Physical methods of examining cultural property

NMR for Cultural Heritage

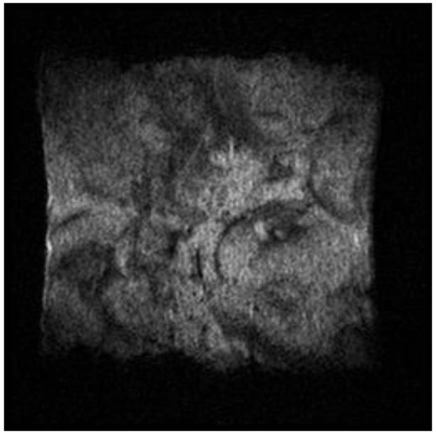
POROSITY
PORE-SIZE DISTRIBUTION

---

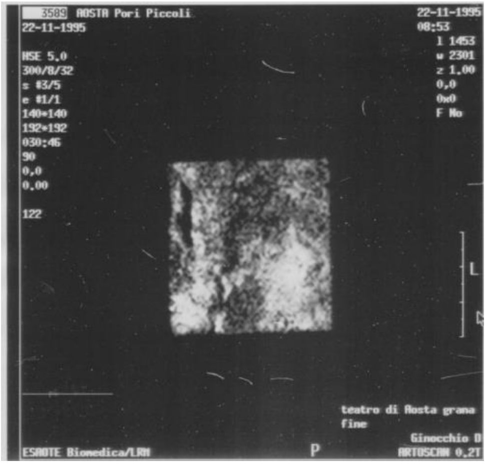
leonardo.brizi2@unibo.it

Examples of images of porous materials

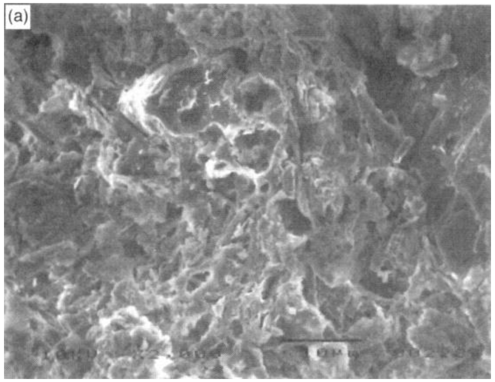
MRI- biocalcarenite

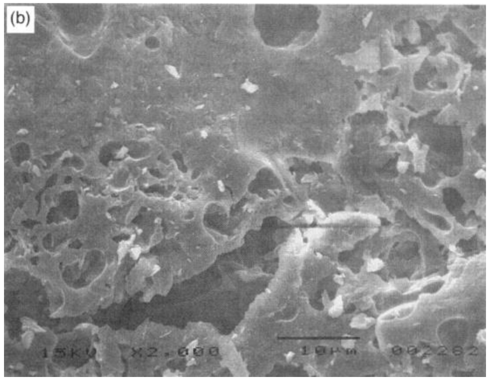


MRI- travertine



electron scanning microscopy (SEM) of ceramic material fired at 1100°C and at 1150°C





The porosity Φ of a material is defined as the ratio of the volume of the void spaces inside a sample of that material to the total volume of the sample (apparent volume)

$$\Phi = V_{\text{pore space}}/V_{\text{apparent}}$$

It is a number in the range 0-1, usually expressed as percent.

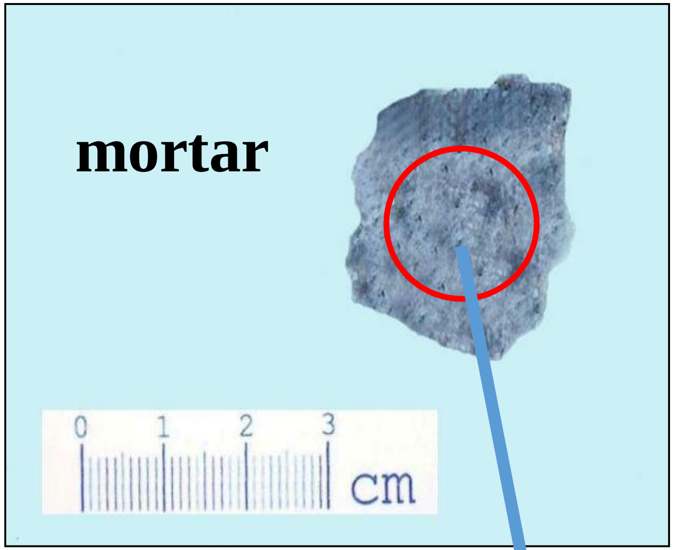
It is important to understand that:

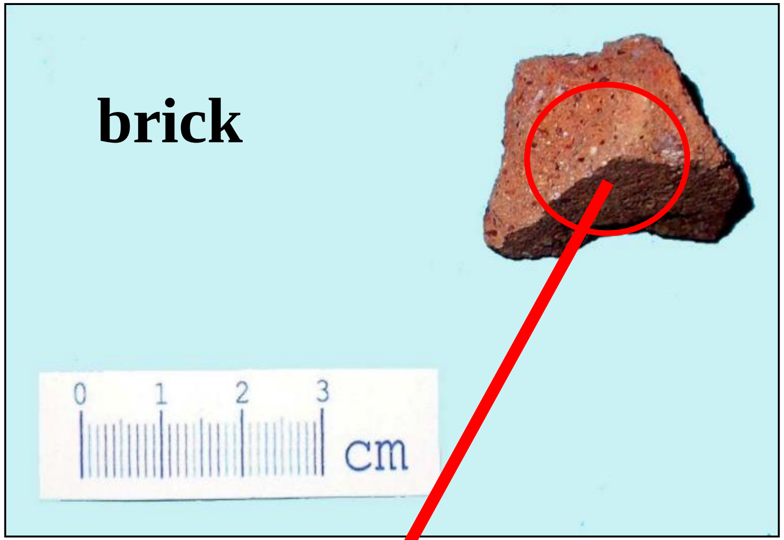
The value of the porosity is strictly dependent on the method used to measure it.

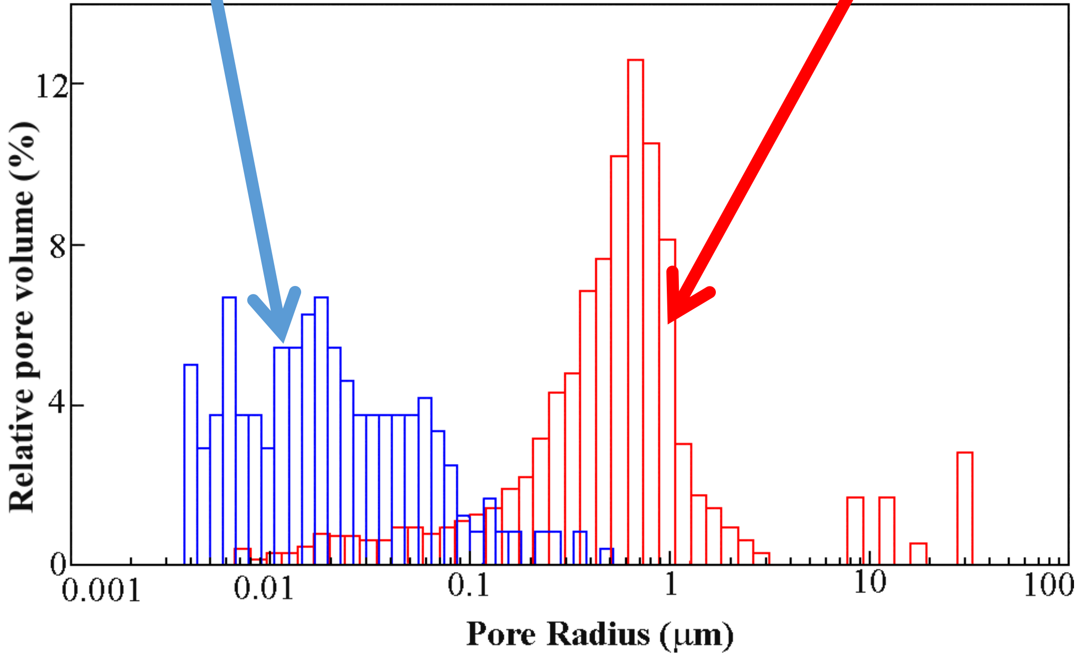
Usually the interconnected porosity is measured.

People tend to overlap the two concepts of porosity and pore-size distribution.

The concept of “pore” is ambiguous.







Pore size distribution

Concept of density

In general the density is defined as the ratio

ρ = Mass / Volume (usually given as g/cm^3)

In the case of a porous material, there are voids inside, so two different densities are defined:

ρ_a the apparent density (mass divided by the total volume occupied by the material, including voids)

ρ_r the real density (mass divided by the total volume occupied by the solid matrix, i.e. excluding voids)

therefore $\rho_a < \rho_r$

Let be

V_a the total volume of the sample (apparent volume)

V_r the volume of the solid matrix (real volume)

V_p the volume of the pore space,

m the mass of the sample,

ρ_a the apparent density,

ρ_r the real density,

(remember that the density is the ratio between mass and volume of a material)

$$\boxed{\Phi = \frac{V_p}{V_a}} = \frac{V_a - V_r}{V_a} = 1 - \frac{V_r}{V_a} = 1 - \frac{m}{V_a}\frac{V_r}{m}$$

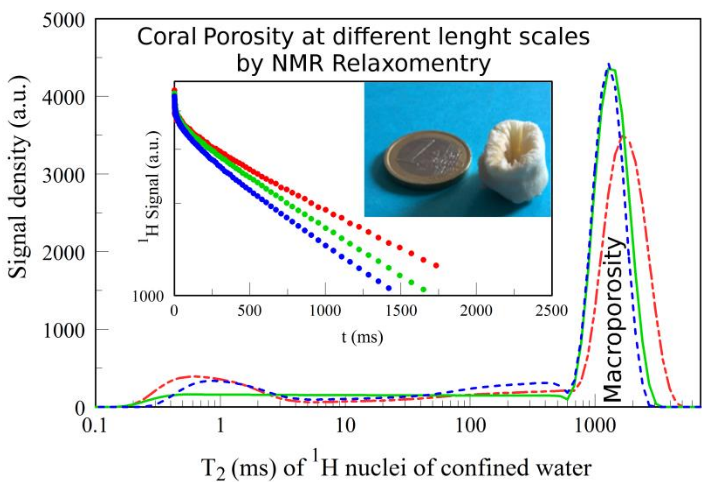
$$\boxed{\Phi = 1 - \frac{\rho_a}{\rho_r}}$$

From internet:

Peso dell'unità di volume g/cm3:

arenaria 1,8 . 2,7; argilla 2,0 . 2,2; basalto 2,7 . 3,2; beola 2,6 2,7; calcare compatto 2,4 . 2,7; calcare tenero 2,0 . 2,4; calcare tufaceo 1,1 . 2,0; ceppo 2,2 . 2,3; diorite 2,7 - 3,0; dolomia 2,3 2,9; gneiss 2,5 . 2,7; granito 2,3 . 2,6; marmo saccaroide 2,7 . 2,8; pomice 0,5 . 1,1; porfido 2,1 . 2,7; scisti 2-3,1; serpentino 2,5 . 2,7; sienite 2,7 . 3,0; trachite 2,4 . 2,7; travertino 2,2 . 2,5; tufo calcareo 1,2 . 1,9; tufo vulcanico 1,1 . 1,8.

We have to observe that there are two errors. First of all “peso” (weight) is not correct, because weight is a force, not a mass. Moreover, it is not specified if those densities are real or apparent. Both, apparent and real densities are reported. The apparent densities are the smallest values.



In the coral skeletons we found:

Apparent density about 1.9 g/cm^3

Real density about 2.5 g/cm^3

Mercury Injection Porometry (MIP)

MIP is the standard technique to measure both porosity and pore-size distribution. Hg does not wet the rock surface. The contact angle is > 90°, therefore it cannot enter spontaneously the pore space. The only way is to force it to enter by applying a pressure in order to overcame the capillary pressure. The capillary pressure to be applied is larger if the pore is smaller. The pressure to be applied is given by the law:

$$P = \frac{2\tau \cos \vartheta}{r}$$

Washburn Equation

where:

P = applied pressure (N/m^2)

τ = interfacial tension (N/m)

θ = contact angle

r = “pore-radius”

Remember that:

1 atmosphere = 760 mm Hg = 101325 N/m^2 (Pa)$\cong$ 0.1 MPa=

=1013 mbar=1.0332 kg/cm^2

The distribution of the pore radius can be very wide, from micropores to ultramacropores.

This is the classification of pores depending on the size of their radius.

Summary of the most frequently used pore size classifications.

Classification	Specified types of pores, d [nm]		
	Macro-	Meso-	Micro-
IUPAC	> 50[4, 16]	$2 \div 50$[4, 16]	< 2[4]; ($0.4 \div 2$[16])
Dubinin [5]	$> 200 \div 400$	$200 \div 400 > d > 3 \div 3.2$	$< 1.2 \div 1.4$
Cheremskoj [6]	> 2000	-	$2000 > d > 200$
Kodikara [9]	$10^4 \div 10^6$	-	$10^3 \div 3 \times 10^4$

By applying the Washburn law,

$$P = \frac{2\tau \cos \vartheta}{r}$$

using the values $\tau = 48.0\ 10^{-2}$ N/m, $\theta = 141.3°$, if the pressure is given in atmospheres, one gets: P ≅ 75000/*r* or

r=75000/P (Å)

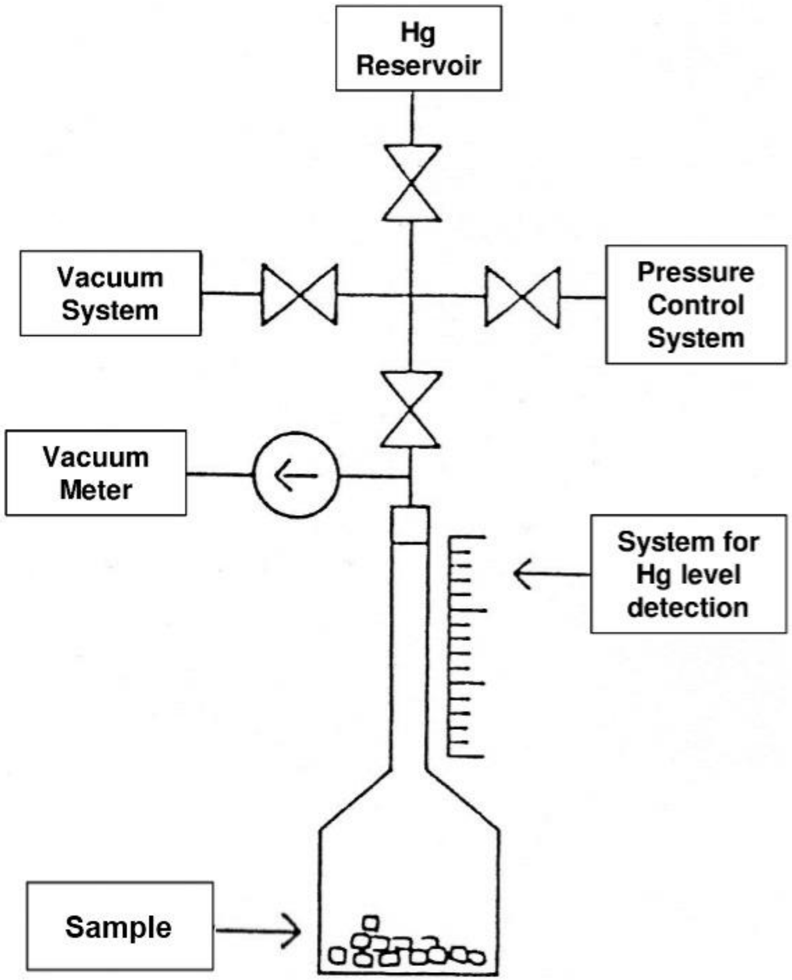
If P=1 atm *r*=75000 Å = 7.5 μm

If P=2000 atm *r*=37Å = 3.7 nm, *that is the minimum value that one can measure by MIP.*

This technique is highly invasive, not only because is based on the intrusion of mercury, that is toxic, but also because high pressures have to be applied with the risk of breaking the samples.

The measure of porosity and pore size distribution is made by the mercury injection porosimeter, as described below.

Mercury Injection Porosimetry method



The sample is dried and weighted at laboratory temperature. Then it is placed in the sample-holder. By means of the vacuum pump, a pressure as low as 10^{-2} mm Hg is reached.

That condition is maintained for 15 minutes to evacuate the sample. Then, Hg is injected and the system is connected to the pressure pump. The pressure is gradually increased step by step. At each step, the level of Hg is registered.

The level of Hg allows one to compute the volume of Hg entered inside the pore-space at each incremental step of pressure.

In this way it is possible to compute not only the total volume of the pore-space and the porosity (if the apparent volume is known), but also the volume occupied by each class of pores invaded by Hg at each step of pressure, by applying the Washburn law.

Thanks to the inverse proportionality between pressure and radius, the radius of each class of pores is computed.

The correspondence between volume of each class of pores and the radius of that class of pores allows one to built the pore-size distribution.

It is clear that in this model the pore is assumed to have a cylindrical shape, so that the radius of the pore is the "radius of the throats connecting the pores" instead of the "pore-body" radius.

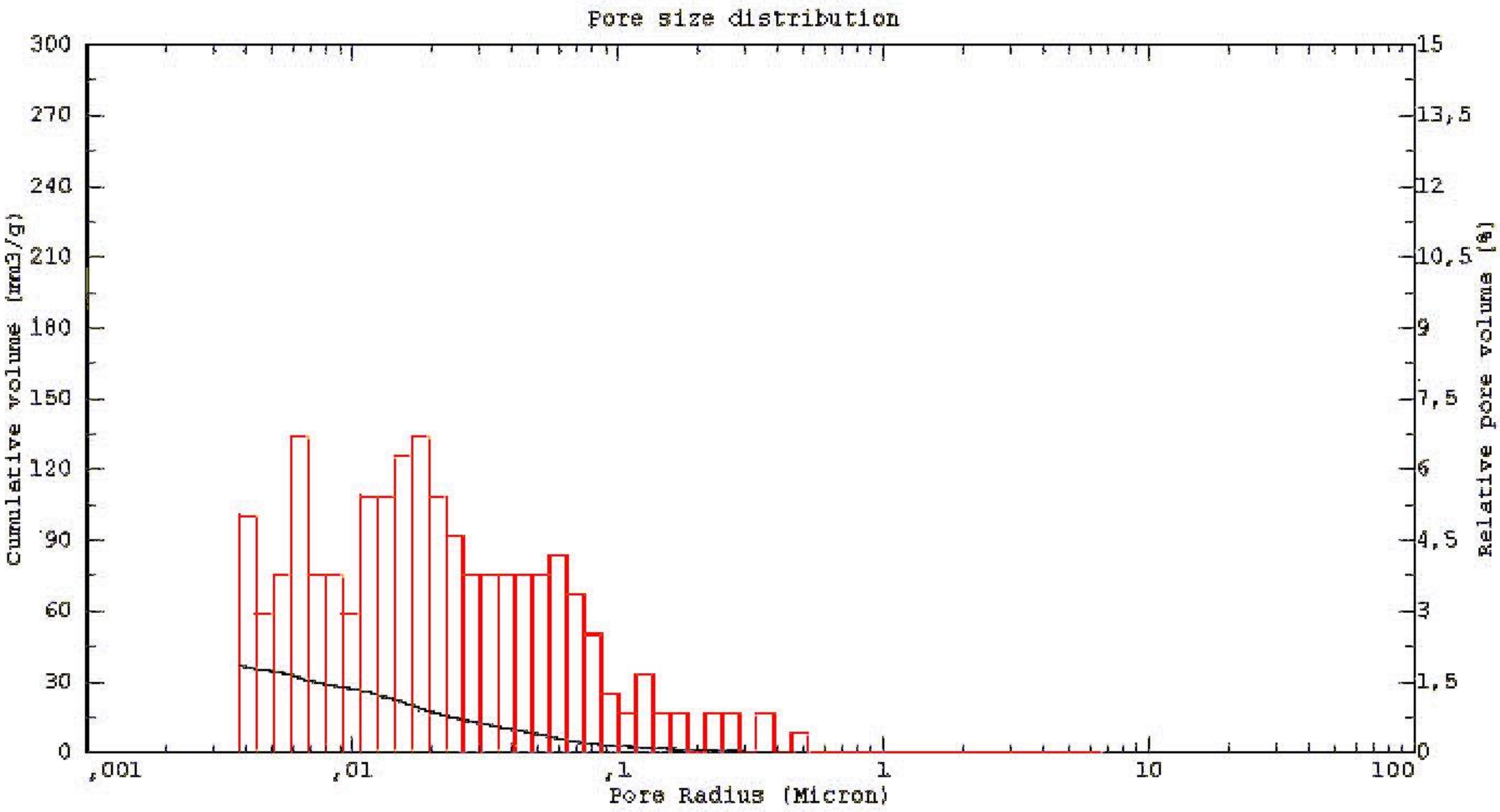
That must to be taken in mind when interpreting MIP results and comparing with other methods, such as porosimetry by NMR.

Greek-Roman Theater of Taormina

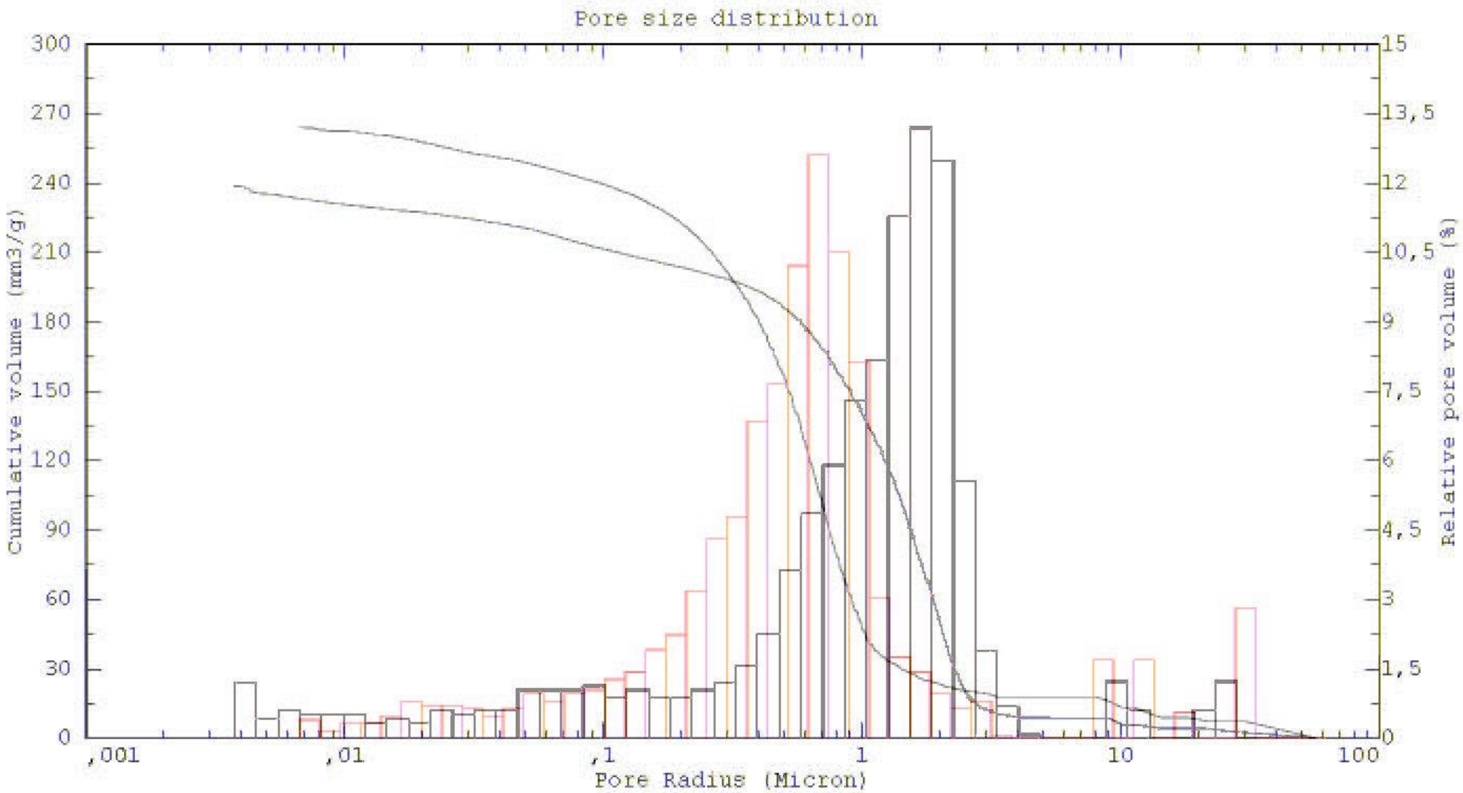
in collaboration with

Dip. Fisica e Tecnologie Relative dell'Università di Palermo

Hg Injection result of a sample of mortar

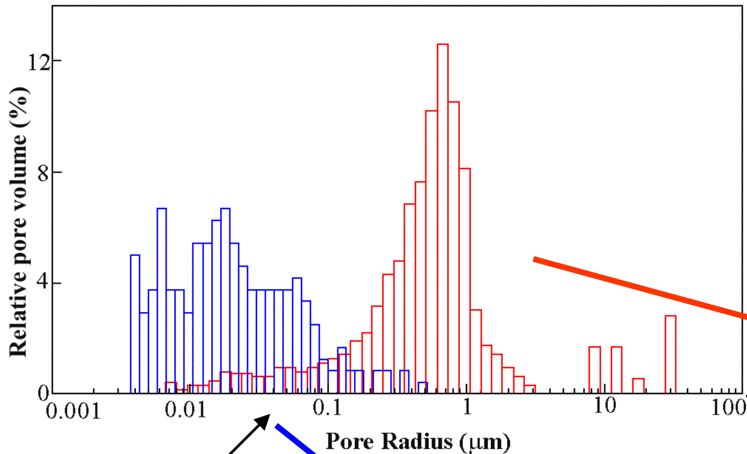


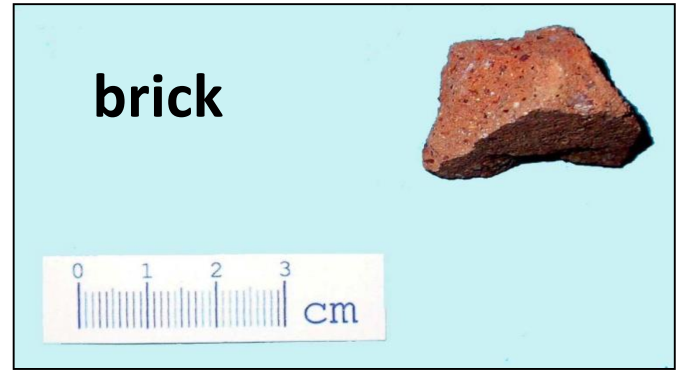
Hg Injection results of two samples of bricks



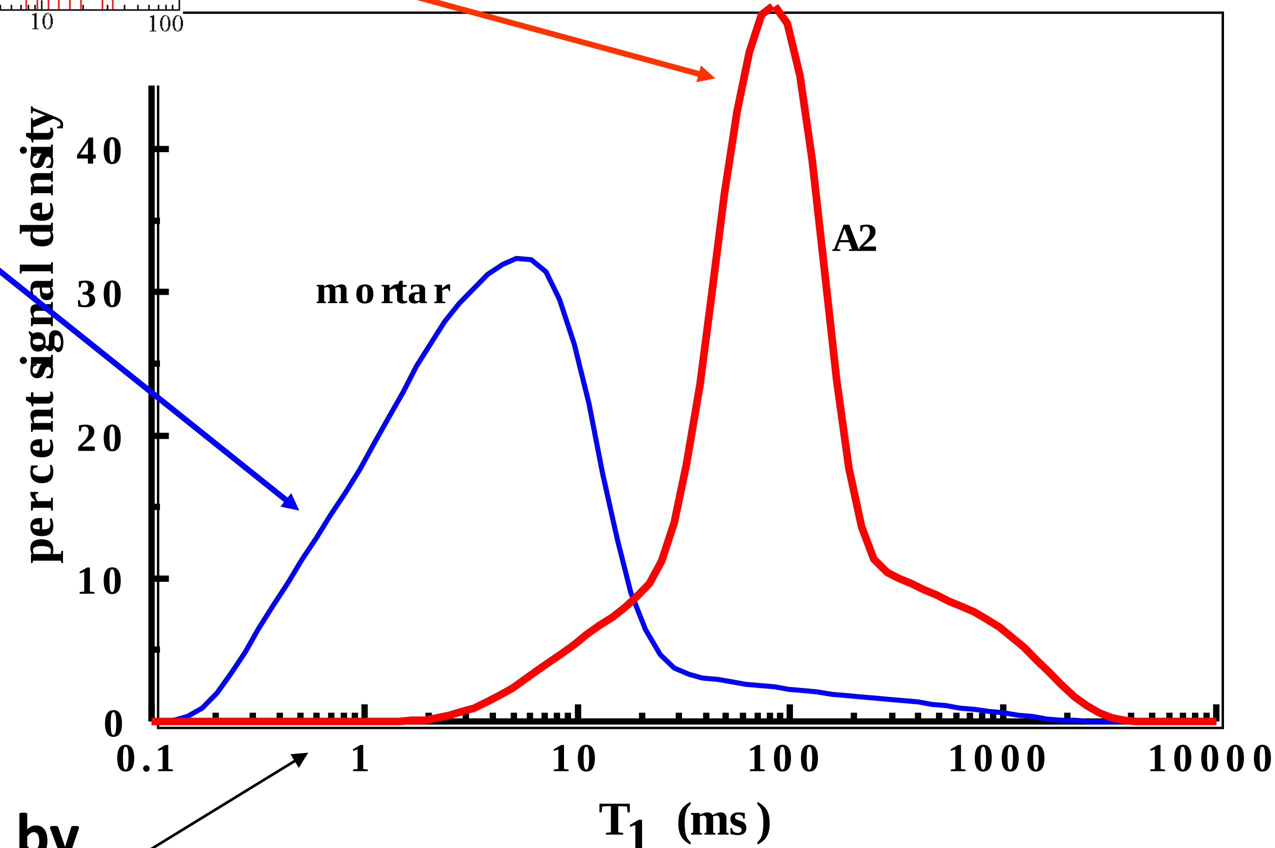
Notes: the logarithmic scale on the x axis;
the radius is the pore-throat radius, not the pore radius;
the computed values for *r* depend on the values
of interfacial tension and contact angle,
assumed to be constant all over the sample.

MPI *vs* NMR Relaxometry





Pore channel size by MIP



Pore body size by Relaxometry

Art'05, Lecce, May 2005