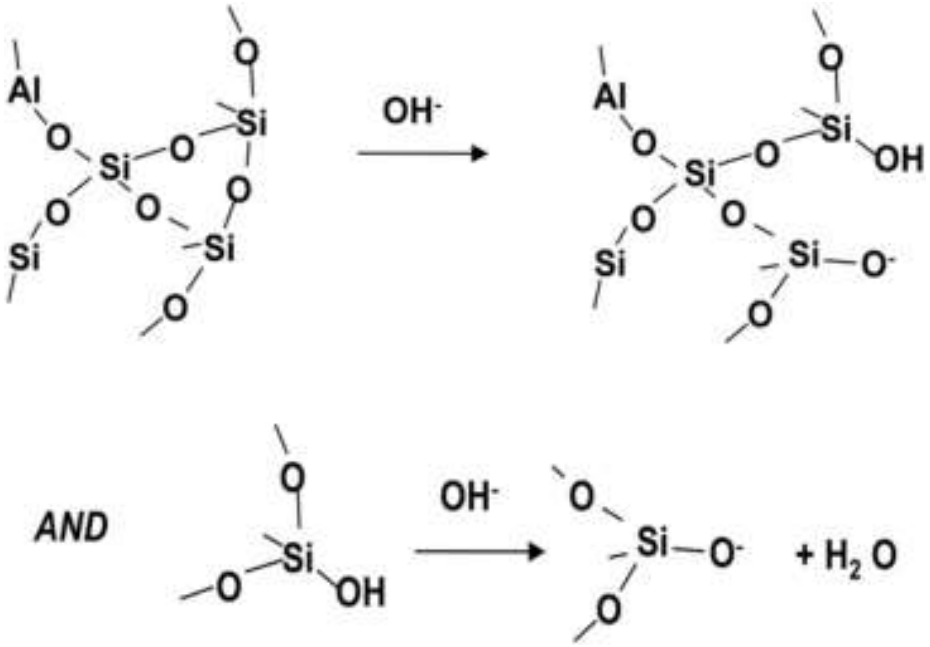
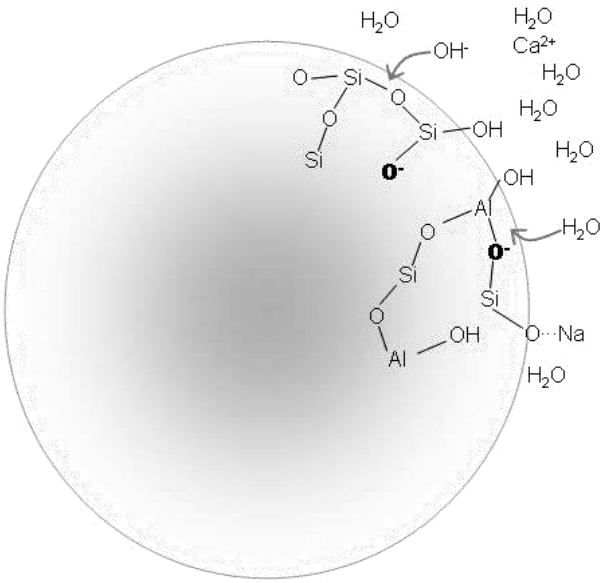
Alkali activation of calcined clays





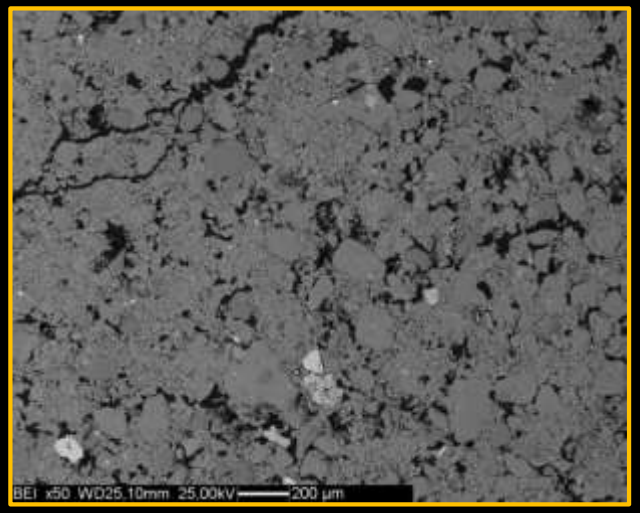
Common alkaline activators:

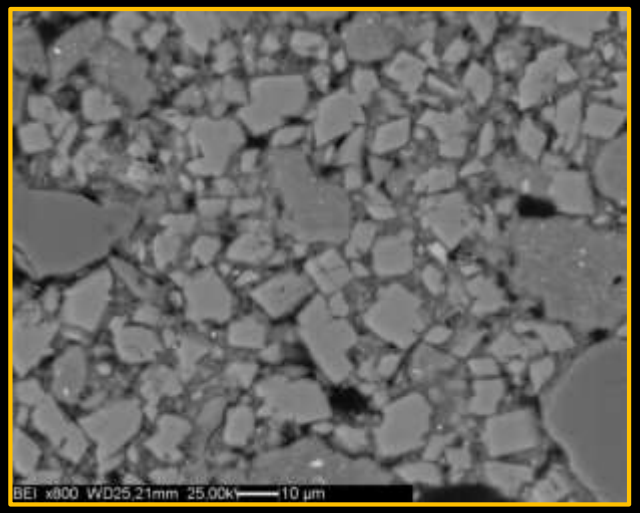
Sodium hydroxide Sodium silicate Sodium carbonate

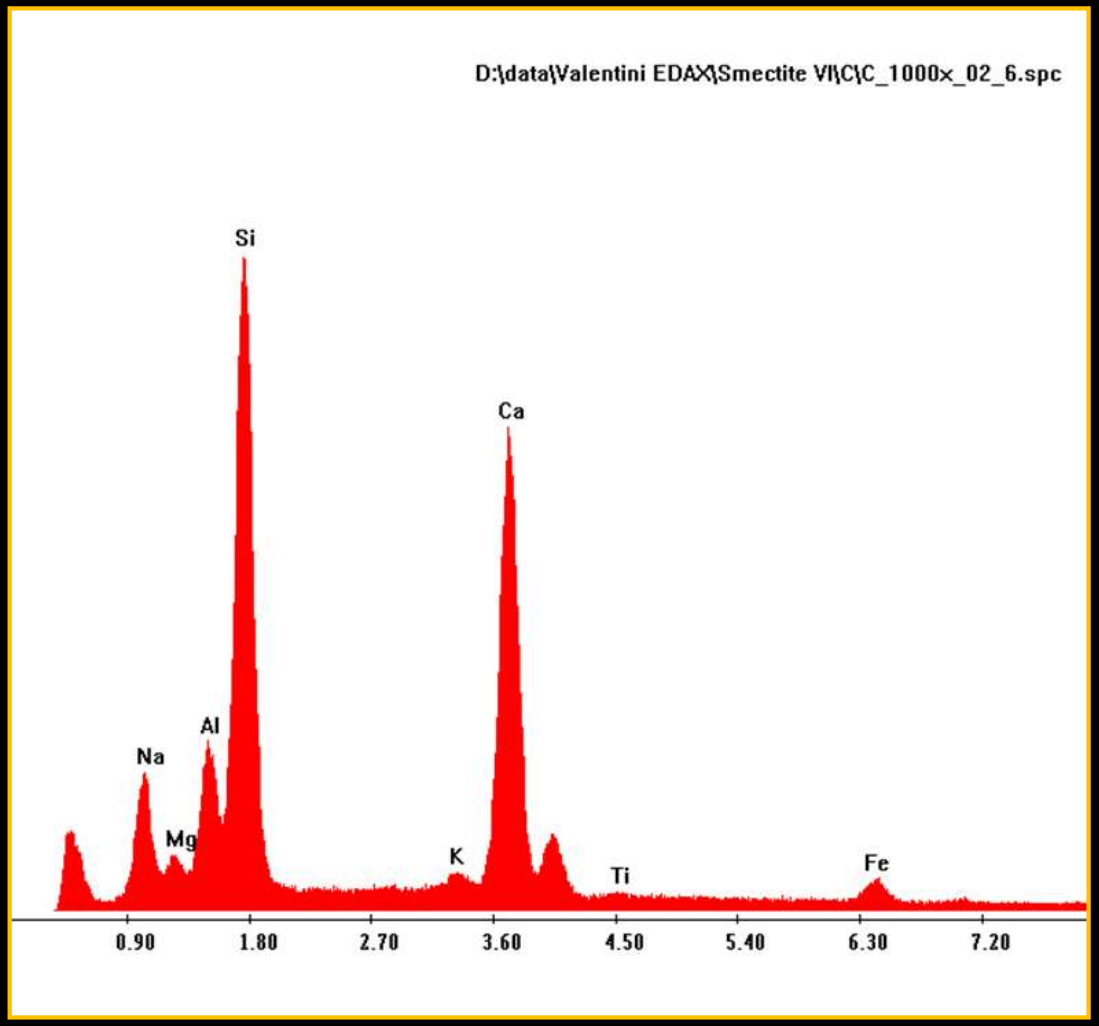
pH

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

Reaction product of alkali-activated blend of calcined smectite and waste marble slurry







BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

Reaction product of alkali-activated blend of calcined smectite and waste marble slurry