

Industrial minerals in the spotlight:

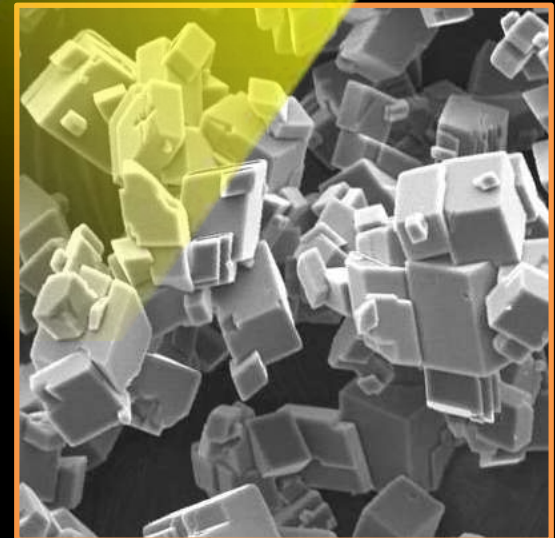
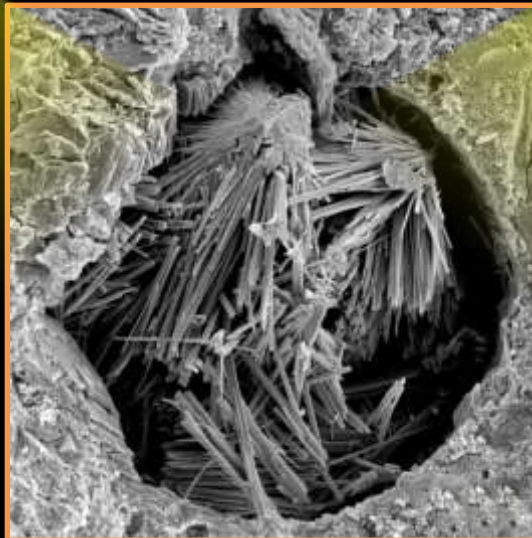
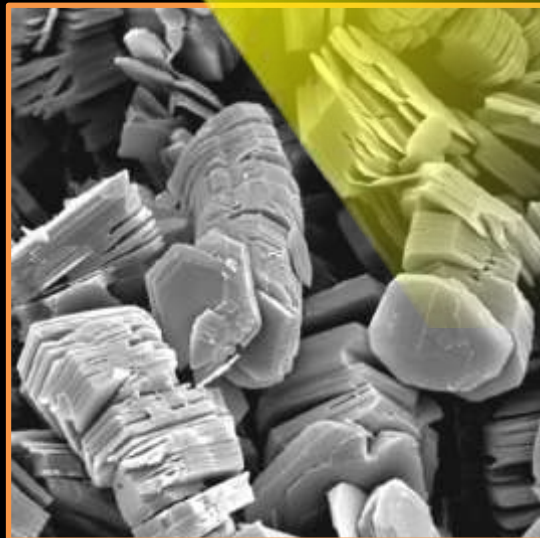
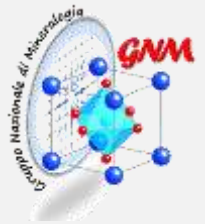
optimizing their environmental performance for sustainable development

Luca Valentini

Università di Padova



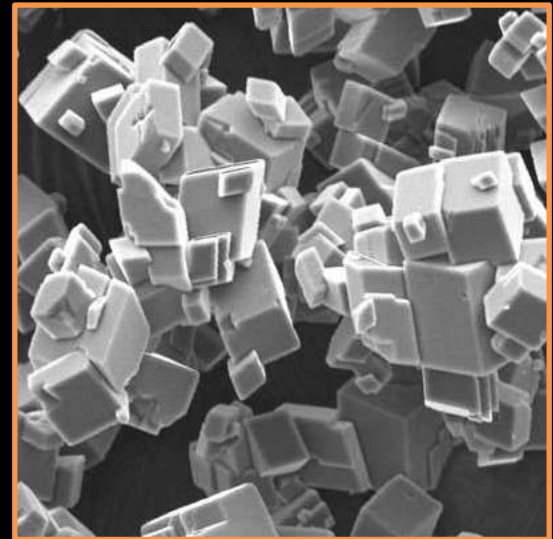
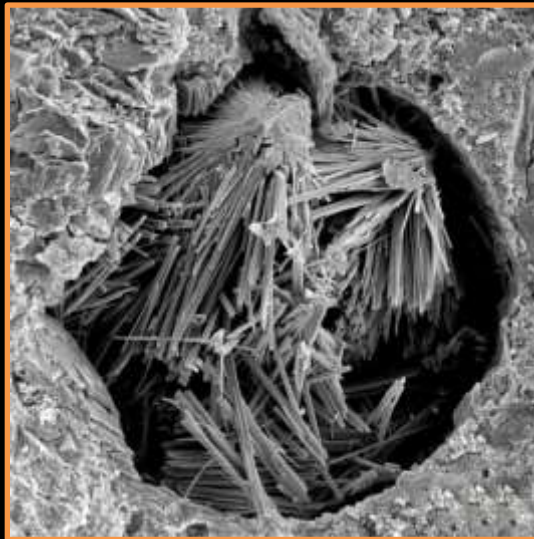
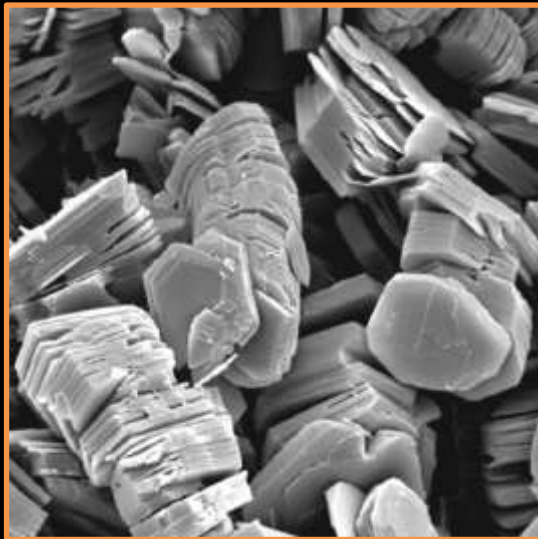
GNM school "physical properties of minerals"
Bressanone/Brixen, 12-15 Feb 2018



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?)

natural

adjective • UK  /'nætʃ.ər.əl/ US  /'nætʃ.ə.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



Cambridge
Dictionary

Make your words meaningful



Industrial minerals in the spotlight

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



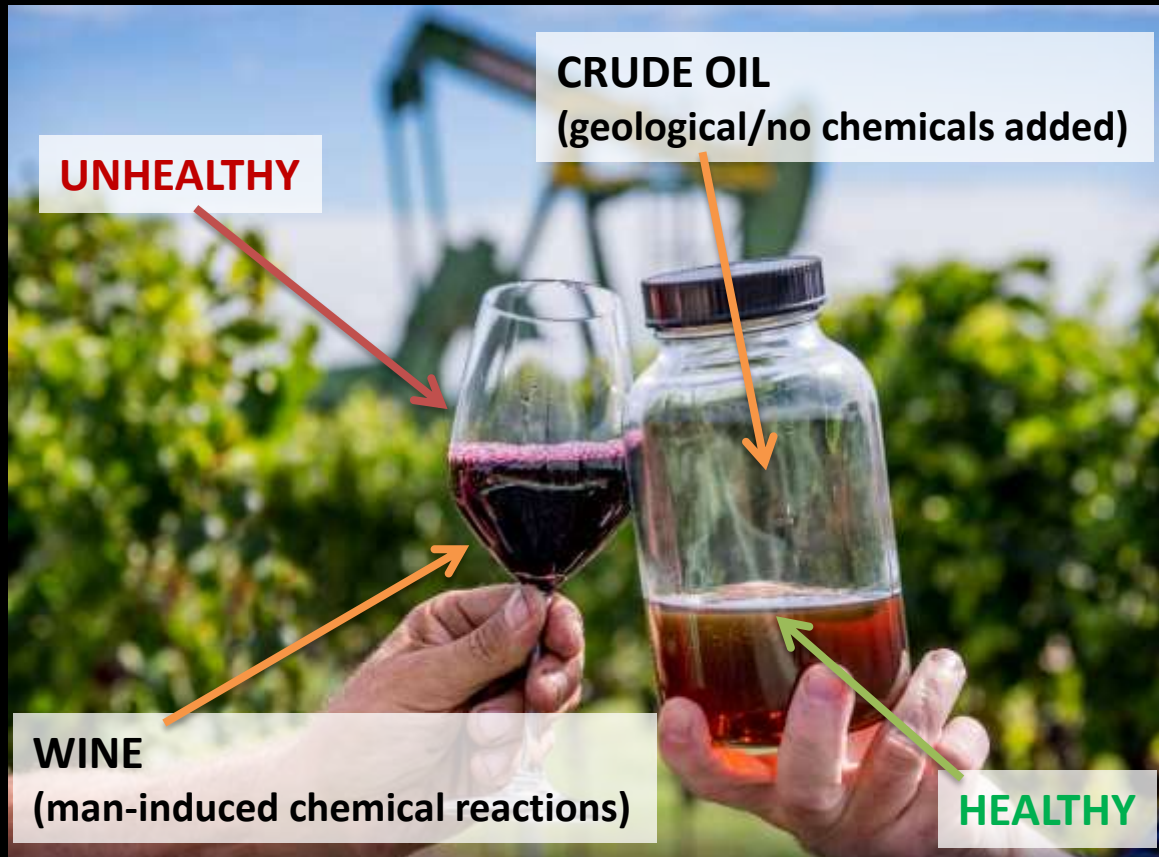
PURE GROWN DIAMONDS
CERTIFIED & SUSTAINABLE



SOME DEFINITIONS...

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

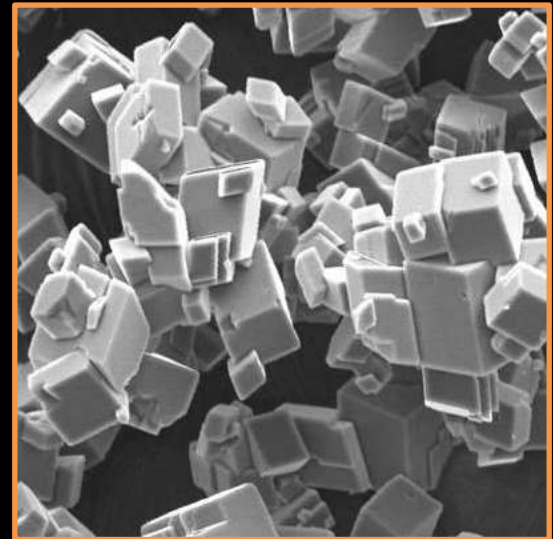
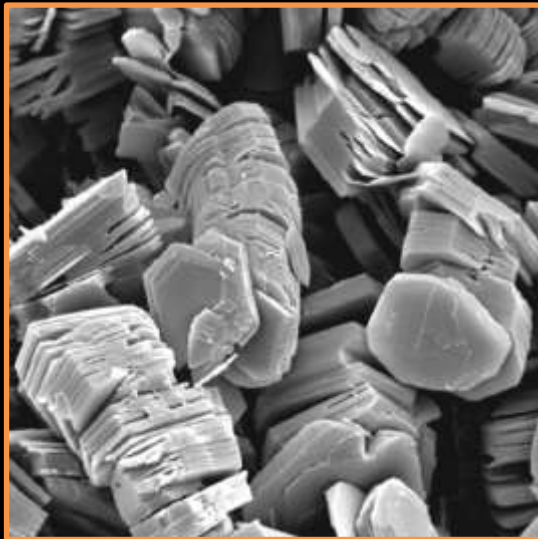
- no chemical substances added and therefore thought to be healthy



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?)



SCIENZA IN CUCINA di Dario Bressanini

Vita da bollicine

19
dicembre
2017

Sono più di due secoli che la regione dello Champagne produce l'omonimo vino, e lo stesso metodo di produzione – il cosiddetto metodo classico – è usato in altre regioni del mondo, anche in Italia, per produrre ottimi vini con le tanto ricercate bollicine. Ma è solo negli ultimi decenni che gli scienziati hanno iniziato ad investigarne [...]

Scritto in [Alcol](#), [Vino](#) | [205 Commenti](#) »

Il mondo dei Cachi

7
dicembre
2017

Quando ero bambino uno dei frutti che più mi piaceva raccogliere e gustare dal giardino di mia nonna Lucia erano i cachi. Aspettavo con ansia l'autunno per poter vedere quei frutti, rassomiglianti a dei grossi pomodori, tingersi via via di un colore arancione sempre più intenso. Ricordo ancora come, tra cugini, si giocasse ad aprire [...]

Scritto in [Chimica](#), [Frutta](#) | [37 Commenti](#) »

Glutammato che spaventa

17
settembre
2017

È una sostanza chimica presente in molti alimenti, leggiamo il suo nome nella lista degli ingredienti di molti cibi confezionati e in tanti leggono con sospetto il suo nome e la sua sigla: E621. Se appartenete a quel vasto gruppo di persone che considerano il glutammato di sodio una «schifezza chimica», beh, forse dovrete considerare [...]

Scritto in [Additivi](#), [Chimica](#), [Etichette](#) | [76 Commenti](#) »

Nobel che sbarellano

3
ottobre
2017

La vitamina C cura il cancro? L'ha detto un premio Nobel, anzi doppiamente Nobel! E non dimentichiamoci della memoria dell'acqua e dell'inesistente legame tra HIV e AIDS. Anche in questi casi "l'ha detto un premio Nobel", quindi, una sorta di "autorità" massima



Industrial minerals in the spotlight

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*)



Industrial minerals in the spotlight



EXAMPLES OF INDUSTRIAL MINERALS

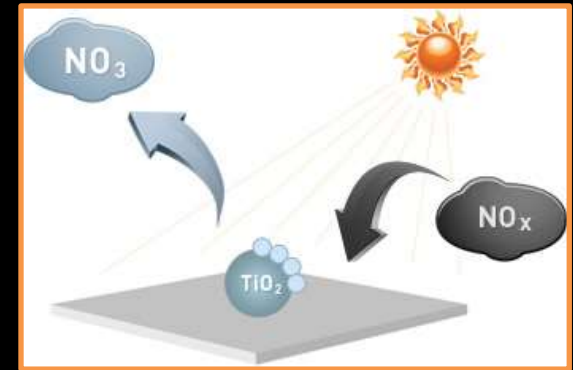
Some metal ores are also used as industrial minerals



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 (BaSO₄)



Sphalerite (ZnS)



Fluorite (CaF₂)





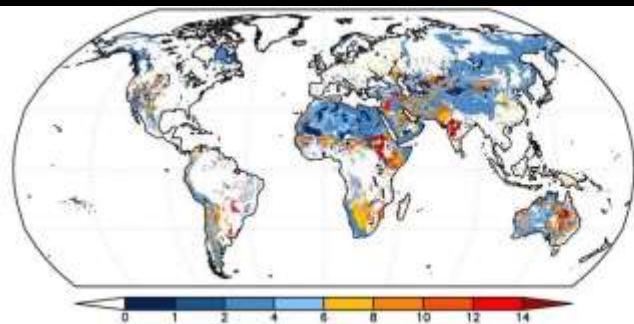
EXAMPLES OF INDUSTRIAL MINERALS

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

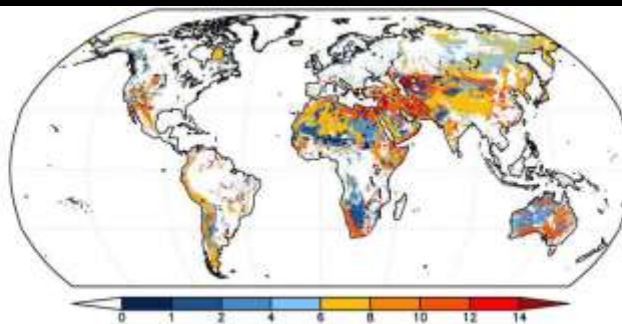


EXAMPLES OF INDUSTRIAL MINERALS

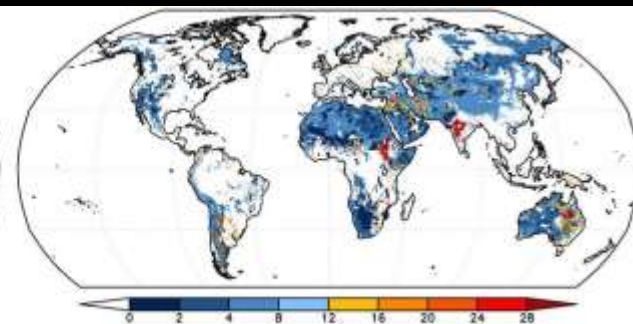
Clay minerals distribution in soils



CAOLINITE



ILLITE



SMECTITE

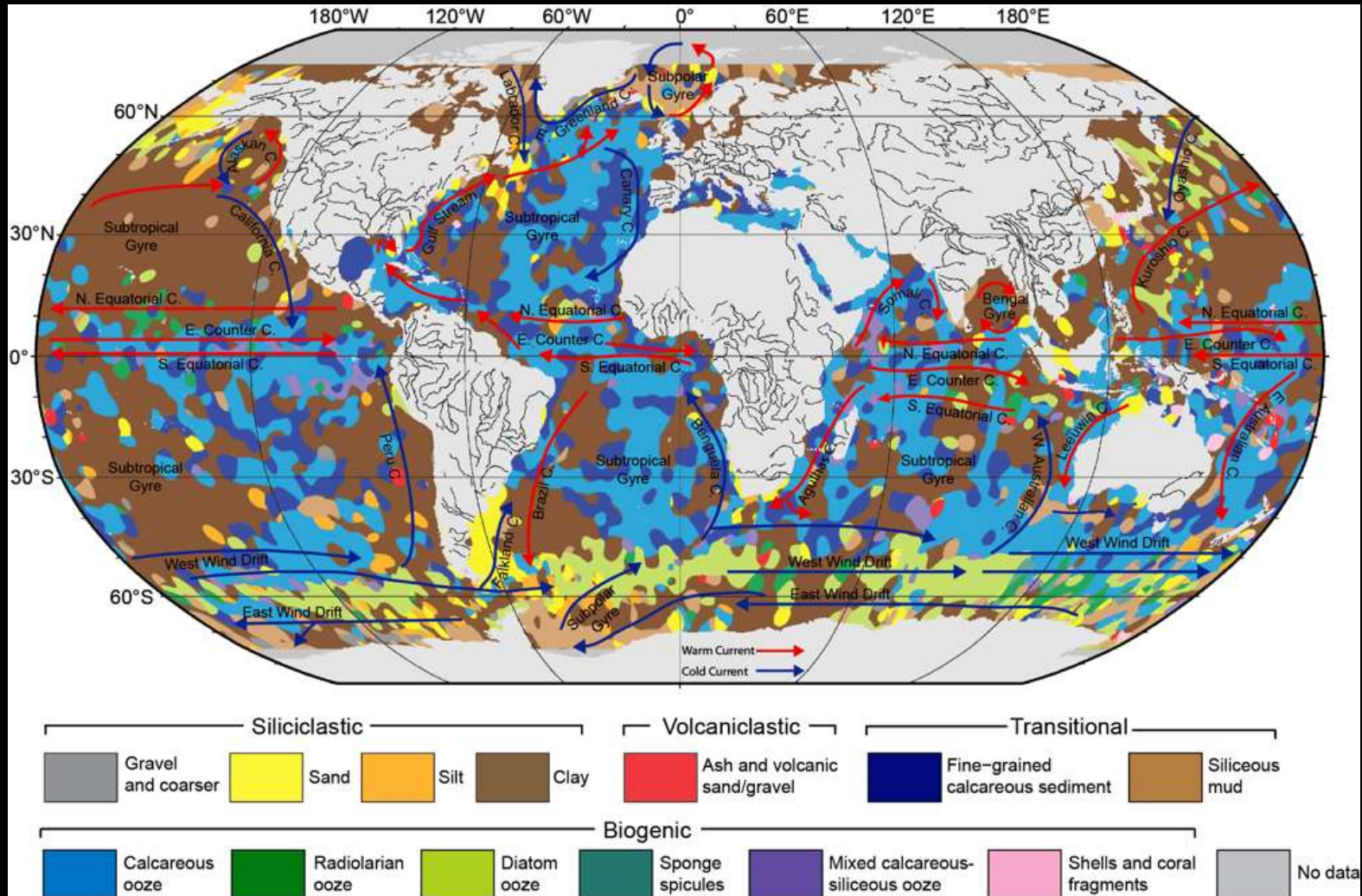


Worldwide kaolinite production (USGS, 2017) 37,000,000 T



EXAMPLES OF INDUSTRIAL MINERALS

Clay distribution in marine sediments



Industrial minerals in the spotlight



EXAMPLES OF INDUSTRIAL MINERALS



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





Properties of materials
made from industrial minerals



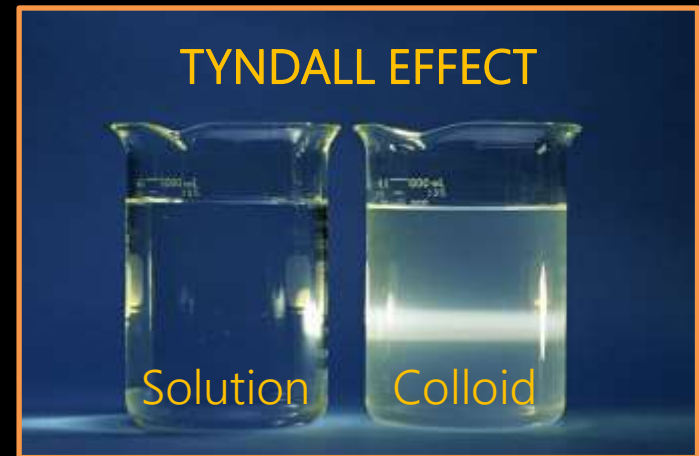
BULK PROPERTIES

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

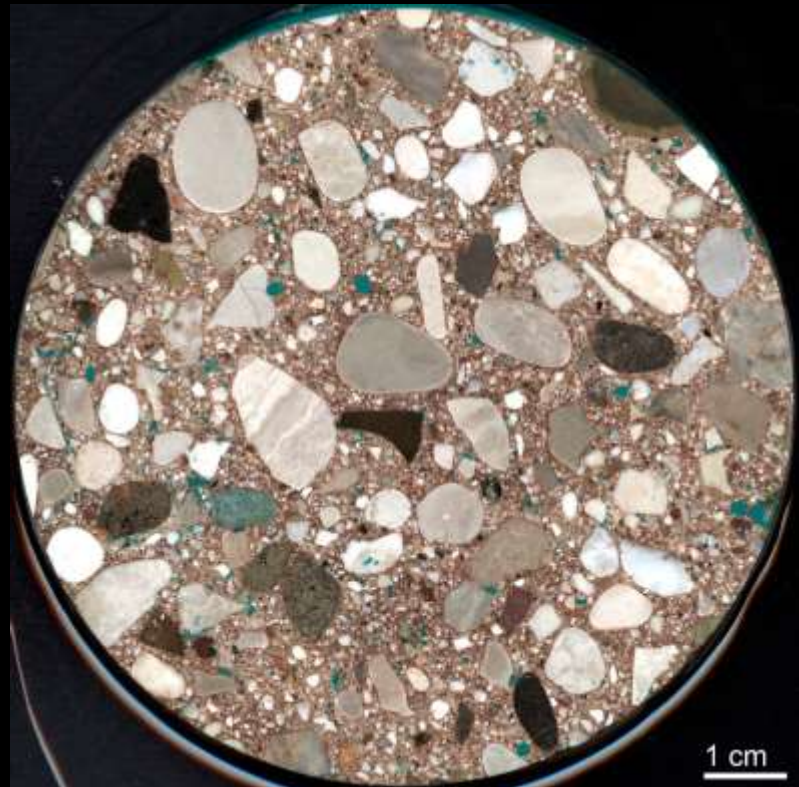
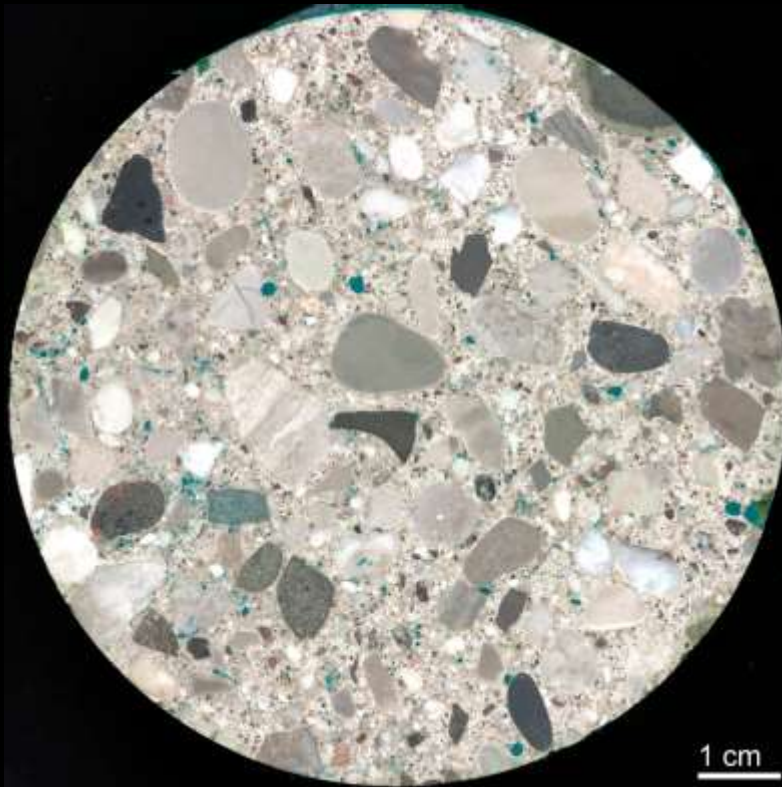




Industrial minerals in the spotlight

BULK PROPERTIES

Microstructural features: optical methods

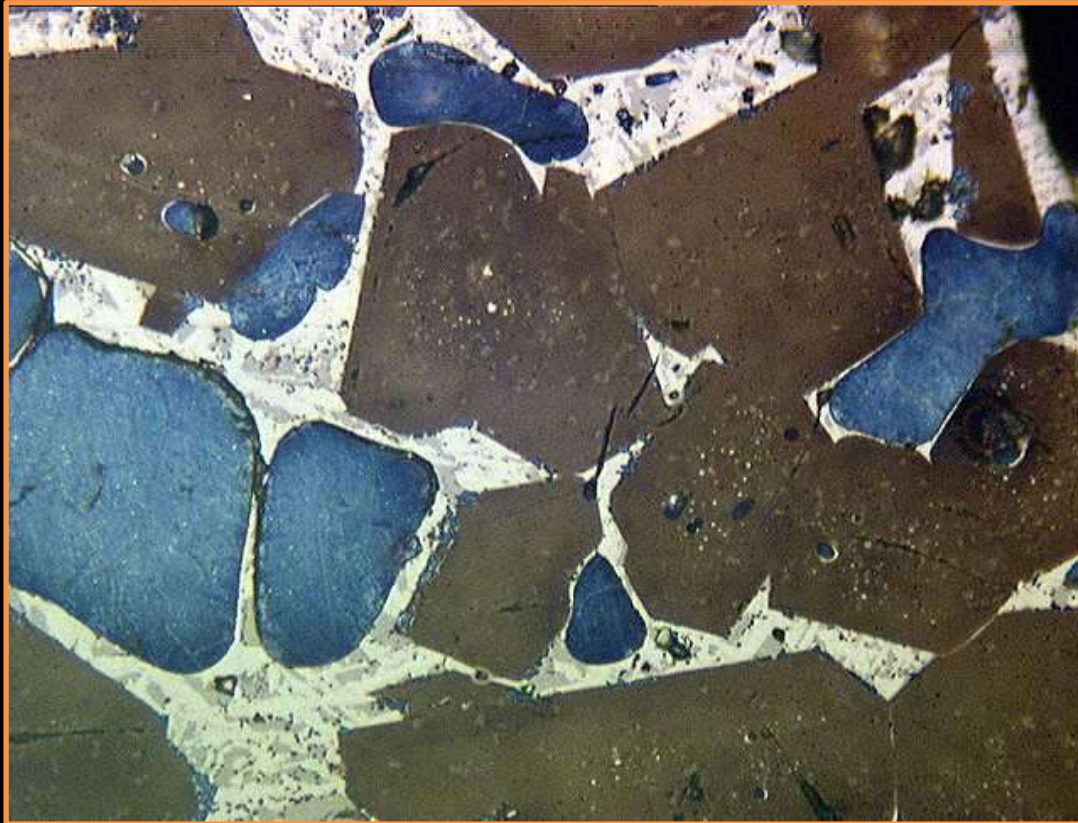


Optical scan of concrete microstructure



BULK PROPERTIES

Microstructural features: optical methods

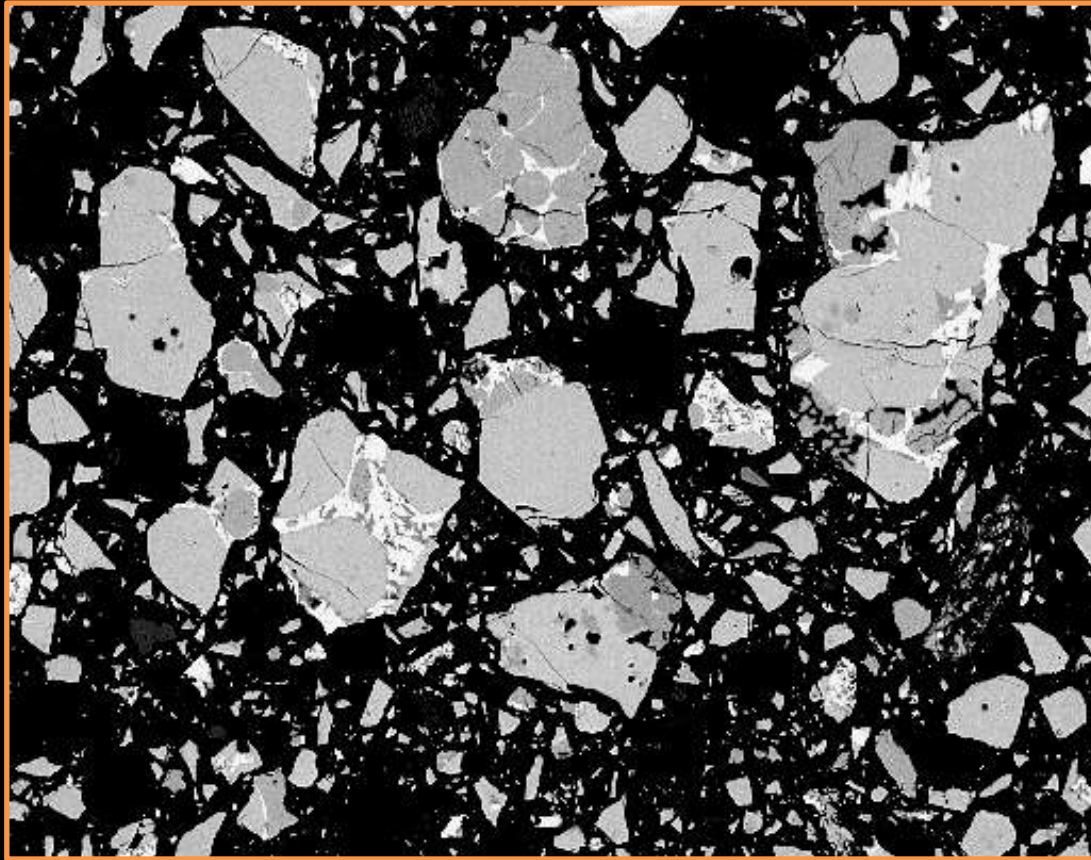


Optical micrograph of clinker microstructure



BULK PROPERTIES

Microstructural features: electron microscopy

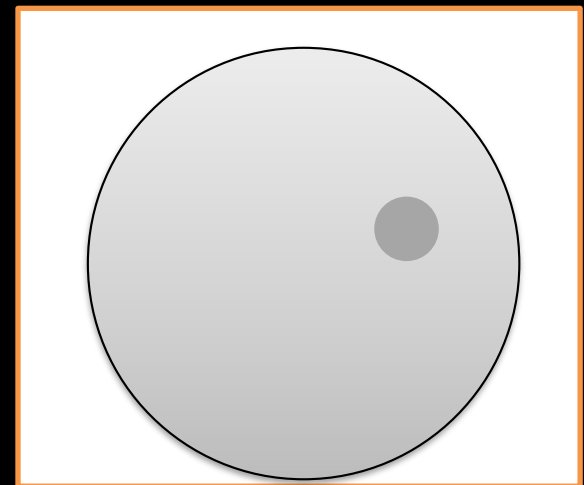
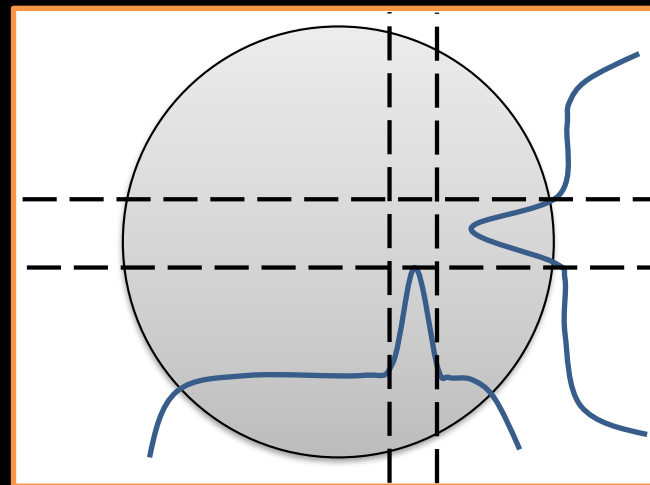
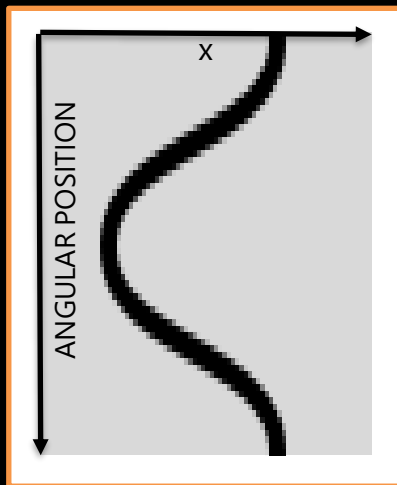
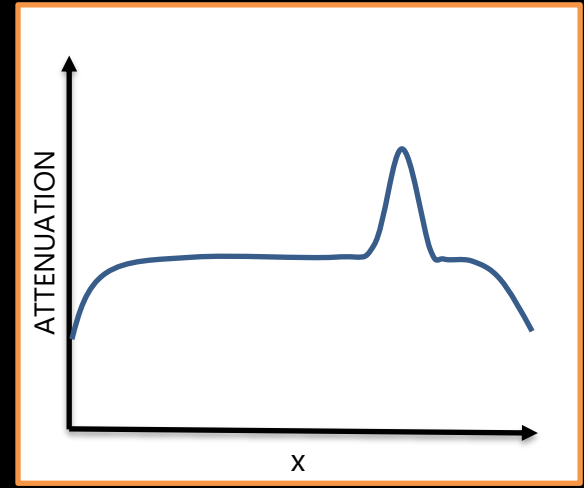
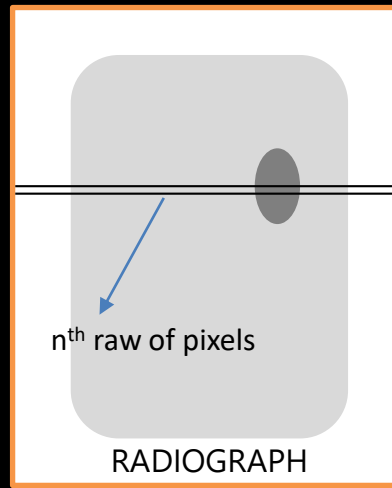
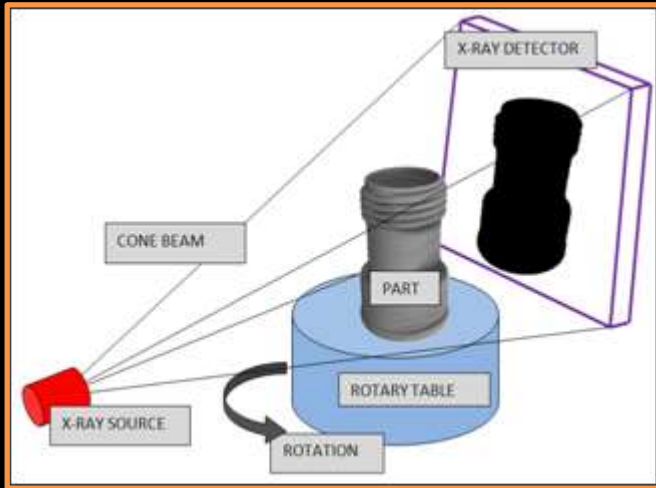


SEM-BSE image of cement powder



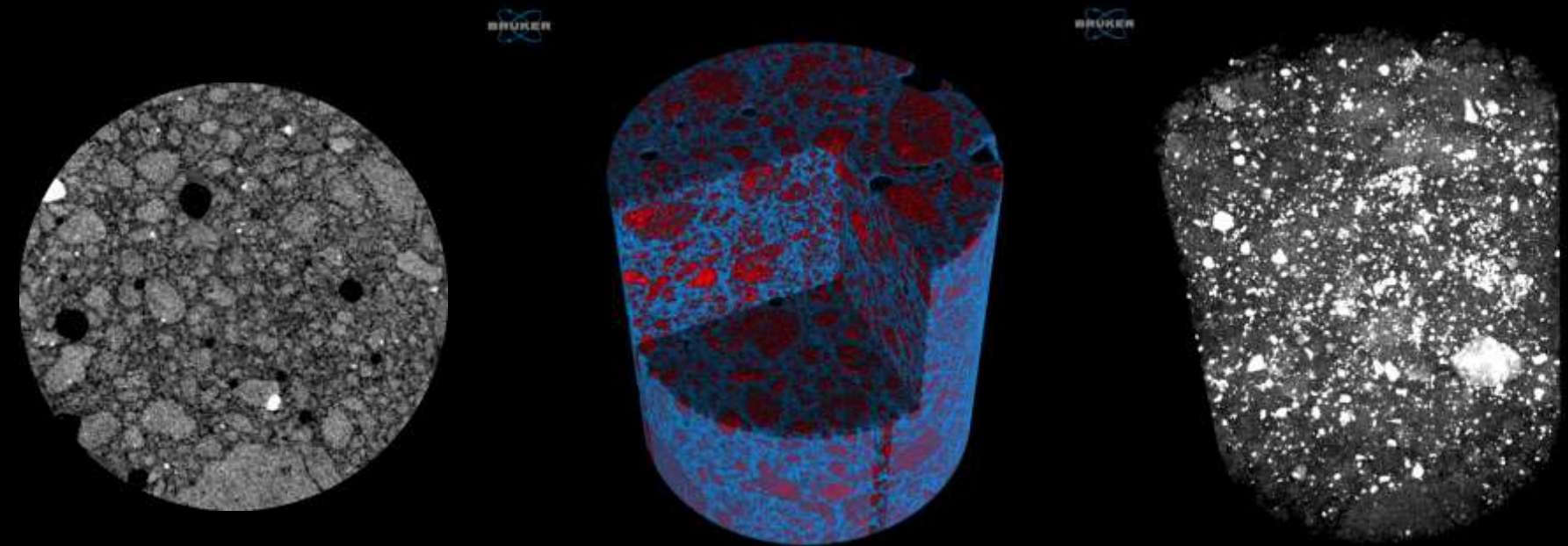
BULK PROPERTIES

Microstructural features: X-ray tomography



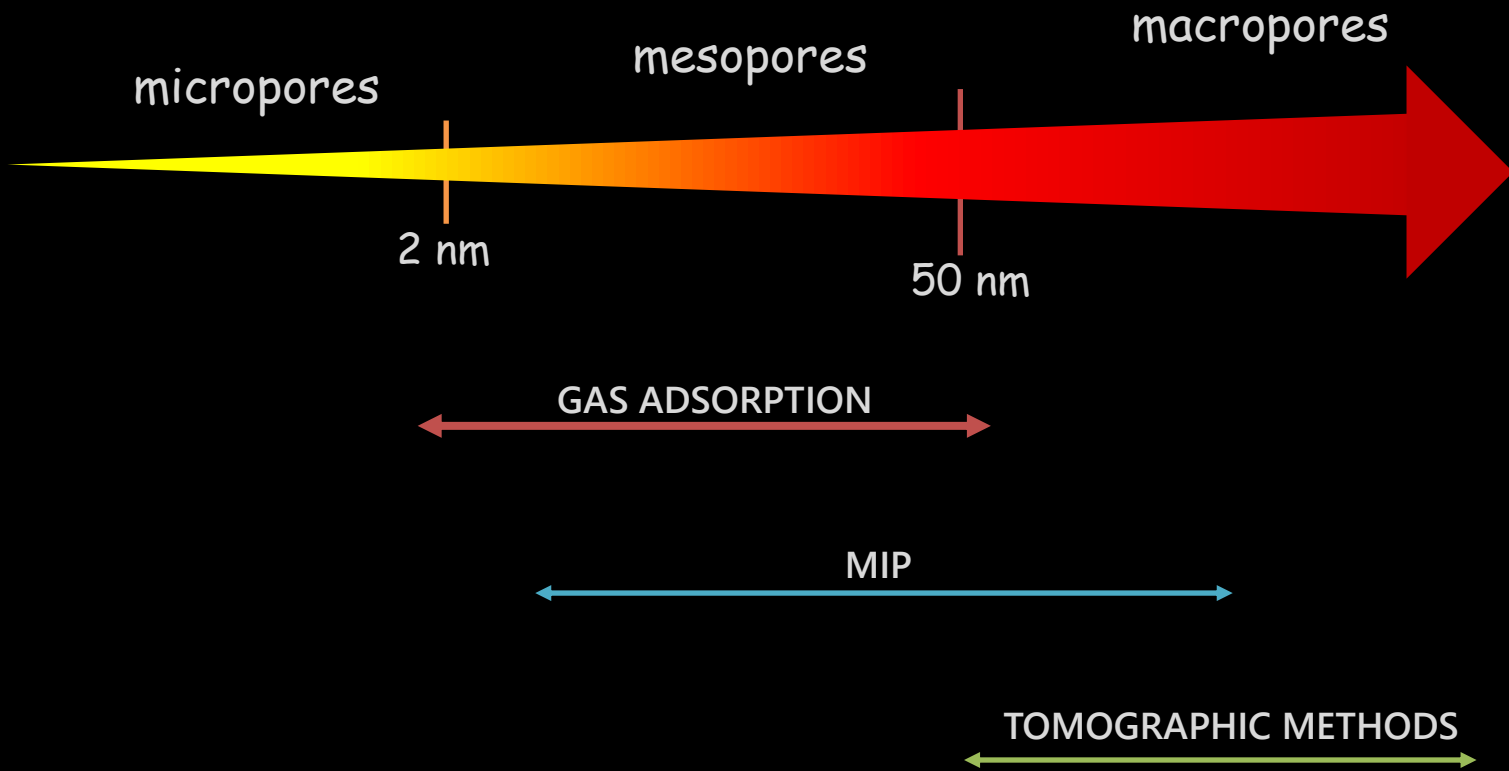
BULK PROPERTIES

Microstructural features: X-ray tomography



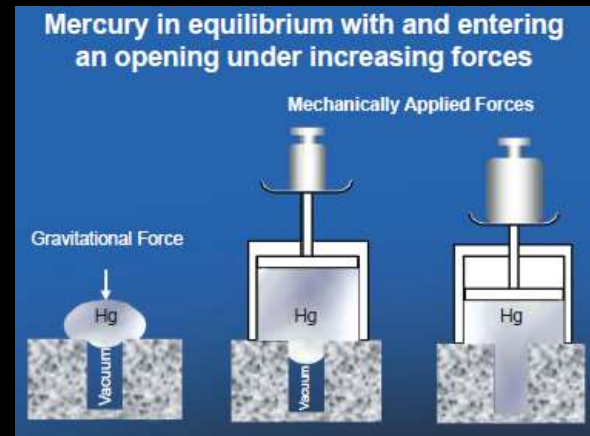
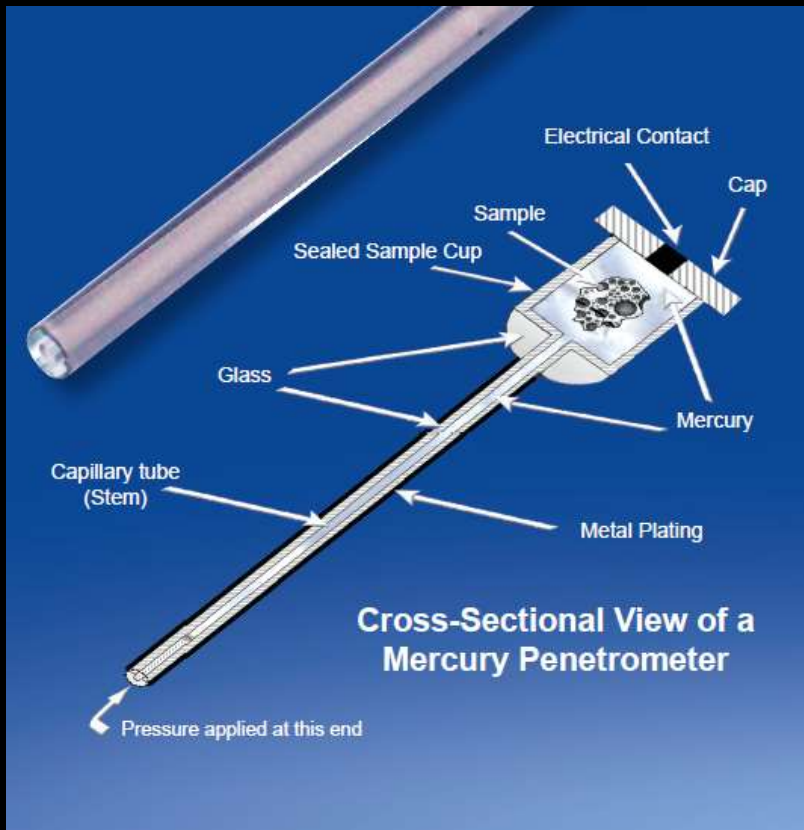
BULK PROPERTIES

Porosity



BULK PROPERTIES

Porosity: Mercury Intrusion Porosimetry

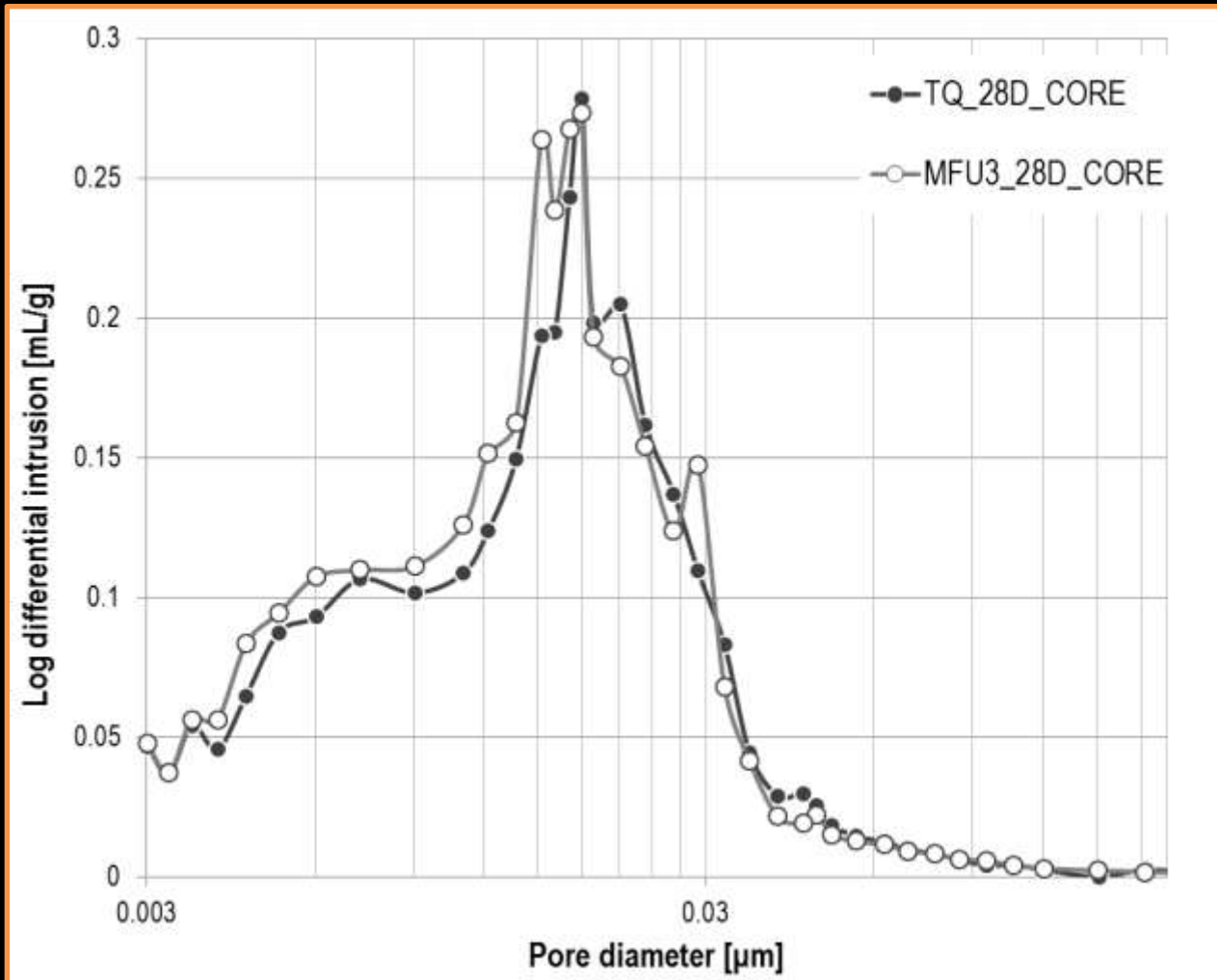


$$D = -4\gamma\cos\theta/P$$



BULK PROPERTIES

Porosity: Mercury Intrusion Porosimetry



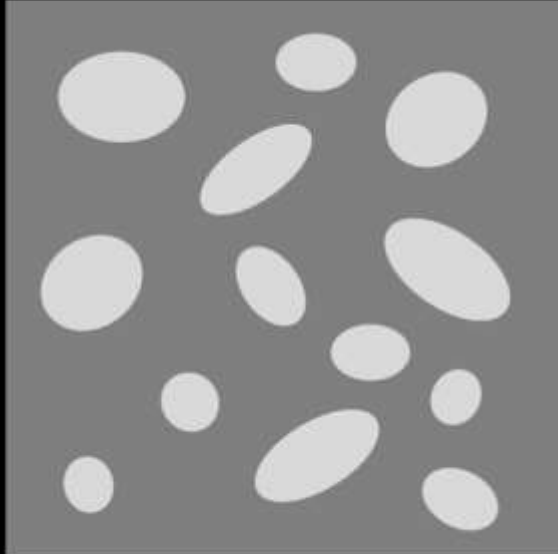


BULK PROPERTIES

Relationship between microstructure and mechanical properties



A percolated



B percolated




“soft” phase



“hard” phase

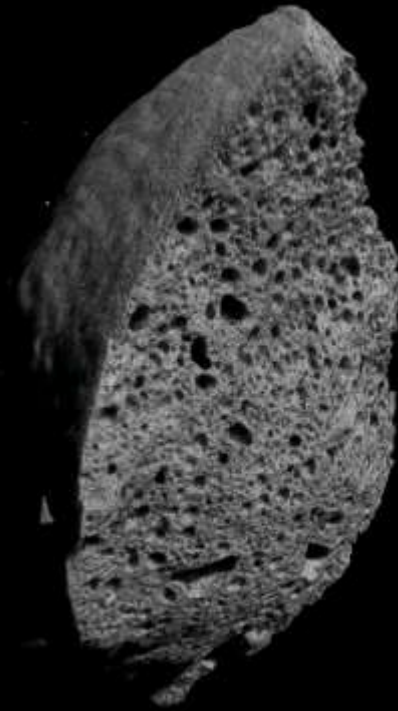
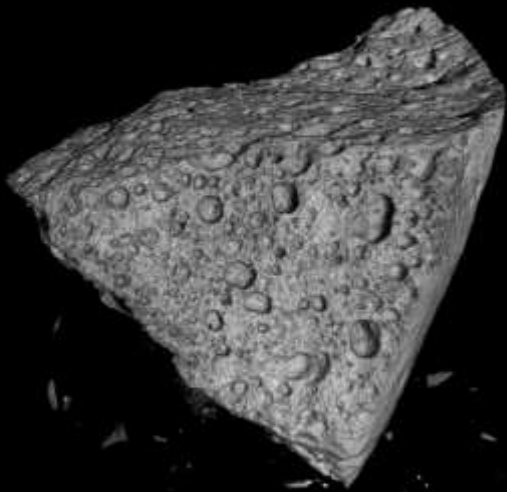
50 % A & 50 % B



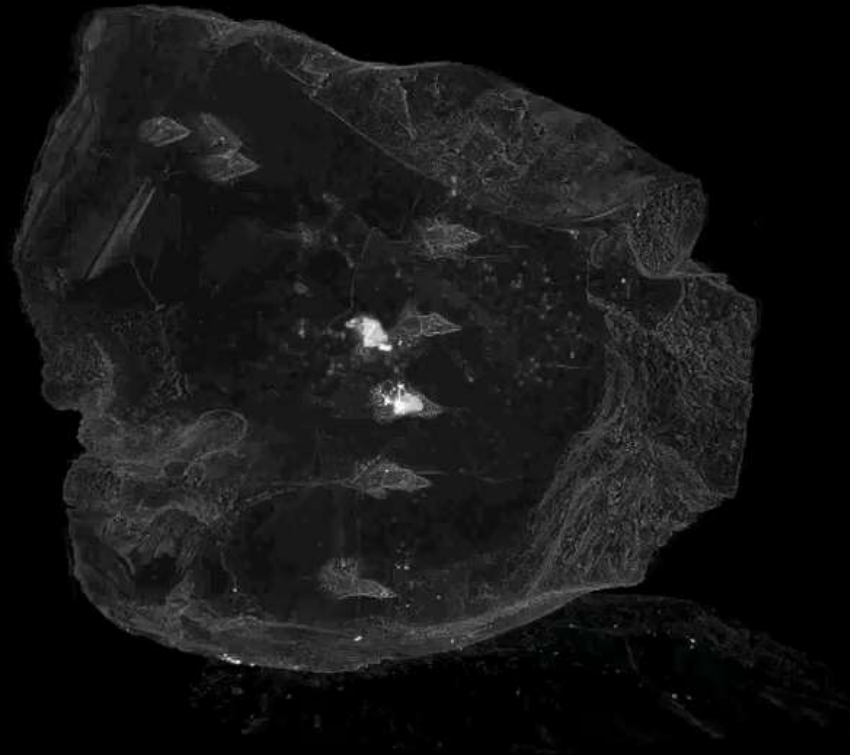


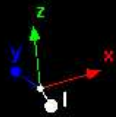
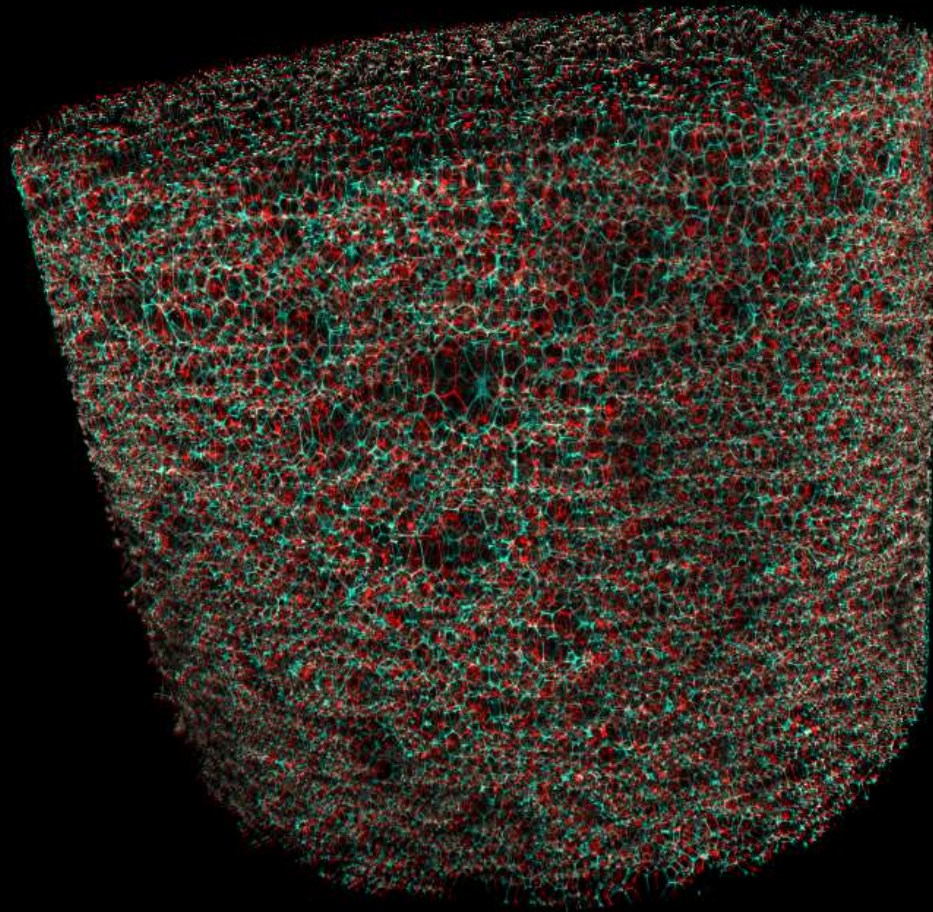
**Gallery of 3D rendered
Tomographic images**

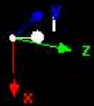
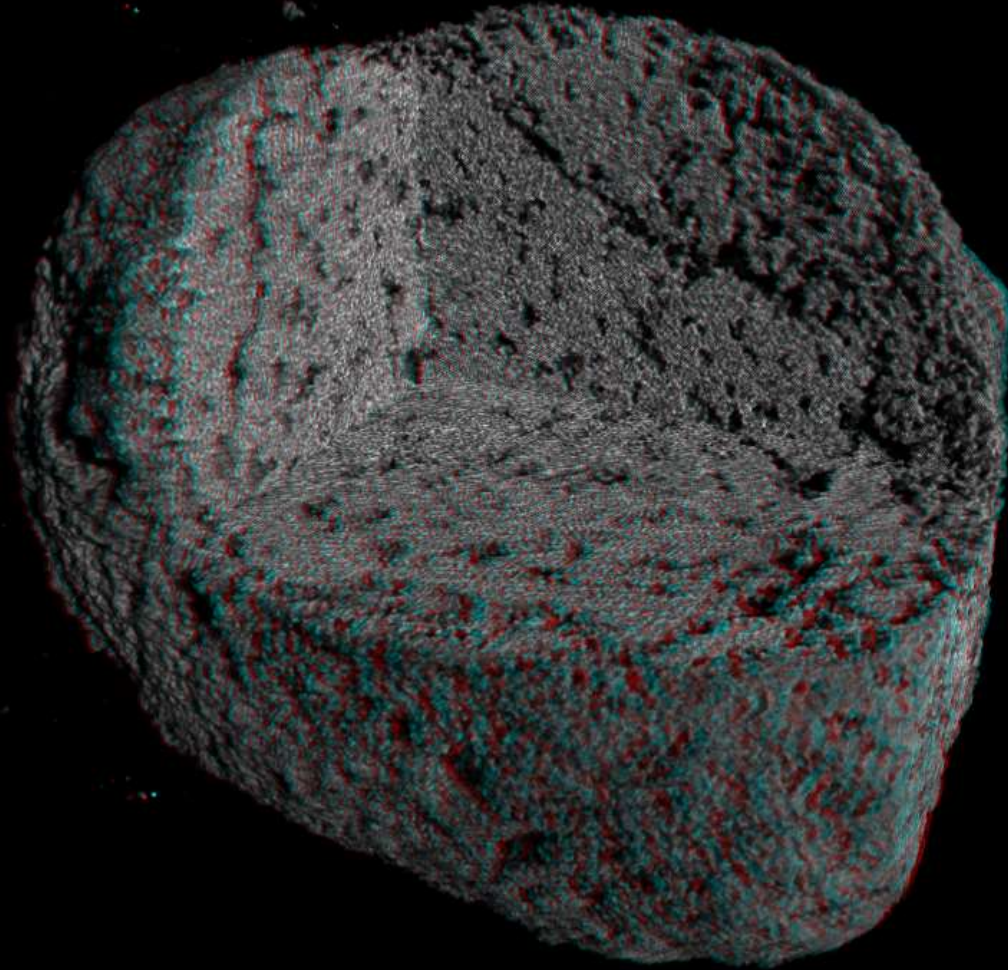


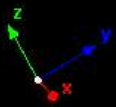
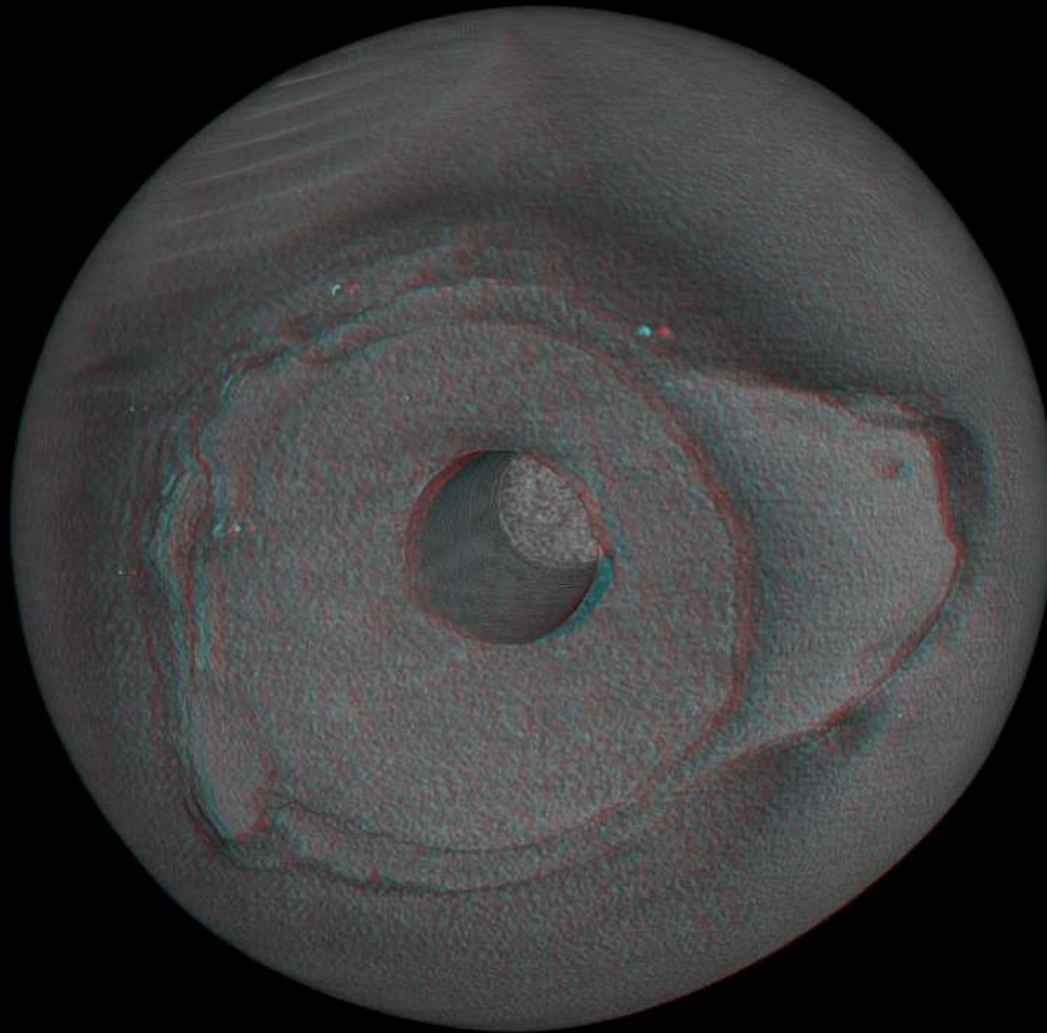


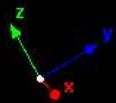
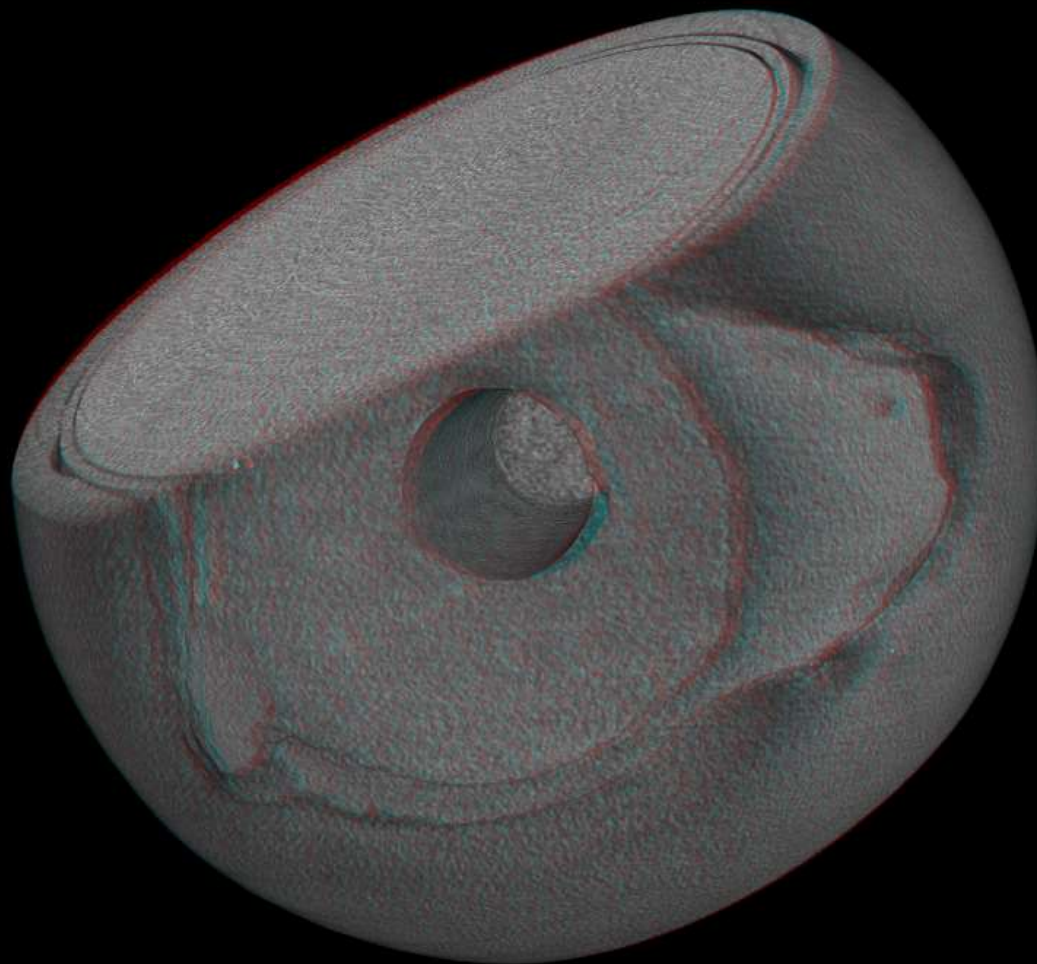
Industrial minerals in the spotlight

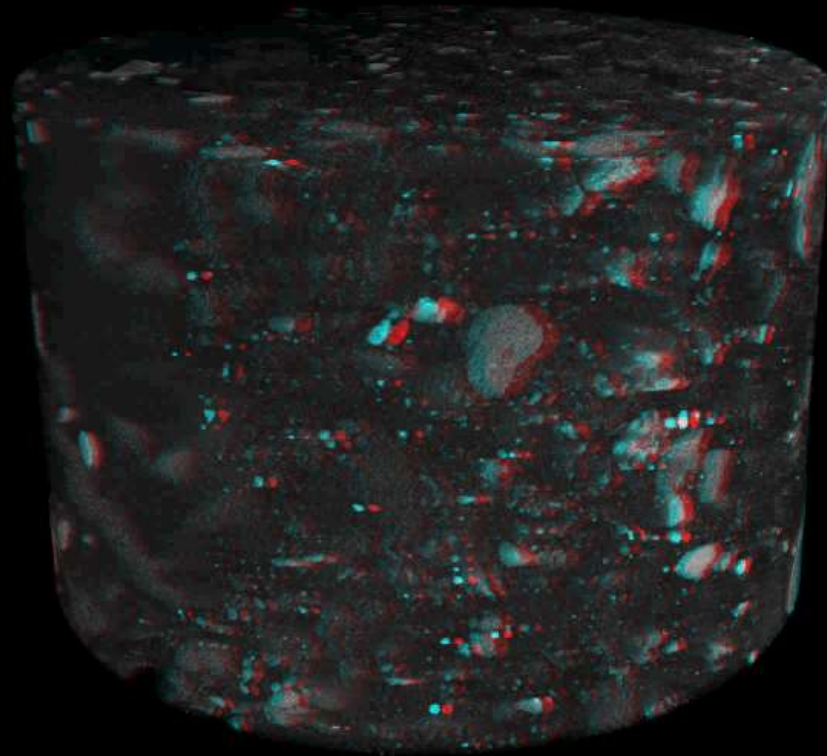


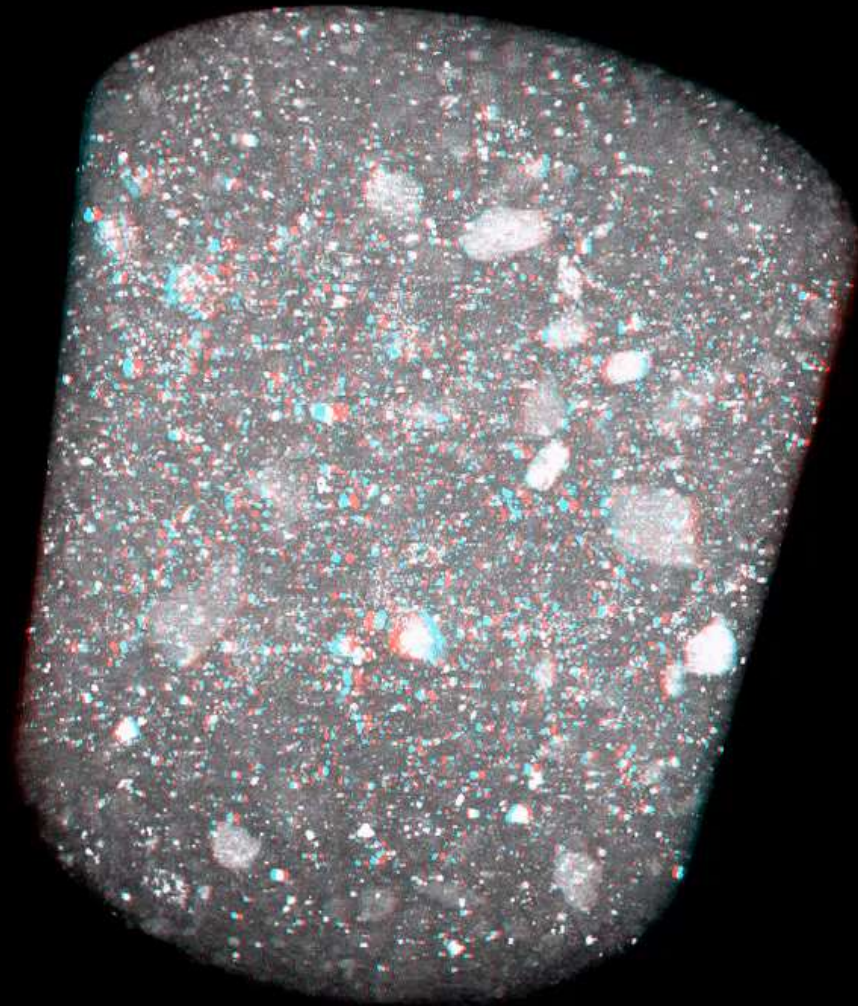














SURFACE PROPERTIES



God made the bulk; the surface was
invented by the devil.

— *Wolfgang Pauli* —

AZ QUOTES



SURFACE PROPERTIES

SURFACE FREE ENERGY

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

I

II

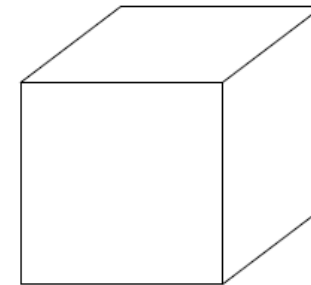
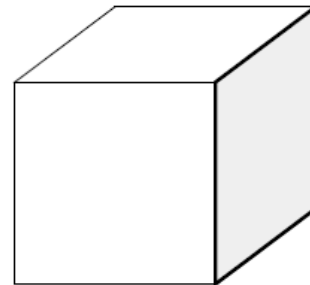
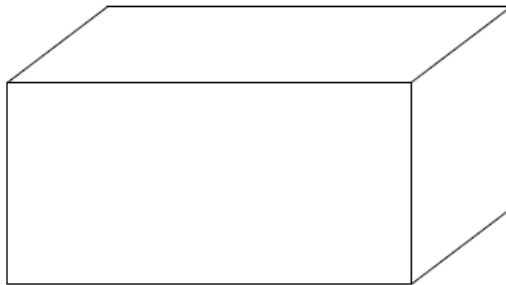


Figure 5.1: Schematic of two configurations of a solid used in defining surface energy.

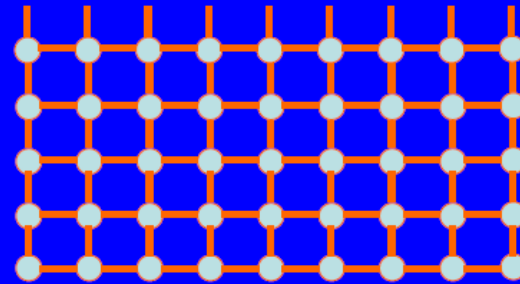
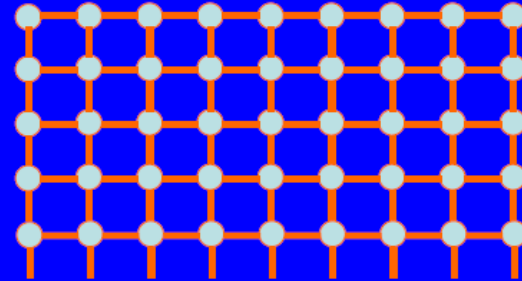
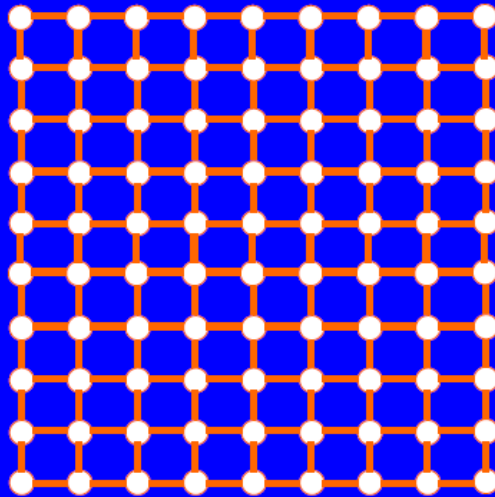
Surfaces behave differently compared to the bulk!



SURFACE PROPERTIES

Concept of ideal flat surfaces (by cleavage process)

A surface is created by cutting a crystal



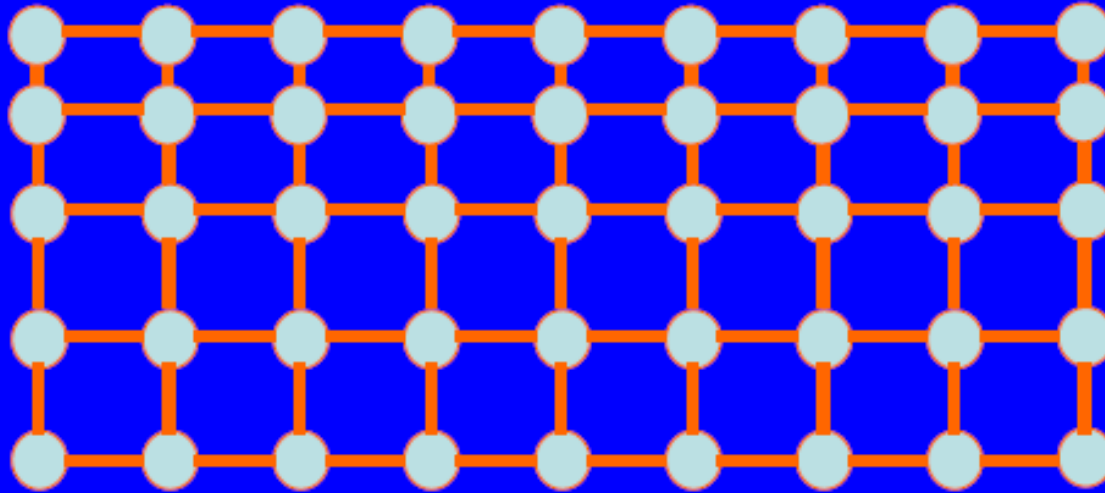
But such ideal surfaces are generally unstable

Surfaces behave differently compared to the bulk!





SURFACE PROPERTIES



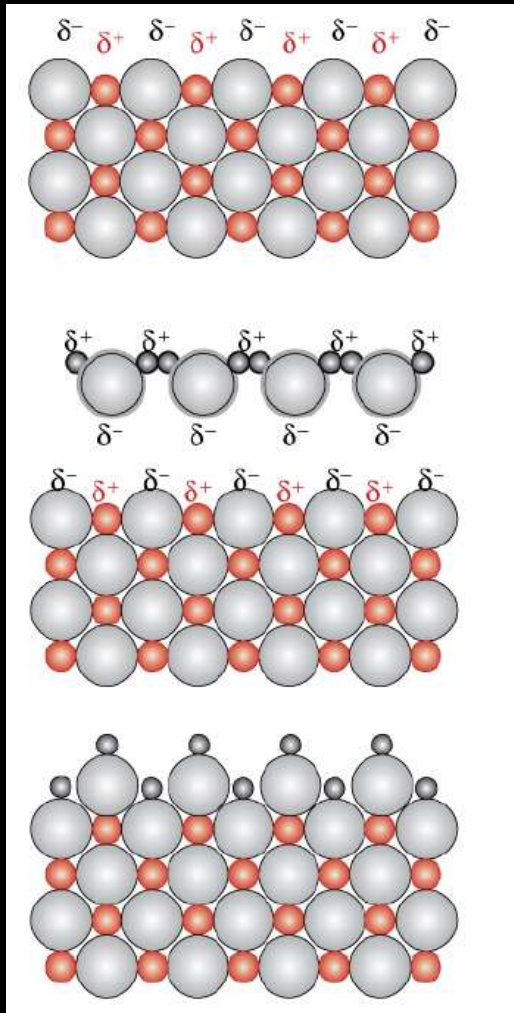
Surface relaxation:
Modification of the near-surface
interplanar distances

Surfaces behave differently compared to the bulk!





SURFACE PROPERTIES



Residual surface charge

H₂O adsorption (wetting)

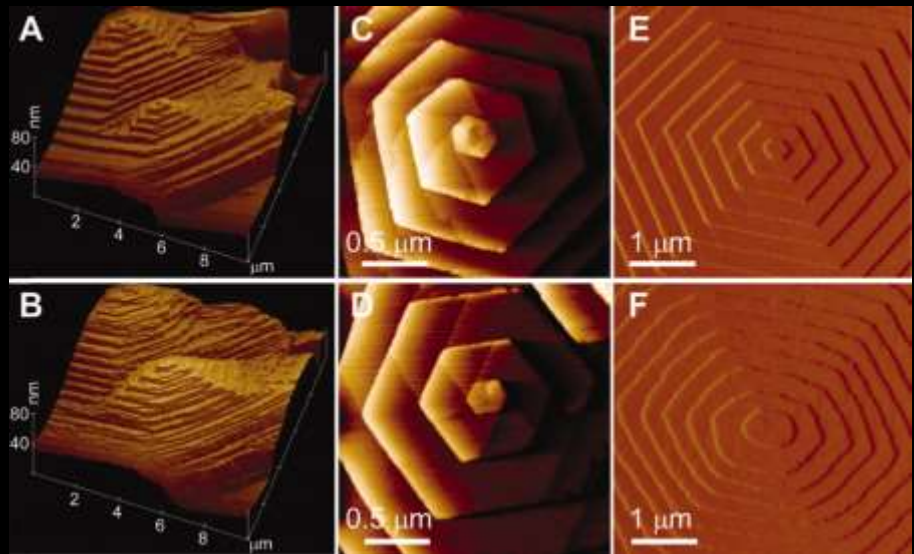
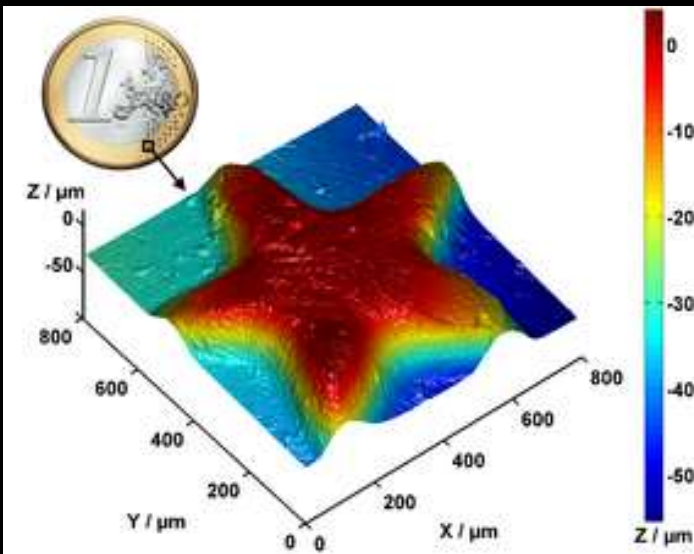
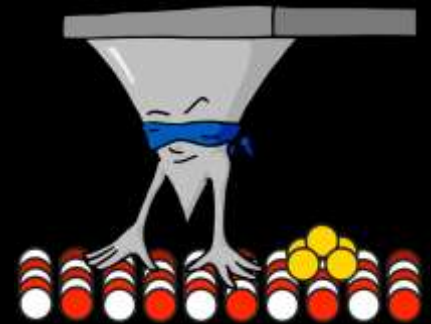
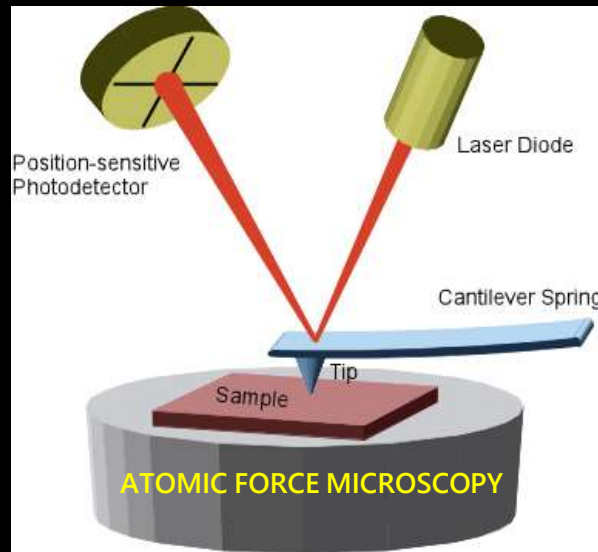
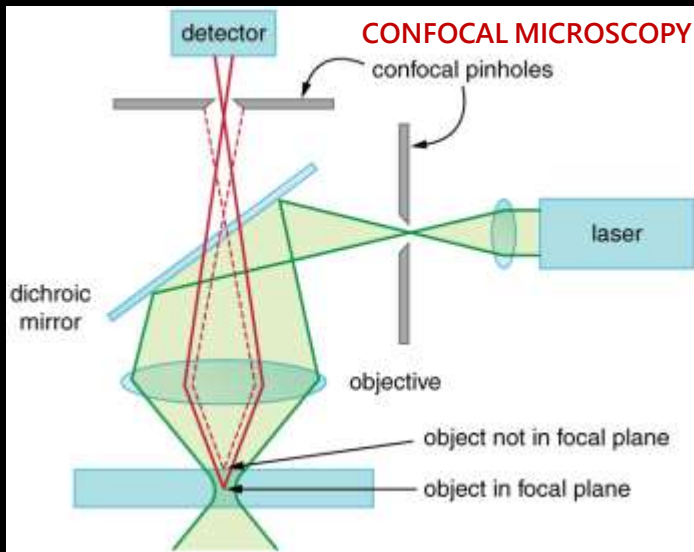
Surface protonation

Surfaces behave differently compared to the bulk!



SURFACE PROPERTIES

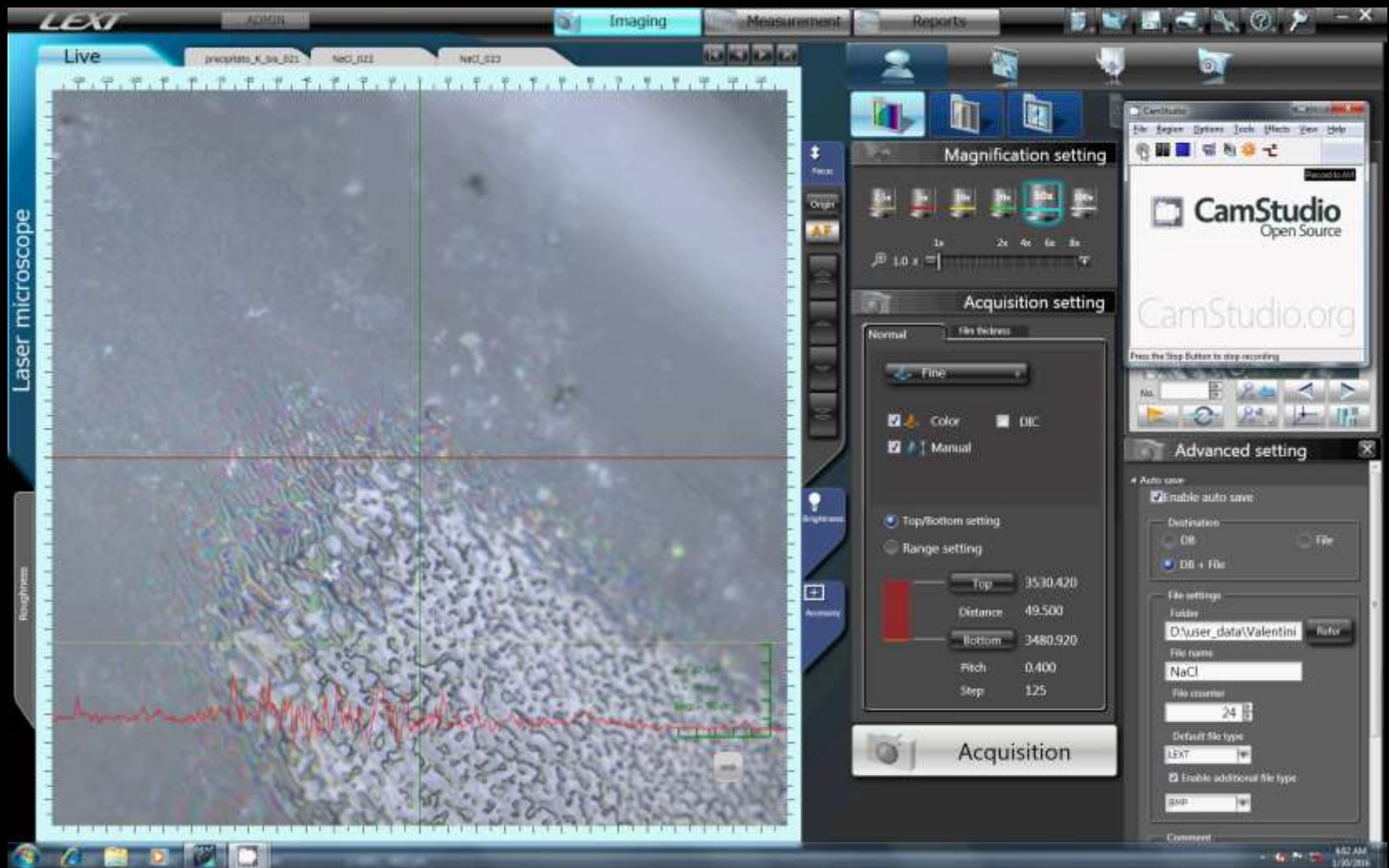
"Observing" surfaces



Industrial minerals in the spotlight



SURFACE PROPERTIES

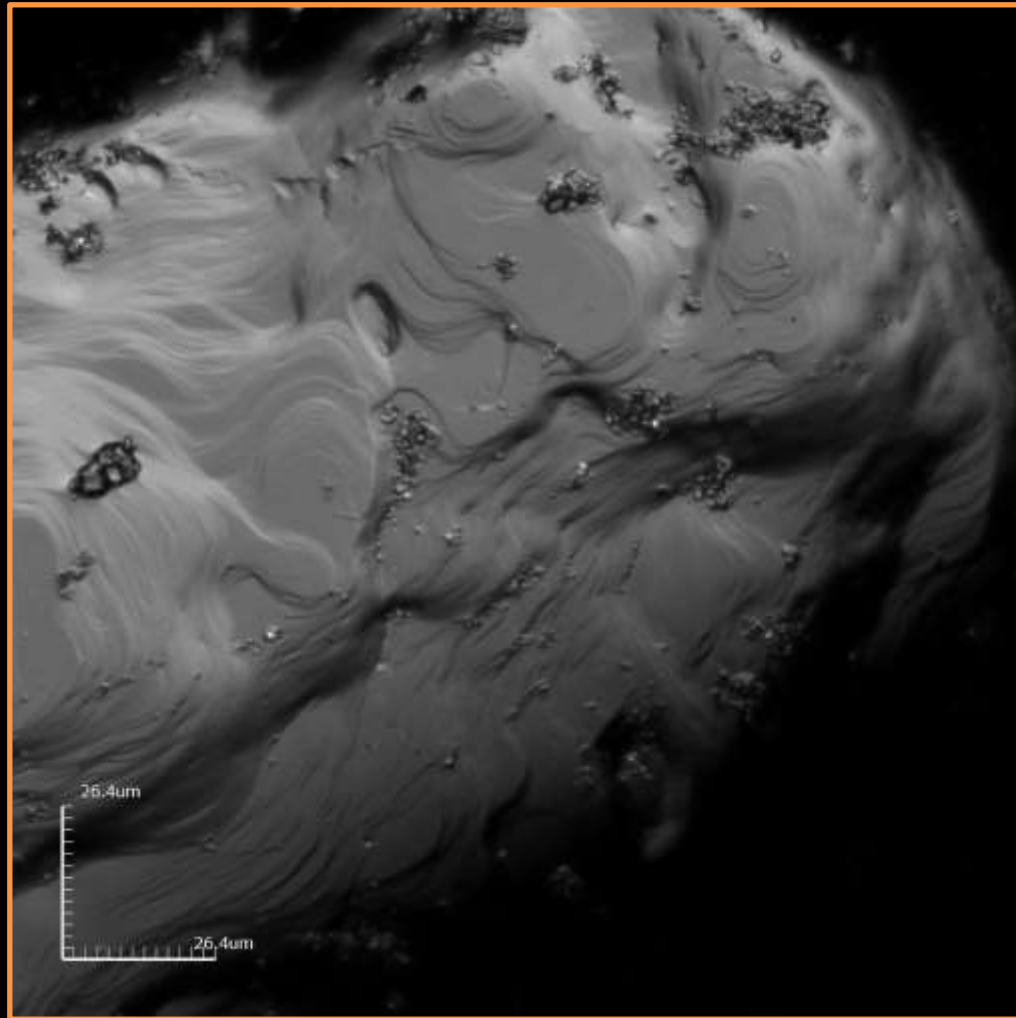


Surfaces are where things happen

Industrial minerals in the spotlight



SURFACE PROPERTIES



Surface of NaCl crystal after partial dissolution





SURFACE PROPERTIES

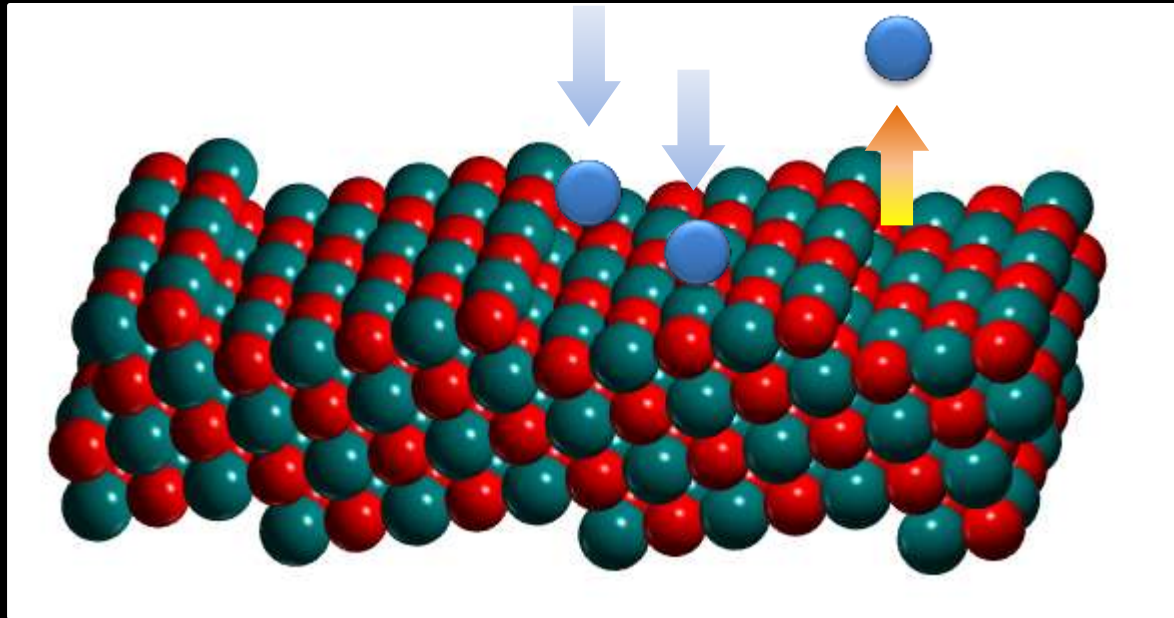
link to video: <https://www.youtube.com/watch?v=8n2AhUYk2WA>

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



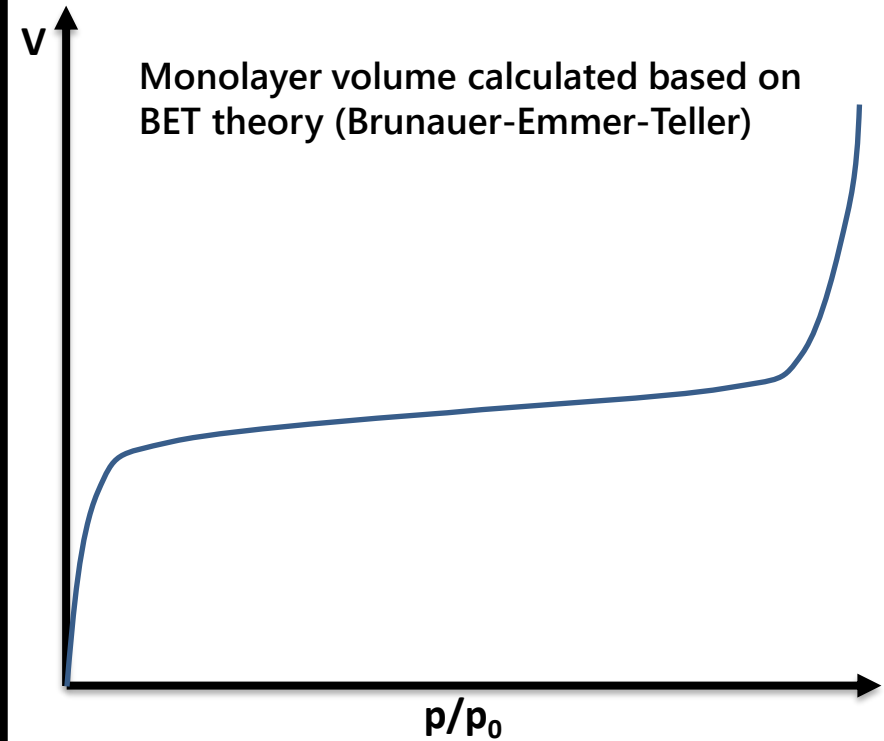
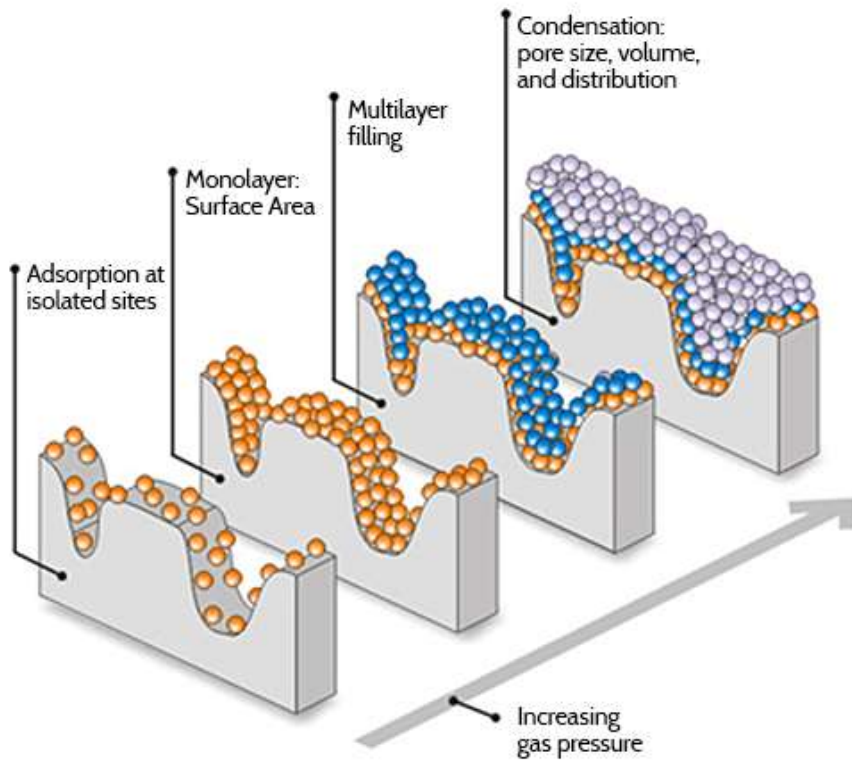
fractional coverage

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



SURFACE PROPERTIES

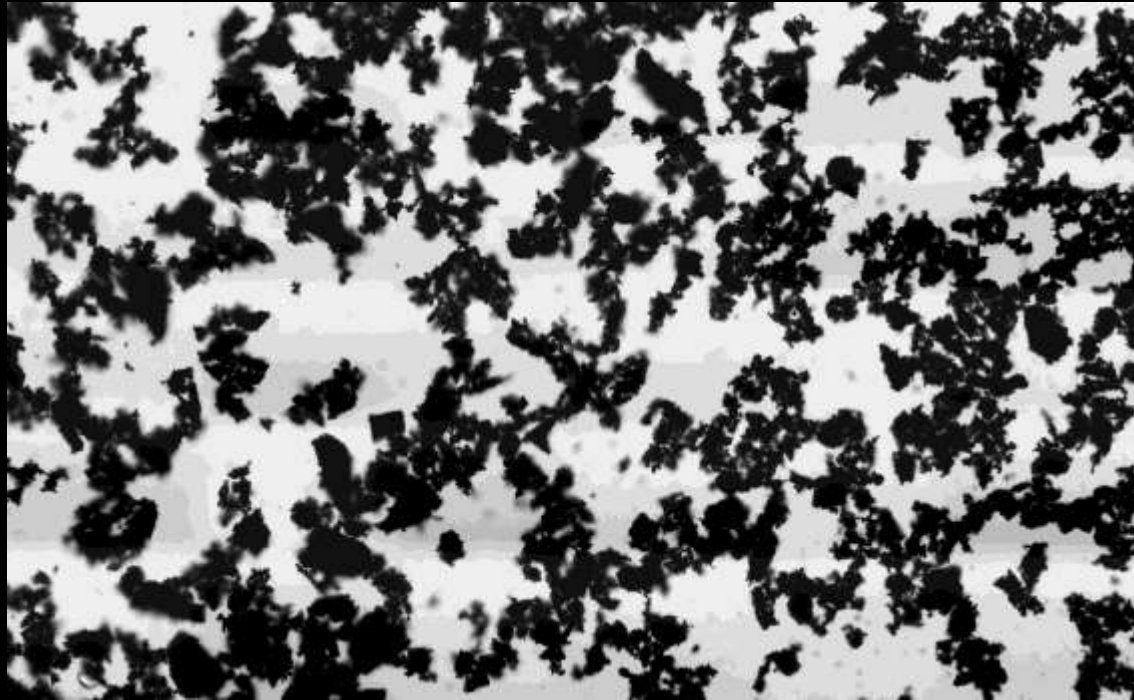
The specific surface area can be measured by controlled adsorption of N_2 (or other gas phases as Ar, Kr, CO_2)



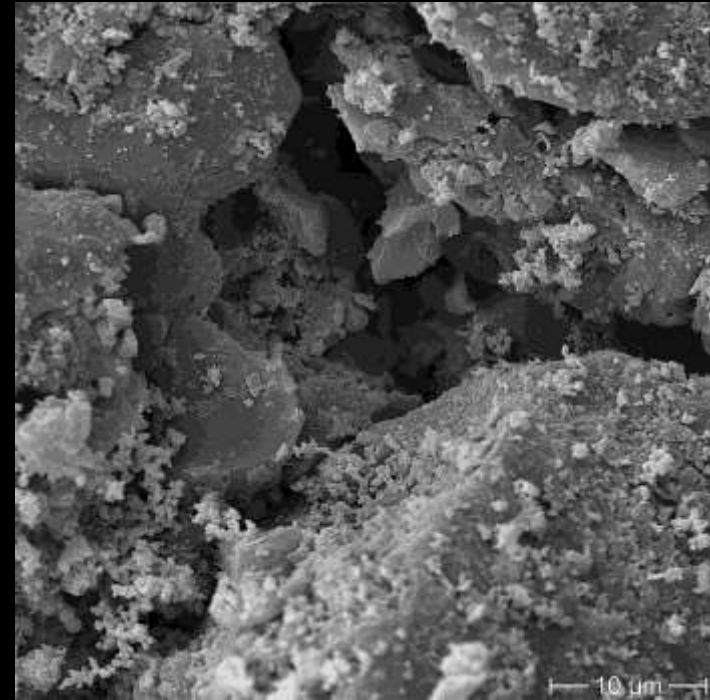


SURFACE PROPERTIES

Activated carbon



1 mm

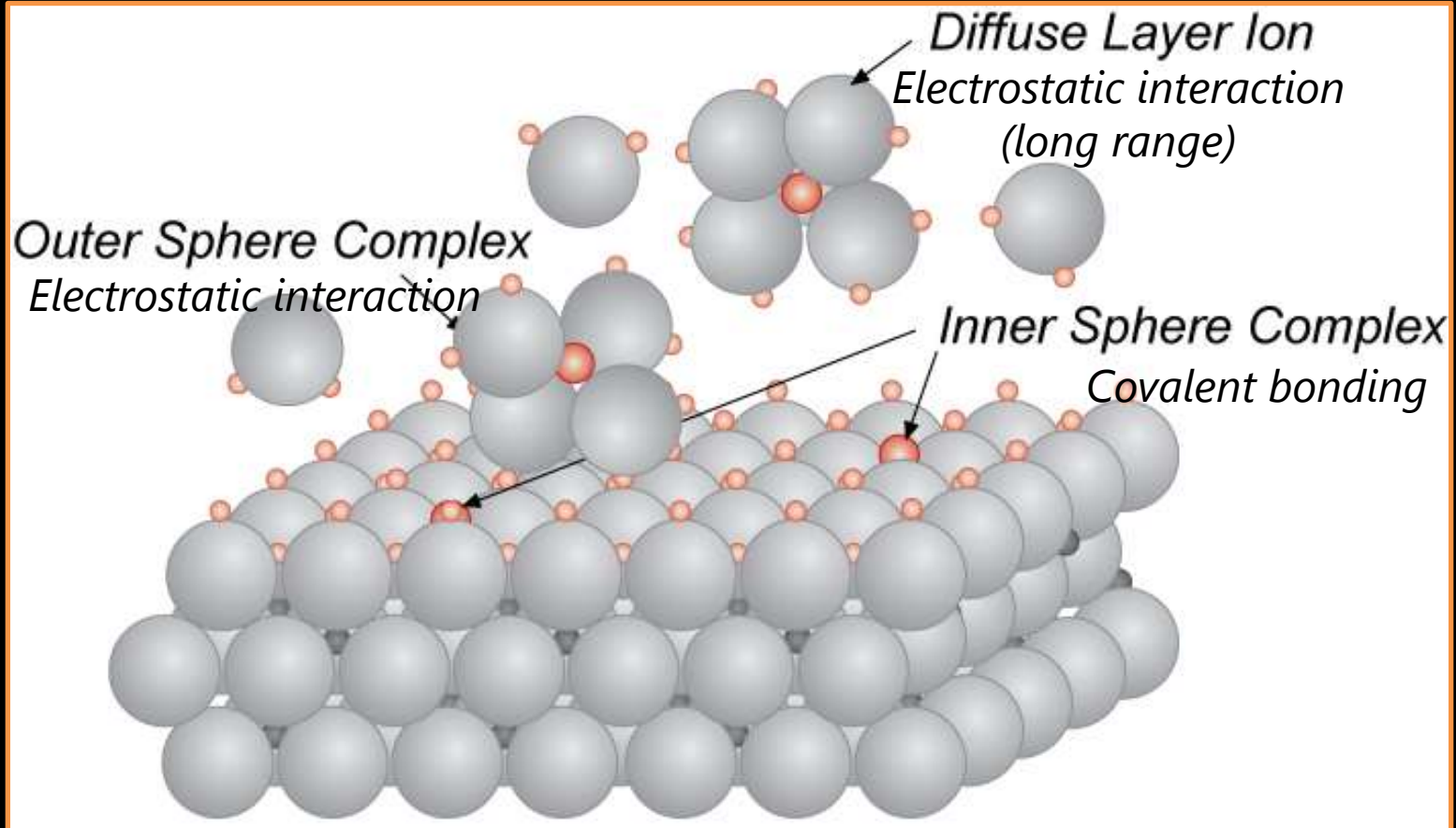


10 μm



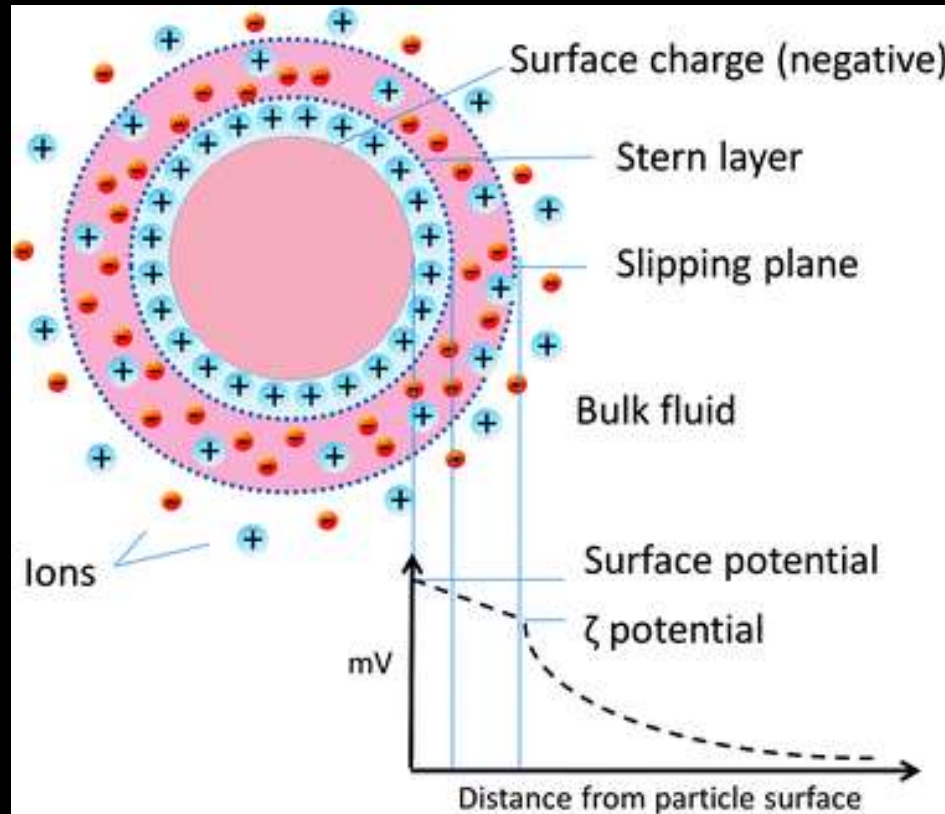
SURFACE PROPERTIES

Electrical double layer



SURFACE PROPERTIES

Electrical double layer



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





SURFACE PROPERTIES

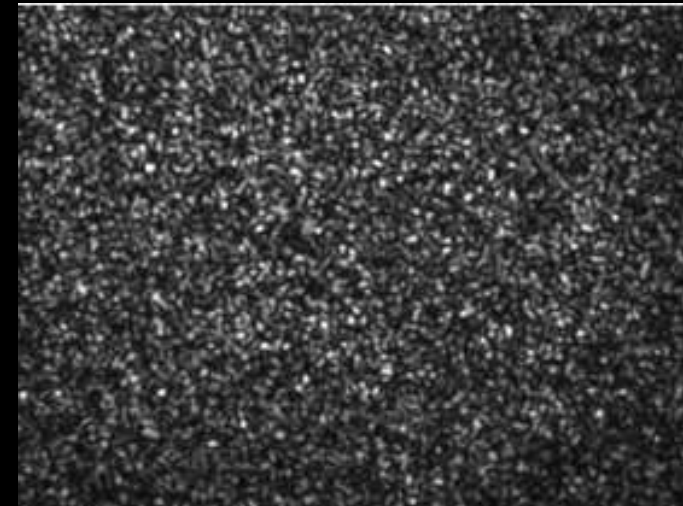
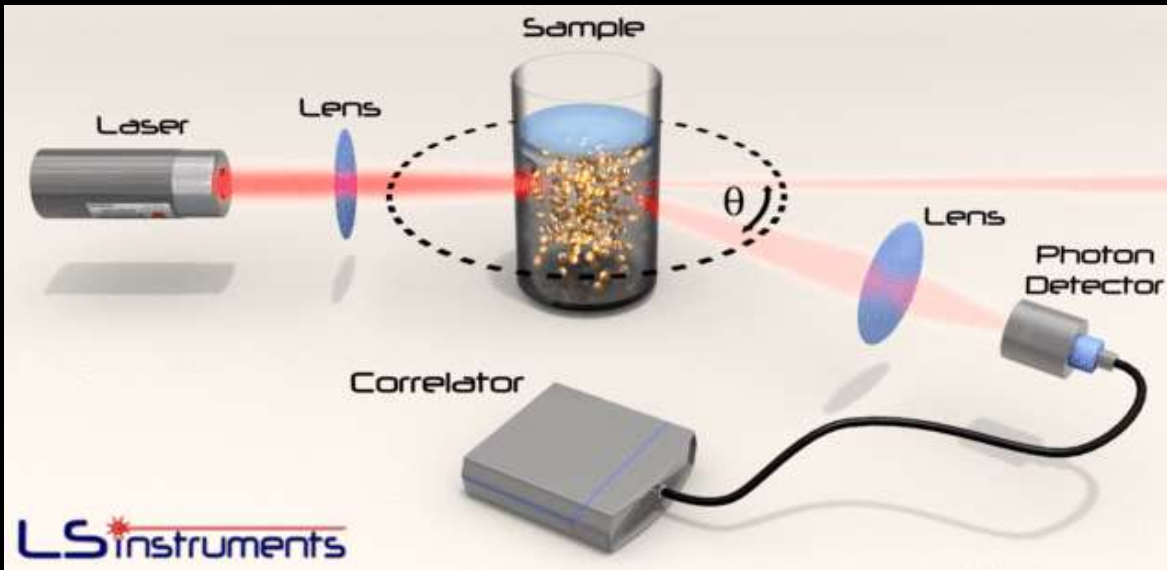
Electrical double layer

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
$> \pm 61$	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: $U = f(\zeta, \epsilon, \eta)$





**Portland cement
and other binders**





ORDINARY PORTLAND CEMENT (OPC)

RAW MATERIALS: LIMESTONE + CLAY + GYPSUM

↑ 1450 °C ↑

CLINKER MINERALOGY

C₃S

Ca₃SiO₅

Alite

C₂S

Ca₂SiO₄

Belite

C₃A

Ca₃Al₂O₆

Aluminate

C₄AF

Ca₄Al₂Fe₂O₁₀

Ferrite

C = CaO

A = Al₂O₃

F = Fe₂O₃

S = SiO₂

\bar{S} = SO₃



PORTLAND CEMENT

CEMENT HYDRATION



MAIN HYDRATION PRODUCTS

C-S-H $(\text{CaO})_{1.7}(\text{SiO}_2)(\text{H}_2\text{O})_4$ **Silicato di calcio idrato**

CH $\text{Ca}(\text{OH})_2$ **Portlandite**

C₃ ASH₃₂ $\text{Ca}_6\text{Al}_2(\text{SO}_4)_3(\text{OH})_{12}\cdot 26\text{H}_2\text{O}$ **Ettringite**

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



PORTLAND CEMENT

OPC Hydration $\text{Ca}_3\text{SiO}_5 + 5.3\text{H}_2\text{O} \rightarrow (\text{CaO})_{1.7} (\text{SiO}_2) \cdot 4\text{H}_2\text{O} + 1.3 \text{Ca}(\text{OH})_2$ Hydraulic binder!

Slaked lime $\text{Ca}(\text{OH})_2 + \text{CO}_2 \rightarrow \text{CaCO}_3 + \text{H}_2\text{O}$ Non-Hydraulic

Roman (pozzolanic) cement $x \text{Ca}(\text{OH})_2 + y \text{SiO}_{2(\text{am})} + z \text{H}_2\text{O} \rightarrow (\text{CaO})_x (\text{SiO}_2)_y \cdot z\text{H}_2\text{O}$



ROMAN CEMENT



Caesarea Maritima (Israel)



ROMAN CEMENT

Alcantara bridge (Spain)

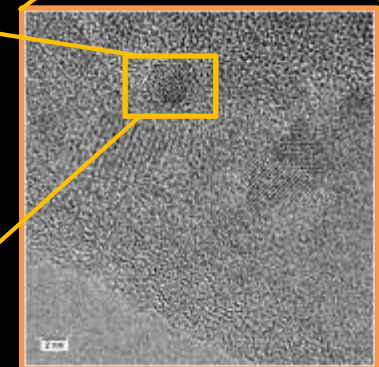
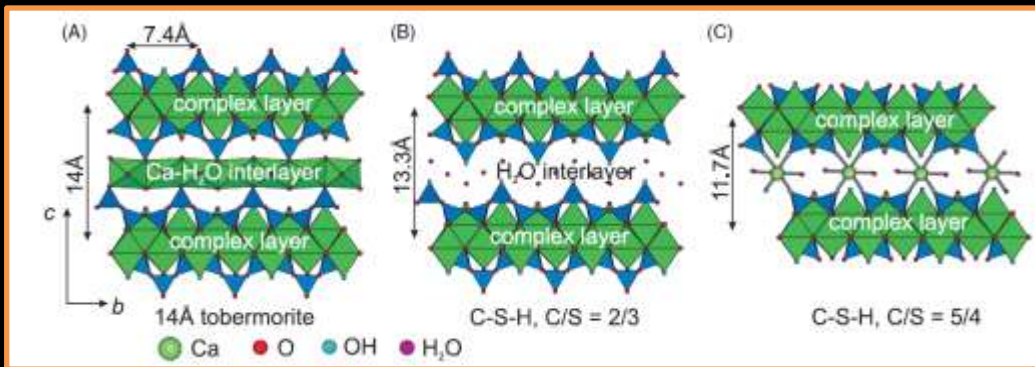
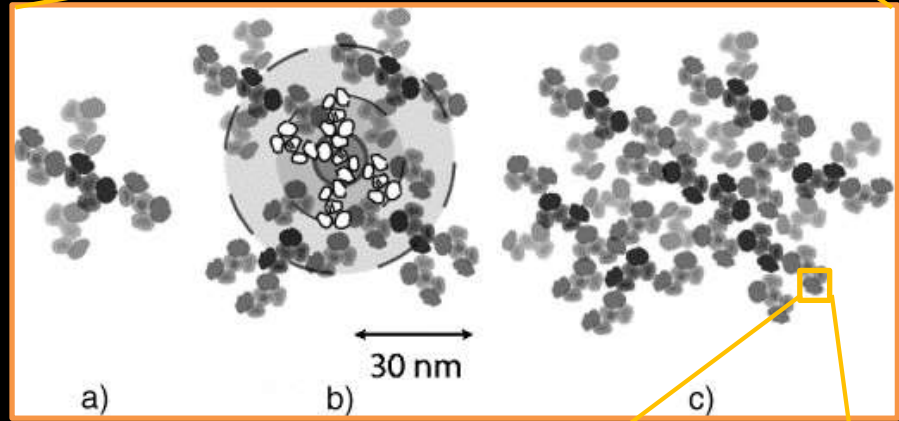
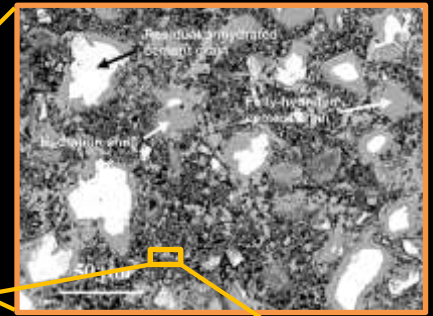
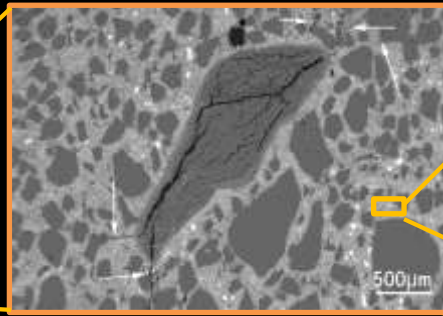
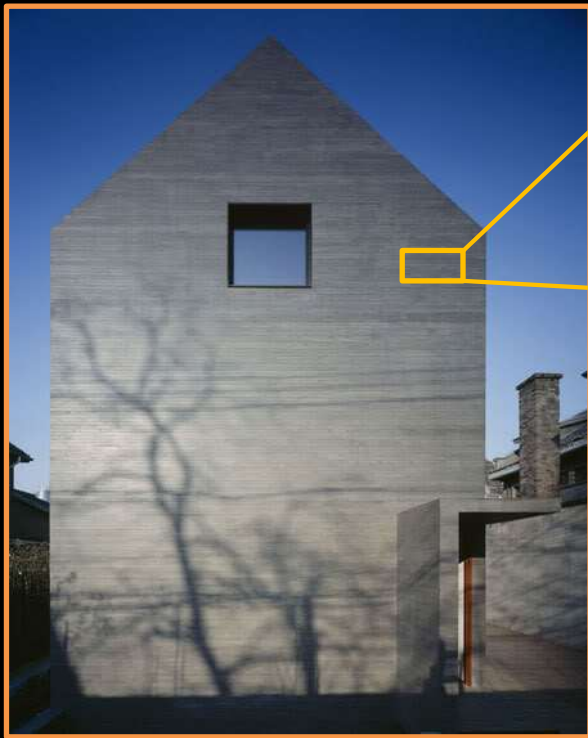


ROMAN CEMENT

Ponte Pietra (Italy)



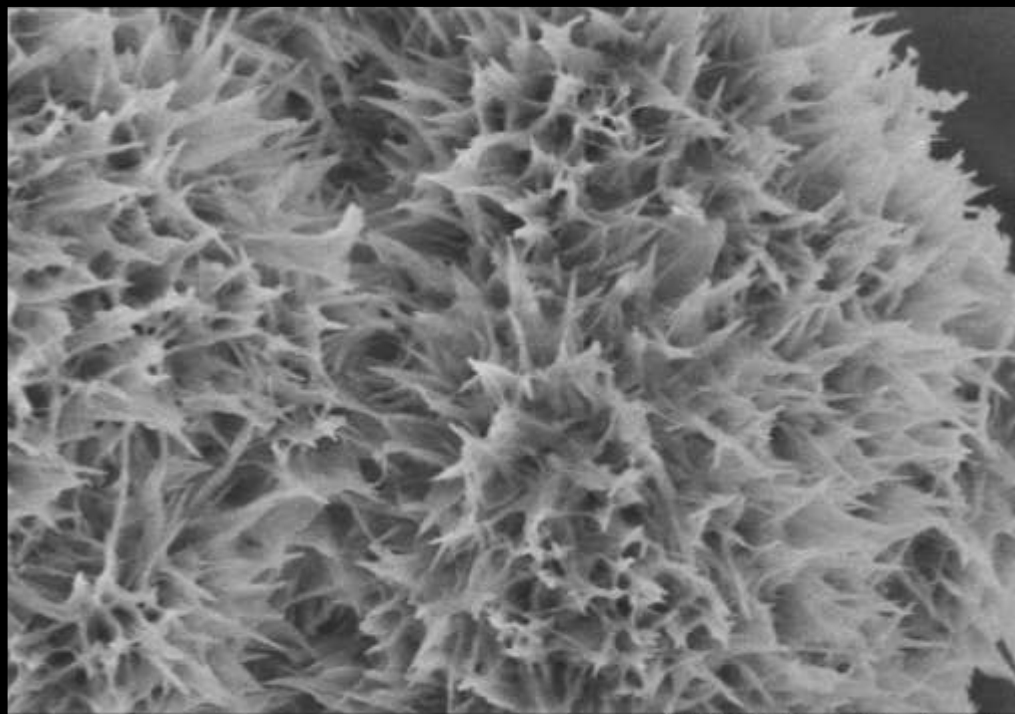
Industrial minerals in the spotlight



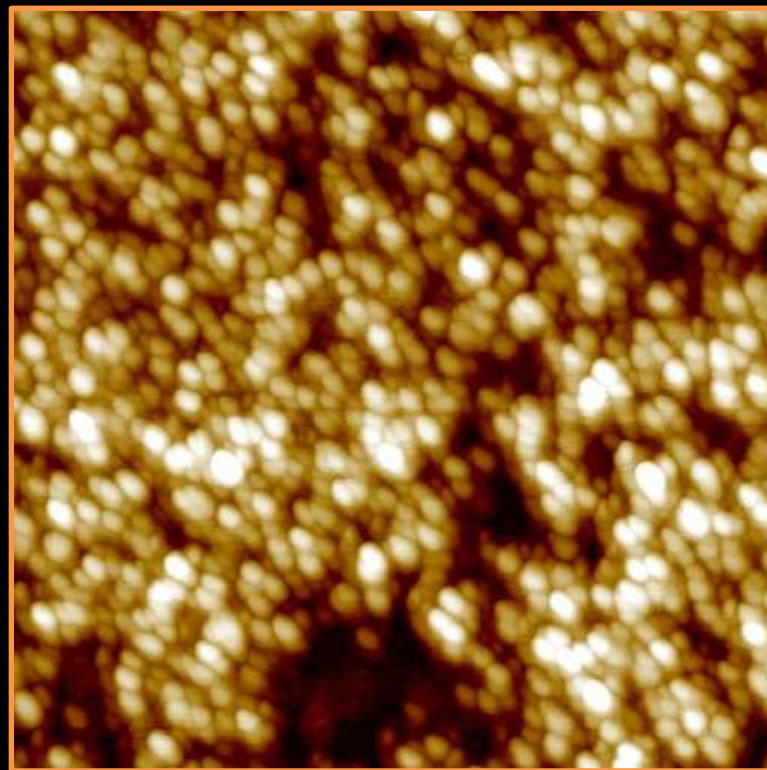


PORTLAND CEMENT

C-S-H: CEMENT HYDRATION PRODUCT



SEM

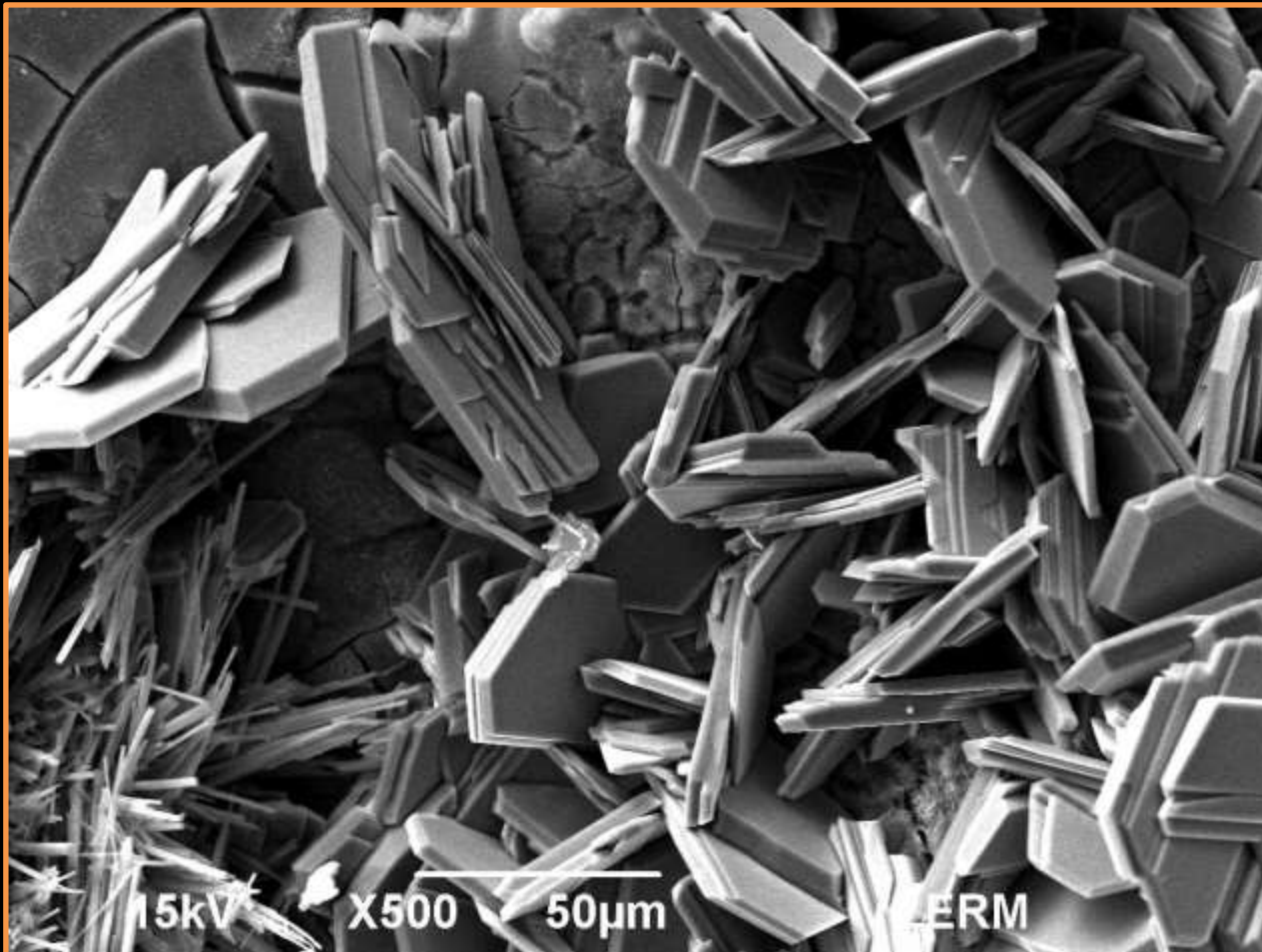


AFM



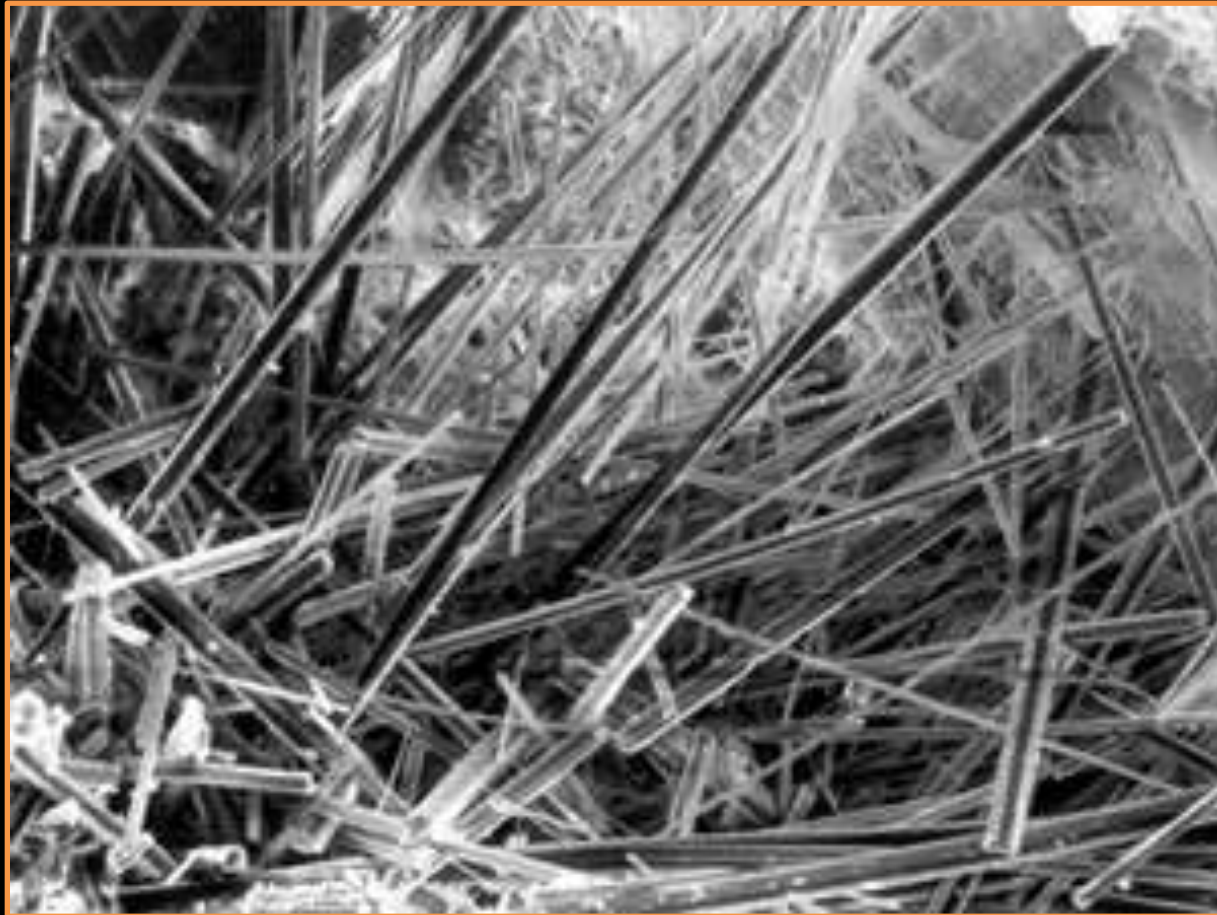
PORTLAND CEMENT

CEMENT HYDRATION PRODUCT: PORTLANDITE

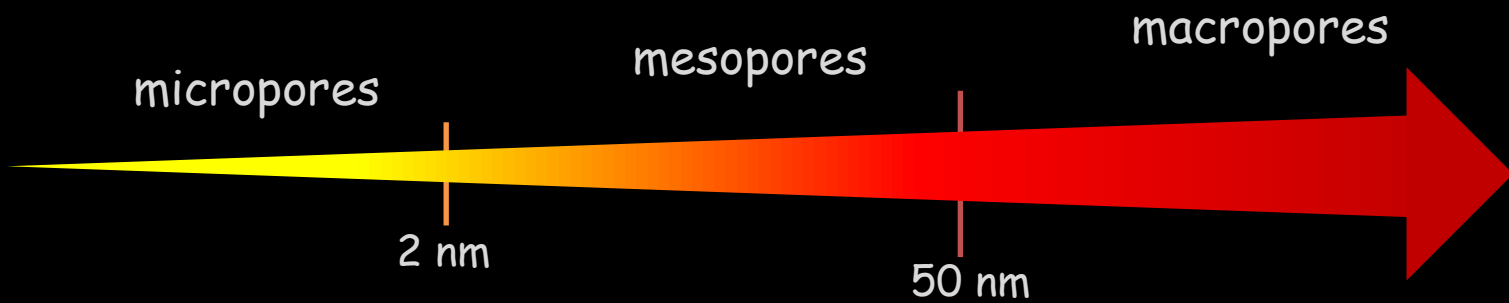


PORTLAND CEMENT

CEMENT HYDRATION PRODUCT: ETTRINGITE



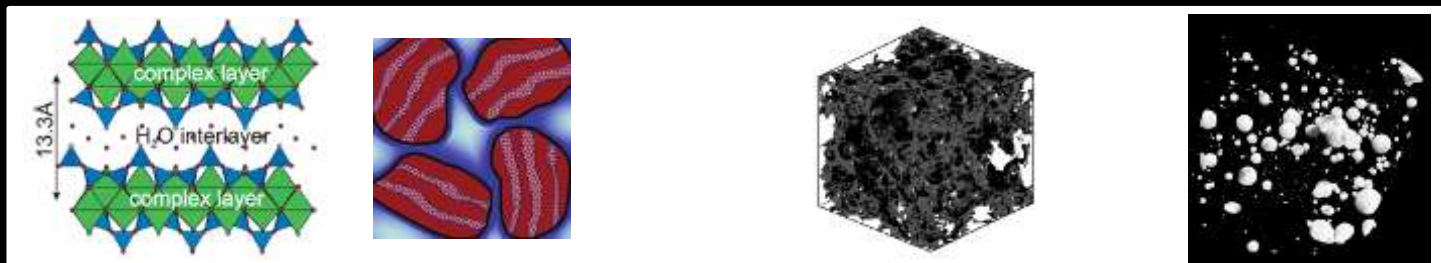
CEMENT POROSITY



GAS ADSORPTION

MIP

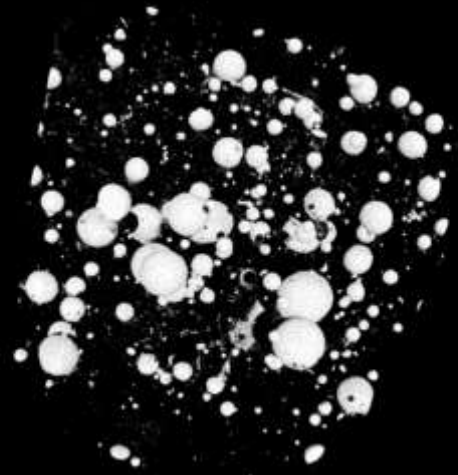
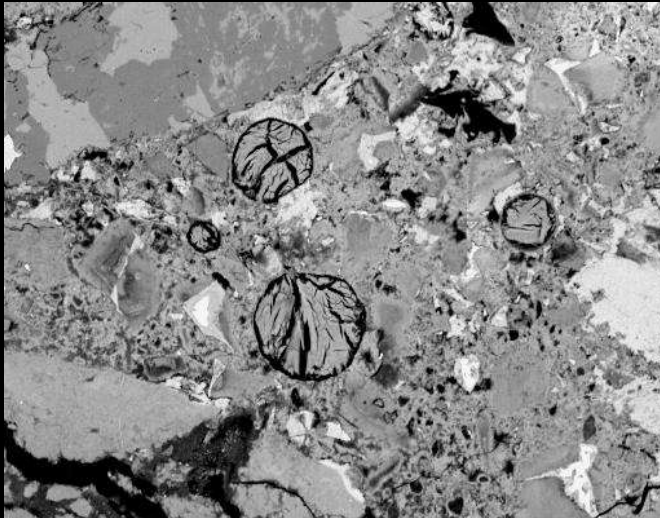
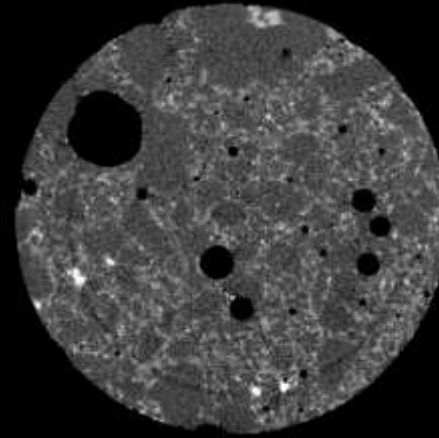
TOMOGRAPHIC METHODS





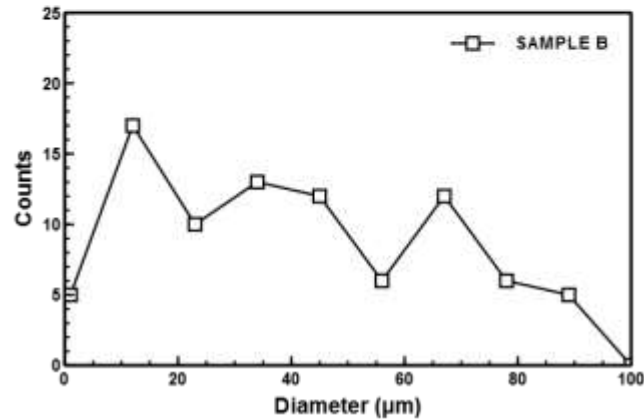
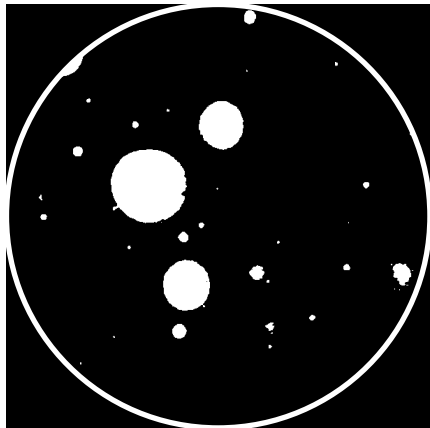
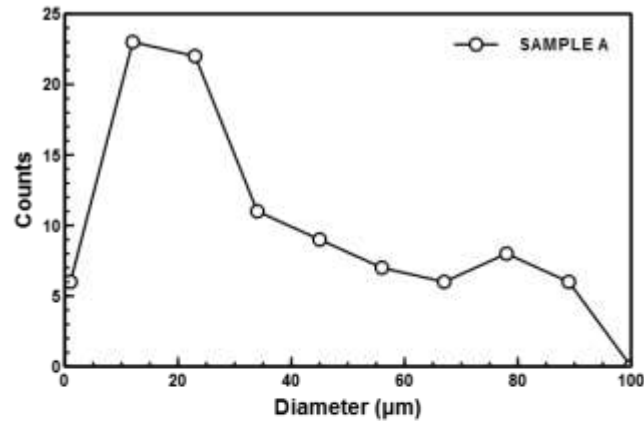
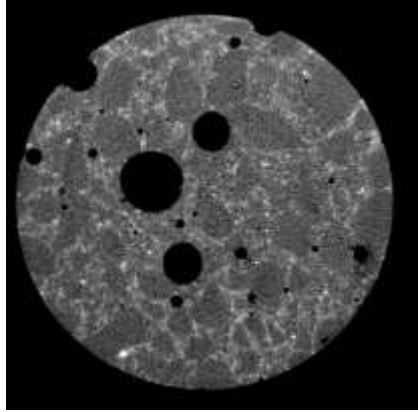
CEMENT POROSITY

Air voids



CEMENT POROSITY

Air voids



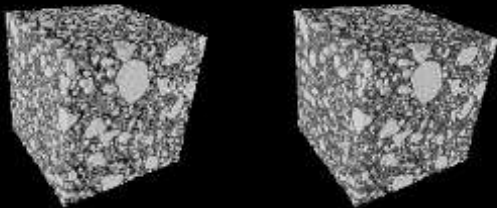
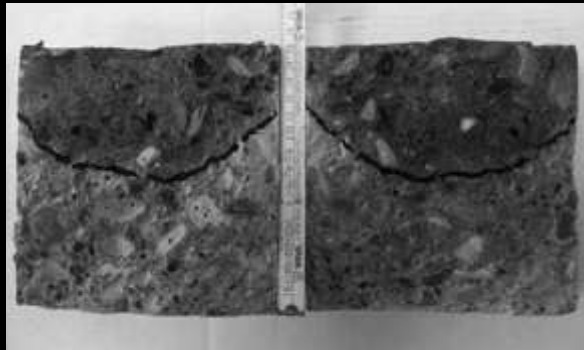
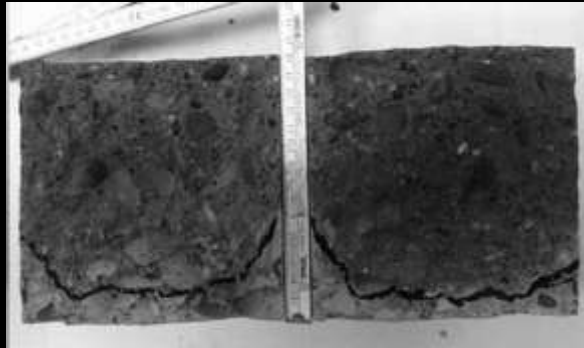
Size distribution by tomographic imaging

Freeze-thaw degradation



CEMENT POROSITY

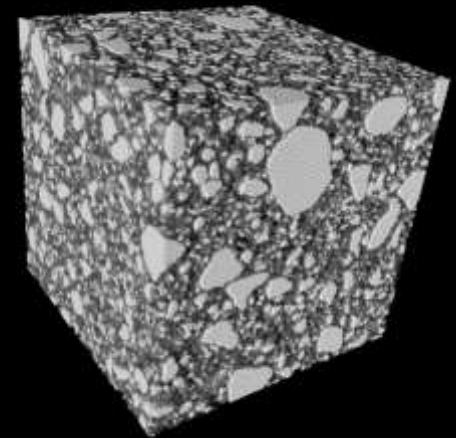
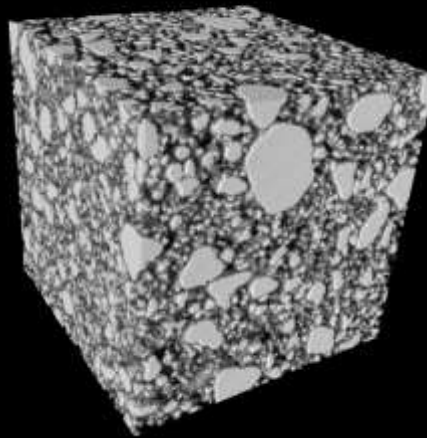
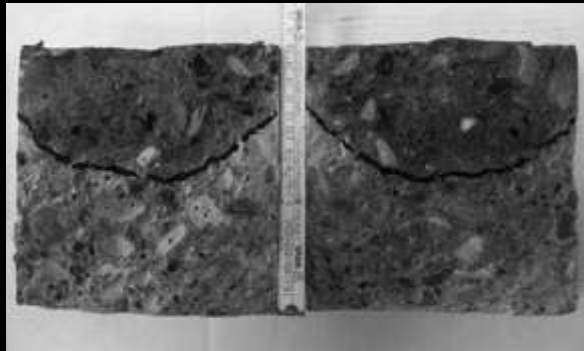
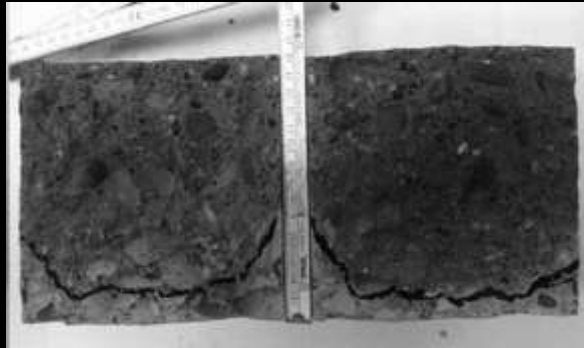
Modulating the pore network tortuosity by the use of nano-seeds





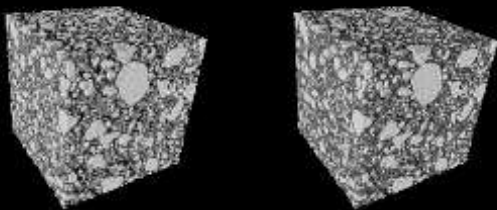
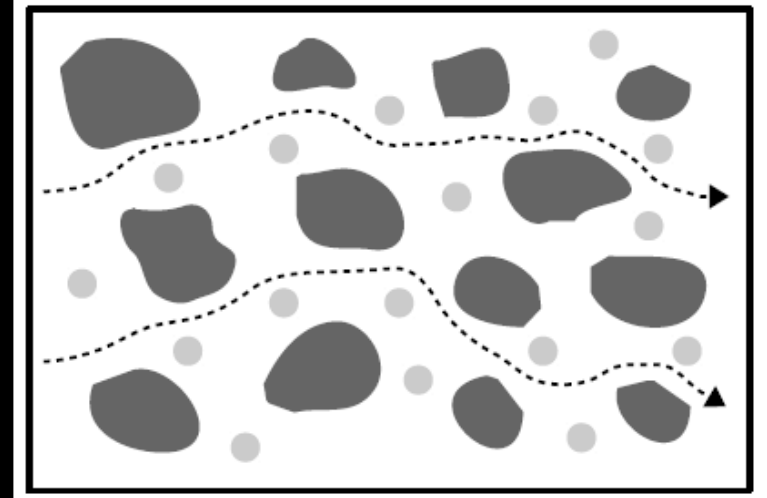
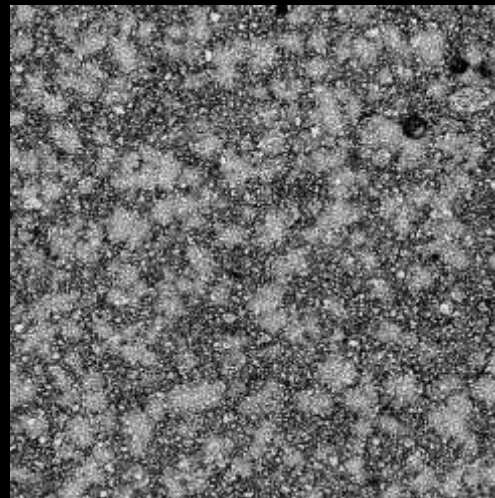
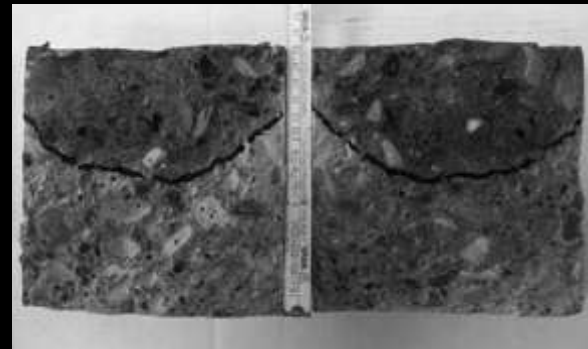
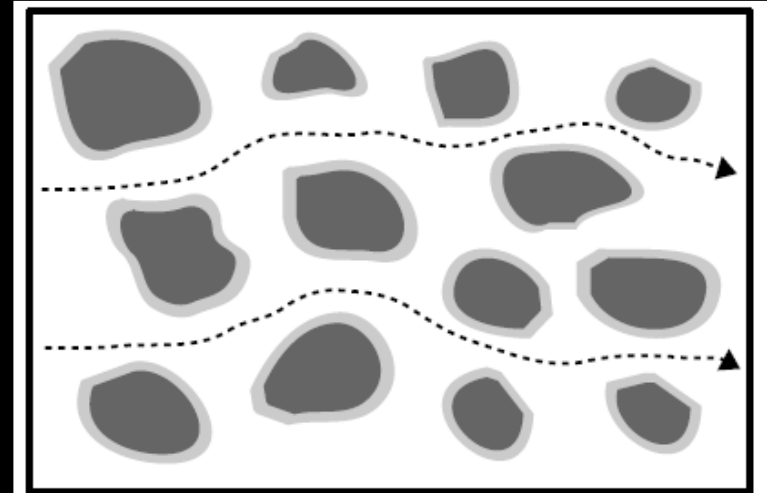
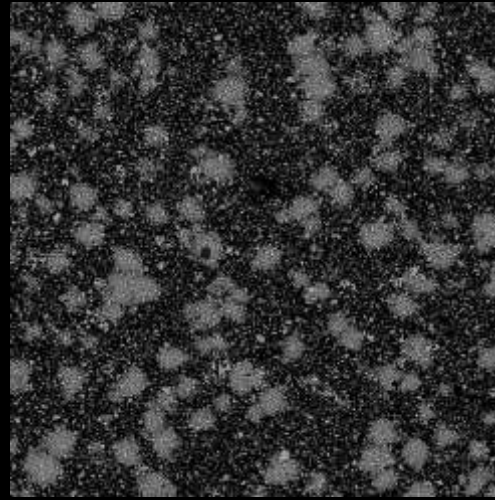
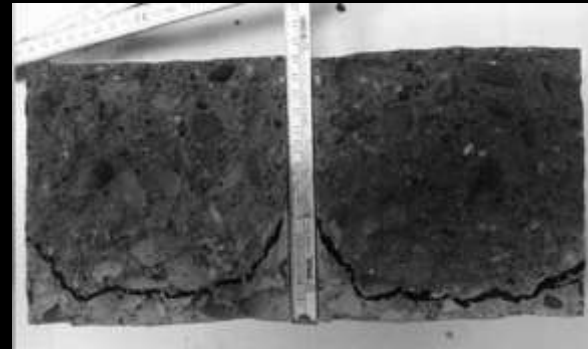
CEMENT POROSITY

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



CEMENT POROSITY

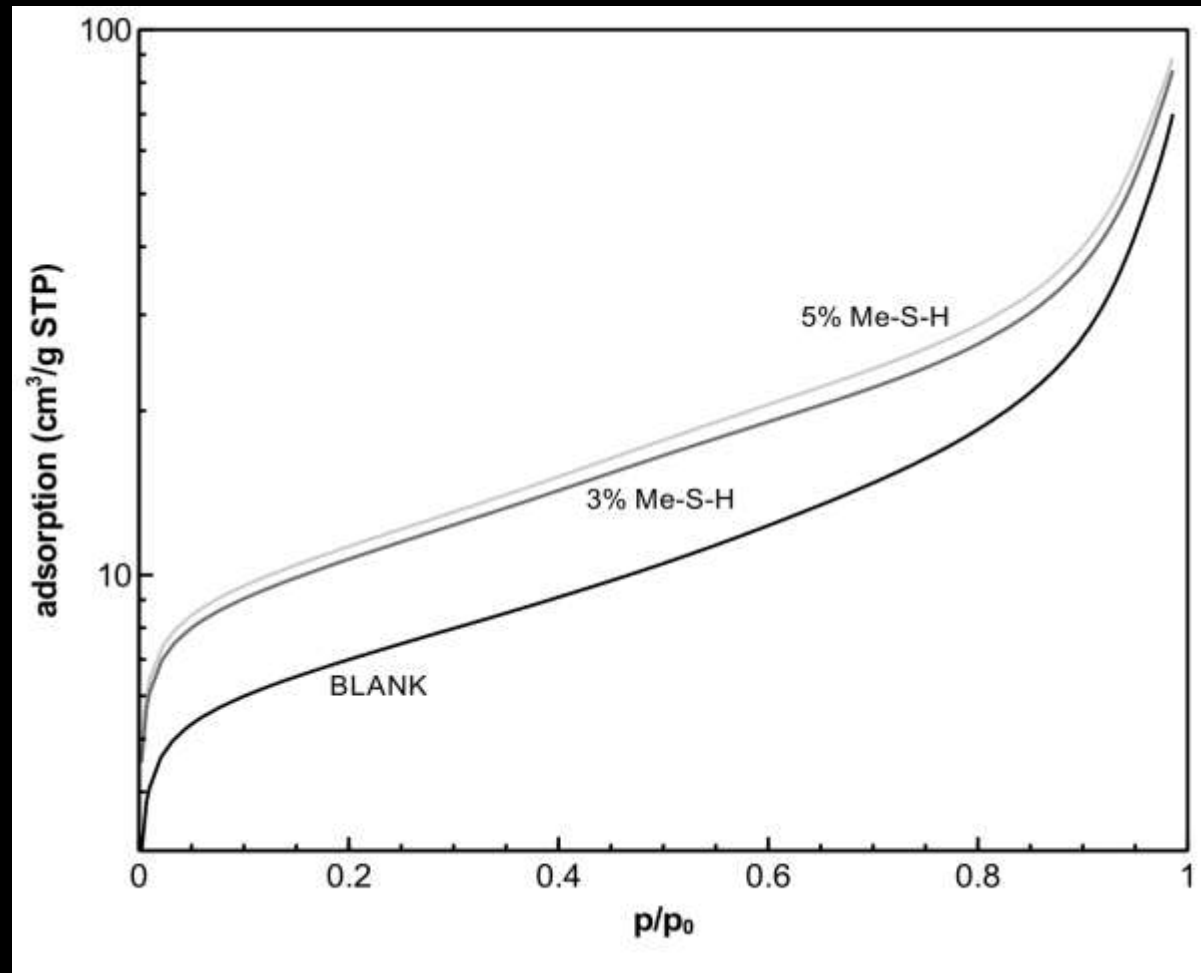
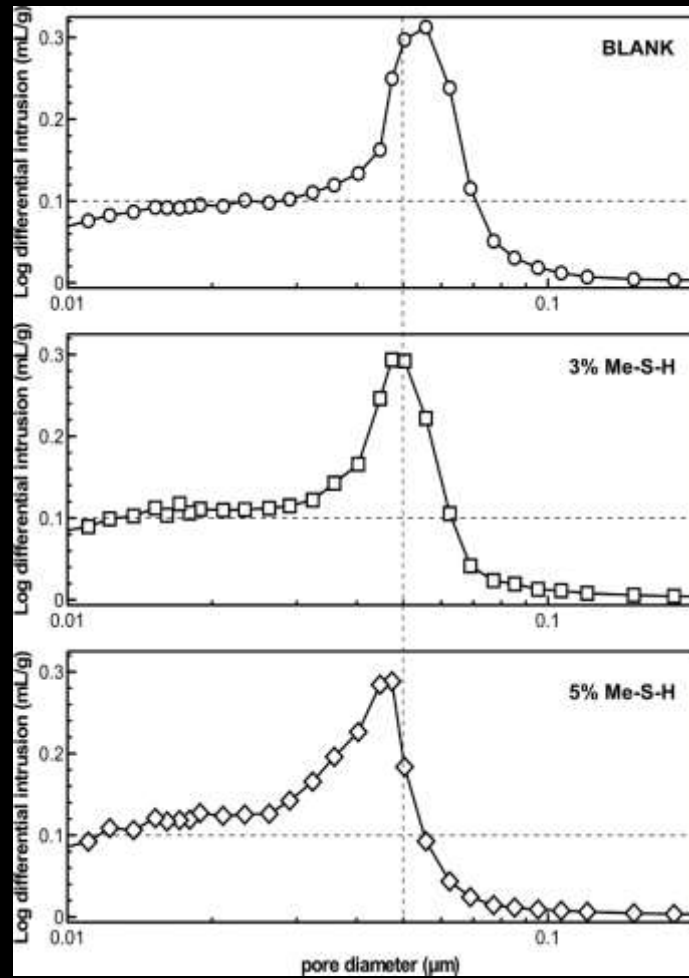
Modulating the pore network tortuosity by the use of nano-seeds





CEMENT POROSITY

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



CEMENT WORKABILITY



CEMENT WORKABILITY



HAND-ARM VIBRATION SYNDROME



Vibration white finger (VWF), also known as hand-arm vibration syndrome (HAVS) or dead finger, is a secondary form of Raynaud's syndrome, an industrial injury triggered by continuous use of vibrating hand-held machinery.

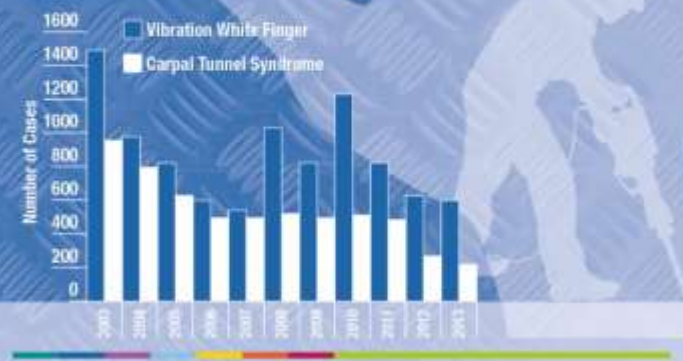
Carpal Tunnel Syndrome (CTS)
 Other ailments may also be caused by vibration. Carpal tunnel syndrome (CTS) is thought to arise in part from microtrauma or compression of nerves in the wrist which could occur from vibration. CTS caused by hand-held vibrating tools was made a prescribed disease from April 2000.

TOTAL 288,000
MEN 255,000
WOMEN 33,000

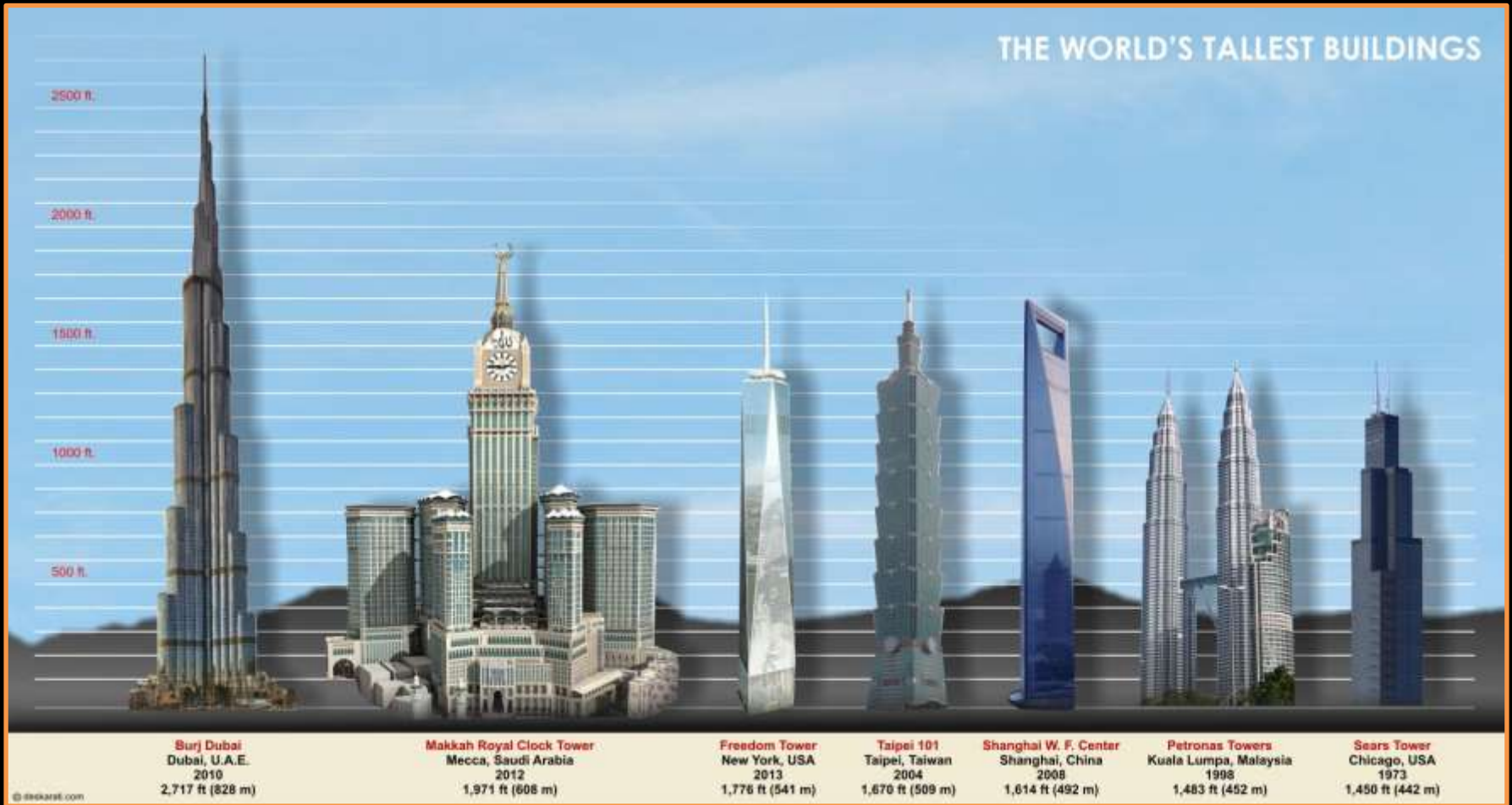


- Tingling 'whiteness' or numbness in the fingers
- Fingers change colour
- Loss of manual dexterity
- In extreme cases, the sufferer may lose fingers.

New cases of Prescribed Vibration White Finger (VWF) and Carpal Tunnel Syndrome (CTS) in Great Britain



CEMENT WORKABILITY



Industrial minerals in the spotlight



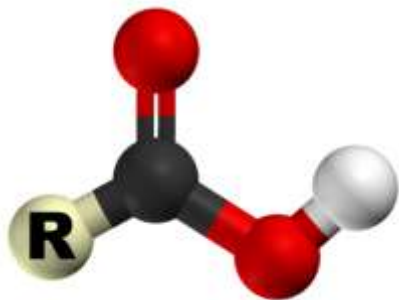
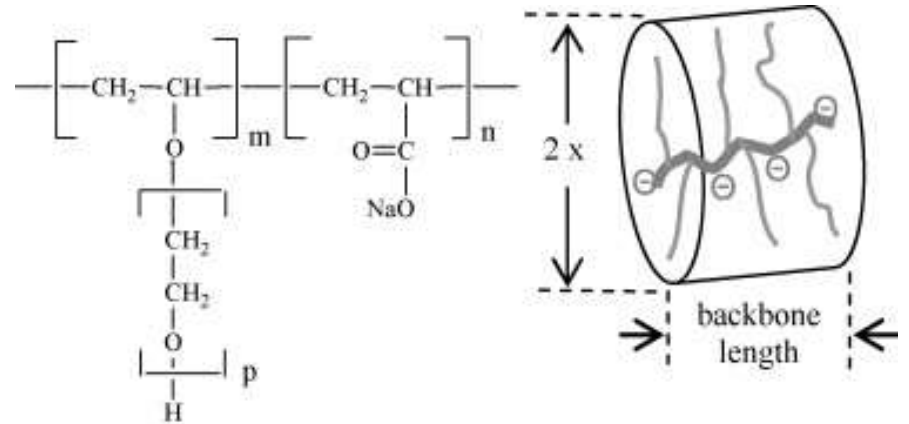
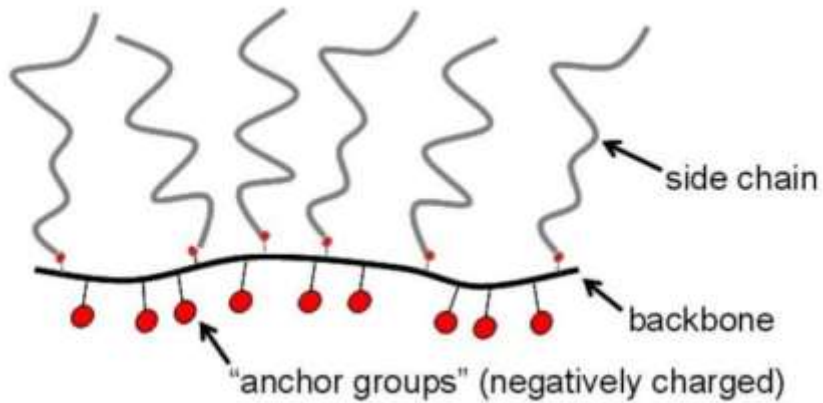
CEMENT WORKABILITY

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

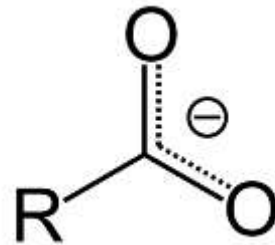


CEMENT WORKABILITY

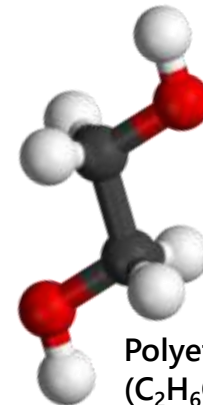
Controlling cement workability by adsorbed organic macromolecules



Carboxylic acid (COOH)



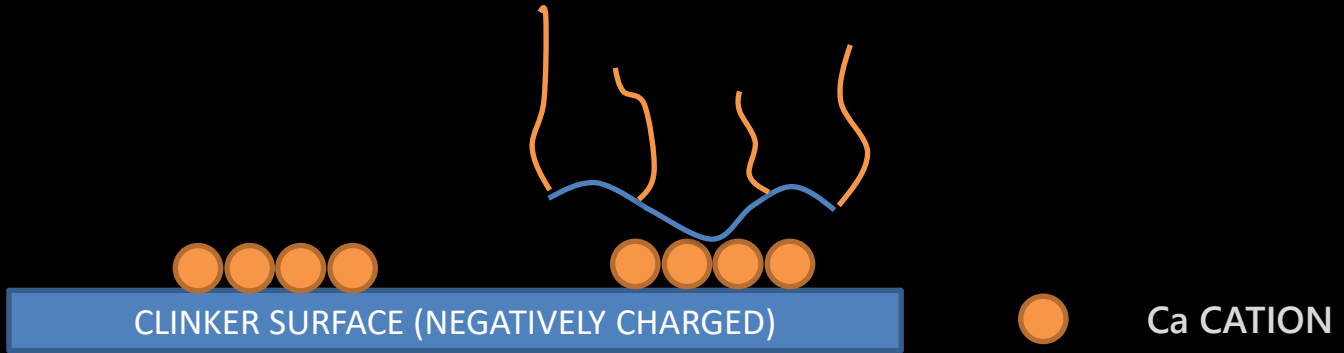
COO-



Polyethylene glycol
(C₂H₆O₂) PEG

CEMENT WORKABILITY

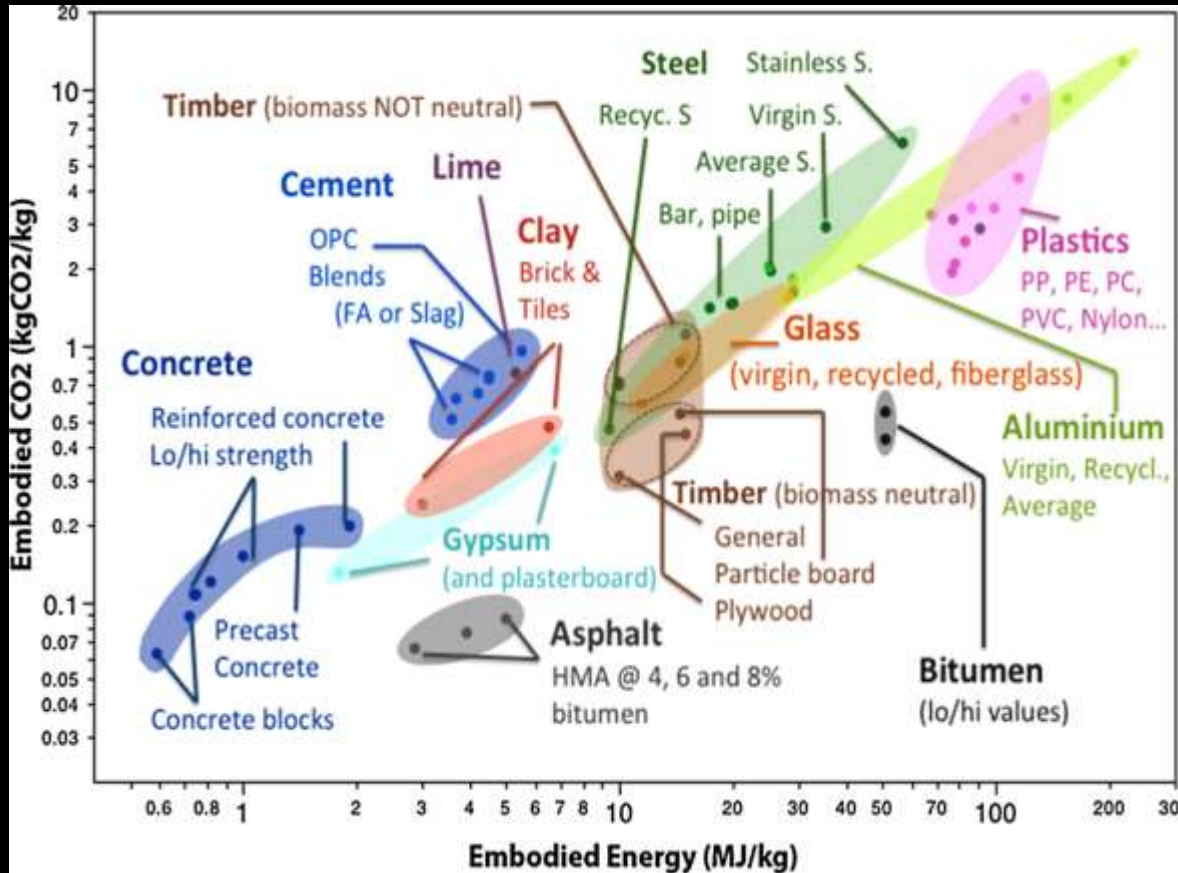
Controlling cement workability by adsorbed organic macromolecules



BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT



5% – 7%
GLOBAL ANTHROPOGENIC EMISSIONS



COP21 MAJOR OUTCOMES

5 Key Elements of the Paris Agreement

- Strengthen Climate Actions:** Countries to strengthen climate actions every 5 years.
- Adaptation:** is a central pillar to help world's most vulnerable.
- Enhanced Transparency:** to ensure commitments are met.
- Finance, Capacity Building:** will scale up support for least developed countries.
- Long-term Goal:** to achieve climate neutral world.

The Paris climate negotiations prompted more than 11,000 new initiatives involving cities, regions, companies, investors and civil society organizations, including:

- 186 COUNTRIES** shared national climate action plans, called NDCs.
- 127+ MILLION HECTARES** of degraded land in Africa and Latin America to be restored.
- 400+ CITIES** SET TARGETS peaking over 70% less of GHGs annually by 2030!
- \$1T IN SOLAR INVESTMENTS** to be financed by new global alliances.
- 114+ COMPANIES** will use Science Based Targets to set emissions-cutting goals.
- 20 COUNTRIES** to double their energy R&D.

These substantial climate actions will transform world and drive us toward a safer, climate-resilient future.

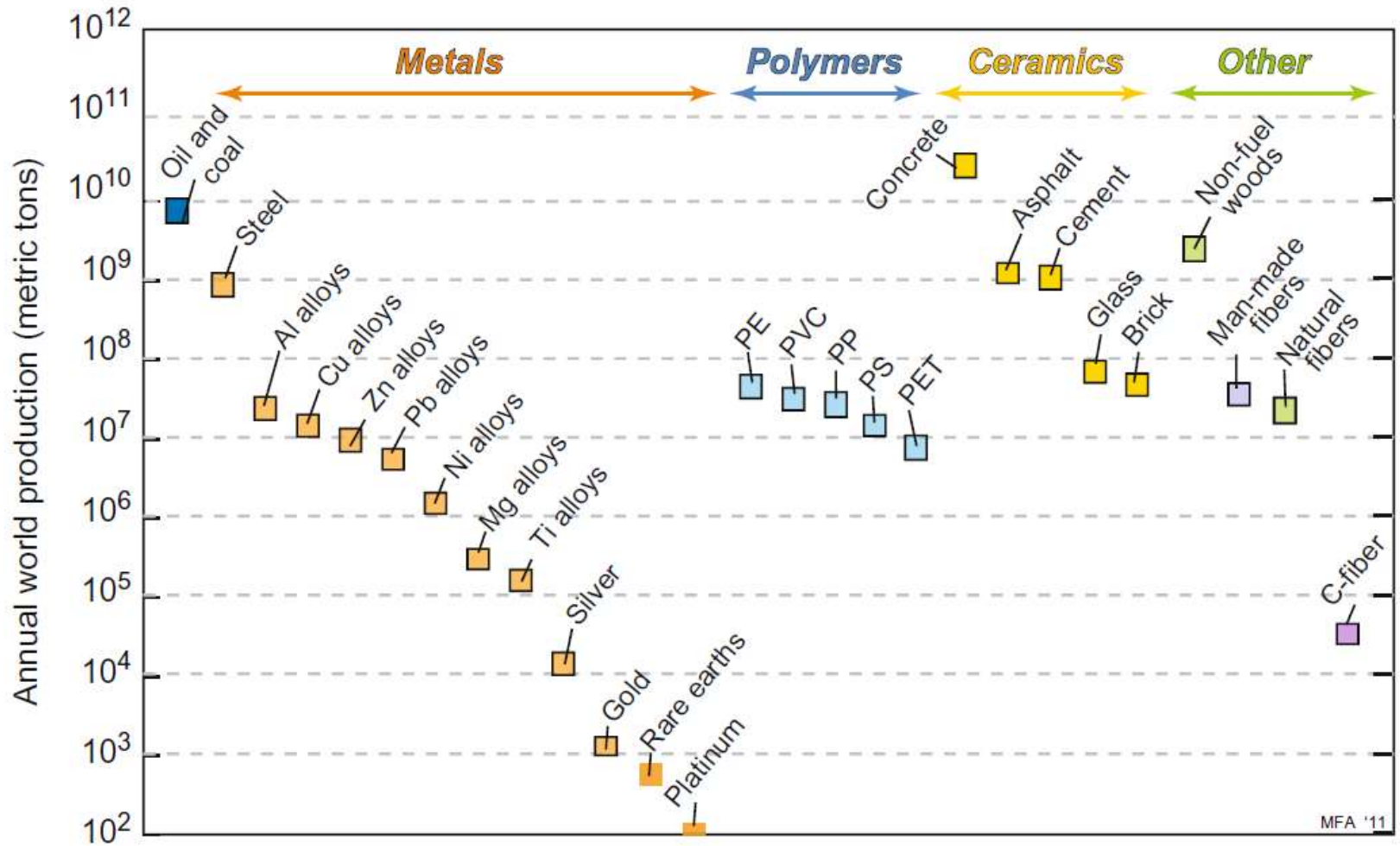
WORLD LEADERS IN CLIMATE ACTION

WORLD LEADERS IN CLIMATE ACTION



Industrial minerals in the spotlight

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

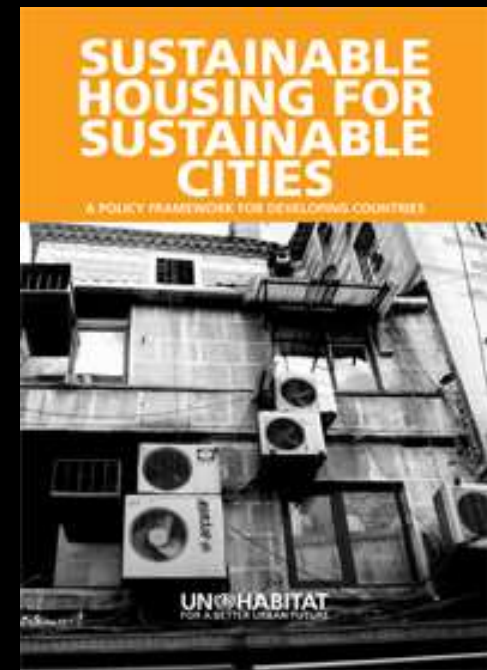
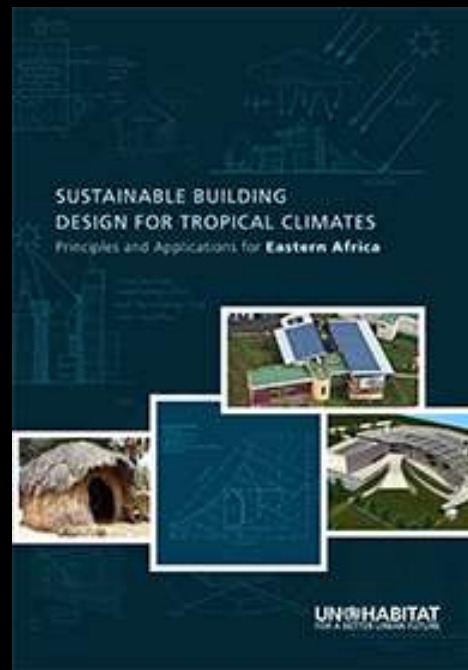


MFA '11



UN HABITAT

FOR A BETTER URBAN FUTURE

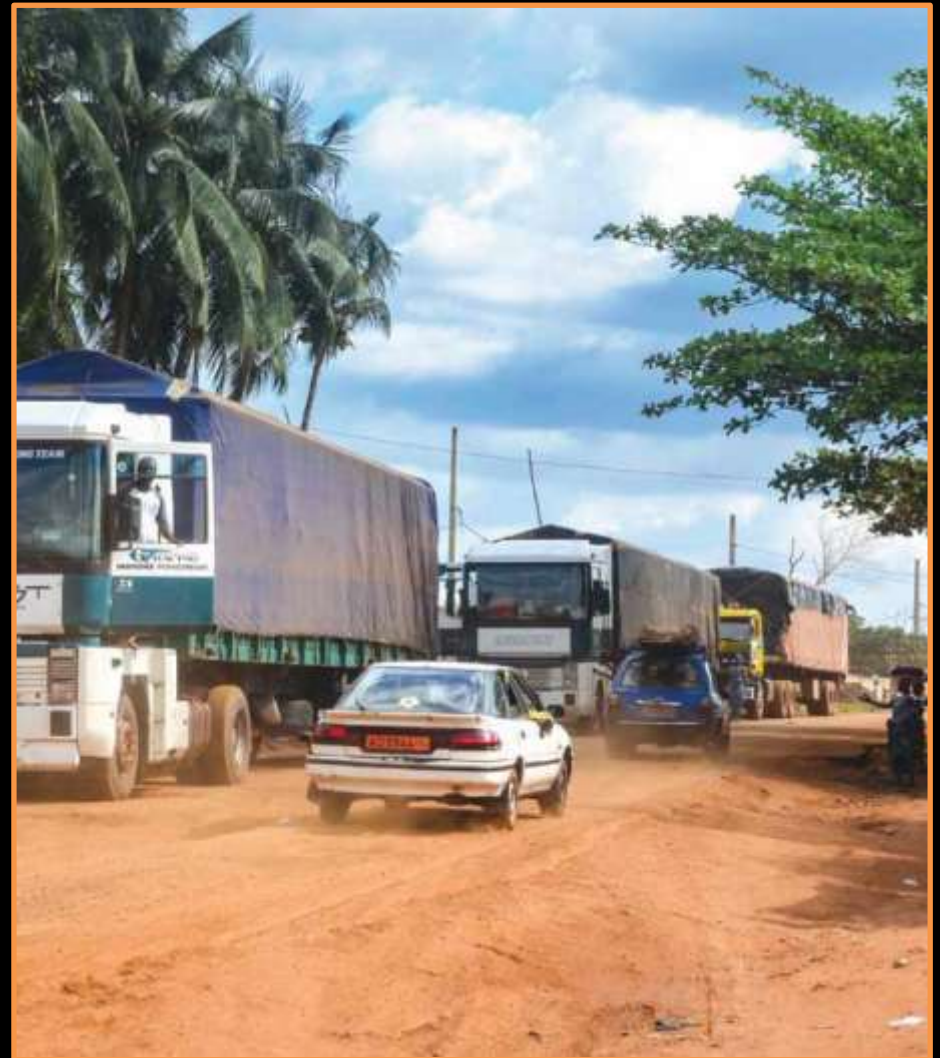
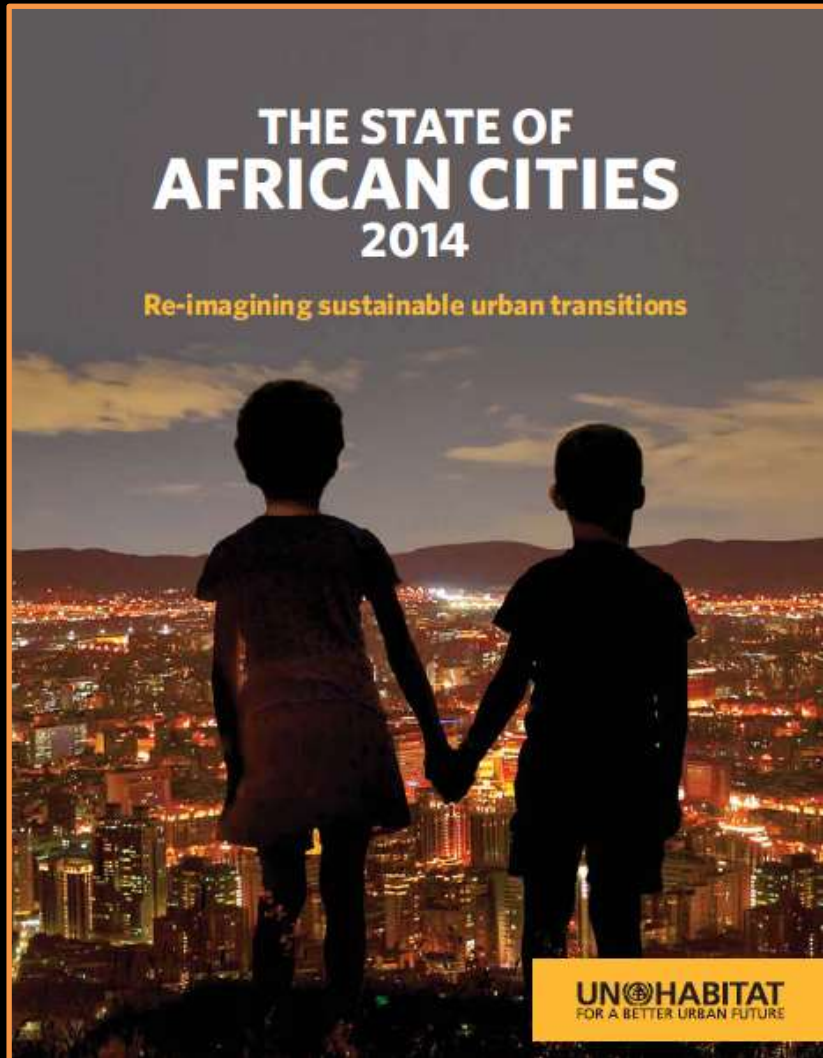


United Nations Human Settlements Programme



Industrial minerals in the spotlight

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

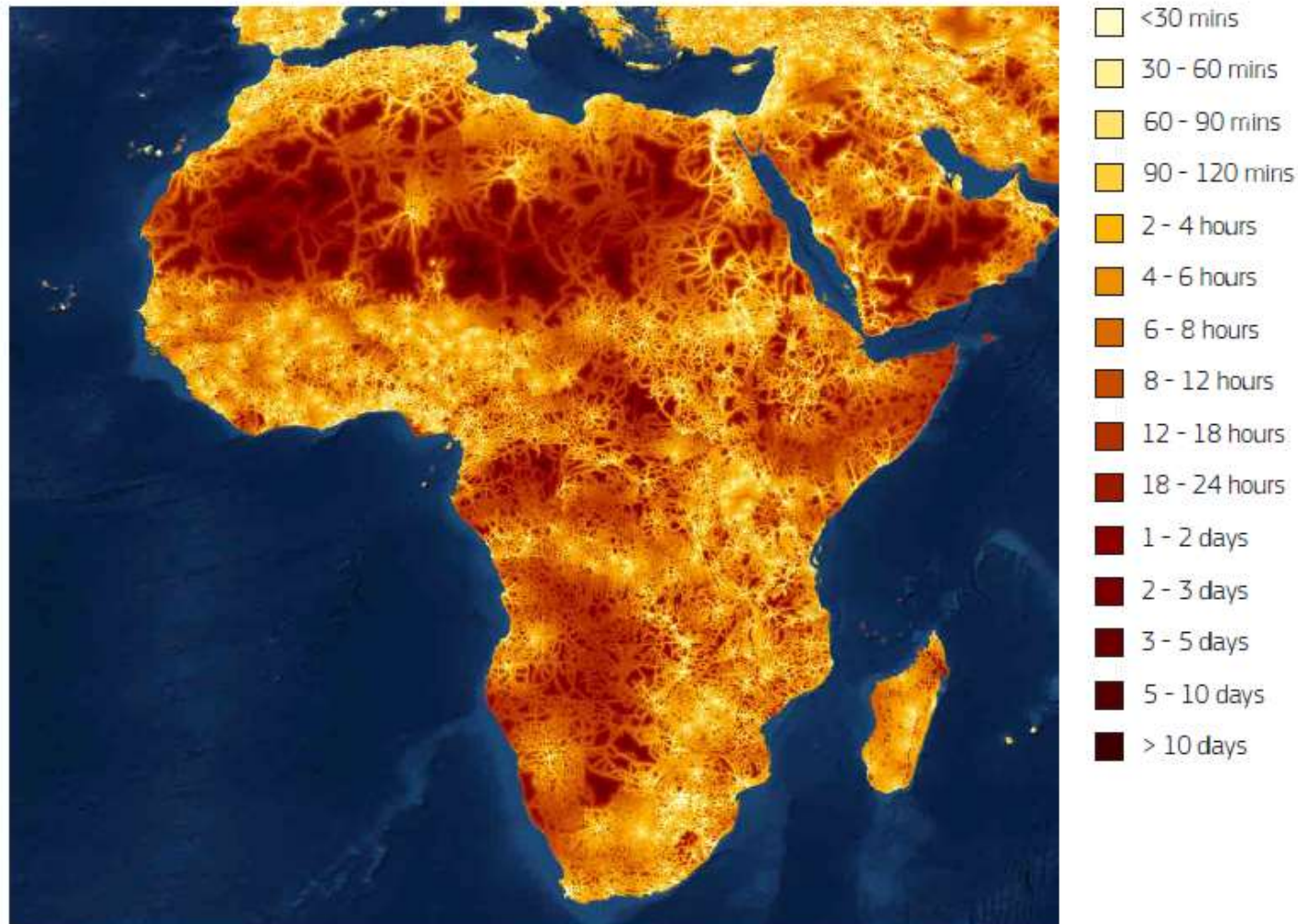


Industrial minerals in the spotlight



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



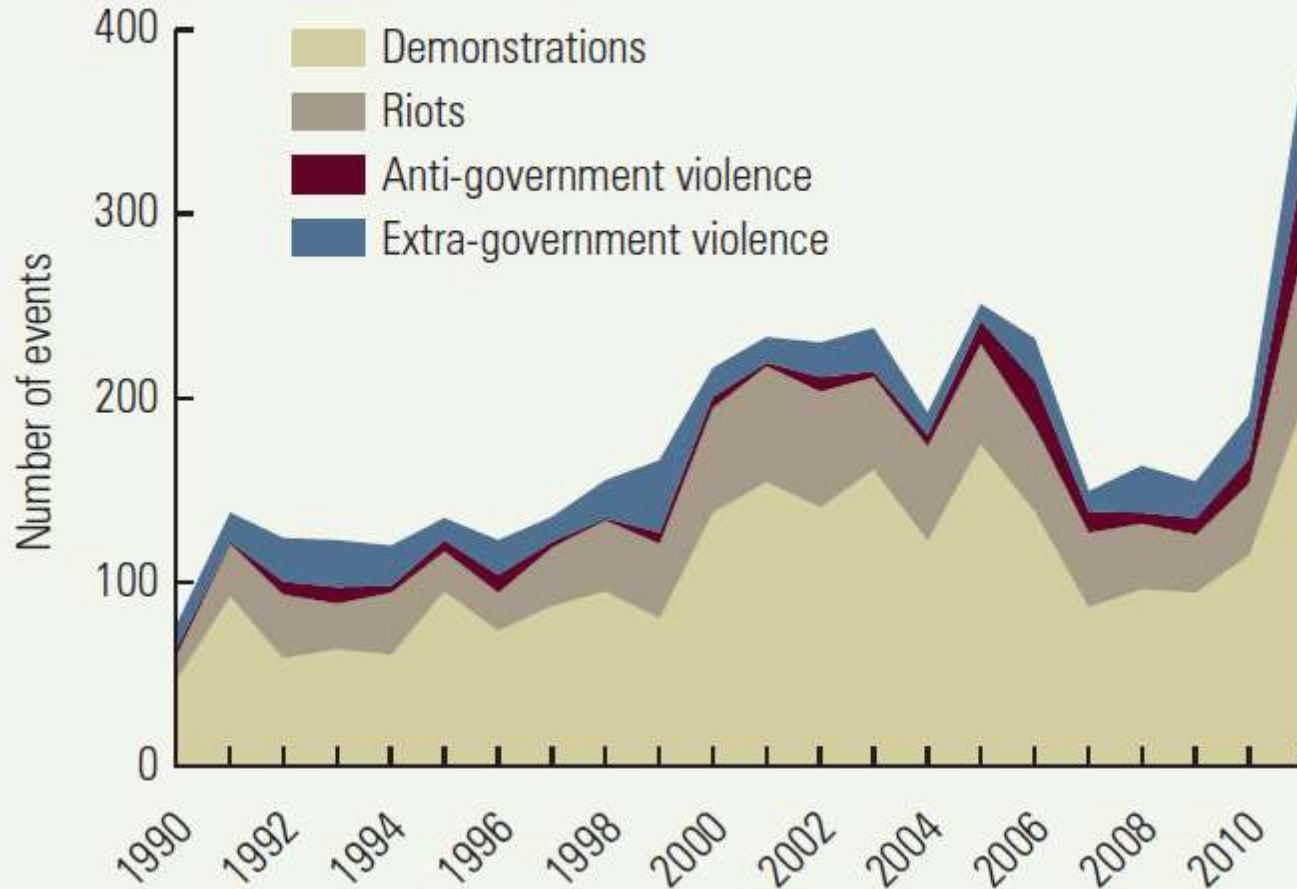
Currently one billion people are living in slums



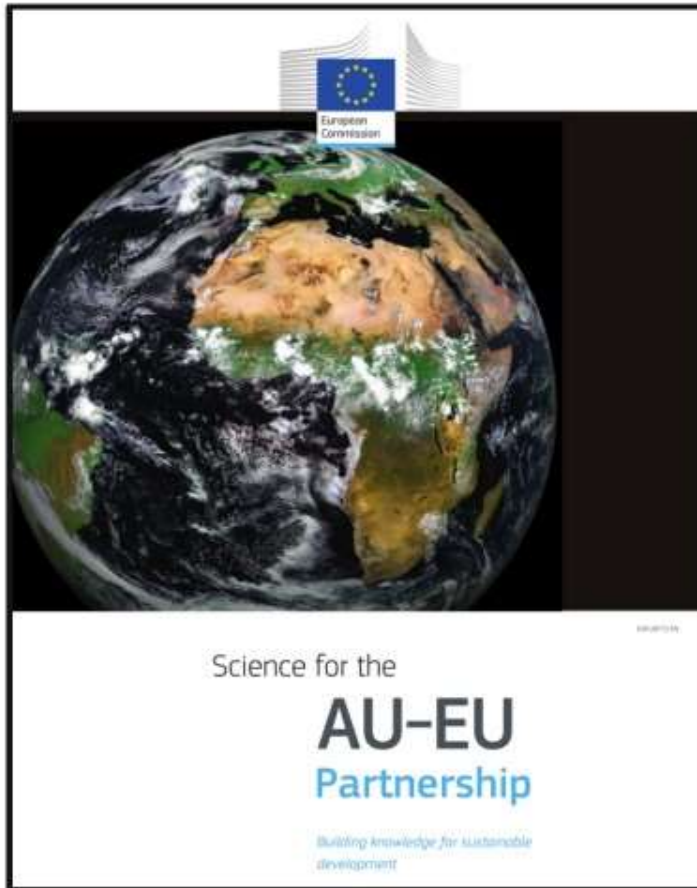
Industrial minerals in the spotlight

BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

Social conflict events in Africa, 1990-2011



BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT



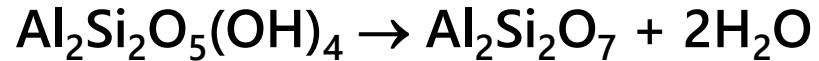
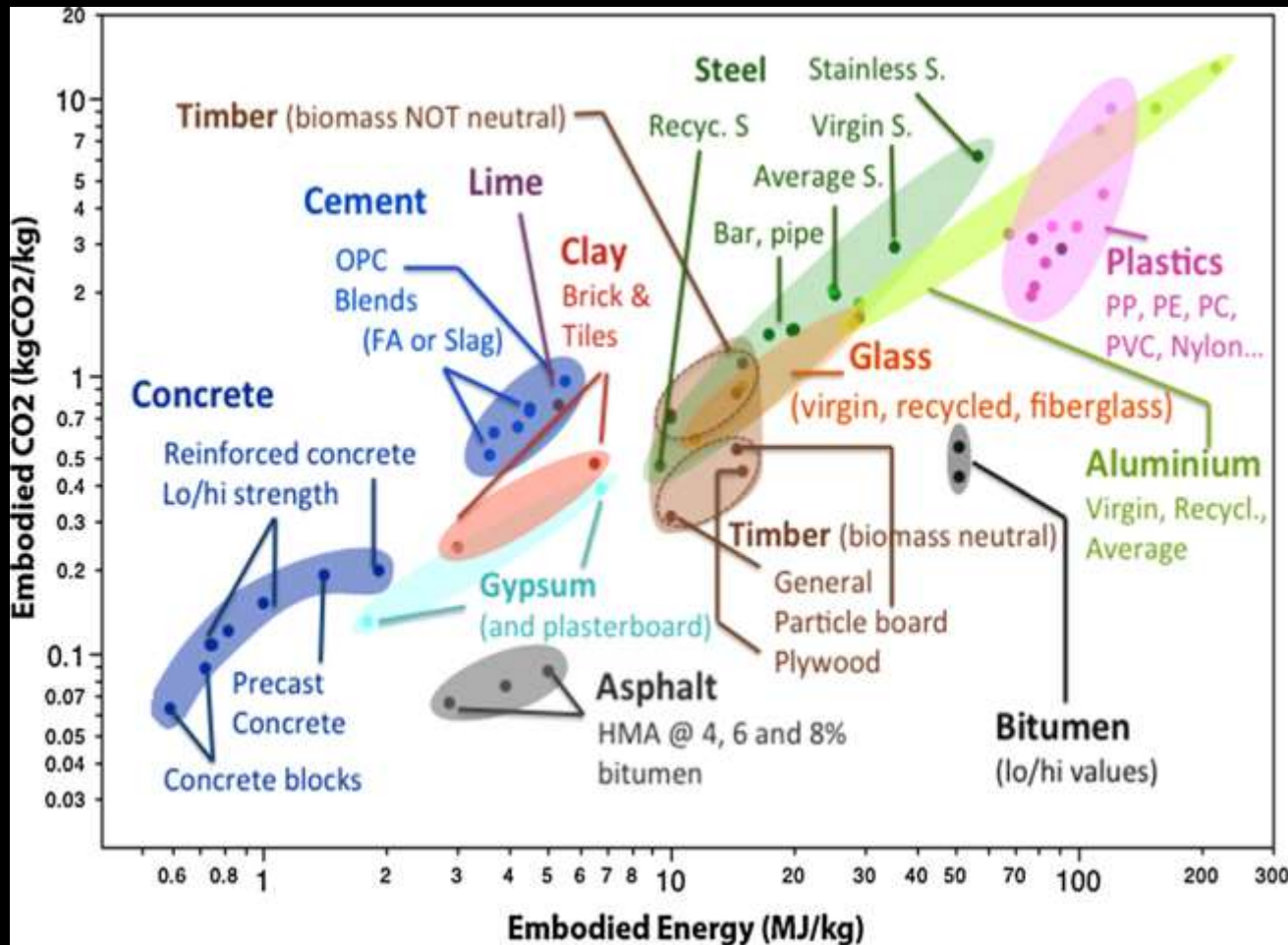
**African Union - EU
Summit 2017**



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

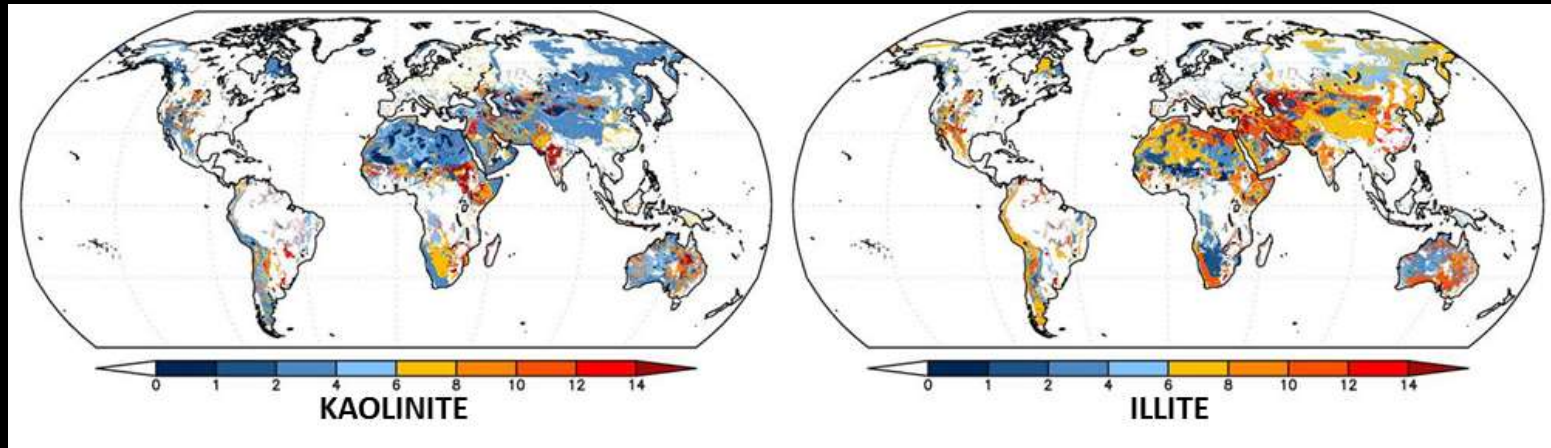


BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT



BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

CLAY MINERALS CONCENTRATION IN SOILS



GDP GROWTH (DATA FROM IMF)



Industrial minerals in the spotlight



BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT



Industrial minerals in the spotlight

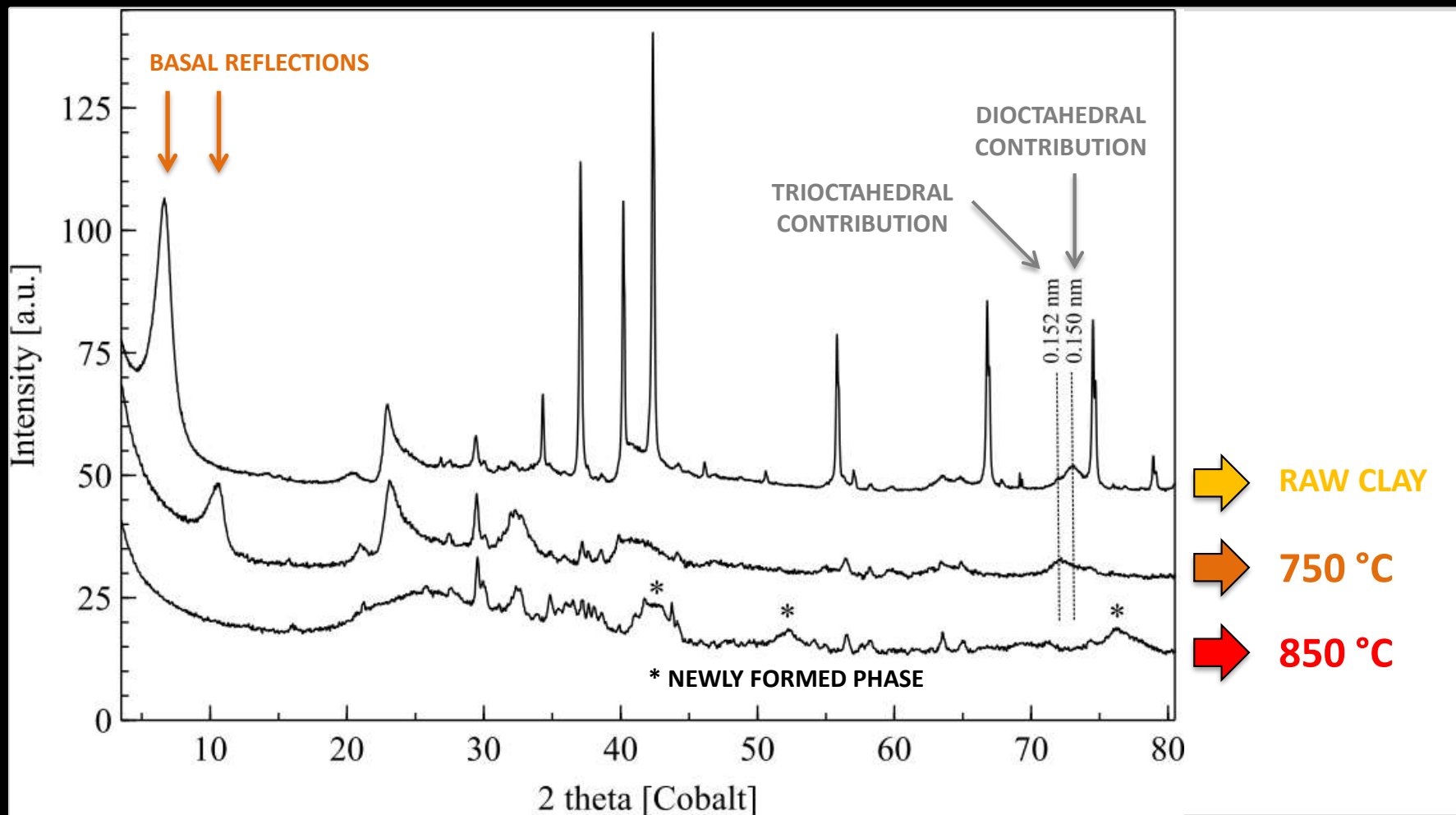
BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT



Industrial minerals in the spotlight

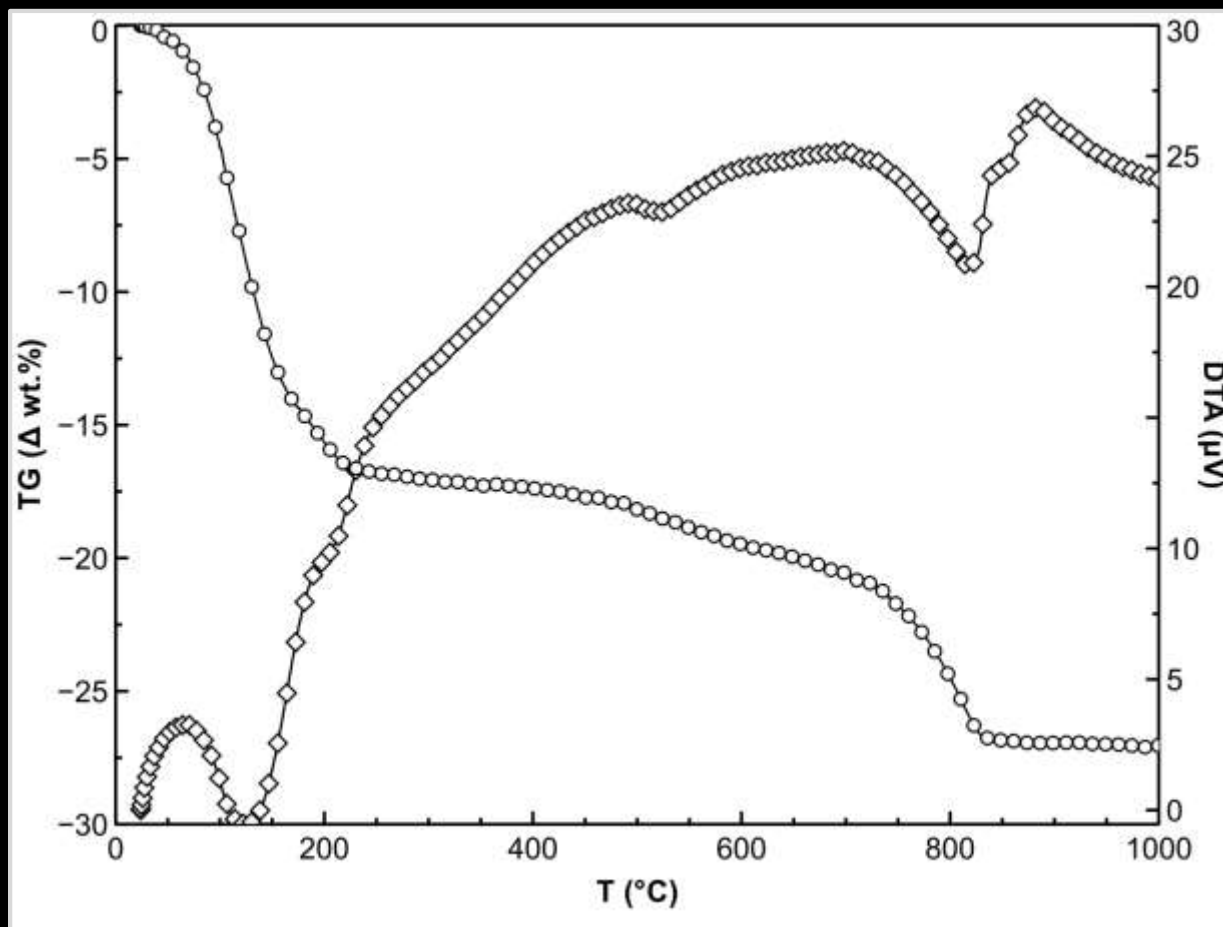
BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

Thermal activation of smectite clay

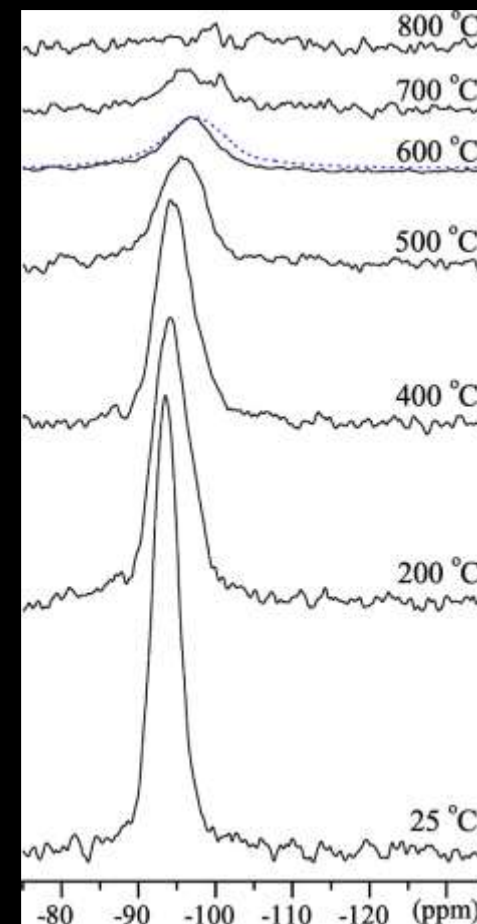


BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

Thermal activation of smectite clay



DTA-TG ANALYSIS

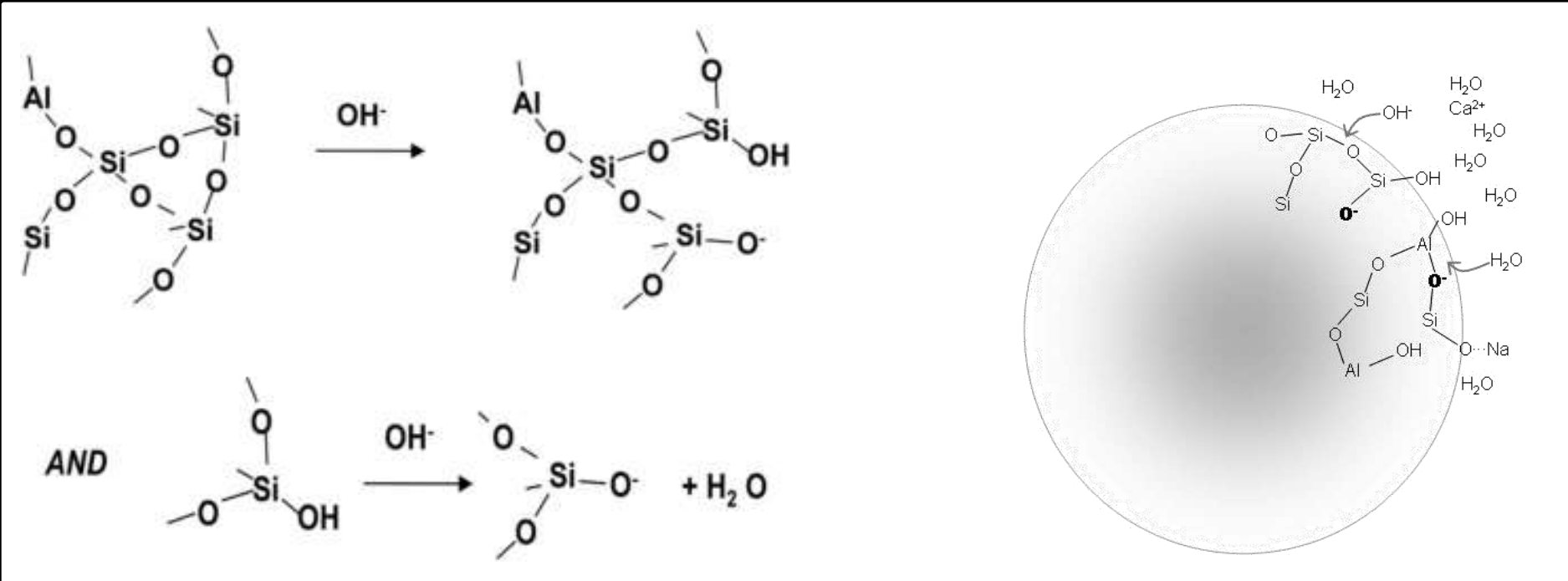


$^{29}\text{Si}\{^1\text{H}\}$ CP/MAS NMR



BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

Alkali activation of calcined clays



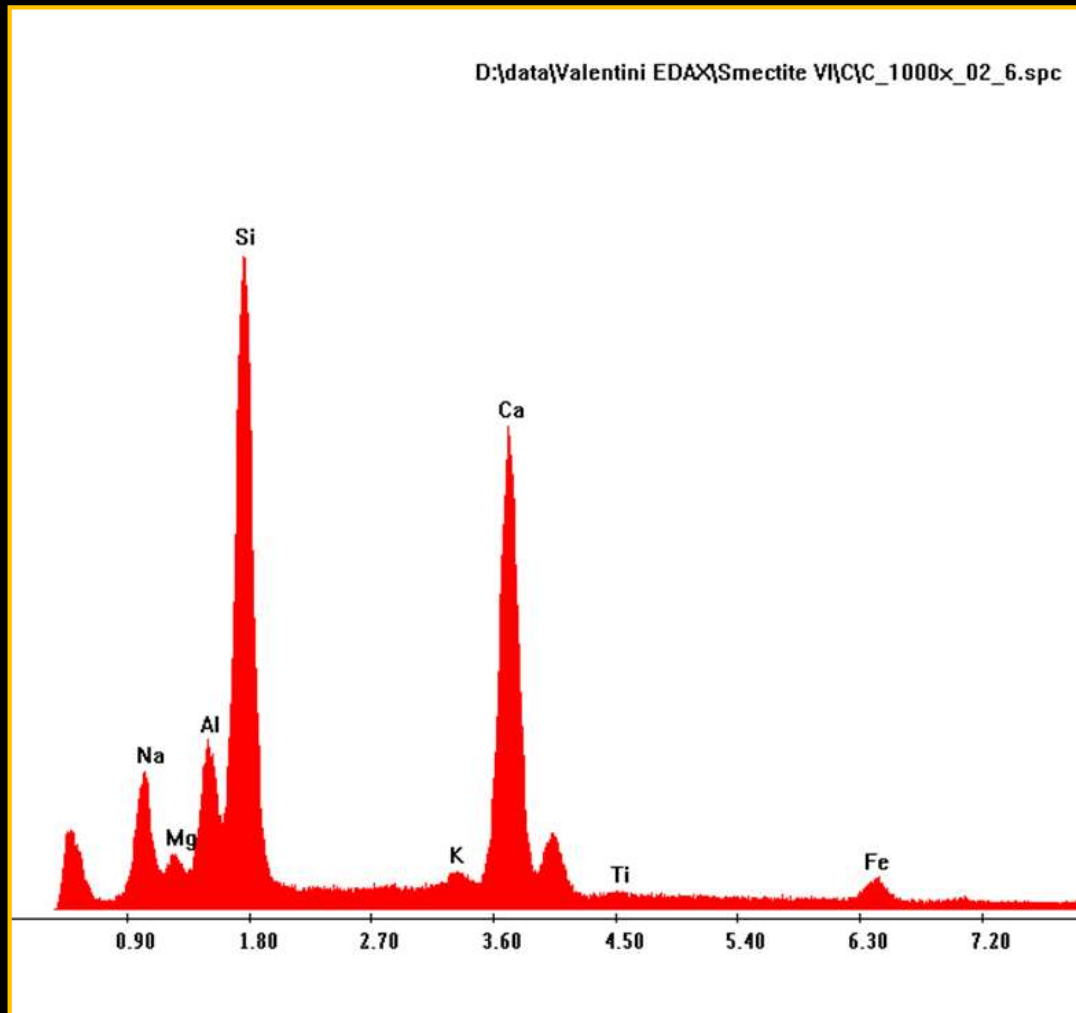
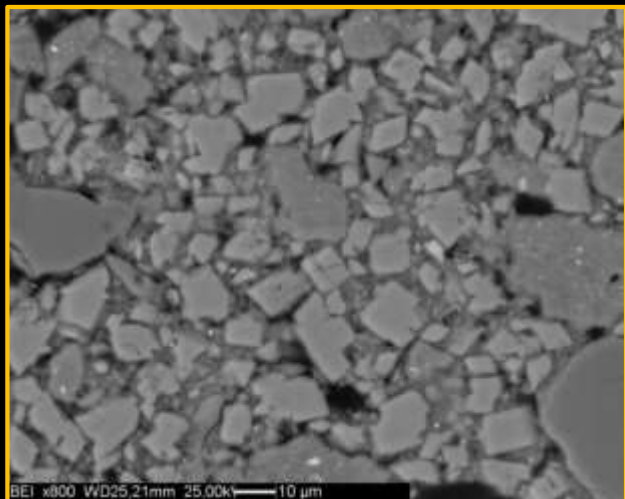
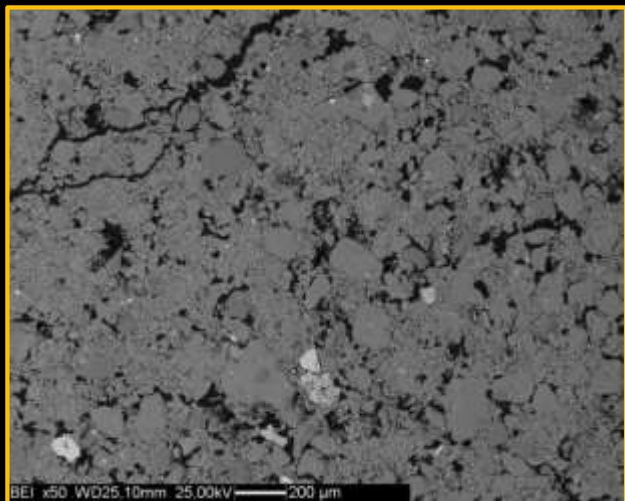
Common alkaline activators:

Sodium hydroxide Sodium silicate Sodium carbonate



BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

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



Industrial minerals in the spotlight





BUILDING MATERIALS AND SUSTAINABLE DEVELOPMENT

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

