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PETROPHYSICS

Physical properties of natural stone and other porous mineral materials

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Depending on the use (cobblestone, stair, façade, carved element, pile of bridge…), stone must have different physical characteristics.

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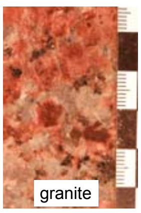
The physical properties of stones depend on cementation, porosity…



☛ they depend on **the origin of stones**

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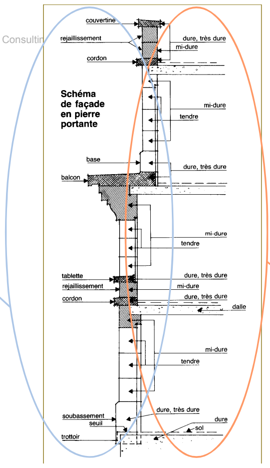
Architectural elements of a façade



Stones qualities:

Très dure: very hard
Dure: hard
mi-dure: half-hard
tendre: soft

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In the same exposure conditions, the durability of stones lying side by side depends on the liquids and gaseous exchanges between them and their environment (=physical properties)


Lausanne, Cathedral, 10.04.2012

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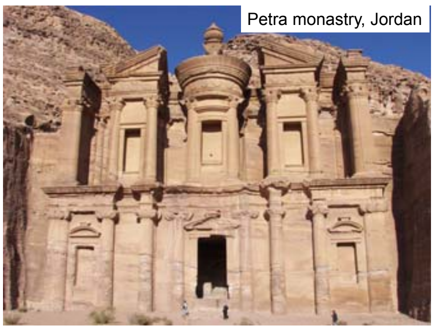
Exchanges between stones and the environment depend on:
- the **quantity** of the **pore space**
- the **quality** of the **pore space** (geometry of pores, mineralogical nature of the inner surfaces…)


Petra monastry, Jordan

Interactions between stones and conservation products are also strongly dependent on quantity and quality of the porous space

Conservation products for stones*, mechanical and/or chemical cleanings -as well as water and salts- can change the physical properties of stones

* (consolidants, water-repellents, anti-graffiti products, paints, …)

(Total) porosity

Definition: fraction of the total volume of a material « occupied » by voids

$$Pt\,(\%) = 100 \times \frac{Vv}{Vt} = 100 \times \frac{Vv}{Vv + Vs}$$

Pt = total porosity
Vv = volume of the voids
Vt = bulk volume
Vs = volume of solid

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Densities and porosity

Density (masse volumique): quantity of solid matter contained in a given volume of material

bulk density $\rho_a = \frac{m}{Vt}$ (m. vol. apparente)	particle or true density $\rho_s = \frac{m}{Vs}$ (m. vol. réelle ou solide)

$$Pt\,(\%) = 100 \times \left(1 - \frac{\rho_a}{\rho_s}\right)$$

If Pt tends to 0, ρ_a tends to ρ_s

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Different kinds of porosity

- **Primary** (primaire): structural arrangement existing since the genesis of the stone
- **Secondary** (secondaire): results from the phenomena of deterioration, diagenesis, metamorphism …
- **Connected**: voids communicating freely between them
- **Occluded**: not inter-connected voids
- **Intergranular**: voids between the constituent grains
- **Intragranular**: voids inside the constituent grains
- **Micro- and macro- porosity** : < or > to 7.5 µm (from mercury injection porosimetry : injection PHg = 1 bar)

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Different kinds of porosity

Porosity and water retention in soils

Pores	diameter	Water
Big pores	> 50 µm	free water - dry quickly and easily (no capillary action)
Medium pores	10 to 50 µm	free/capillary water - take time to the dry out ("coarser" part of the capillary porosity)
Fine pores	0.2 to 10 µm	capillary water - slow to dry, high capillary tension
Very fine pores	< 0.2 µm	linked (adsorbed) water - very difficult/impossible to dry

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Total porosity ranges for various natural rocks

Rock type	**Porosity *(%)***
sandstones	5 – 50
limestones	5 - 55
crystalline rocks	0 – (10)
volcanic rocks	0 – (90)
metamorphic rocks	0 – (50)

Sources: Freeze and Cherry (1979); McWorter and Sunada (1977).

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Total porosity ranges for various natural swiss rocks

PIERRES NATURELLES	Masse volumique apparente	Résistance à la compression	Résistance à la flexion	Porosité totale (connectée)	Porosité capillaire	Dilatation hydrique
	t/m^3	N/mm^2	N/mm^2	Vol.%	Vol.%	mm/m
R. MAGMATIQUES						
Plutoniques	2.6-3.0	80-300	10-40	0.4-1.5	0.2-1.2	0.06-0.2
Volcaniques effusives	1.6-3.1	10-400	5-60	0.2-30	0.1-25	0.06-0.4
R. SEDIMENTAIRES						
Calcaire/ dolomite dures	2.6-2.8	50-200	3-30	0.6-2	0.5-1.5	0.09-0.16
Travertin / tuf calcaire	1.7-2.5	10-80	3-20	2-25	1.5-20	
Calcaire tendre	1.5-2	8-25	2-8	5-25	5-20	0.3-0.5
Grès à ciment siliceux	2-2.6	40-250	7-33	1-25	1-20	0.3-0.6
Grès à ciment calcaire	2-2.6	30-180	3-18	2-20	1-18	0.4-0.8
Conglomérats	2.4-2.6	14-160	2-12	0.5-5	0.5-4	0.1-0.2
R. METAMORPHIQUES						
Gneiss / migmatite	2.5-2.8	70-200	8-45	0.4-2.0	0.25-1.5	
Quarzite	2.6-2.7	100-300	14-60	0.4-2.0	0.2-1.5	
Schistes	2.5-2.7	50-150	8-40	0.6-3.0	0.5-2.5	0.2-0.6
Serpentinite	2.6-2.75	55-200	11-60	0.3-2.0	0.25-0.18	
Marbre	2.5-2.7	40-230	10-40	0.3-0.8	0.2-0.5	

D'après Kündig R. et al., 1997. Die mineralischen Rohstoffe der Schweiz.
Commission Géotechnique Suisse, Zürich, ETHZ

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(connected) Porosity measurement

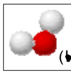
The « triple weighing* » method: (method of imbibition)

M_1 = mass of the dried sample weighing in the air
M_2 = m. of the water saturated s.**, weighing in the air
M_3 = m. of the water saturated s.**, weighing underwater

$M_1 = (\rho_s \times Vs)$
$M_2 = (\rho_s \times Vs) + (\rho_{H2O} \times Vv)$
$M_3 = (\rho_s \times Vs) - (\rho_{H2O} \times Vs)$
avec $\rho_{H2O} = 1\ g/cm^3$

$$\mathbf{Pt} = \frac{M_2 - M_1}{M_2 - M_3}$$

☛ water soluble phases !!!



Ø of the H_2O molecule
~0.343 nm
(☛ big pores are not accessible)

*méthode de la triple pesée
** the connected porosity of samples are saturated with water under vaccum

(connected) Porosity measurement

The gas pycnometry method: (method of imbibition)
Measurement of the volume of a sample (solid or powder). Principle: injection of a gas (He) from a closed volume of reference with a known pressure and a known volume to a closed volume containing the sample. According to the Boyle-Mariotte law, the difference in change of pressure gives the volume of the sample.

V_1 = closed volume of reference
V_0 = volume of the container with sample
V_s = "solid" volume of the sample
P_1 = gas pressure in the reference container
P_2 = gas pressure in the container with sample after expansion of the gas

$$V_s = V_0 - V_1 \left(\frac{P_1}{P_2} - 1 \right)$$

Ø of the He atom ~0.12 nm ?

(connected) Porosity measurement

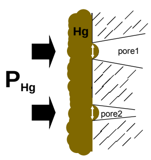
Mercury intrusion porosimetry (MIP): (method of drainage)
The technique involves the intrusion of mercury, a non-wetting liquid, at high pressure into a material through the use of a porosimeter. The pore size can be determined based on the external pressure needed to force the liquid into a pore against the opposing force of the liquid's surface tension (at 25° C γ = 0,474 N/m and the contact angle α = 130°)

$$P_{Hg} - P_{vap} = \frac{2\gamma \cos\alpha}{R} \quad \text{as } P_{vap} << P_{Hg} \Rightarrow P_{Hg} = \frac{2\gamma \cos\alpha}{R}$$

deformable materials ?

Ø of the Hg atom 0.3 nm
BUT the Ø of the smallest accessible pores depends on the max. PHg (and the largest ones depends on the min. PHg

(connected) Porosity measurement

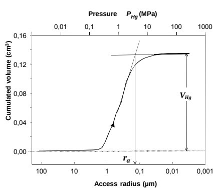


MIP:
With a known **P_{Hg}** on a known volume of mercury, all the pores with an access radius ≥ **R** can be filled

As **P_{Hg}** ↗, the radius **R** of the pores that can be filled ↘

V_{Hg} = bulk volume of intruded mercury (≈ Pt)

ra = threshold radius (the smallest radius giving access to the maximum porous volume)



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Speed of sound, porosity and cementation

The time of transmission of the P waves (longitudinal) through the thickness of a porous material ↗ when:
- the percentage of the void volume ↗
- the cementation degree ↘

The Hooke's law (very) simplified allows to estimate the modulus of elasticity or Young's modulus (E):

$$Vp = \sqrt{\frac{E}{\rho_a}} \quad \Rightarrow \text{relative value}$$

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Microscopic observation of thin sections of rocks (polarizing petrographic microscopy)

A thin section *(lame mince)* is a 30 µm thick strip of stone which is sticked on a glass slide. This sample can be observed with transmitted light because of its transparency.

Stages of manufacture:
- sawing a stone to « suger cube » (3 x 2 cm) size
- hardening using an epoxy resin
- polishing of one side which is then glued on the glass slide
- sawing, grinding, then polishing up to a thickness of 30 µm

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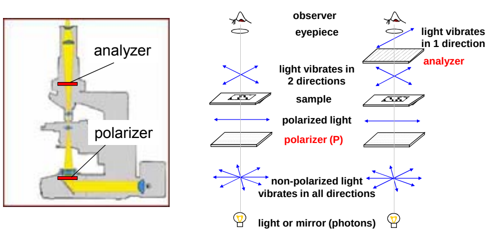
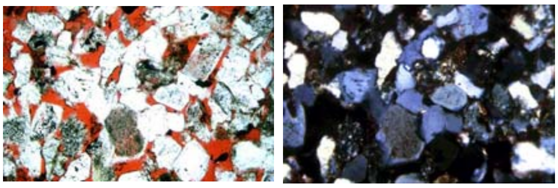
The polarizing petrographic microscope



The optical properties of the minerals in a thin section alter the colour and intensity of the observed light. Minerals can be identified but porosity can also be observed

Microscopic observation of thin sections of rocks



(Photos: D. Jeannette) Sandstone of the Basel cathedrale. Width ≈ 5 mm

⇒ mineralogy
⇒ geometry of the porous network (only for voids >1 µm)

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Notion of climate:

In french
http://c2rmf.fr/sites/c2rmf.fr/files/quest-ce_que_le_climat.pdf
(29.10.2015)

http://www.kasuku.ch/pdf/hygrometrie.pdf
jusqu'à la page 9
(29.10.2015)

In English
http://www.conservationphysics.org/intro/fundamentals.php
(29.10.2015)

Température

Humidité
(relative et absolue)

Point de rosée

Conservation Scie

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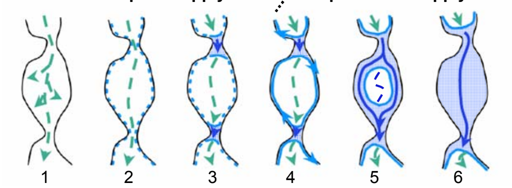
Water transfer in porous media



1 - vapour diffusion; 2 – vapour adsorption + diffusion; 3 - capillary condensation; 4 - capillary migration along the walls (beginning of filling); 5 - hydraulic flow in unsaturated media (filling in progression or finished); 6 - hydraulic flow in saturated media

According to Rose (1963)

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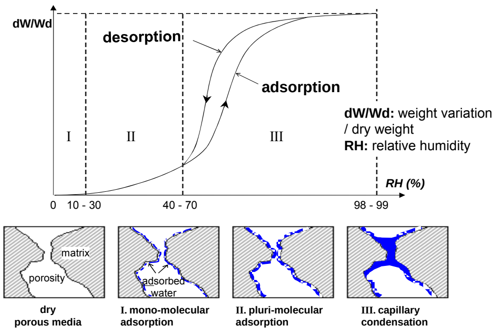
Water vapour in porous media: adsorption



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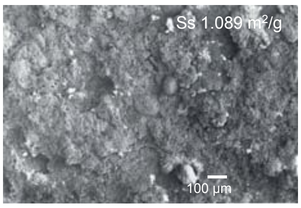
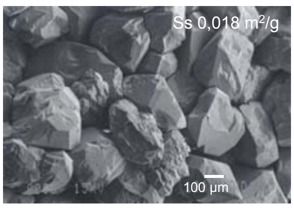
Water vapour in porous media: adsorption



Lourdines micrite MCL



Fontainebleau sandstone GFT

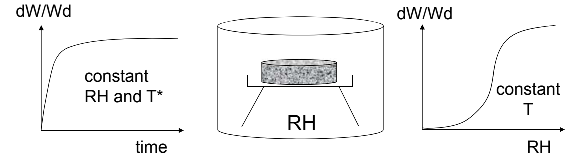
Hygroscopicity increases when:

- specific surface ➚ (microporosity, content of clays – for example MCL hygroscopicity > GFT one)

- content of soluble salts ➚

Water vapour in porous media: adsorption

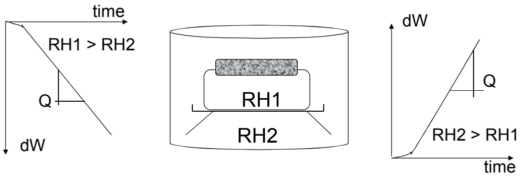
To determine the kinetic adsorption and the adsorption isotherm, samples are first dried at 60ºC then, they are placed in closed boxes where relative humidity is controlled. Then, they are weighted regularly until their mass becomes constant.

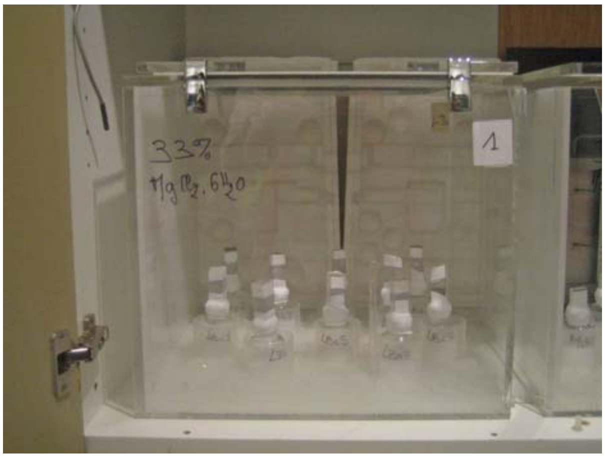


*T = temperature

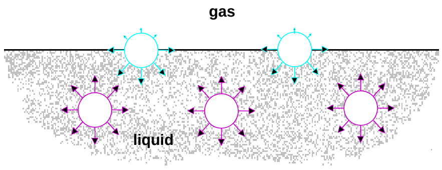
Water vapour in porous media: permeability

To determine the water vapour diffusivity or the permeability to water vapour samples are first dried at 60ºC. Then they are packed in such a way that two opposite faces can exchange with two different relative humidities.



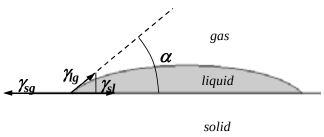


Liquid water in porous media – surface tension



The cause of surface tension in a liquid: a molecule in contact with a neighbour is in a lower state of energy than if it weren't in contact with a neighbour. The boundary molecules have fewer neighbours than interior molecules and are therefore in a higher state of energy than interior molecules => to minimize its energy state, a liquid must minimize its number of boundary molecules and therefore minimize its surface area => formation of "film" => formation of a drop **…**

Liquid water in porous media – surface tension



γ_{sg} **surface tension solid/gas**
γ_{lg} **surface tension liquid/gas**
γ_{sl} **surface tension solid/liquid**
α **contact angle solid/liquid**

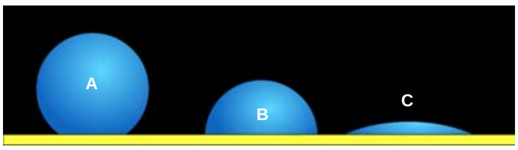
When a drop of liquid is deposited on a solid surface, the interface geometry depends on the affinity of each phase (solid, liquid, gas) to the other, or on their relative surface tensions

Young-Dupré equation:

γ_{lg} **cos**α **=** γ_{sg} **-** γ_{sl}

wetting liquid: $\alpha < 90°$
non-wetting liquid: $\alpha > 90°$

Liquid water in porous media – surface tension



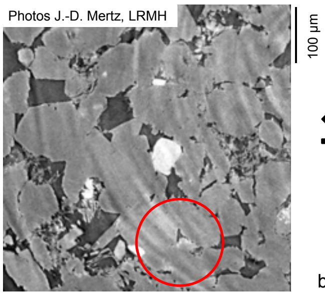
Wetting of different fluids. ***A*** shows a fluid with very **high surface tension** (and thus little wetting), while ***C*** shows a fluid with **very low surface tension** (more wetting action.) A has a high contact angle, and C has a small contact angle.

Examples: drops of oil, water and water + detergent

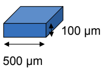
Liquid water in porous media – surface tension

For example, inorganic salts (in general!) increase the surface tension (decrease the wettability) of a solution, but alcohols or surfactants decrease the surface tension (increase the wettability) of the solutions

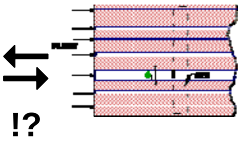
Some treatment effects:
Hydrophobic and consolidating treatments decrease the wettability of the façade surfaces whereas cleaning products tend to increase this wettability



Buntsandstein sandstone
« Grès à Meules »
Micro computed tomography
(x ray - synchrotron)
slice thickness ~ 1.35 µm



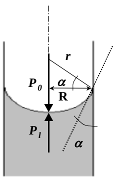
Modeling of the rock porosity



Despite the complexity of the porous structures, it seems that a bundle of parallel capillaries, all of different diameters, embedded in a solid, is a perfect morphology model of a porous medium !!!

Liquid water in porous media – capillarity

If a tube is sufficiently narrow and the liquid adhesion to its walls is sufficiently strong, surface tension can draw liquid up the tube in a phenomenon known as capillarity.
In such a case, surface tensions are responsible for the capillary pressure (a tension in fact) and the formation of a meniscus at the liquid interface



=> $Pc = P_0 - P_l$

Laplace equation:

$$\boxed{Pc = \frac{2\gamma}{r}}$$

Pc = capillary pressure (= tension !)
P_0 = pressure in the gas
P_l = pressure in the liquid
r = radius of curvature of the meniscus
R = radius of the capillary
γ = surface tension liquid/gas

Liquid water in porous media – capillarity

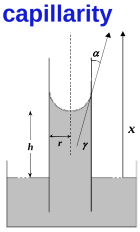
When the radius of the capillary **R** is very small, the meniscus is hemispherical and the radius of curvature ***r*** can then be connected to **R**:

$$\boxed{r = \frac{R}{\cos\alpha}} \quad \Rightarrow \quad \boxed{Pc = \frac{2\,\gamma\cos\alpha}{R}}$$

The more wetting fluid moves spontaneously the less wetting fluid towards the outside of the capillary: this is called a capillary imbibition, succion or absorption

(When a pressure is applied on the less wetting fluid, the more wetting fluid is forced out: this is called a drainage; the MIP for ex.)

Liquid water in porous media – capillarity



When a capillary tube is plunged in a liquid, the meniscus moves allong the tube.

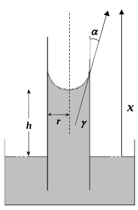
The kinetic follows the **Poiseuille law** which is (if acceleration due to gravity is neglected) :

$$Q\,(x) = \frac{\pi\,\gamma\cos\alpha\, r^3}{4\,\eta\, x}$$

=> when r ↗, Q ↗

γ = surface tension liquid/gas
r = radius of the capillary
η = dynamic viscosity
α = contact angle solid/liquid

Liquid water in porous media – capillarity



When a capillary tube is plunged in a liquid, the meniscus moves allong the tube.

The height *h* of the liquid column at stady state is given by the Jurin's equation :

$$h = \frac{2\,\gamma\cos\alpha}{r\, g\,\rho}$$

=> when r ↗, h ↘

γ = surface tension liquid/gas
g = gravitiy
ρ = density of liquid
r = radius of the capillary
α = contact angle solid/liquid

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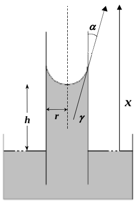
Calculation examples



For a water-filled glass tube in air at sea level,

γ = 0.0728 J/m² at 20°C
θ = 20° (0.35 rad)
ρ = 1000 kg/m³
g = 9.8 m/s²

=> the height of the water column is given by:

$$h = \frac{2\,\gamma\cos\alpha}{r\,g\,\rho} \approx \frac{1.4 \times 10^{-5}}{r}$$

Thus for a 2 m wide (r = 1 m) tube, the water would rise an unnoticeable 0.014 mm.
For a 2 cm wide tube (r = 1 cm), the water would rise 1.4 mm and for a capillary tube with r = 0.1 mm, the water would rise 14 cm.

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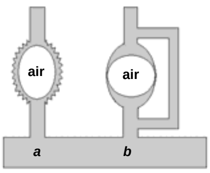
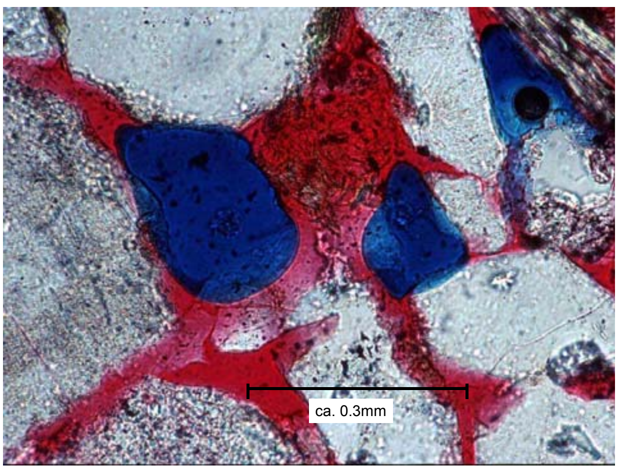
Liquid water in porous media – capillarity



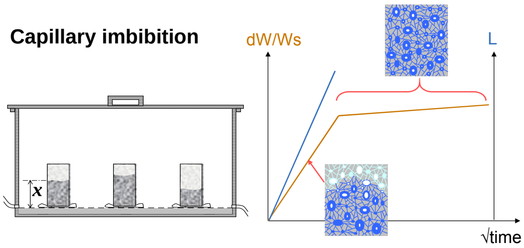
Less wetting fluid trapped by the more wetting fluid during an imbibition because of:
a. rugosity
b. derivation

The porosity of a rock (or a mortar, a concrete,…) is a complex system formed by inter-connected wide and tiny pores. As a result, there are always many parallel ways for the capillary water during an **imbibition**.
This great complexity allows the water (more wetting fluid) to trap air (less wetting fluid) in parts of the porosity.



Liquid water in porous media – capillarity

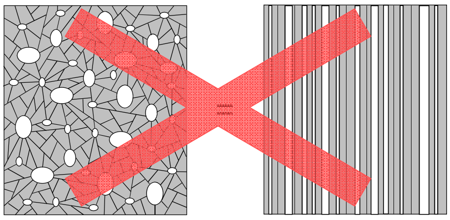
Capillary imbibition



The kinetics of linear and mass capillary imbibitions of a stone show the complexity of the porous network

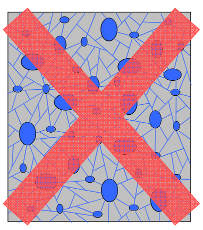
Materials and conservation of built cultural heritage – Petrophysics _ BR 43

Liquid water in porous media – capillarity



Materials and conservation of built cultural heritage – Petrophysics _ BR 44

Liquid water in porous media – capillarity



In a porous network partly formed of (connected) macropores, the water saturation of the porosity is not reached by simple capillarity

Materials and conservation of built cultural heritage – Petrophysics _ BR 45

Liquid water in porous media – capillarity

During a **capillary imbibition**:

Porosity freely accessible to water = **free porosity**
Portion of porous space inaccessible = **trapped porosity**

The trapped porosity is caracterised by the capillary saturation coefficient or **Hirschwald coefficient (S%)**

$$S\% = \frac{P_i}{Pt} \times 100 \quad \text{where} \quad Pi\ (\%) = \frac{M_i - M_1}{M_2 - M_3} \times 100$$

P_i = porosity filled by water imbibition
M_i = sample weight after water imbibition
M_1, M_2, M_3: see page 15

Liquid water in porous media – gelivity

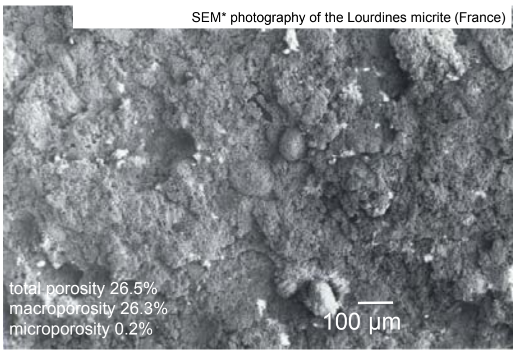
The ability to be more or less filled with water in the presence of air **is one of the lot of parameters** controling the frost resistance of a stone

Estimation of frost resistance :

In a "simplistic" way, a stone is described as
- **frost susceptible** if S% is > 0,85
- **not frost susceptible** if S% is < 0,75

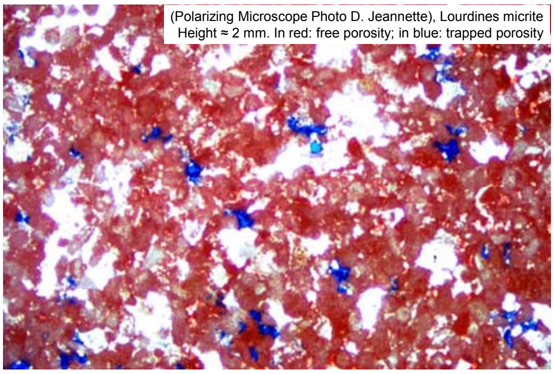
A high water saturation makes the stone frost susceptible (because of the volume expansion of about 9% - or a linear expansion of 3% - of this liquid when it freezes)

SEM* photography of the Lourdines micrite (France)



micro- < r = 7.5 µm < macro-porosity (p.11)

*SEM: Scanning Electron Microscope



(Polarizing Microscope Photo D. Jeannette), Lourdines micrite
Height ≈ 2 mm. In red: free porosity; in blue: trapped porosity

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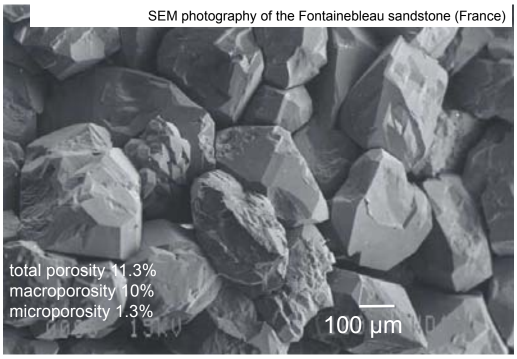

SEM photography of the Fontainebleau sandstone (France)

micro- < r ≈ 7.5 µm < macro-porosity (p.11)

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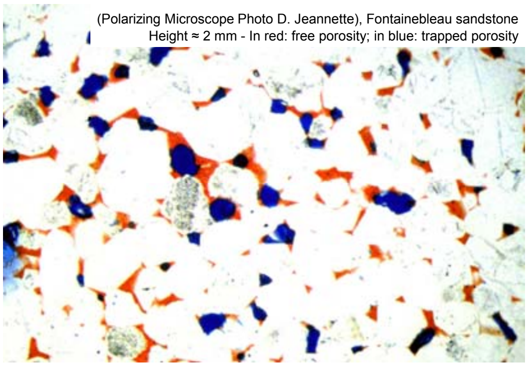

(Polarizing Microscope Photo D. Jeannette), Fontainebleau sandstone
Height ≈ 2 mm - In red: free porosity; in blue: trapped porosity

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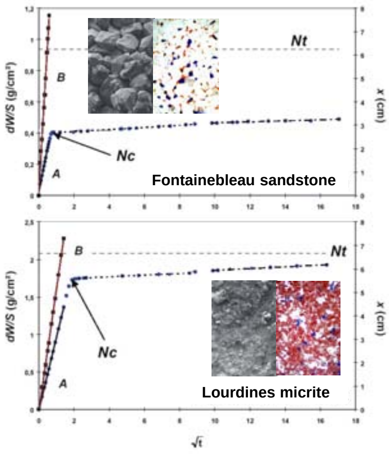
Capillary imbibition
(RH 100%, T 23° C)

dW = weight variation
S = imbibition surface
Nc = capillary porosity
Nt = total porosity



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Liquid water in porous media – capillarity

- **In general**, the higher the dimension of the pores, the higher is the capillary imbibition velocity

- if the linear capillarity is much faster than the massic one, the trapped porosity is high => even if water goes up high, the water saturation of the porosity remains low

- the more varied the pore sizes, the bigger is the trapped porosity: media with very homogeneous porosity can reach very high water saturation of the porosity (at least near the water source)

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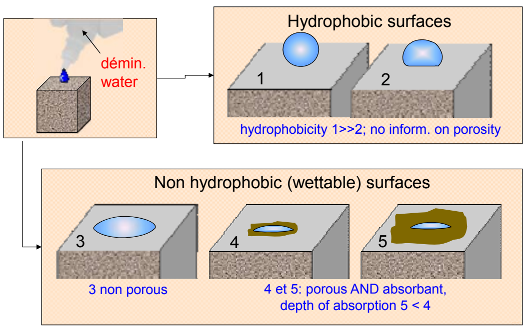
The (field) drop test to estimate if a material is porous and/or hydrophobic and/or absorbant



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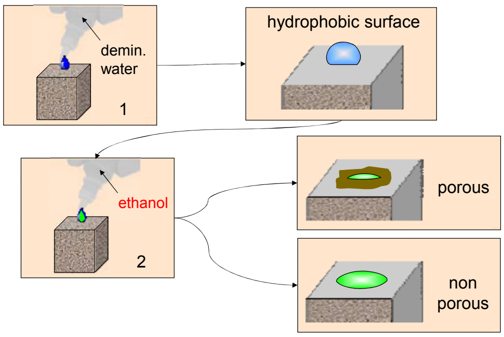
The (field) drop test to estimate if a material is porous and/or hydrophobic and/or absorbant



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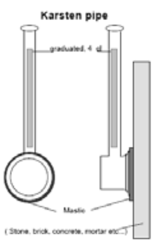
How to estimate the initial water absorption in the field: Karsten pipes

http://www.reedconstructiondata.com



Final Report for the Research and Development Project Non-Destructive Field Tests in Stone Conservation Literature Study Rapport från Riksantikvarieämbetet 2006:3 // http://www.raa.se/publicerat/9172094345.pdf

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How to estimate the initial water or alcool absorption in the field: Mirowski pipes

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How to estimate the initial water absorption in the field: contact sponge

Marini P., Bellopede R., 2009- Bowing of marble slabs: Evolution and correlation with mechanical decay. Construction and Building Materials, Vol. 23, Issue 7, pp 2599–2605

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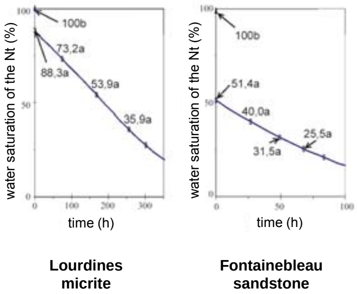
Liquid water in porous media – drying



Drying of a specific material is always much slower than its capillary imbibition

In general, the bigger the dimension of the pores of a material, the faster it dries

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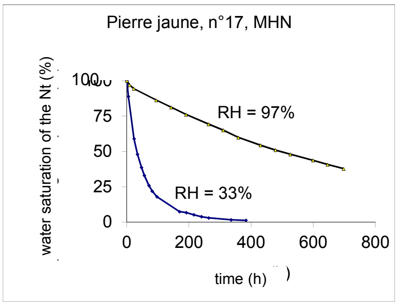
Liquid water in porous media – drying



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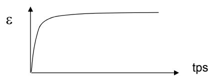
Liquid water in porous media – dilation (dilatation)

Every porous material changes more or less its dimensions when it adsorbs (vapor) or absorbs (liquid) water (because of a loss of cohesion between grains and or the swelling of clays). This phenomenon is called **hydric dilation** (with liquid water) or **hygric dilation** (with water vapour).

Hydric dilation measurement: the dried sample (length: L_0) is fixed under a dial test indicator *(comparateur)*, then it is entirely immersed in water. The extension which is obtained after 72 hours of immersion allows to calculate the hydric dilation coefficient:

$$\varepsilon(72) = \frac{\Delta L\ (72\ h)}{L_0}$$



$\varepsilon(72) \geq 2$ mm/m is regarded as high and dangerous

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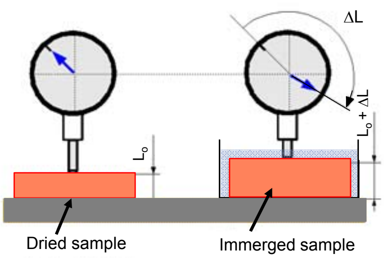
Liquid water in porous media – dilation (dilatation)



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Notion of R.V.E.

Rocks are **heterogeneous materials** (mineralogy, porosity) on a scale of:

- **pores**
- **samples**
- **outcrops** *(affleurements)*

Therefore to be representative, measurements of physical and mechanical properties of rocks must be done on **Representative Volume Elements** *(volumes élémentaires représentatifs)*.

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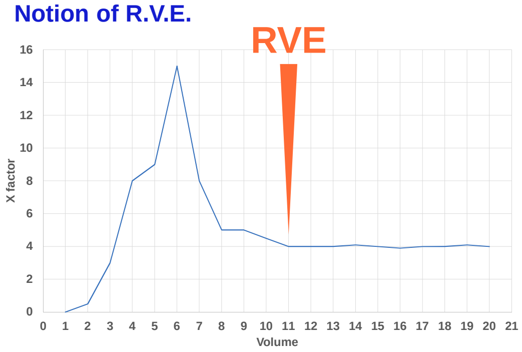
Notion of R.V.E.



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