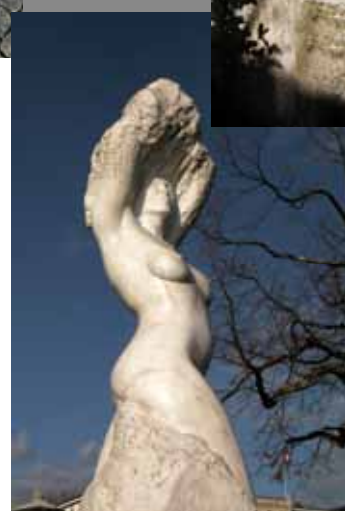




PETROPHYSICS

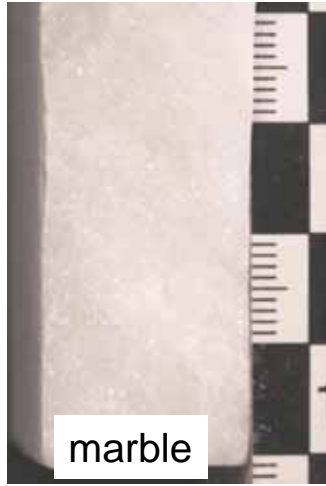
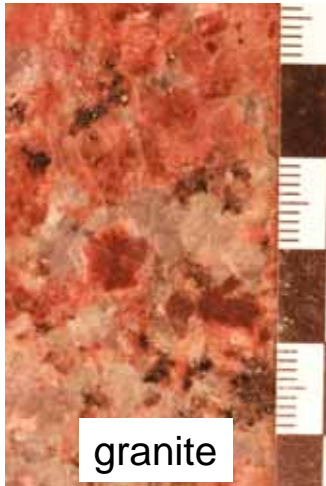
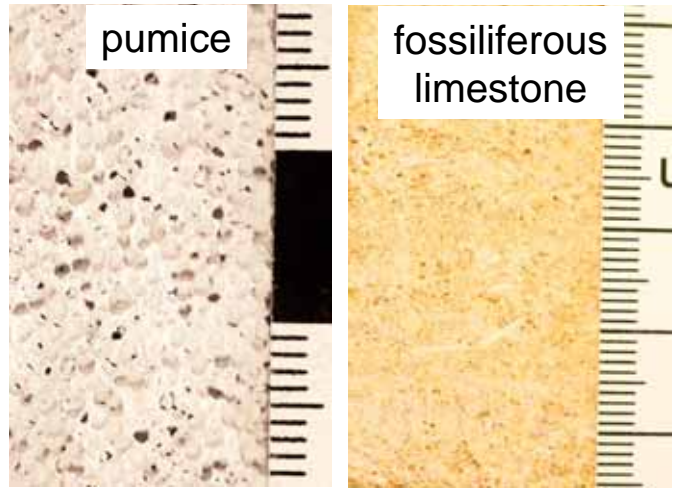
Physical properties of natural stone and other porous mineral materials



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



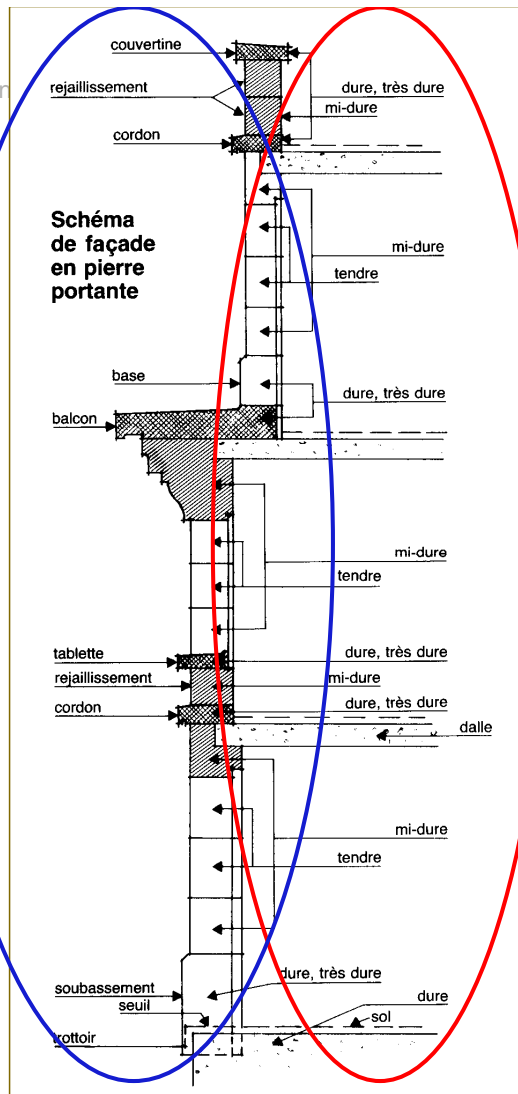
The physical properties of stones depend on cementation, porosity...



they depend on the origin of stones



Architectural elements of a façade



Stones qualities:

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

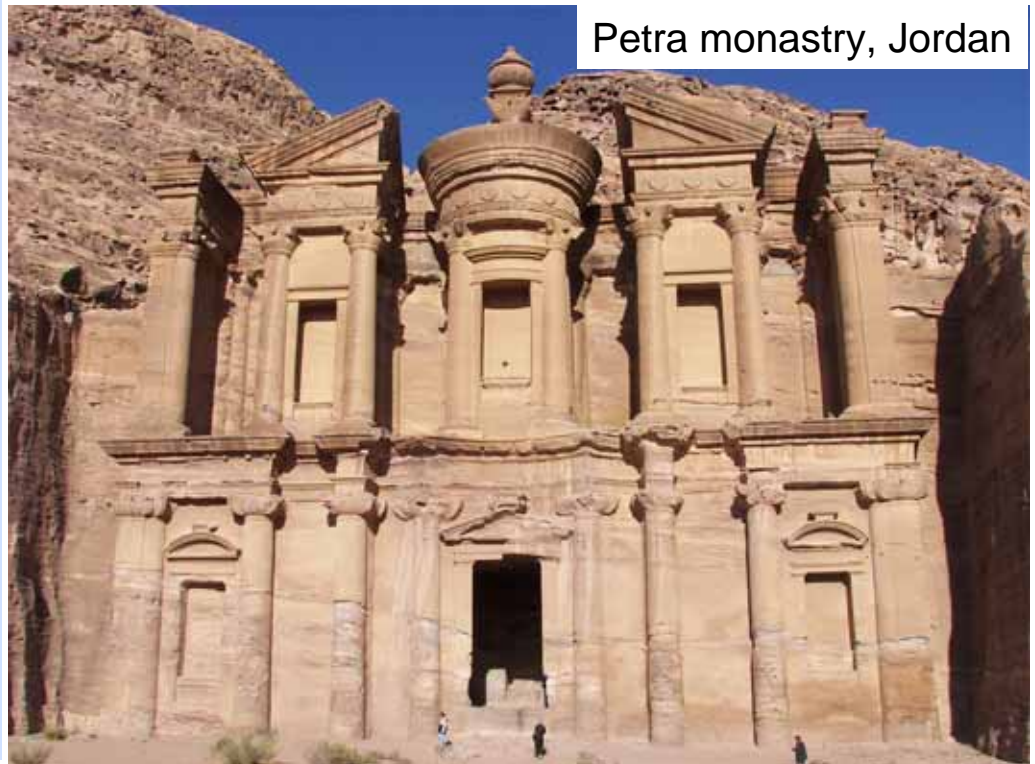


In the same exposure conditions, the durability of stones lying side by side depends on the liquids and gaseous exchanges between them and their environment (=physical properties)



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...)





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, ...)



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



Densities and porosity

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

bulk density

(m. vol. apparente)

$$\rho_a = \frac{m}{Vt}$$

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**



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



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).



(connected) Porosity measurement

The « triple weighing* » method:

M1 = mass of the dried sample weighing in the air

M2 = m. of the water saturated s.**, weighing in the air

M3 = m. of the water saturated s.**, weighing underwater

$$M1 = (\rho_s \times Vs)$$

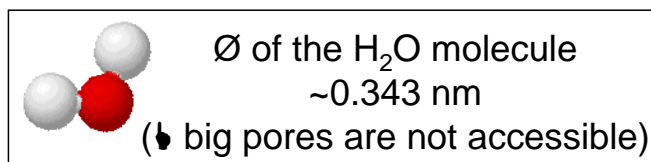
$$M2 = (\rho_s \times Vs) + (\rho_{H_2O} \times Vv)$$

$$M3 = (\rho_s \times Vs) - (\rho_{H_2O} \times Vs)$$

$$\text{avec } \rho_{H_2O} = 1 \text{ g/cm}^3$$

$$Pt = \frac{M2 - M1}{M2 - M3}$$

👉 water soluble phases !!!



*méthode de la triple pesée

** the connected porosity of samples are saturated with water under vacuum



(connected) Porosity measurement

The gas pycnometry method:

Measurement of the volume of a sample (solid or powder). Principle: injection of a gas 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.

V1 = closed volume of reference

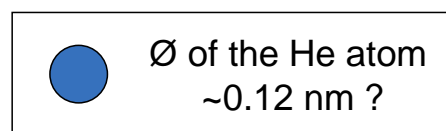
V0 = volume of the container with sample

Vs = "solid" volume of the sample

P1 = gas pressure in the reference container

P2 = gas pressure in the container with sample after expansion of the gas

$$Vs = V0 - V1 \left[\frac{P1}{P2} - 1 \right]$$






(connected) Porosity measurement

Mercury intrusion porosimetry (MIP):

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 $\gamma = 0,474$ N/m and the contact angle $\alpha = 130^\circ$)

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

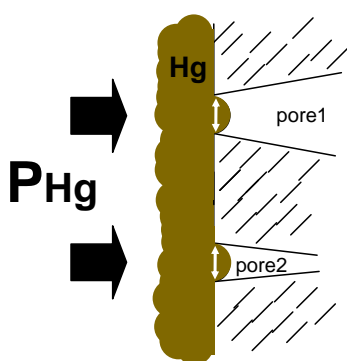
↳ deformable materials ?



\emptyset of the Hg atom 0.3 nm
BUT the \emptyset of the smallest accessible pores depends on the max. P_{Hg} (and the largest ones depends on the min. P_{Hg})



(connected) Porosity measurement



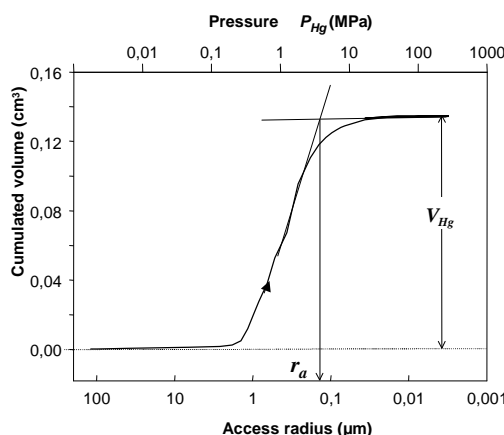
MIP:

With a known P_{Hg} on a known volume of mercury, all the pores with an access radius $\geq R$ can be filled

As $P_{Hg} \nearrow$, the radius R of the pores that can be filled \searrow

V_{Hg} = bulk volume of intruded mercury ($\approx Pt$)

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





Speed of sound, porosity and cementation

The time of transmission of the P waves (longitudinal) through the thickness of a porous material \nearrow when:

- the percentage of the void volume \nearrow
- the cementation degree \searrow

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

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



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

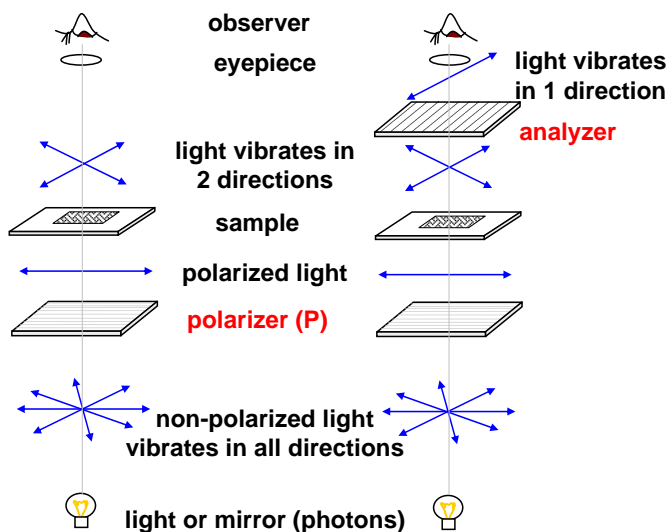
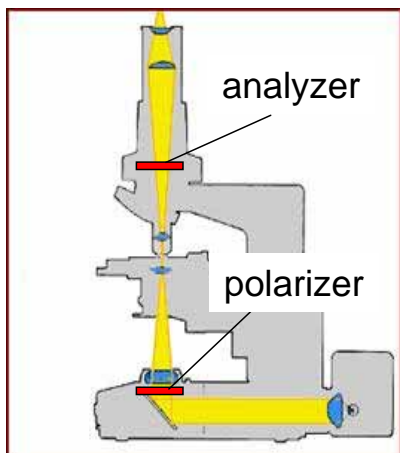
A thin section (*lame mince*) is a 30 μm thick strip of stone which is stuck on a glass slide. This sample can be observed with transmitted light because of its transparency.

Stages of manufacture:

- sawing a stone to « sugar 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



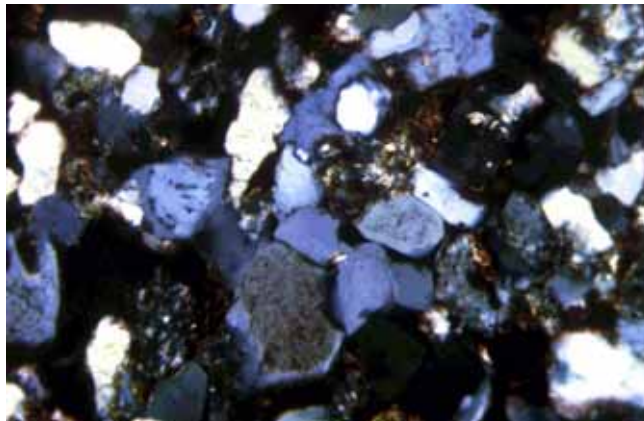
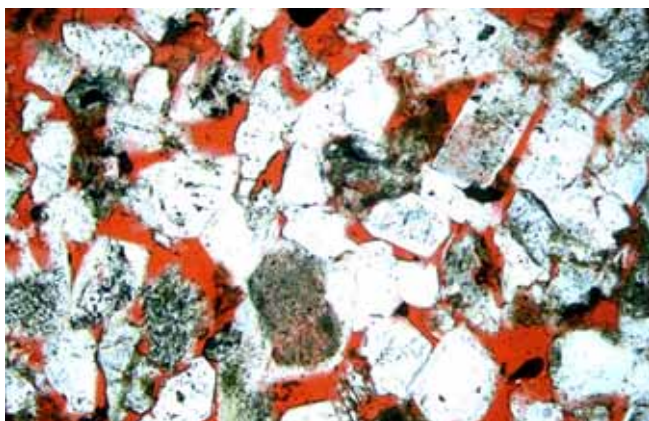
The polarizing petrographic microscope



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)



Notion of climate:

In french

http://www.c2rmf.fr/documents/Climat_fiche1.pdf

In english :

<http://www.conservationphysics.org/atmcalc/atmoclc1.php#svc>

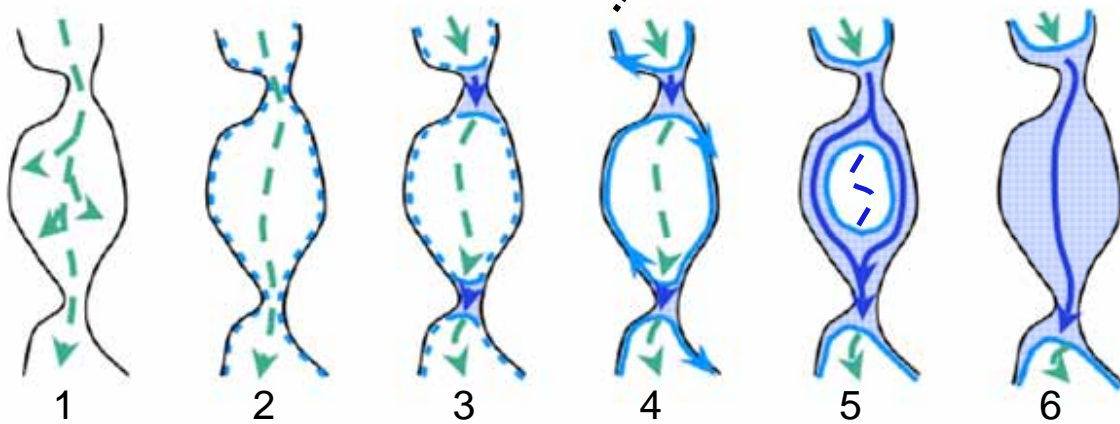


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Water transfer in porous media

	vapour transfer
	liquid transfer
	adsorbed vapour

→ water vapour supply ↗ → → liquid water supply ↗ →

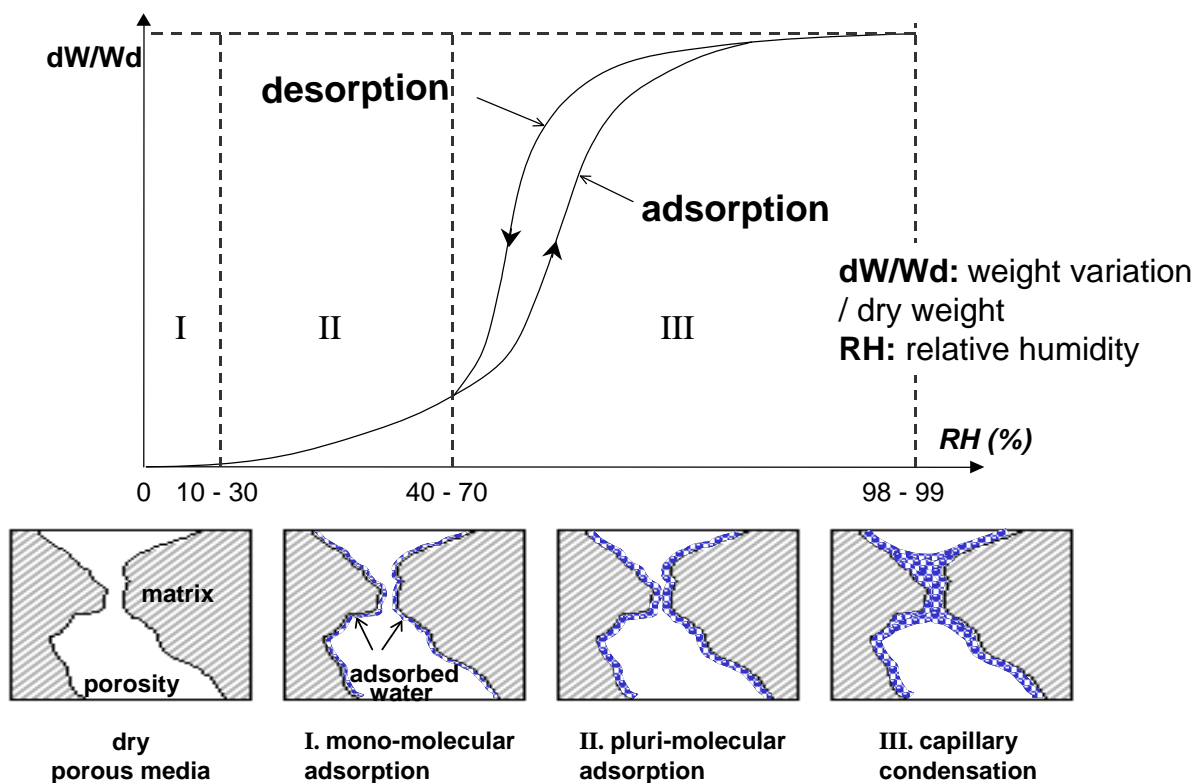


- 1 - vapour diffusion; 2 – vapour adsorption + diffusion; 3 - capillary condensation; 4 - capillary migration along the walls (beginning of filling); 5 - hydraulic flow in unsaturated media (filling in progression or finished); 6 - hydraulic flow in saturated media

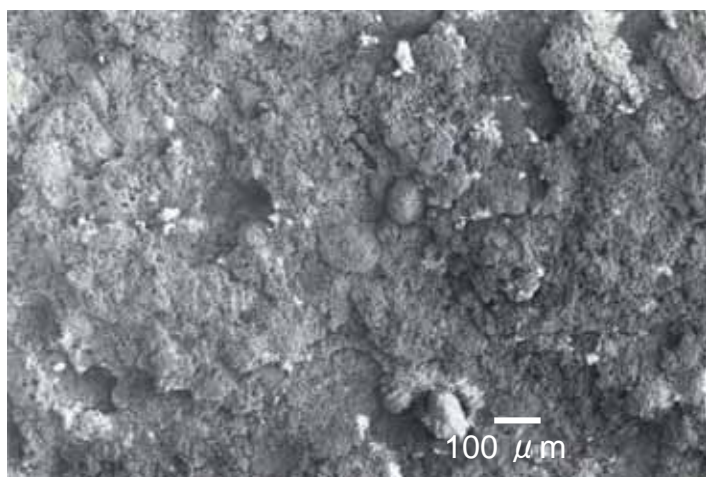
According to Rose (1963)



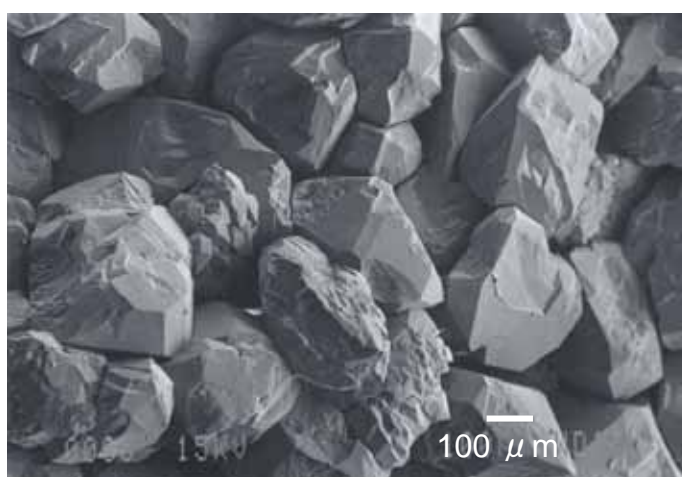
Water vapour in porous media: adsorption



Water vapour in porous media: adsorption



Lourdines micrite MCL



Fontainebleau sandstone GFT

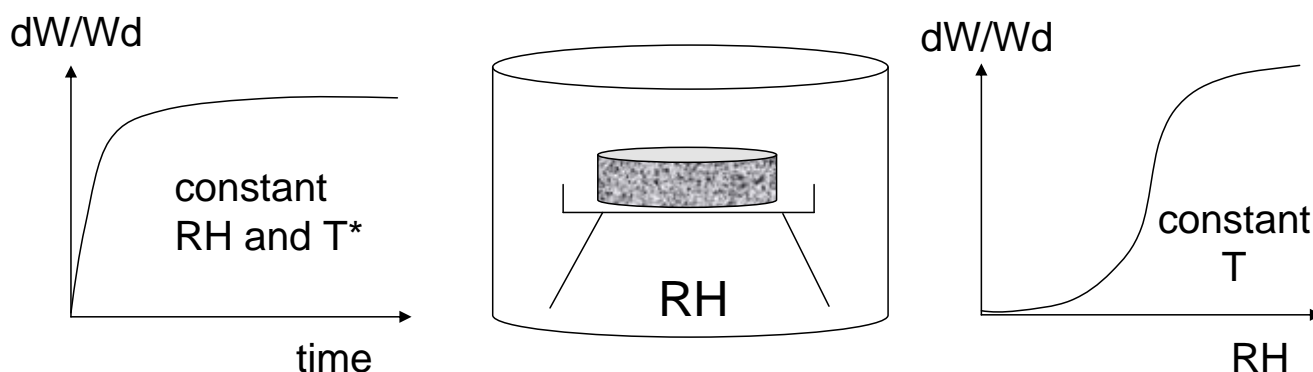
Hygroscopicity increases when:

- 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 60°C then, they are placed in closed boxes where relative humidity is controlled. Then, they are weighted regularly until their mass becomes constant.

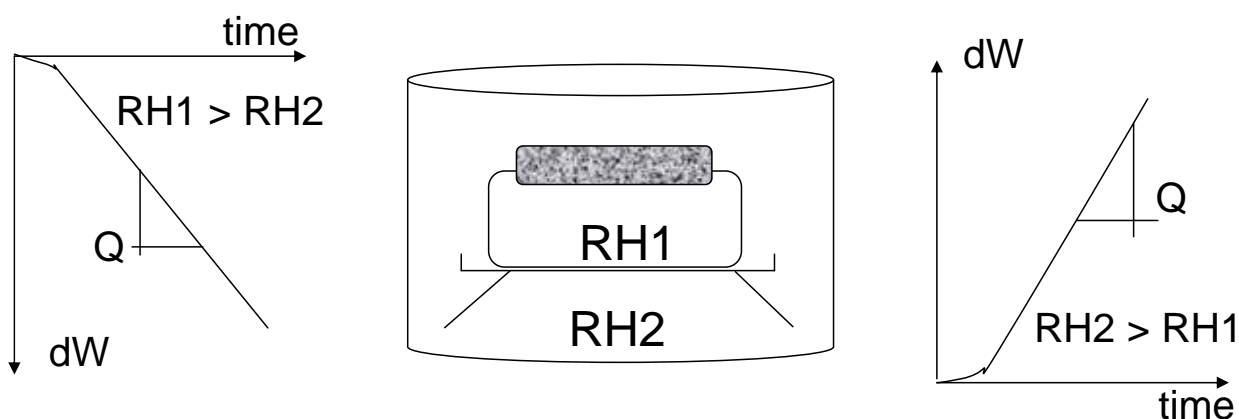


*T = temperature



Water vapour in porous media: permeability

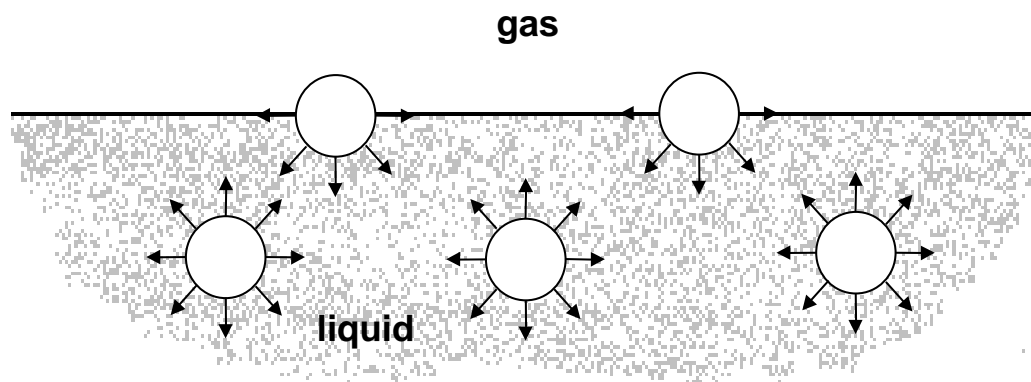
To determine the water vapour diffusivity or the permeability to water vapour samples are first dried at 60°C. Then they are packed in such a way that two opposite faces can exchange with two different relative humidities.





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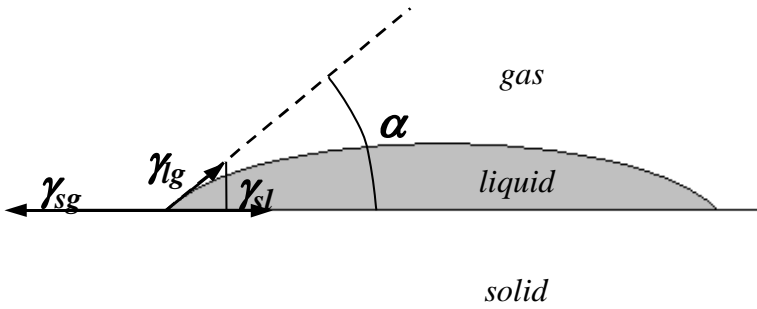
Liquid water in porous media – surface tension



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.



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

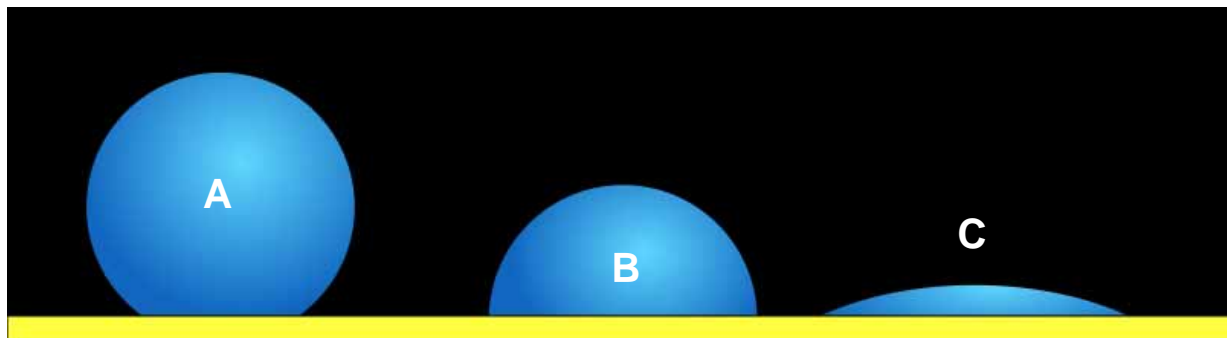
Young-Dupré equation:

$$\gamma_{lg} \cos \alpha = \gamma_{sg} - \gamma_{sl}$$

- wetting liquid: $\alpha < 90^\circ$
- non-wetting liquid: $\alpha > 90^\circ$



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

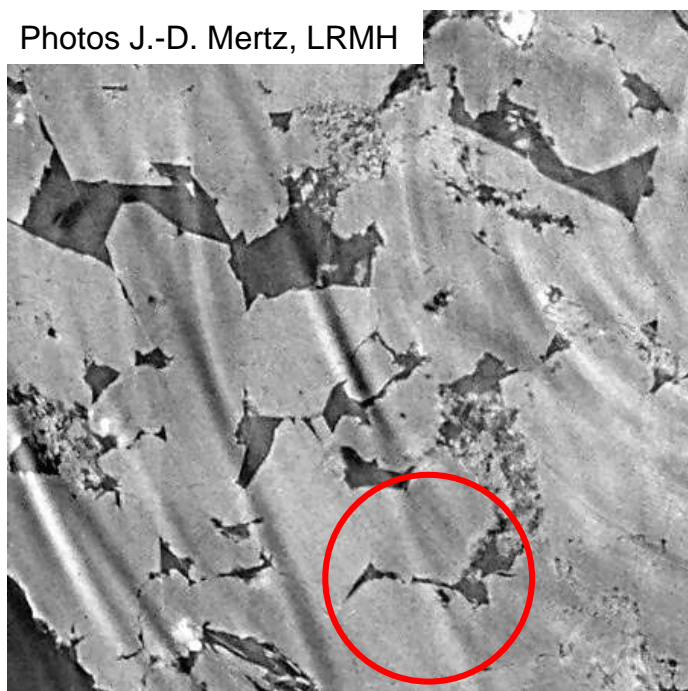
For example, inorganic salts increase the surface tension of a solution, but alcohols or surfactants decrease the surface tension of the solutions

Some treatment effects:

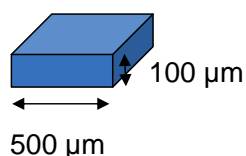
Hydrophobic and consolidant treatments decrease the wettability of the façade surfaces whereas cleaning products tend to increase this wettability



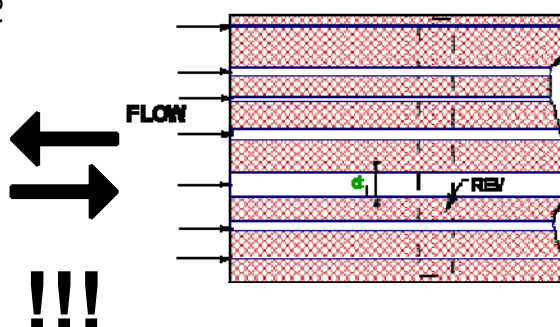
Photos J.-D. Mertz, LRMH



Buntsandstein sandstone
« Grès à Meules »
Micro computed tomography
(x ray - synchrotron)



Modeling of the rock porosity



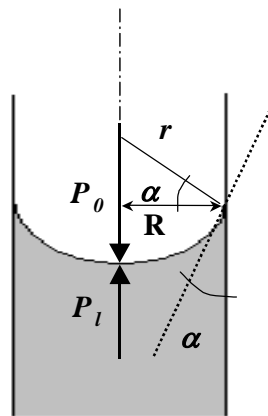
Despite the complexity of the porous structures, it seems that a bundle of parallel capillaries, all of different diameters, embedded in a solid, is a perfect morphology model of a porous medium !!!



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



$$\Rightarrow P_c = P_0 - P_l$$

Laplace equation:

$$P_c = \frac{2\gamma}{r}$$

- P_c = 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 :

$$r = \frac{R}{\cos\alpha} \quad \Rightarrow \quad P_c = \frac{2\gamma \cos\alpha}{R}$$

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

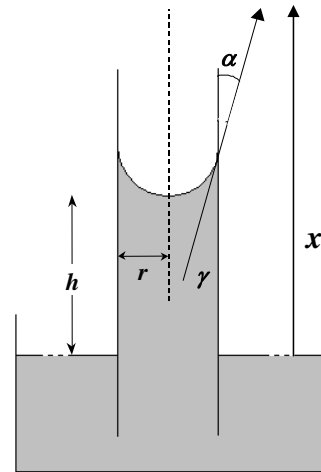
When a capillary tube is plunged in a liquid, the meniscus moves along the tube.

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 $r \nearrow$, $Q \nearrow$

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



Liquid water in porous media – capillarity

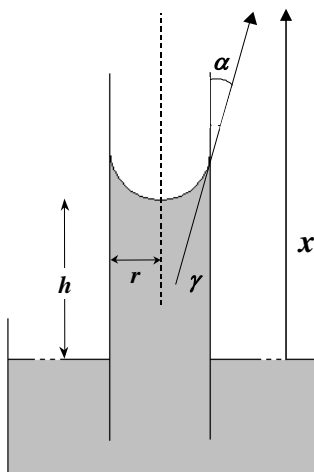
When a capillary tube is plunged in a liquid, the meniscus moves along the tube.

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

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

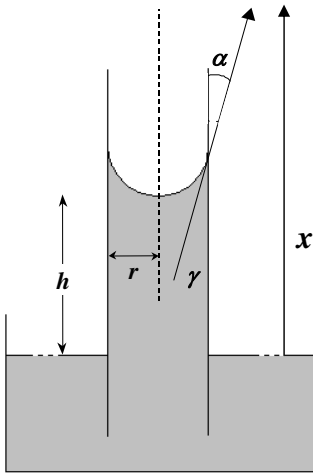
=> when $r \nearrow$, $h \searrow$

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





Calculation examples



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

$$\gamma = 0.0728 \text{ J/m}^2 \text{ at } 20^\circ\text{C}$$

$$\theta = 20^\circ (0.35 \text{ rad})$$

$$\rho = 1000 \text{ kg/m}^3$$

$$g = 9.8 \text{ m/s}^2$$

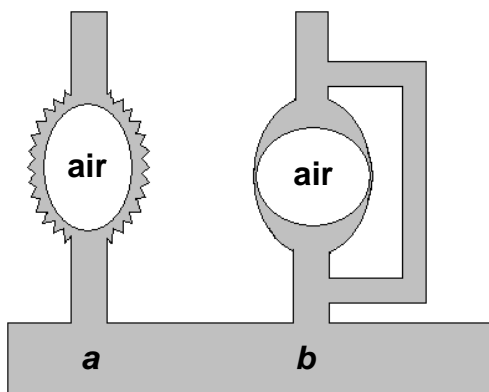
=> the height of the water column is given by:

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

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



Liquid water in porous media – capillarity

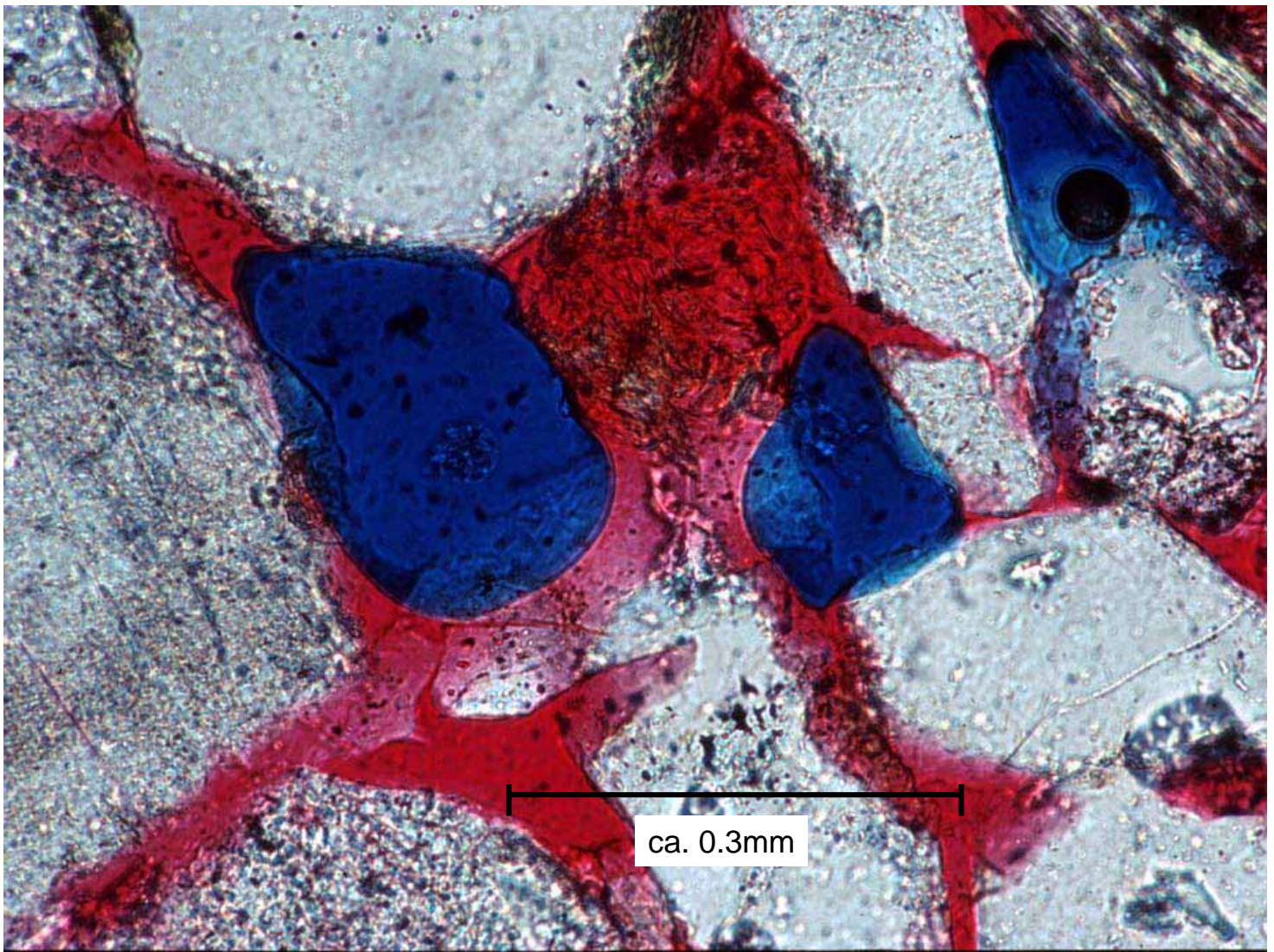


Less wetting fluid trapped by the more wetting fluid during an imbibition because of:

- a. rugosity
- b. derivation

The porosity of a rock (or a mortar, a concrete,...) is a complex system formed by interconnected wide and tiny pores. As a result, there are always many parallel ways for the capillary water during an **imbibition**.

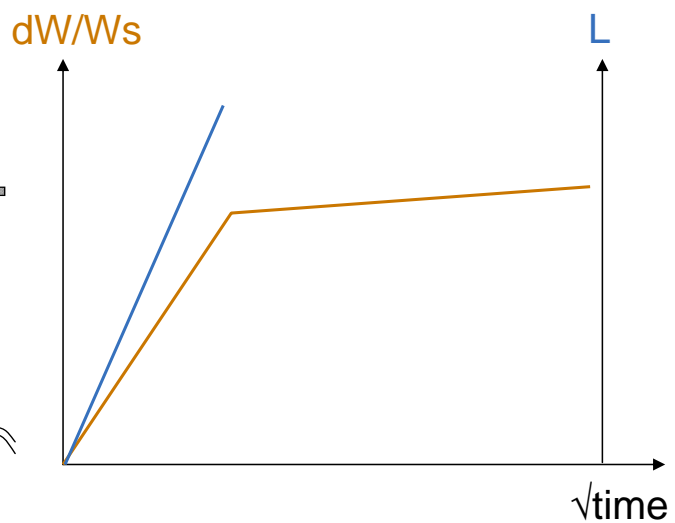
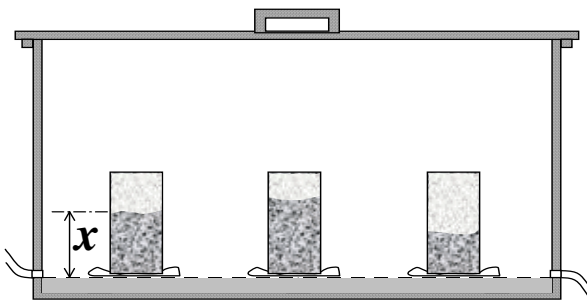
This great complexity allows the water (more wetting fluid) to trap air (less wetting fluid) in parts of the porosity.



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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



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 characterised by the capillary saturation coefficient or **Hirschwald coefficient (S%)**

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

P_i = porosity filled by water imbibition

M_i = sample weight after water imbibition

M_1, M_2, M_3 : see page 13



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** controlling the frost resistance of a stone

Estimation of frost resistance :

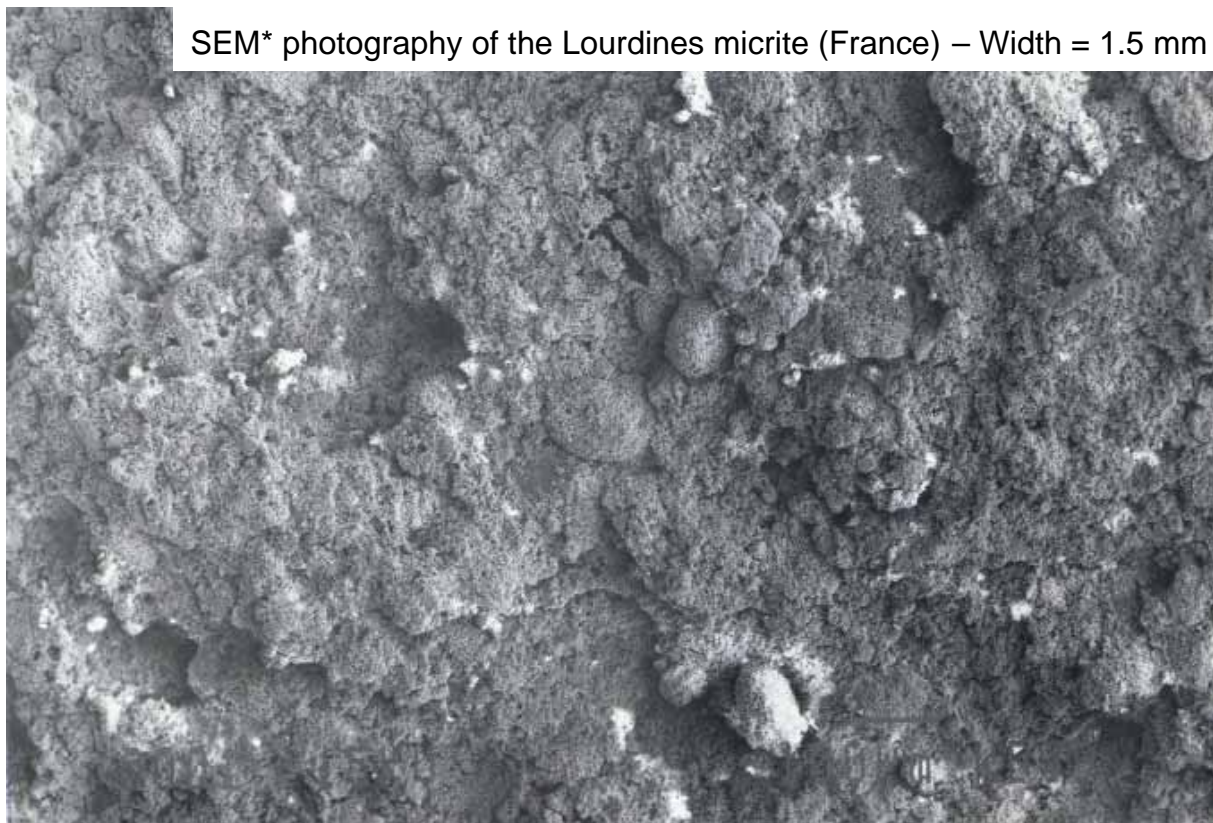
In a “simplistic” way, a stone is described as

- **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)



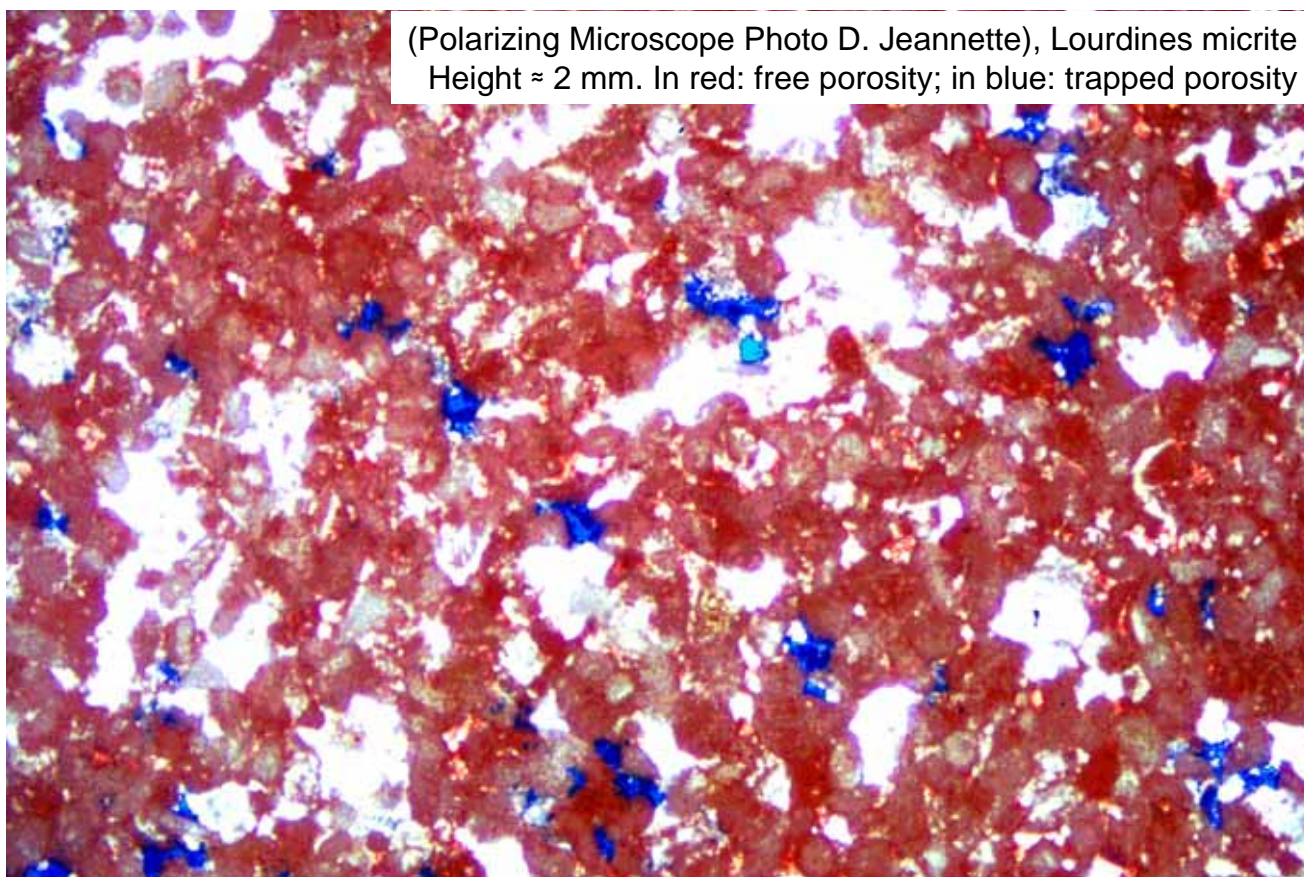
SEM* photograph of the Lourdines micrite (France) – Width = 1.5 mm

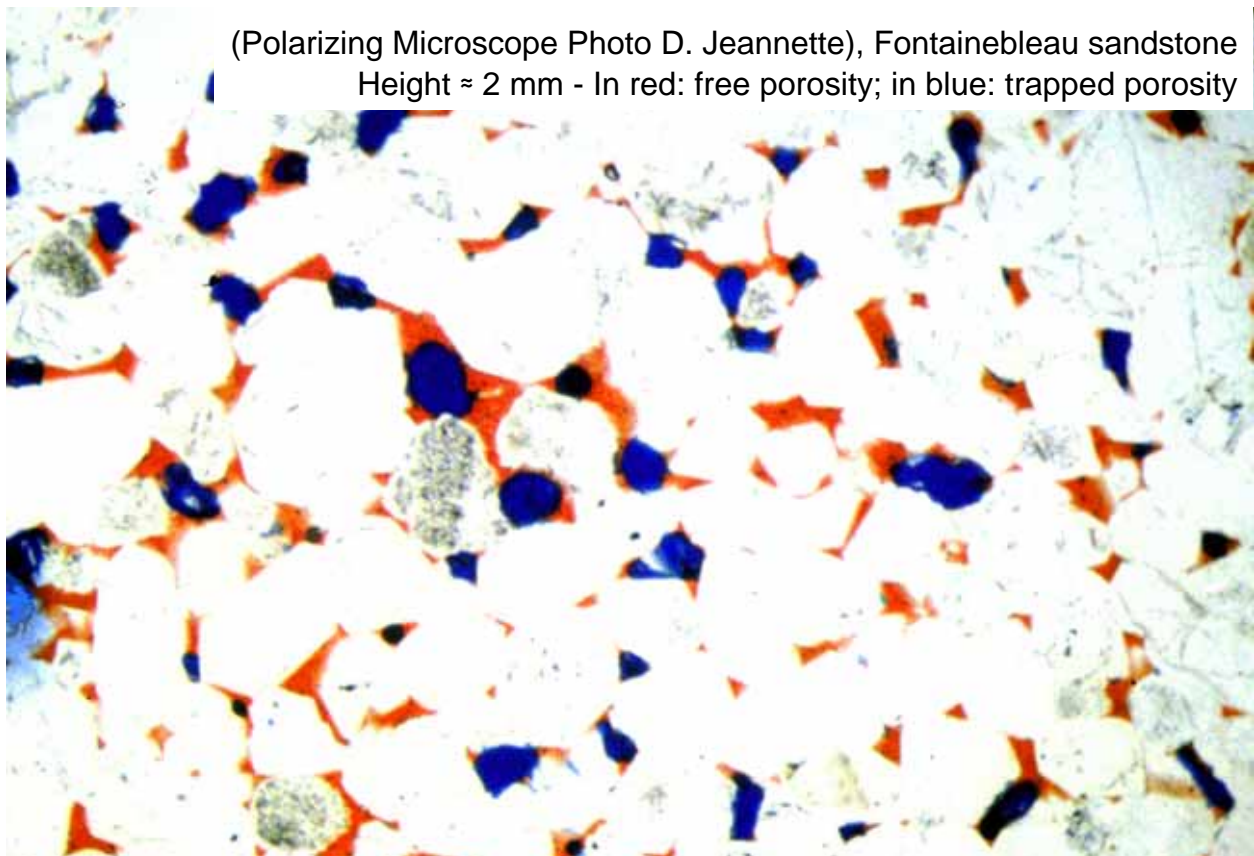
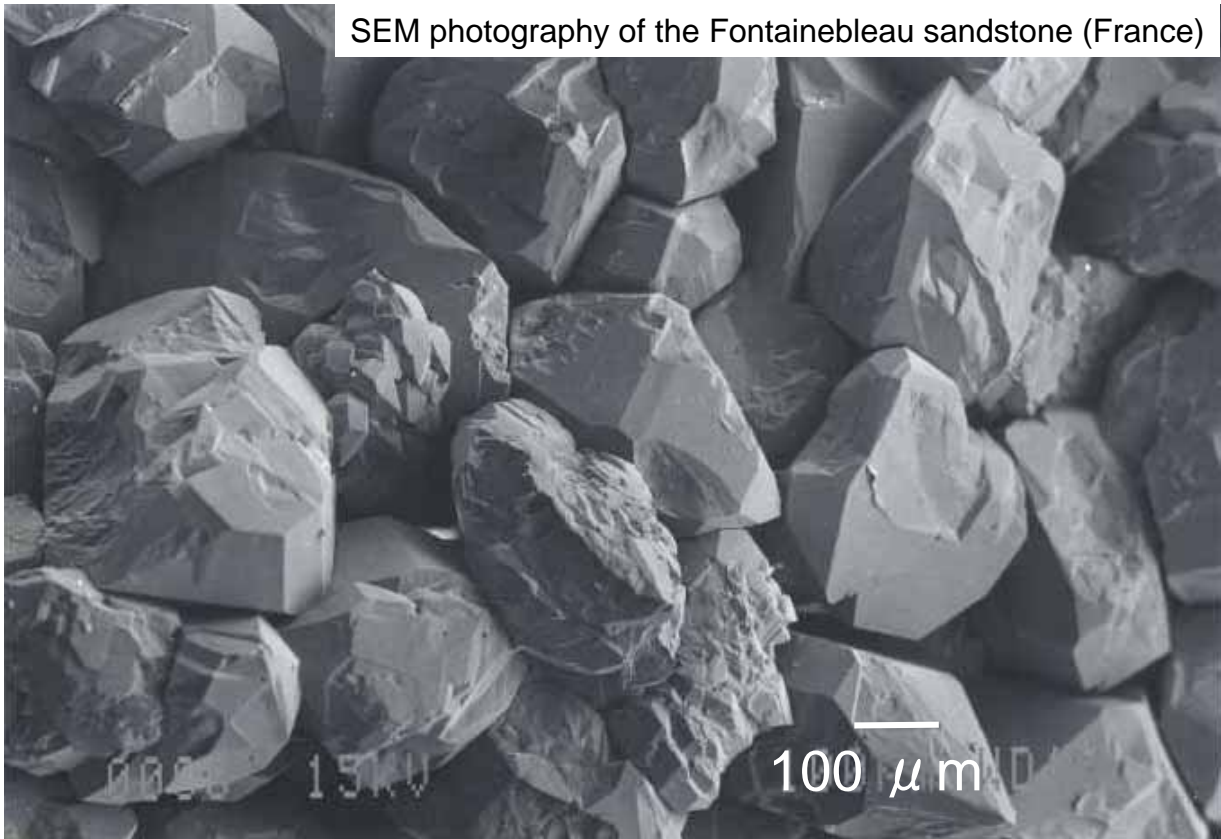


*SEM: Scanning Electron Microscope



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

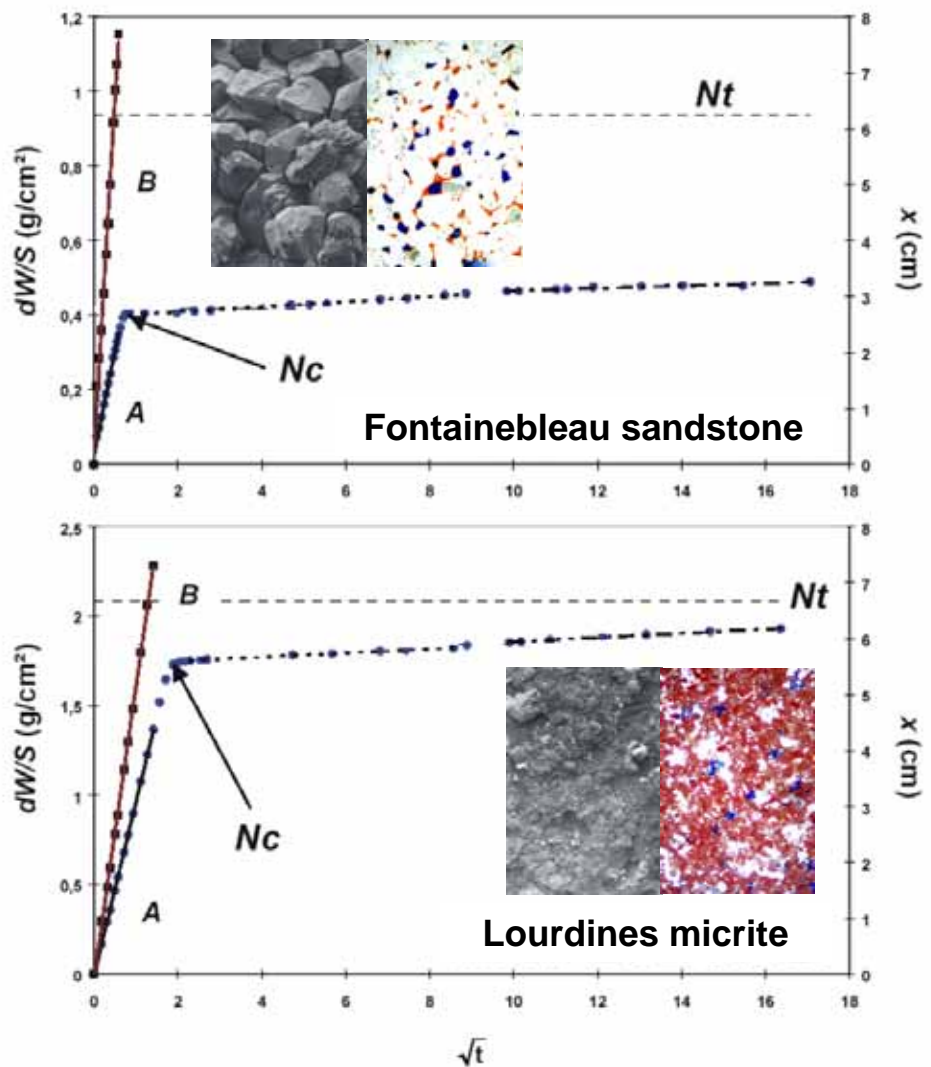






Capillary imbibition
(RH 100%, T 23° C)

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

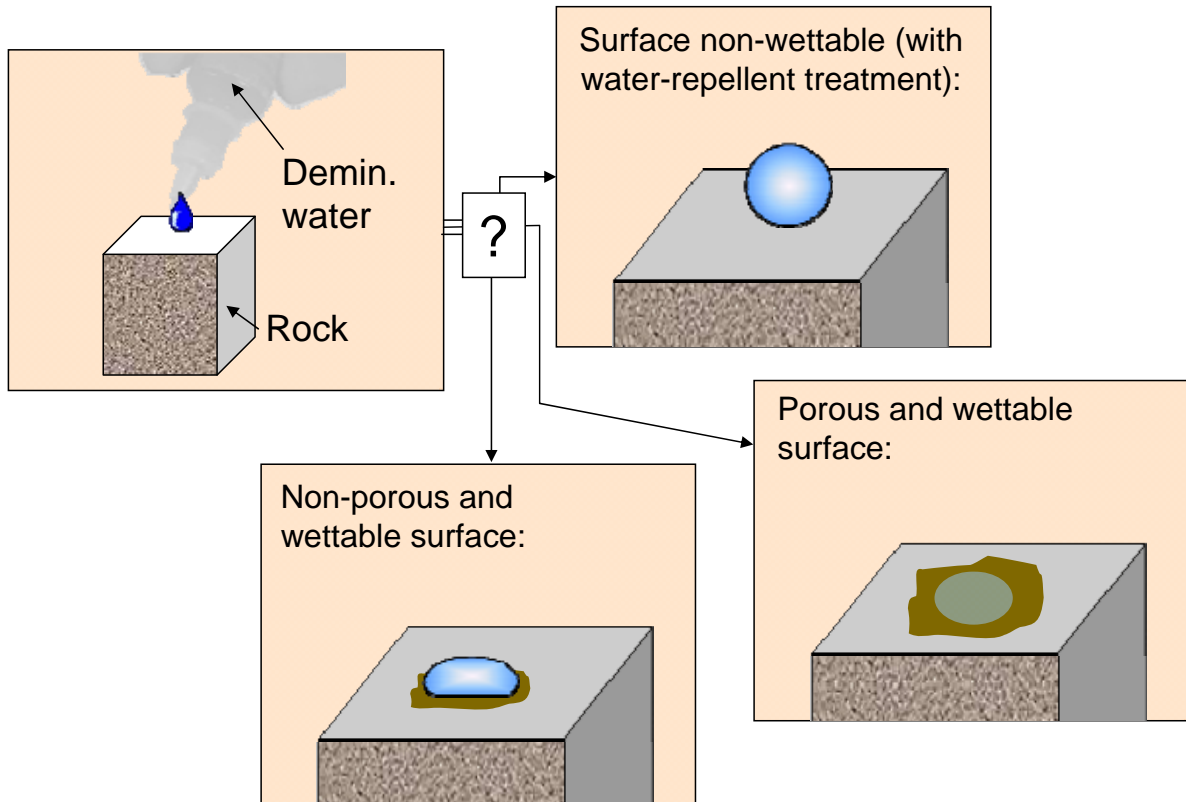


Liquid water in porous media – capillarity

- **In general**, the higher the dimension of the pores, the higher is the imbibition velocity
- if the linear capillarity is much more rapid than the massic one, the trapped porosity is high => even if water goes up high, the water saturation remains low
- the more varied the pore sizes, the bigger is the trapped porosity: media with very homogeneous porosity can reach high water saturation

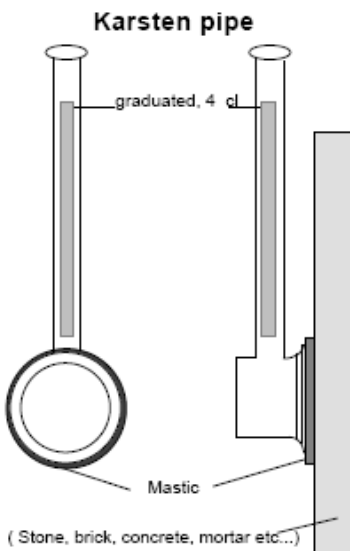


How to quickly estimate the wettability and the water absorption in the field: the drop of water- test



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>



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



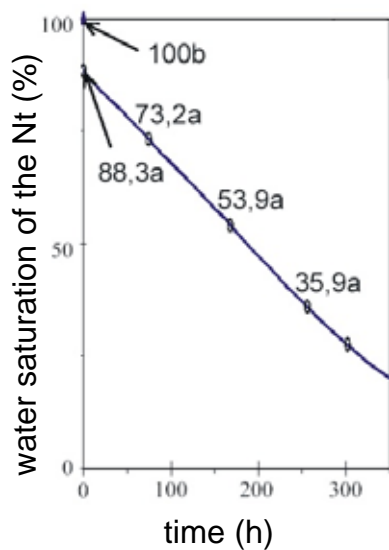
How to estimate the initial water absorption in the field: contact sponge



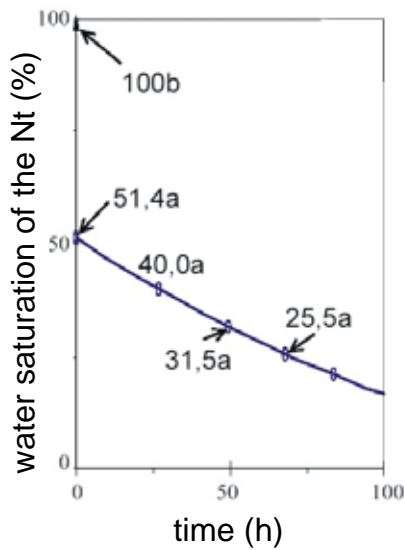
Marini P., Bellopede R., 2009- Bowing of marble slabs: Evolution and correlation with mechanical decay. Construction and Building Materials, Vol. 23, Issue 7, pp 2599–2605



Liquid water in porous media – drying



Lourdines micrite



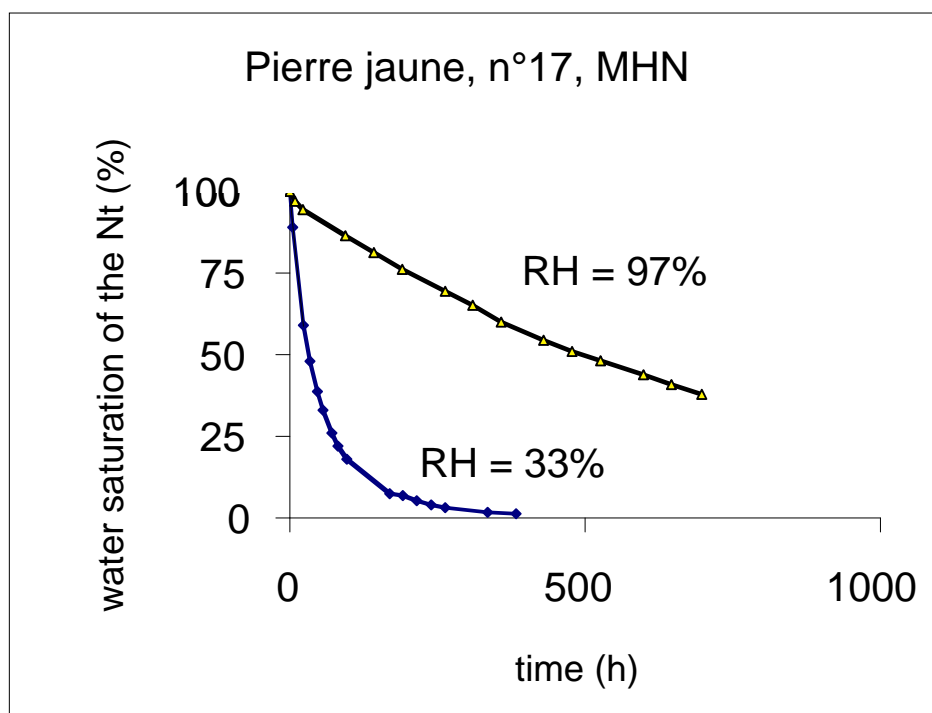
Fontainebleau sandstone

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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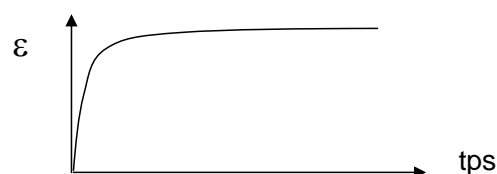


Liquid water in porous media – dilation (dilatation)

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:

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



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



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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