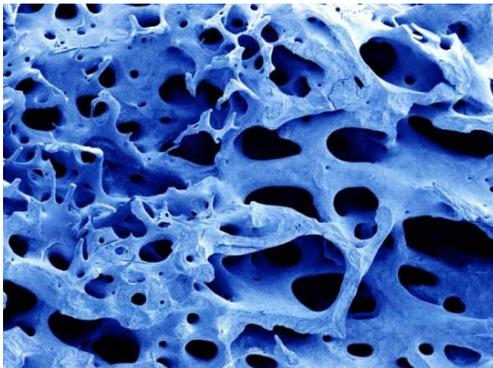


SUMMER SCHOOL

CERAMIC & GLASS SCIENCE & TECHNOLOGY,
APPLICATION TO BIO CERAMICS & BIOGLASSES

Processing of bioceramic scaffolds: state of the art and current trends



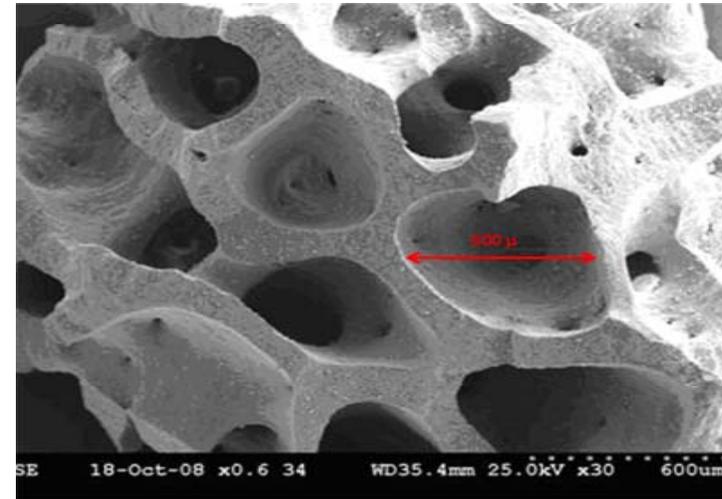
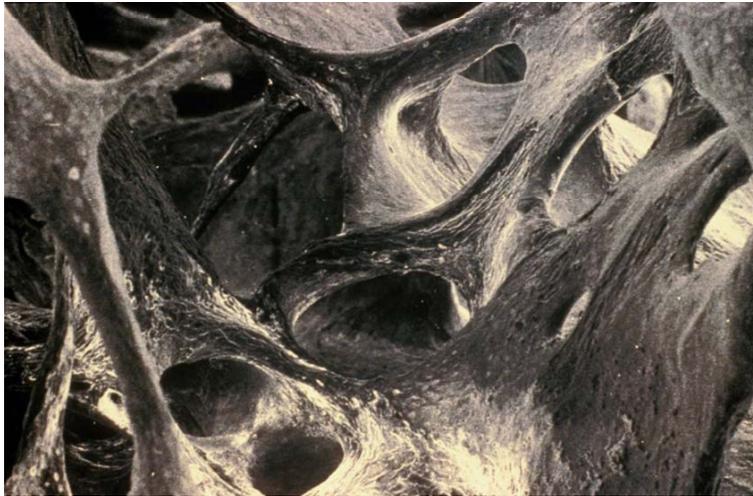
A.Leriche

Université
de Valenciennes
et du Hainaut-Cambrésis

LMCPA - UVHC
Pôle universitaire de Maubeuge
Boulevard Charles de Gaulle
59600 Maubeuge FRANCE

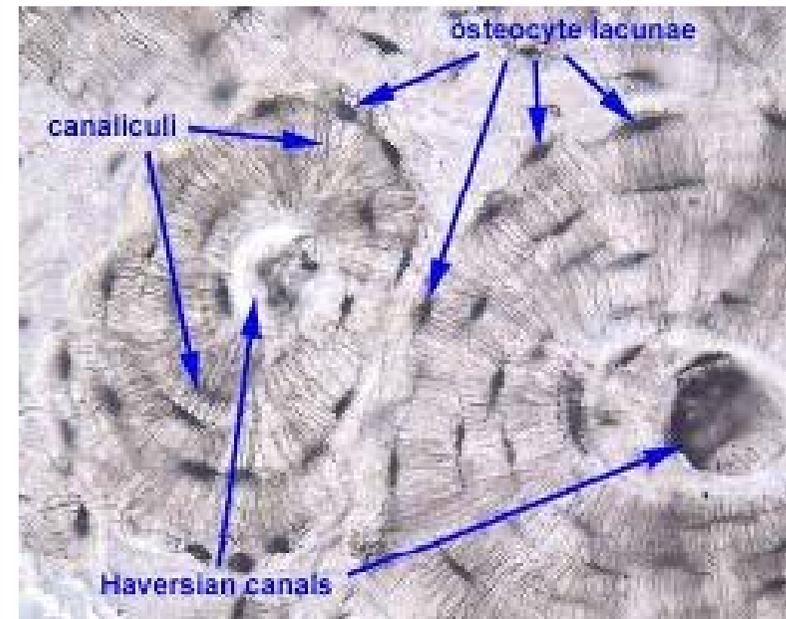
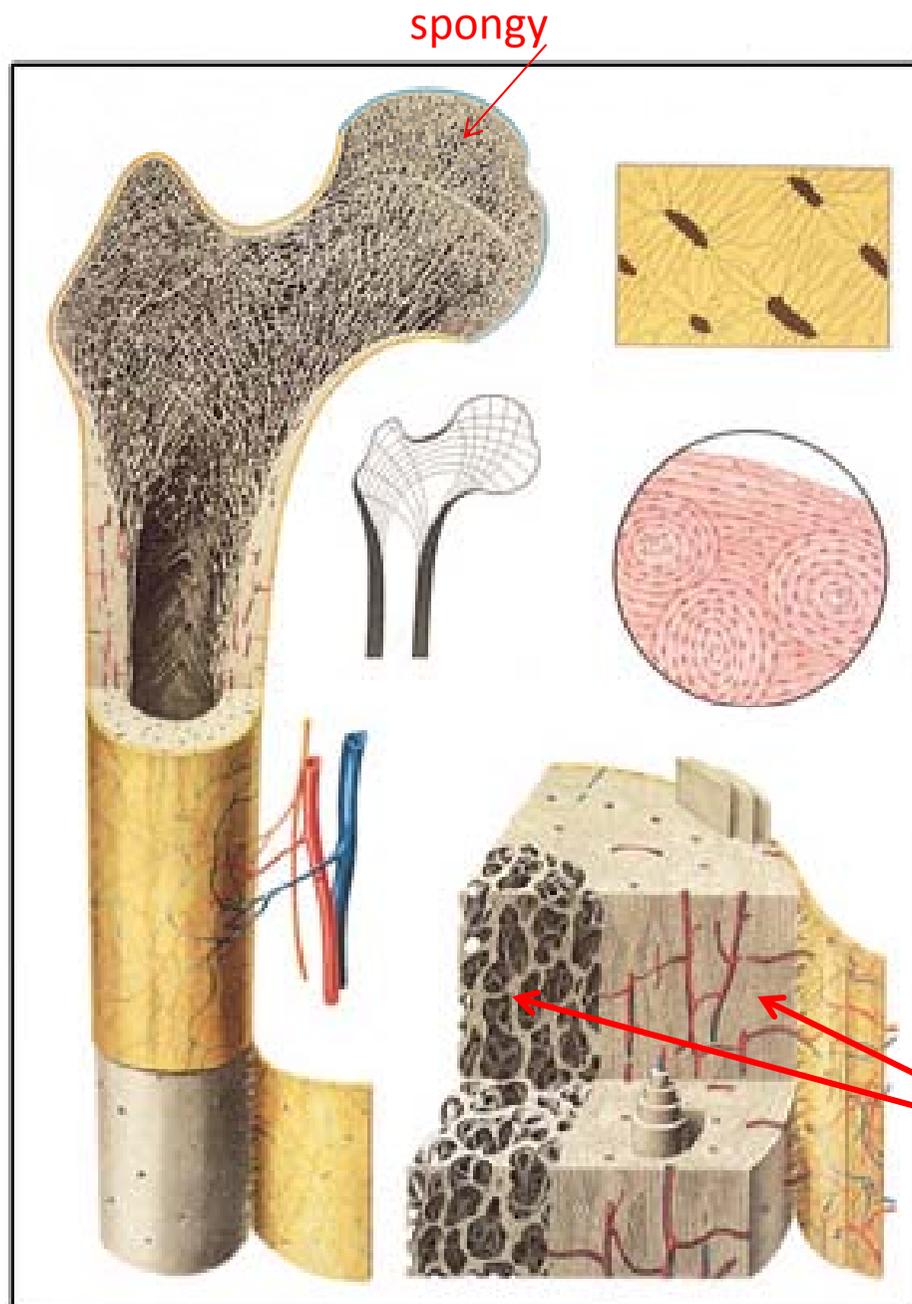


Processing of bioceramic scaffolds: state of the art and current trends



How to mimic natural bone for substitute processing?

Bone structure



Natural composite of collagen and mineral.

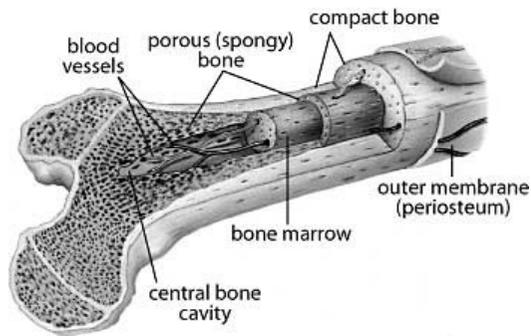
2 types of bone:

- cortical with dense structure →

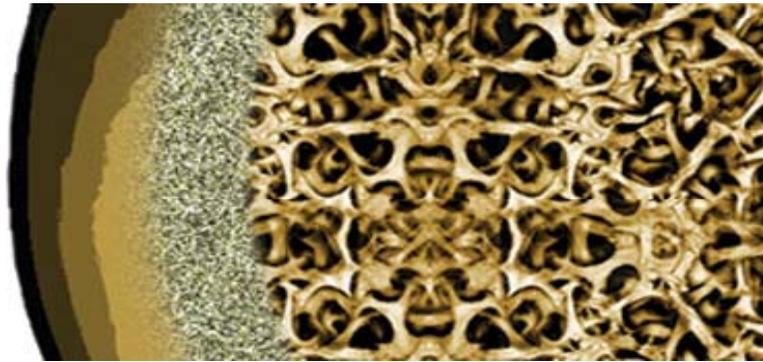
compact bone

- cancellous or trabecular bone with high porosity → **spongy bone**

How to mimic natural bone?



Carlyn Iverson



**Compact
bone**

Spongy bone

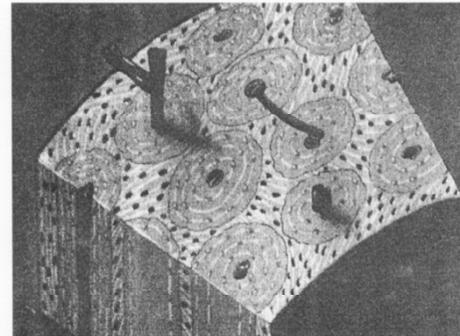


Porosity

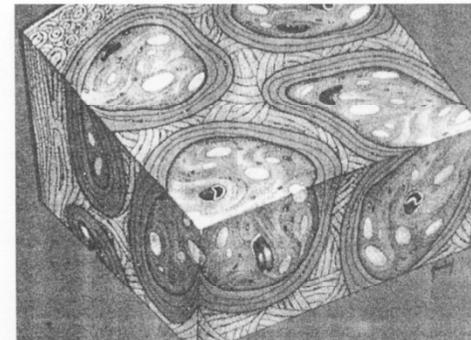
Φ : 190-230 μm

V : 65%

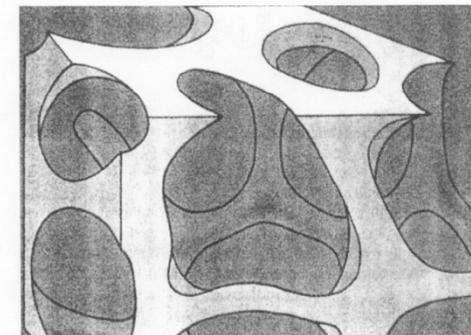
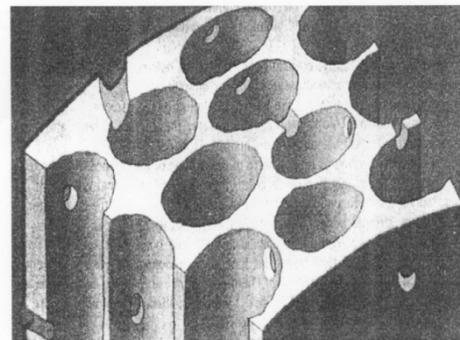
$\sigma_c = 80-200 \text{ MPa}$



Os compact



Os spongieux



Porosity

Φ : 500-600 μm

V : 80%

$\sigma_c = \text{a few tenths MPa}$

How to mimic natural bone?

Criteria for an ideal scaffold for bone regeneration:

- 1 - Is made from a biocompatible material,
- 2- acts as template for tissue growth in 3 dimensions,
- 3- has an interconnected macro-porous network with diameters > 100 μ m for cell penetration, tissue ingrowth and vascularisation, and nutrient delivery to the centre.
- 4- bonds to the host tissue
- 5- exhibits a surface texture favorable to cell adhesion
- 6- resorbs at the same rate as the tissue is repaired
- 7- is made from processing technique that can produce irregular shapes to match that of the defect in the bone of the patient,
- 8- exhibits mechanical properties sufficient to be able to regenerate tissue in bone in load bearing sites,
- 9- has the potential to be commercially producible to the required ISO or FDA standards.

J.R.Jones, L.L.Hench *Current opinion in solid state and materials science* 7 (2003) 301-307

High level of porosity: value higher than 60 vol%

→ cellular ceramics

Various technologies

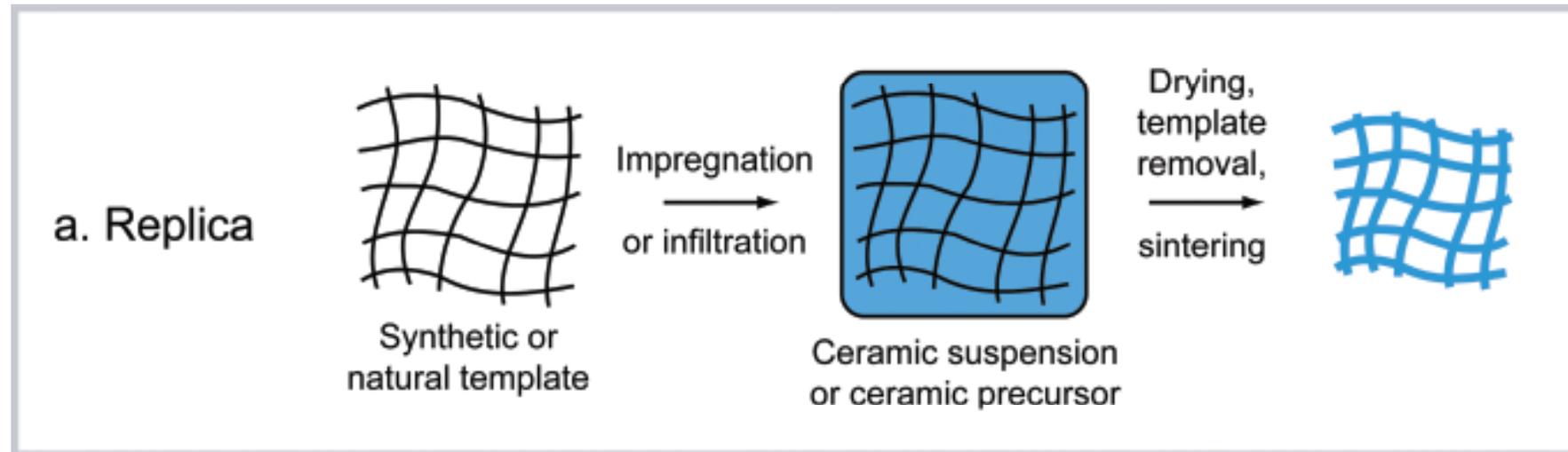
1: Replica

2: Sacrificial templates

3: Direct foaming

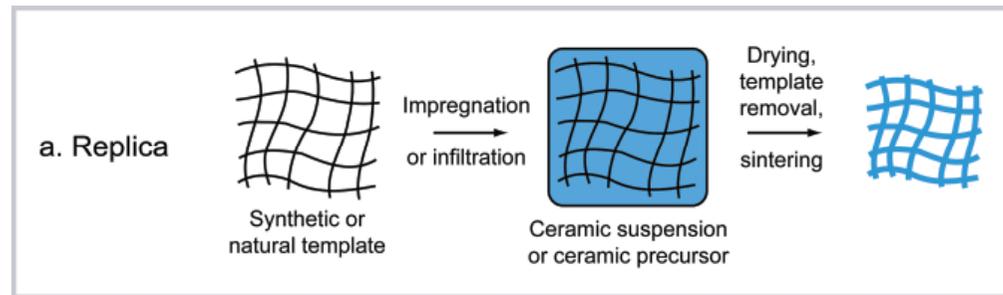
4: 3D-Additive Manufacturing

1. Replica techniques



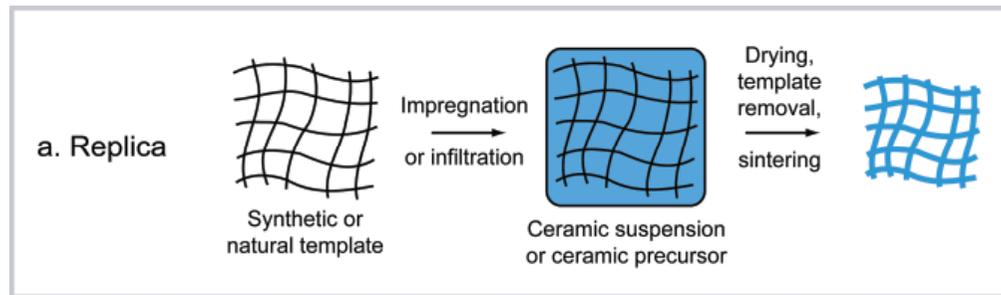
Replica technique is based on the impregnation of a cellular structure with a ceramic slurry in order to produce a macroporous ceramic exhibiting the same morphology as the original porous material.

Many **synthetic** or **natural** cellular structures can be used as templates.

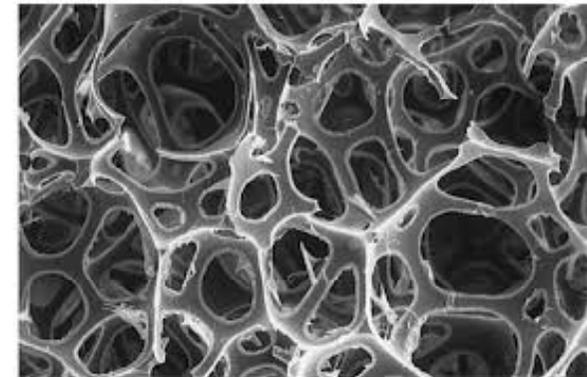
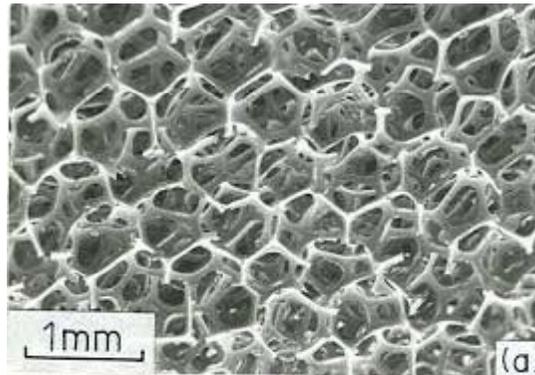
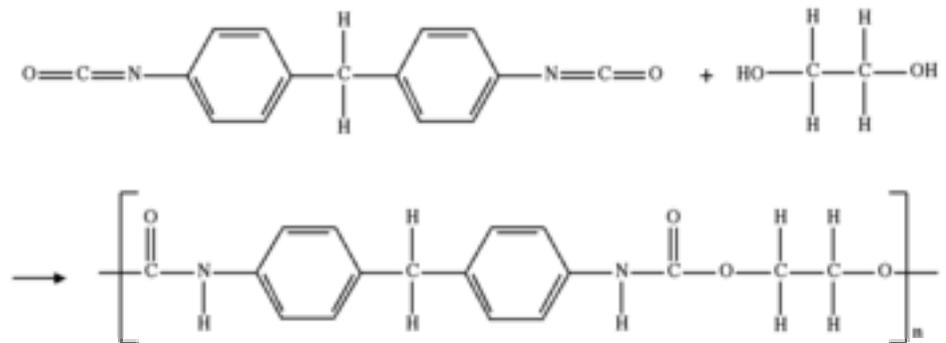


Synthetic templates:

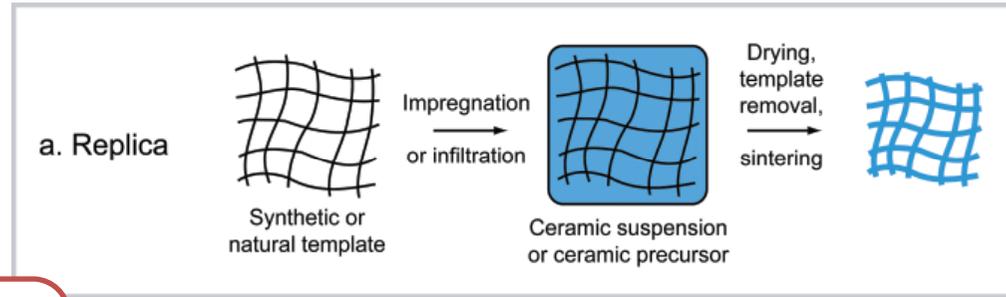
- **Highly porous polymeric sponge (typically polyurethane)** is initially soaked into a ceramic suspension until the internal pores are filled in with ceramic material.
- The impregnated sponge is then passed through rollers to remove the excess suspension and enable the formation of a thin ceramic coating over the struts of the original cellular structure.
- The ceramic coated polymeric template is dried and pyrolysed and finally the ceramic coating is sintered.



Polyurethane foam: currently called carbamate, product of reaction between isocyanate and alcohol



Replica from sponge



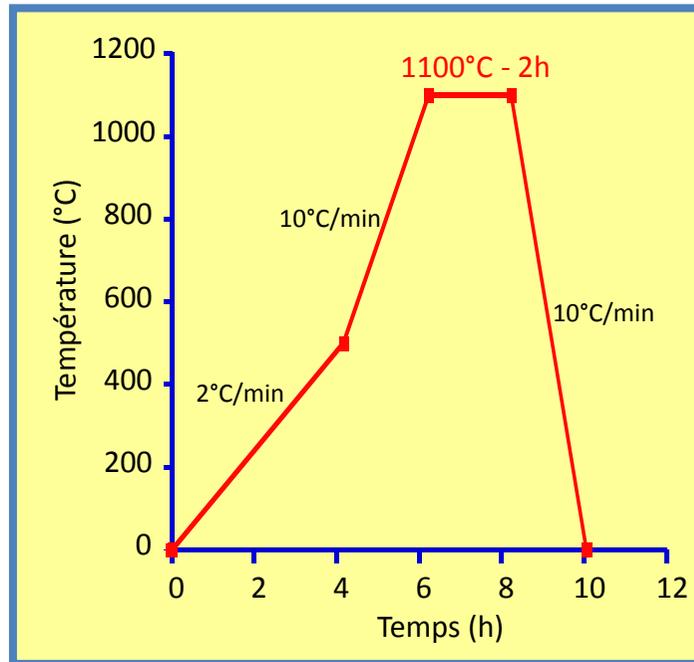
Impregnation of the foam by calcium phosphate slurry



Pyrolysis and sintering

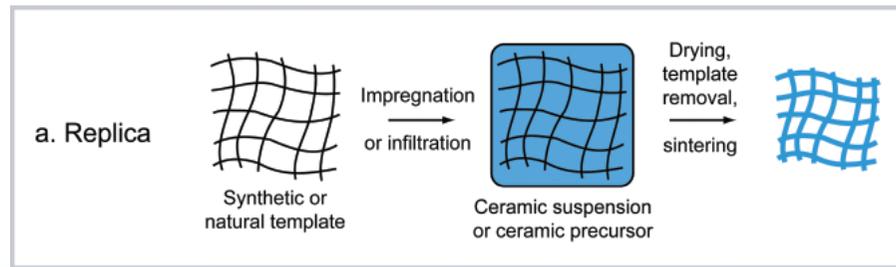


Sintered scaffold

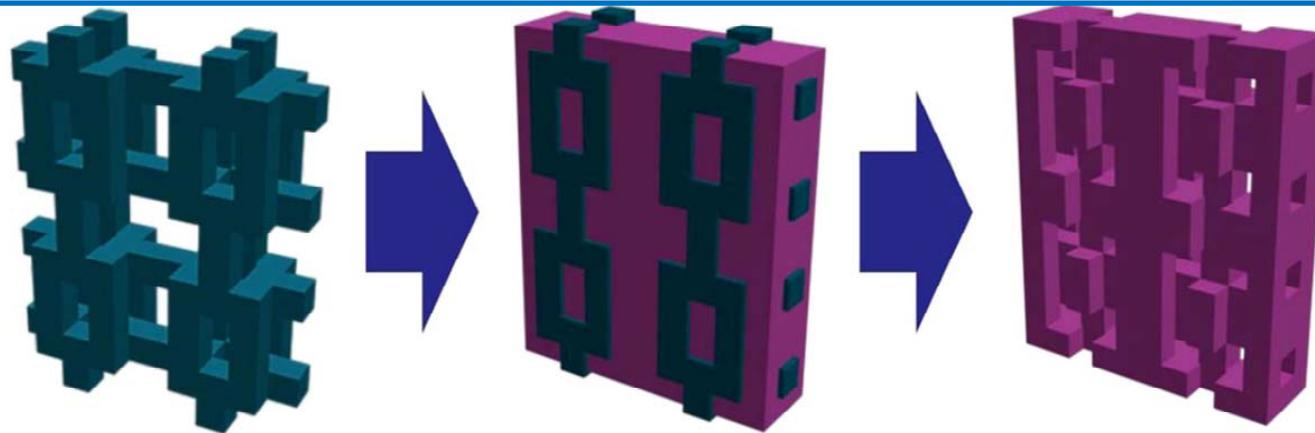


► Macropore and interconnection sizes depend on foam characteristics and on CaP slurry properties

*F. Lelièvre & A. Destainville ,
Thèses, Limoges, 1992 & 2005*

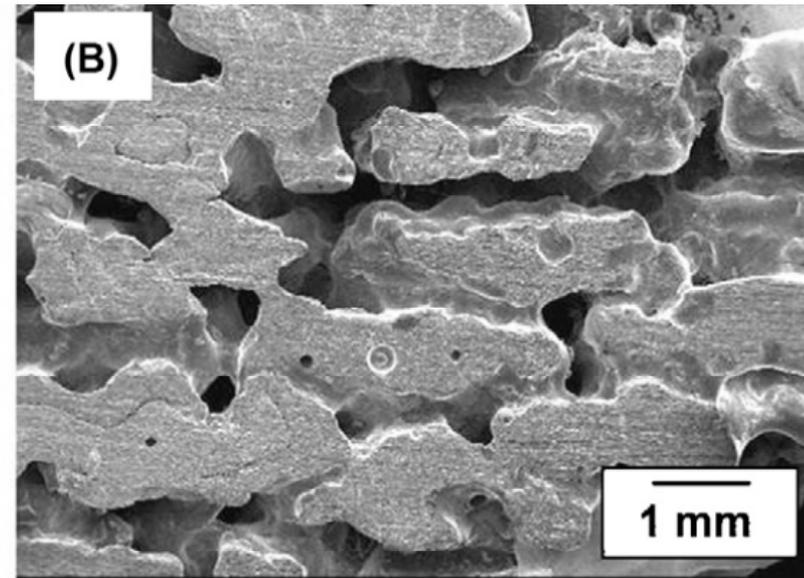
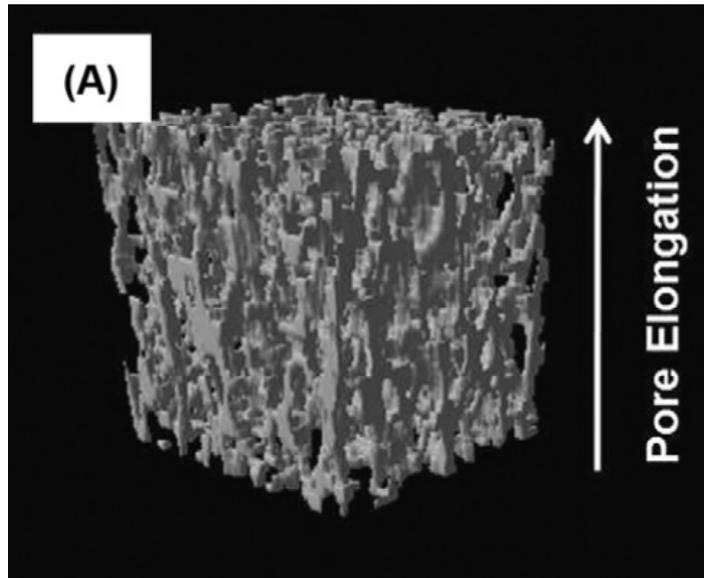
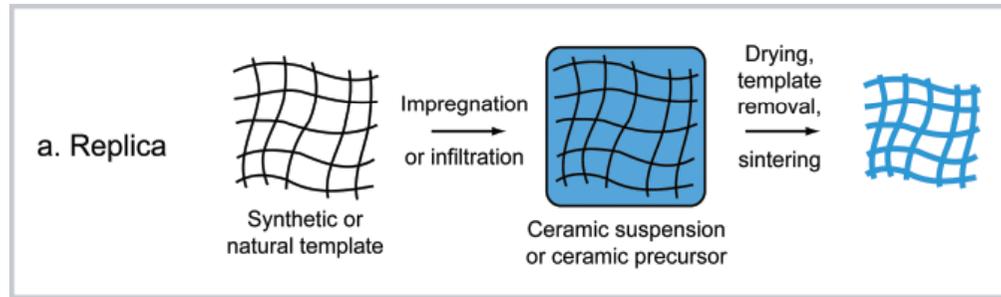


Synthetic templates: polyurethane sponges coated with a carbon slurry: The carbon coating layer would result in the formation of large pores suitable for bone ingrowth.



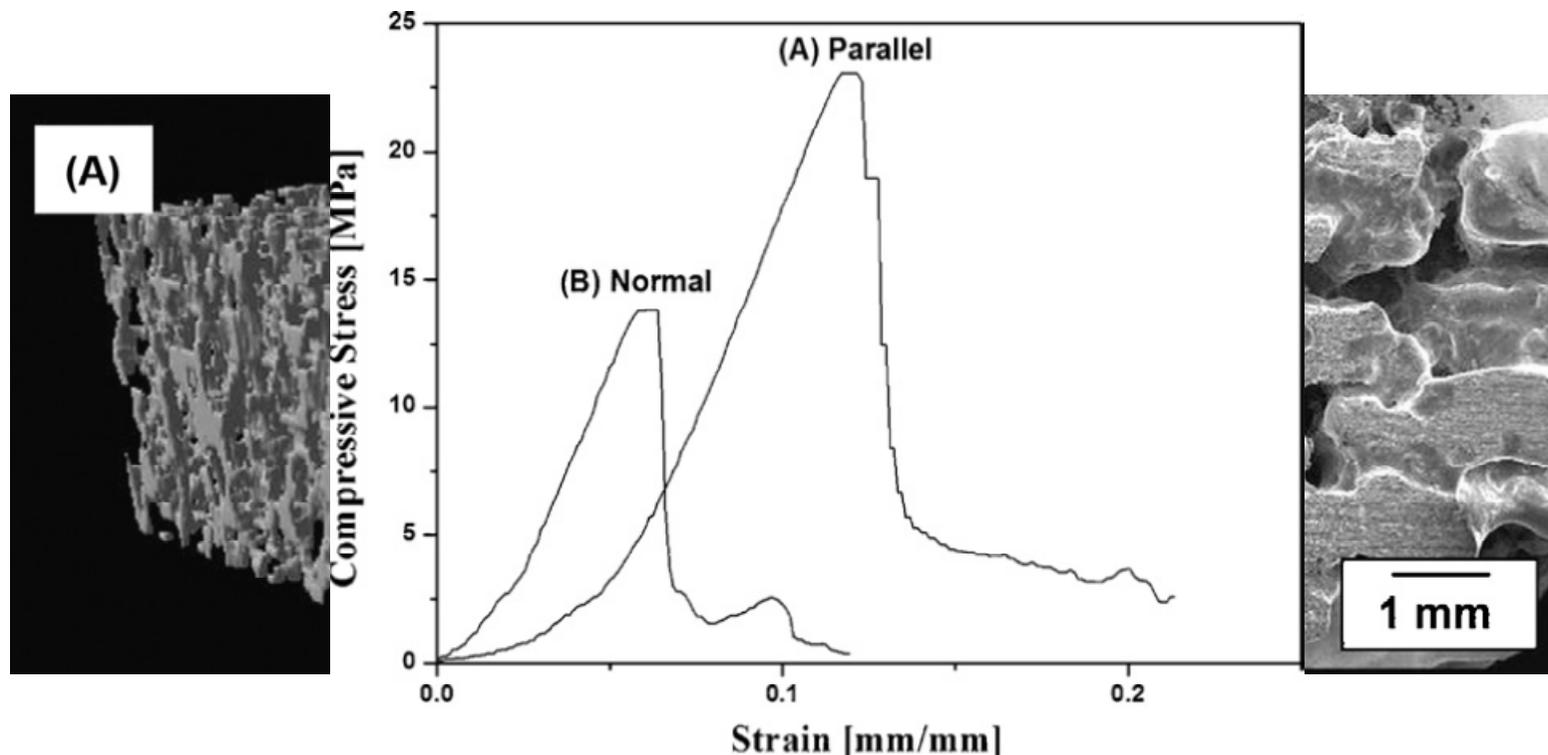
Porous CaP ceramics with highly elongated pores

- 1°) Coating of stretched polymeric sponge with carbon slurry/ drying
- 2°) Casting a CaP/camphene slurry into carbon-coated polymeric templates, followed by freeze-drying to remove the solid camphene.
- 3°) Heat-treatment at 800 °C for 3 h to remove the template and at 1250 C for 3 h to sinter the CaP walls.

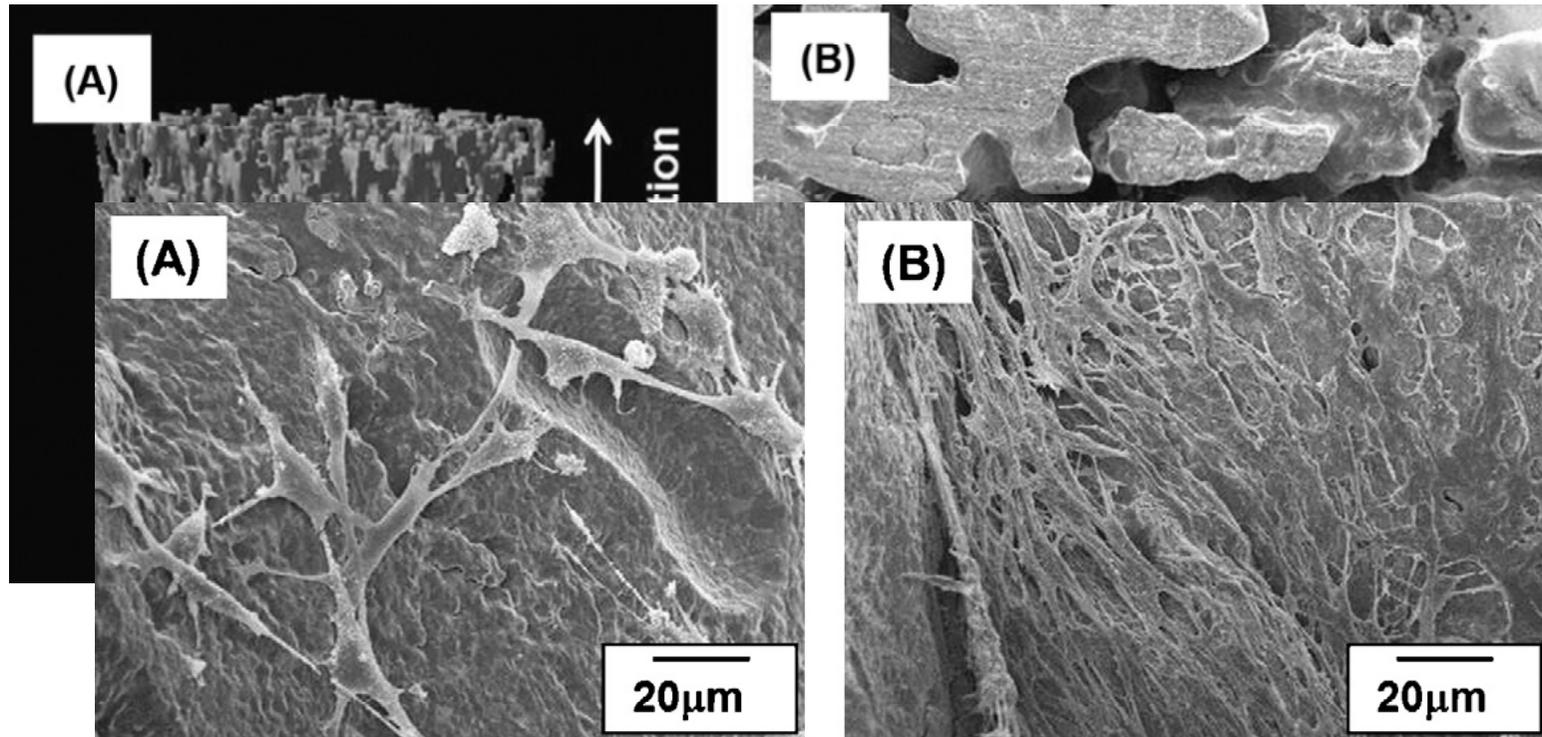


► Creation of highly elongated pores with a size of $512 \pm 96 \mu\text{m}$, surrounded by dense CaP walls with a thickness of $841 \pm 239 \mu\text{m}$.

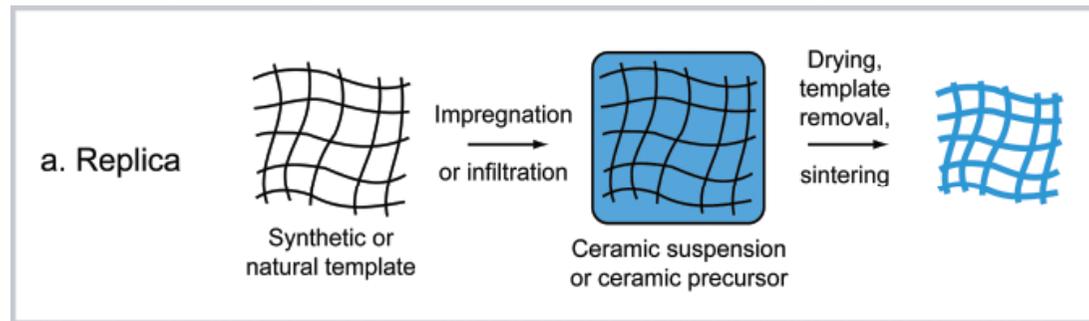
Ji-Hyun Sung *Ceramics International* 38 (2012)



The compressive strength (21 MPa) of the sample tested parallel to the direction of pore elongation was much higher than that (12 MPa) of the sample tested normal to the direction of pore elongation $\rightarrow \sigma_c$ can be improved significantly by creating highly elongated pores, which can be achieved using stretched polymeric sponges with a carbon coating layer as a template.



The cells appeared to grow and spread actively on the sample surface after culturing for 1 day Fig A. Furthermore, the surface was covered almost completely with the cells after culturing for 3 days Fig B.



Natural templates: Coral CaCO_3

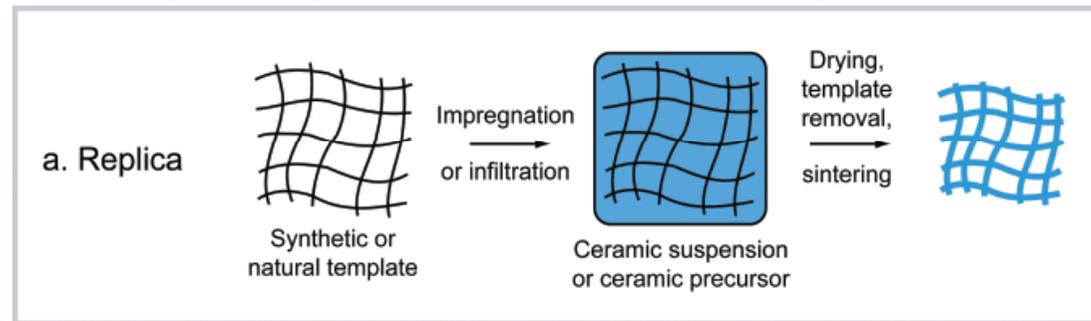
The coral exhibit the presence of both calcite and aragonite phases and presents a porous structure which depends on coral species:

- Acropora (20% porosity) near to compact bone
- Porites (50% porosity) near to spongy bone

The pore size varies between 150 and 500 microns versus species.

→ **coral can be directly used as bone substitute**

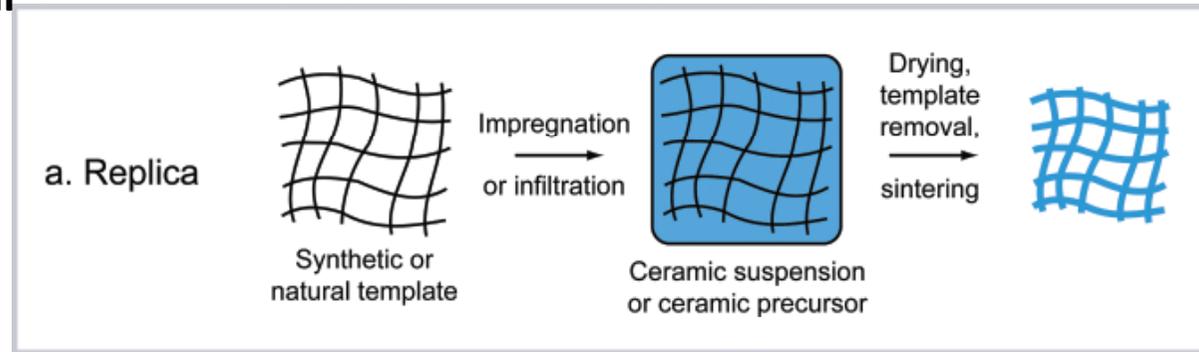




Natural templates: Coral

First method: 1970 White et al. lost-wax method named "replamineform"

- The coral is first impregnated with wax under vacuum to obtain a negative form of the cellular form.
- After hardening the wax, the calcium carbonate of the coralline skeleton is leached out using a strong acidic solution.
- The wax model is impregnated with a ceramic suspension and subsequently removed by pyrolysis.

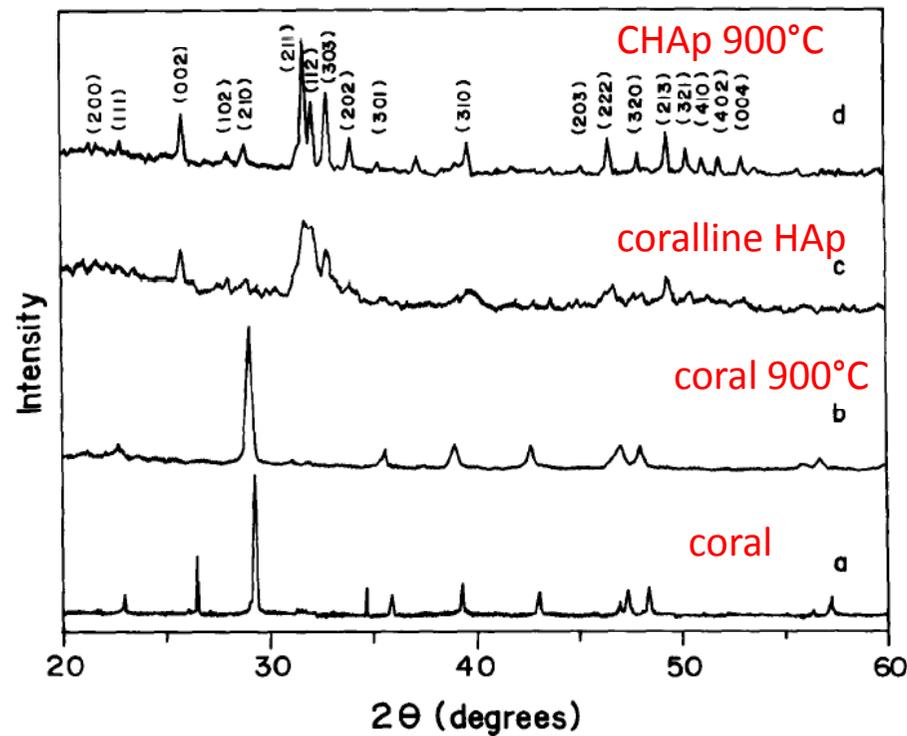


Natural templates: Coral:

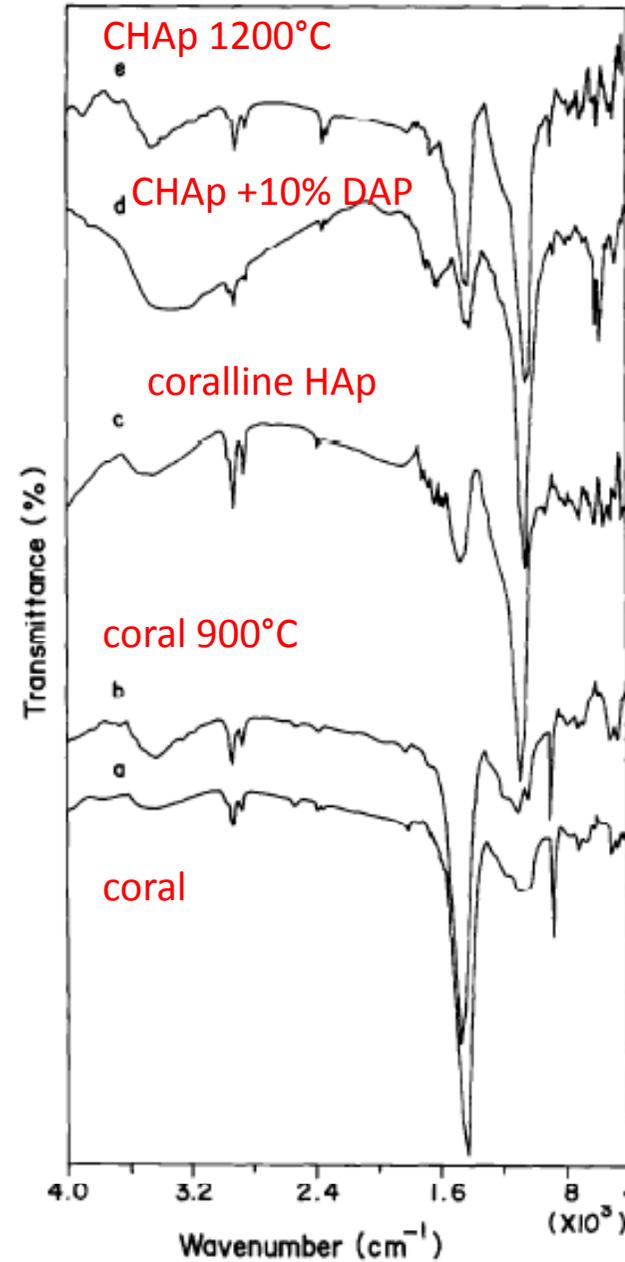
Second method: 1974 D. M. Roy and S. K. Linnehan

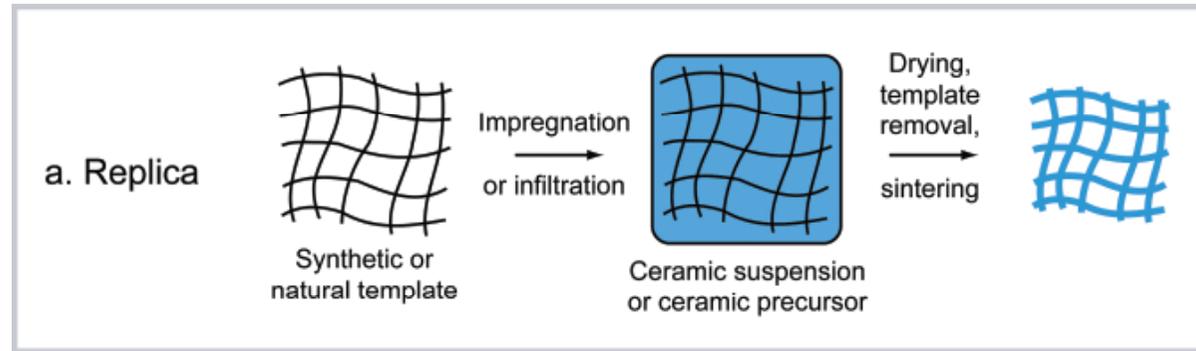
The coral is directly converted into macroporous scaffolds by hydrothermal treatments at high temperatures and pressures in a phosphate solution. The carbonate ions from the aragonite material (CaCO_3) originally present in the coral are partially or totally replaced by phosphate ions to form hydroxyapatite.

Exchange reaction with diammonium phosphate (DAP) : carbonate to phosphate



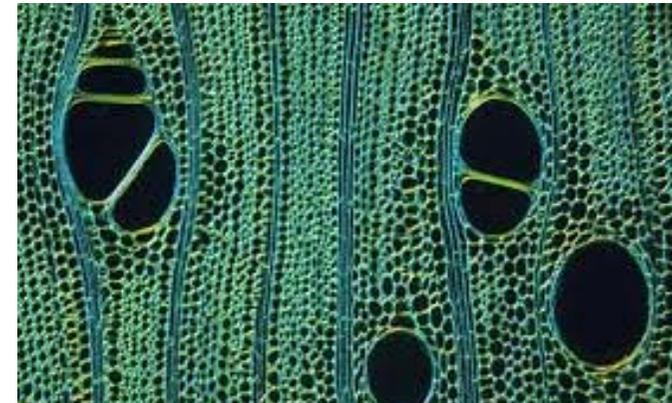
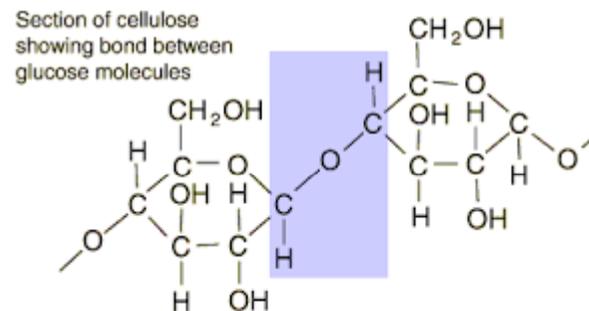
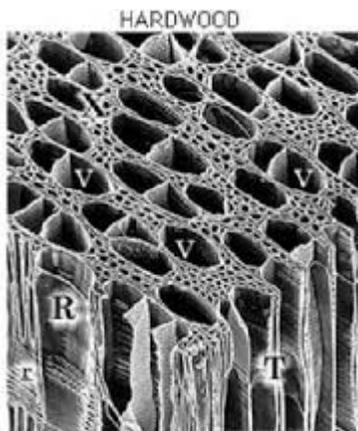
M. Sivakumar et al Biomaterials 1996, Vol17, N°17





Natural templates: wood

The presence of oriented vessels in the structure of wood enables the preparation of macroporous ceramics with highly anisotropic aligned pores.

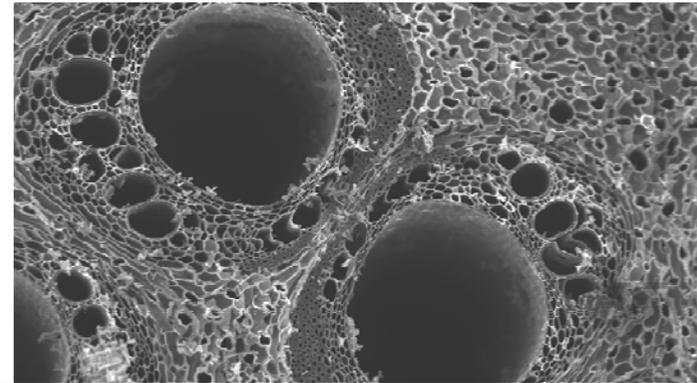
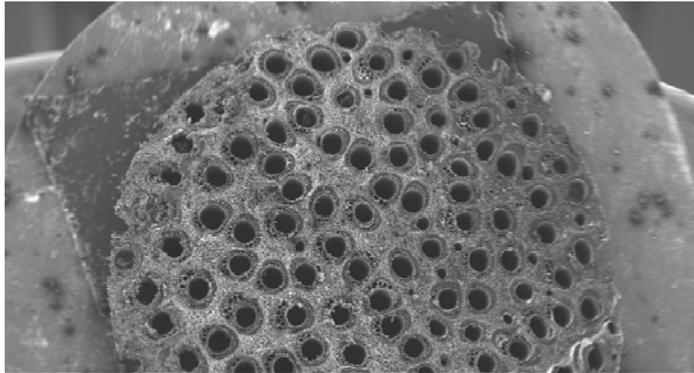


CRITERIA OF SELECTION:

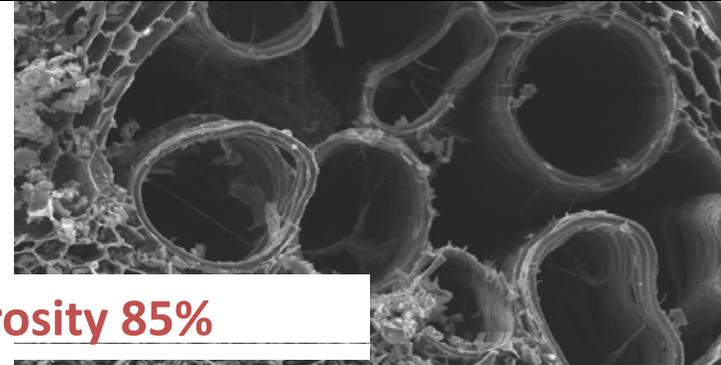
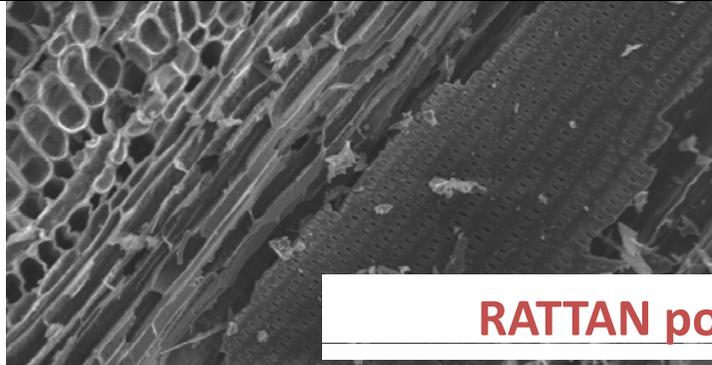
- Hierarchical and anisotropic structure
- Microstructural properties (pore size and distribution, pore interconnection)

RATTAN wood



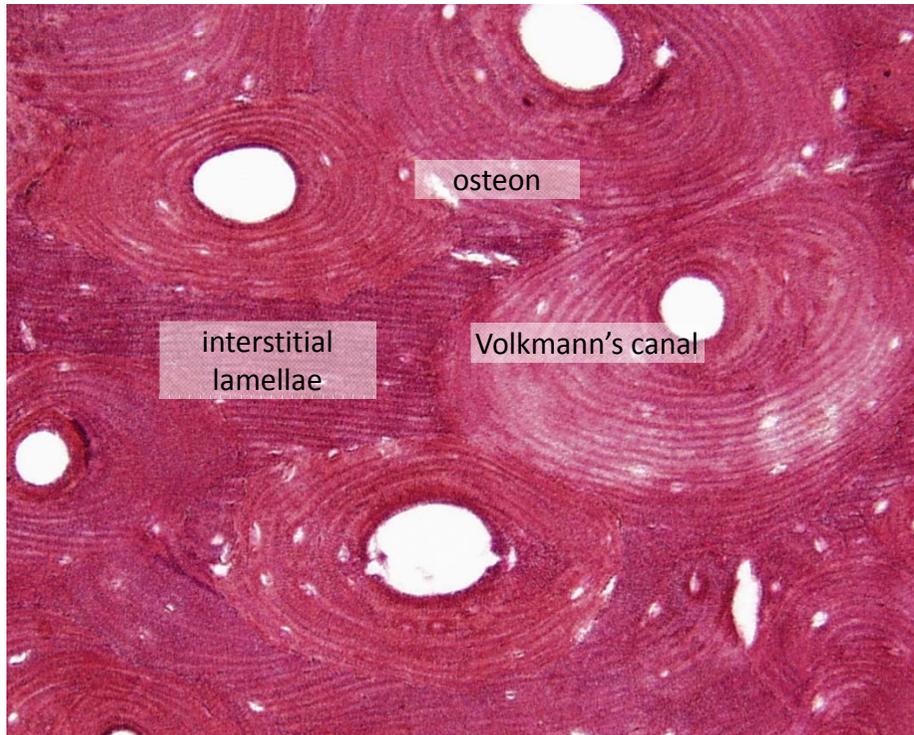


Pores surface fraction distribution	58.1% Large pores ($\varnothing = 250 \pm 40 \mu\text{m}$)
	15.0% Medium pores ($\varnothing = 12 \pm 4 \mu\text{m}$)
	26.9% Small pores ($\varnothing = 4 \pm 1 \mu\text{m}$)

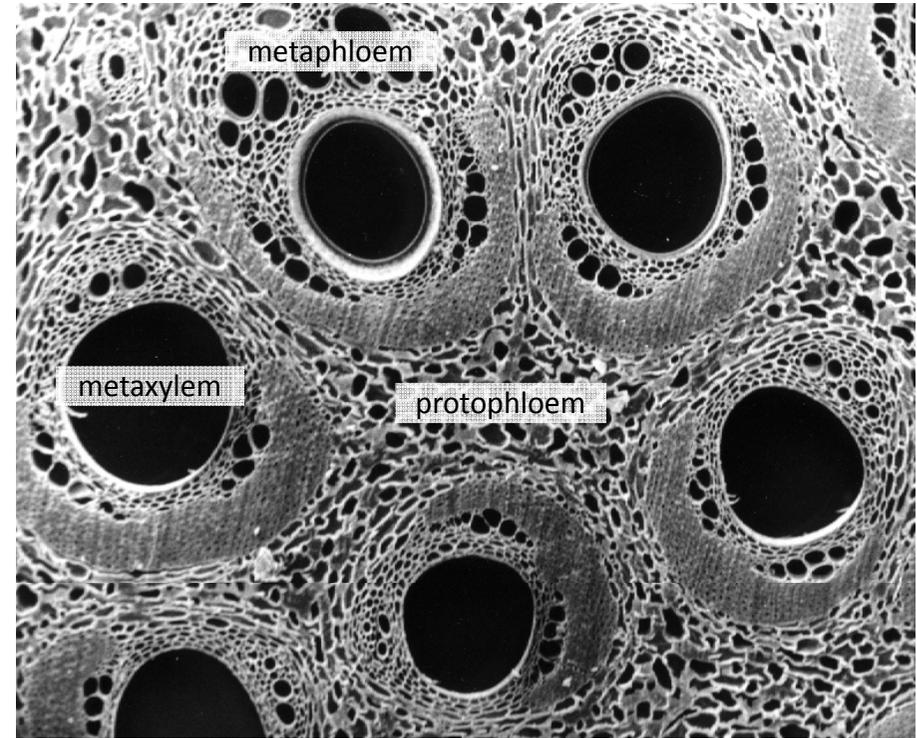


RATTAN porosity 85%

RATTAN WOOD REPRODUCES SPONGY BONE



Bone



Rattan wood



CERAMISATION PROCESS OF NATIVE WOOD

1) PYROLYSIS
Wood → Carbon

A.Tampieri et al. *J Mater Chem* (2009) 19, 4973

A.Ruffini et al (2012) *Chem Eng J.* 217: 150

2) CARBURIZATION
Carbon → CaC_2

3) OXIDATION
 $\text{CaC}_2 \rightarrow \text{CaO}$

4) CARBONATION
 $\text{CaO} \rightarrow \text{CaCO}_3$

5) PHOSPHATION
 $\text{CaCO}_3 \rightarrow \text{Hydroxyapatite}$

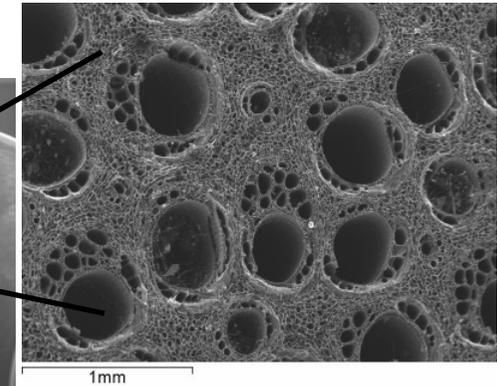
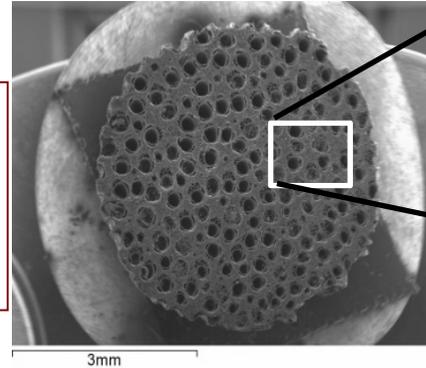
Transformation of the natural wood template and preserving its initial morphology

Replica from wood

STAGES OF BIOMORPHIC TRANSFORMATION OF WOOD

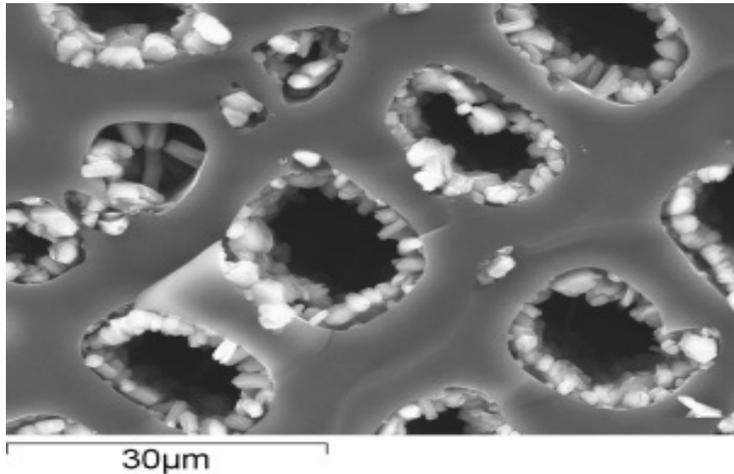
Pyrolysis
Wood → Carbon

Slow heating/cooling (1°C/h) to decompose the organic component and maintain the wood structure



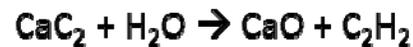
Carburization
Carbon → CaC₂

Highly controlled heterogeneous gas/solid reaction between gaseous Ca and solid carbon.

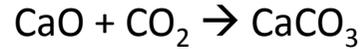


Oxidation
CaC₂ → CaO

Two chemical reactions are competing in the oxidation process.



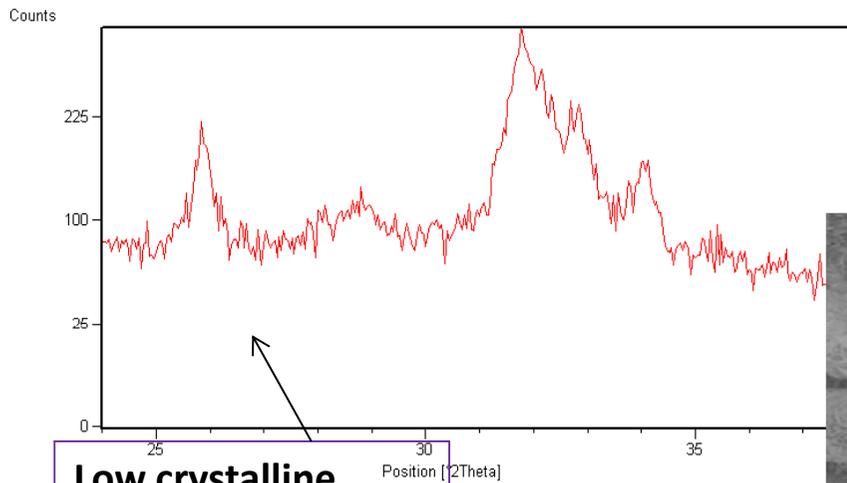
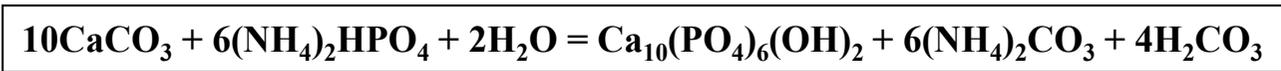
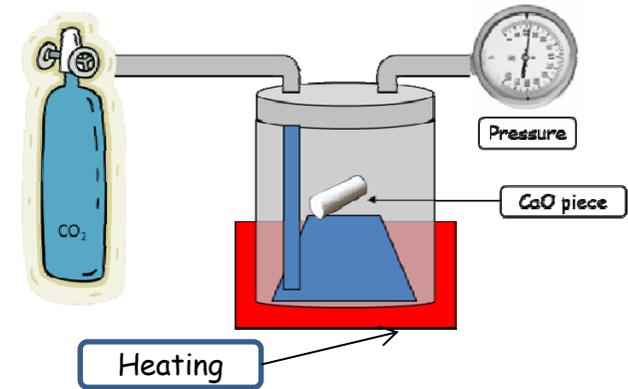
STAGES OF BIOMORPHIC TRANSFORMATION OF WOOD



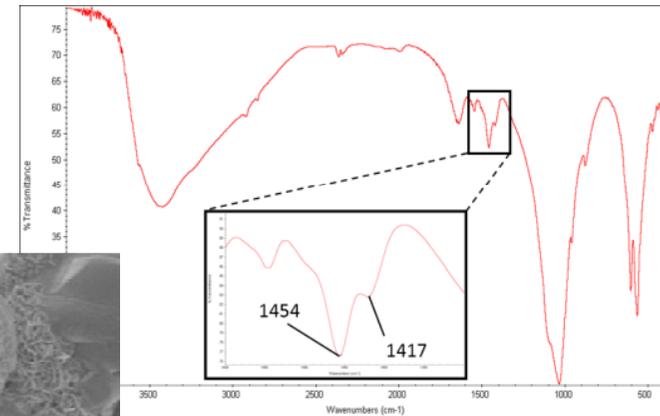
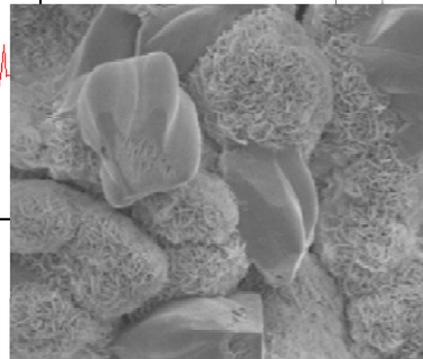
Carbonation
 $\text{CaO} \rightarrow \text{CaCO}_3$

Phosphatization
 $\text{CaCO}_3 \rightarrow \text{HA}$

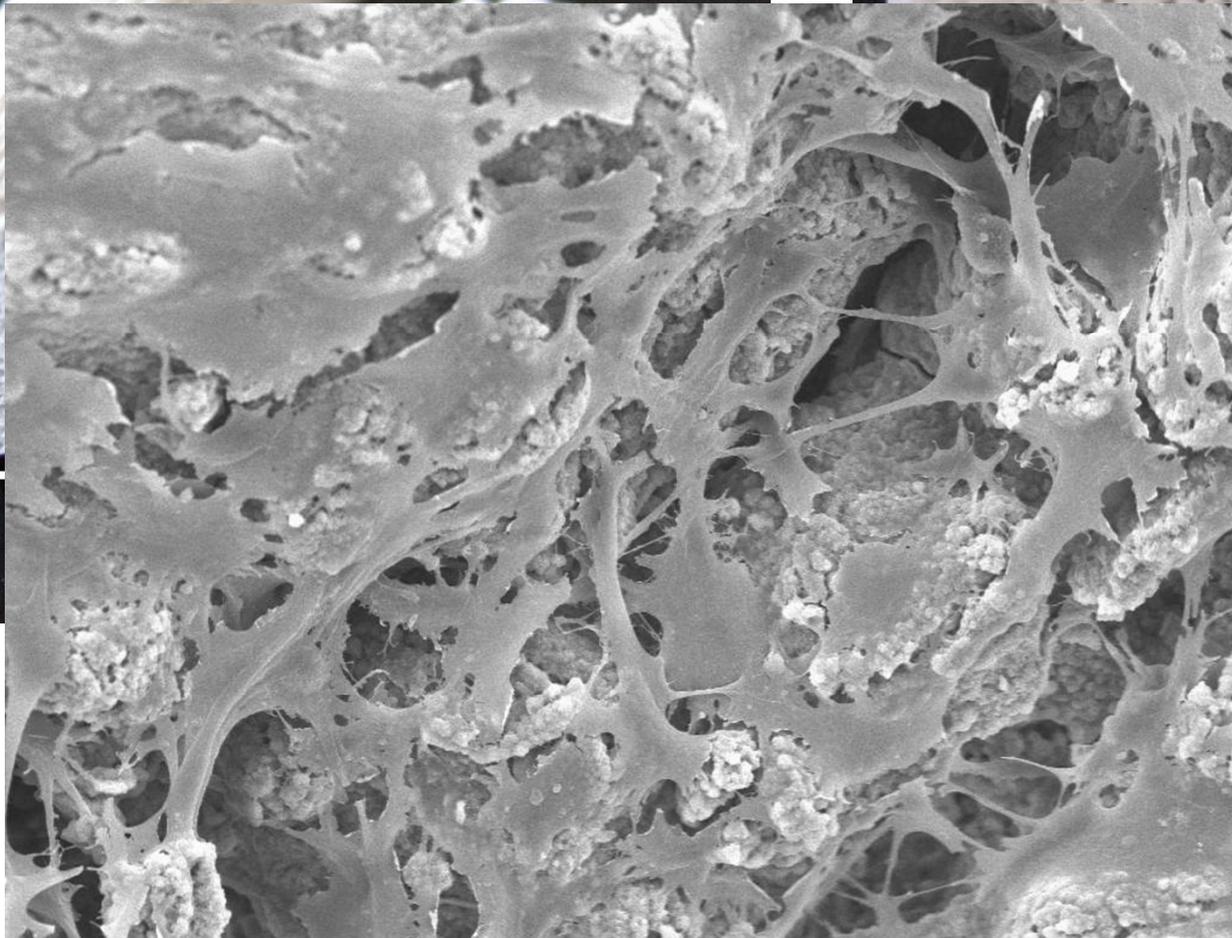
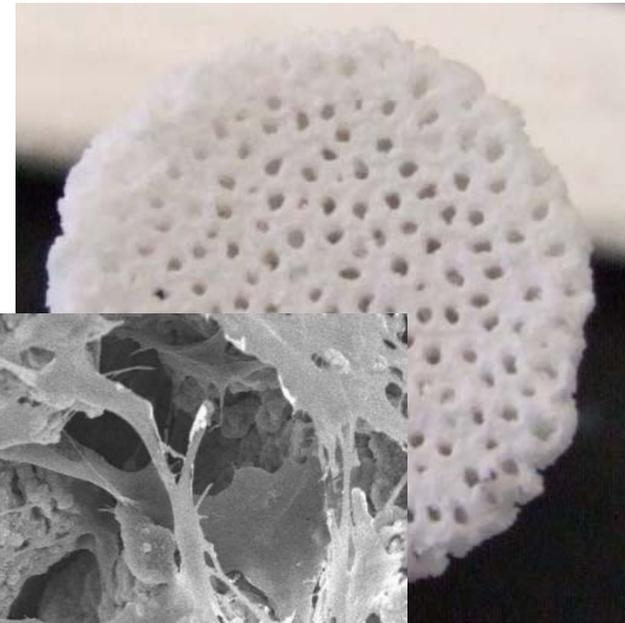
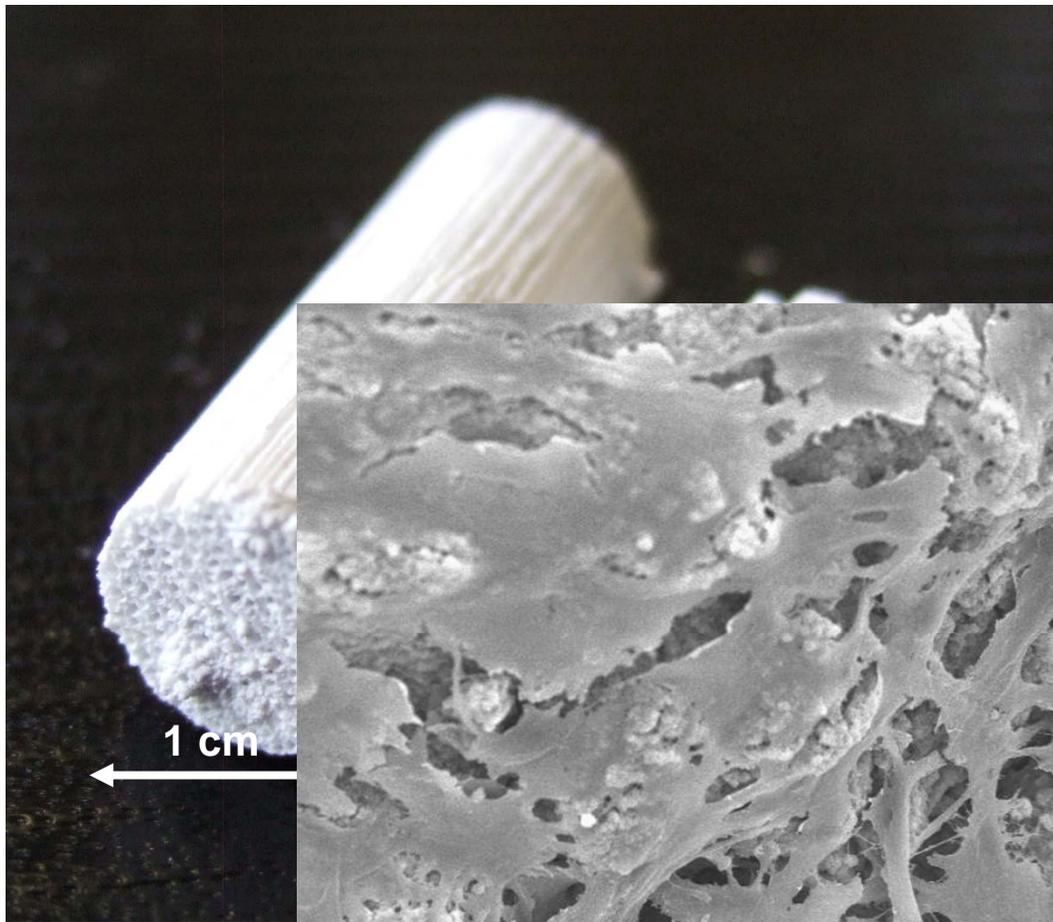
Carbonation of CaO is carried out at high temperature and CO₂ pressure to achieve effective CO₂ diffusion in the whole scaffold.



Low crystalline, bone-like HA phase

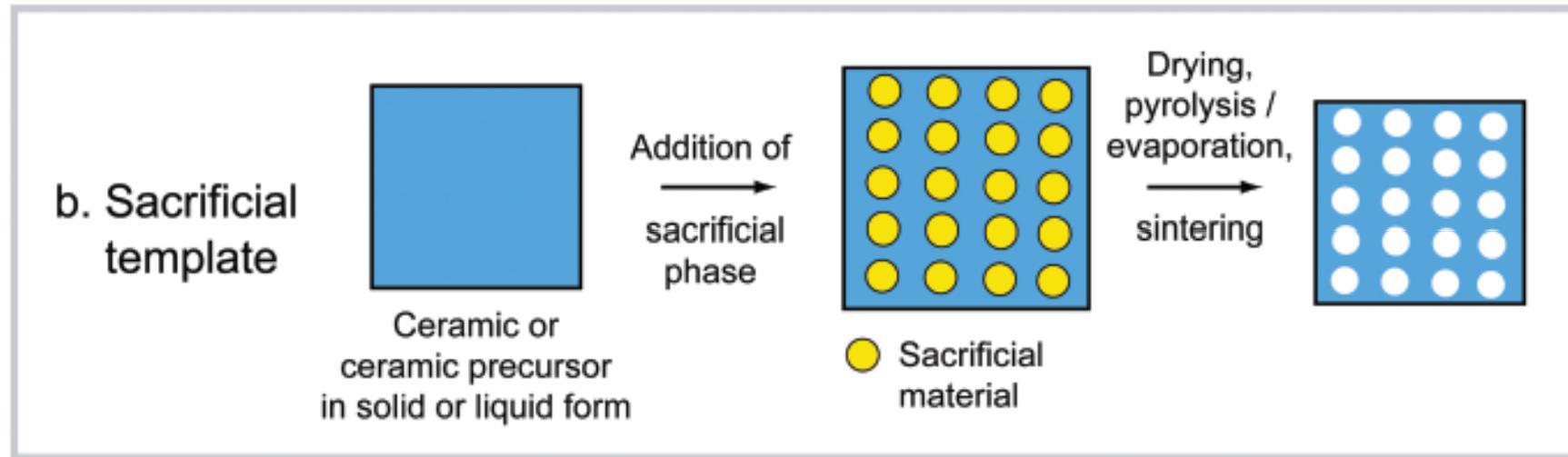


B-site carbonation (2-4 wt%)

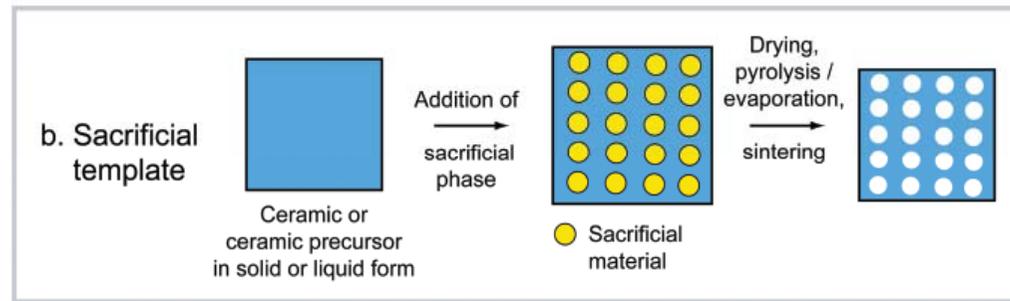


MG63
osteoblast-like
7 days

2.Sacrificial template technique



Sacrificial template technique consists of the preparation of a biphasic composite comprising a continuous matrix of ceramic particles and a dispersed sacrificial phase. This phase is extracted to generate pores within the structure. This method leads to porous materials displaying a negative replica of the original sacrificial template contrarily to the previous replica methods.



Wide variety of sacrificial materials:

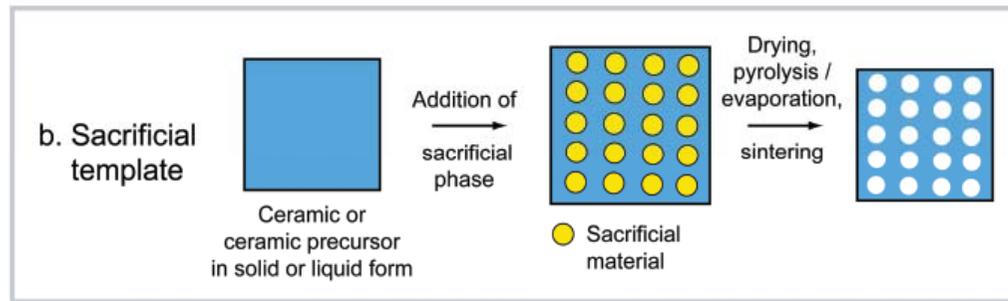
synthetic organics : PVB beads, PMMA or PMMA-PEG beads, ...

natural organics: sucrose, wax, starch...

The biphasic composite is prepared by various ways:

- a) Pressing a powder mixture of the two components
- b) Forming a two-phase suspension that is processed by wet colloidal routes such as slip or tape casting
- c) Impregnating previously consolidated preforms of the sacrificial material with the ceramic suspension.

The organics are after extracted through pyrolysis by applying long heating times at temperatures between 200 and 600°C depending on organic species.



Wide variety of sacrificial materials:

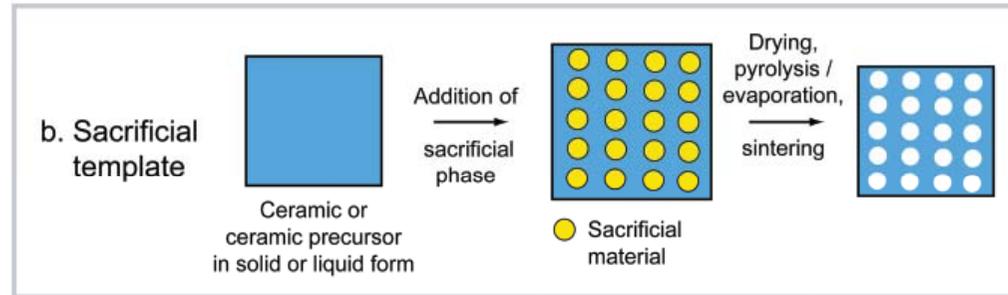
synthetic organics : PVB beads, PMMA or PMMA-PEG beads, ...

natural organics: sucrose, wax, starch...

The biphasic composite is prepared by various ways:

- a) Pressing a powder mixture of the two components
- b) Forming a two-phase suspension that is processed by wet colloidal routes such as slip or tape casting
- c) Impregnating previously consolidated preforms of PMMA beads scaffold with the CaP powder suspension.

The organics are after extracted through pyrolysis by applying long heating times at temperatures between 200 and 600°C depending on organic species.



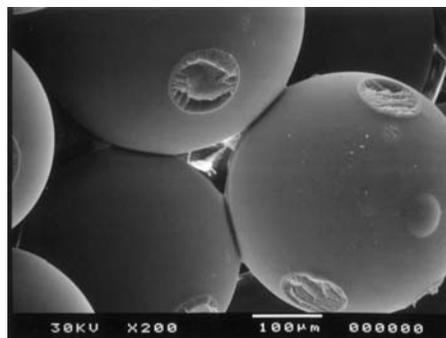
Impregnation of PMMA beads consolidated preforms with CaP powder suspension.



**Chemical forming
with acetone**



under pressure



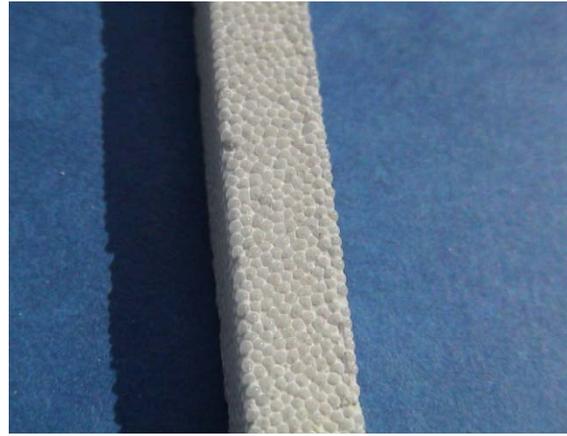
- **Bonding between PMMA beads (scaffold)**
- **Controlled diameter bonding (Interconnection) depends on time, temperature, pressure**



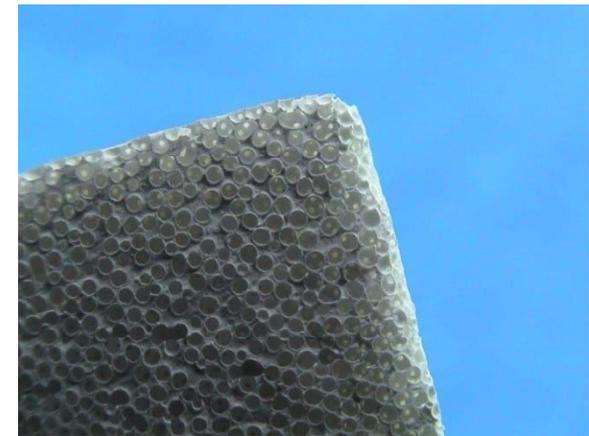
Impregnation of PMMA beads consolidated preforms with CaP powder suspension.



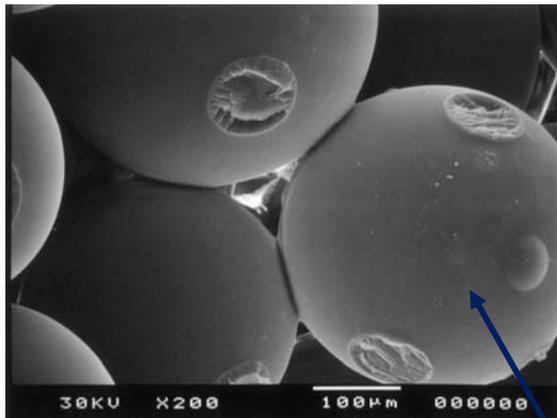
Shaping



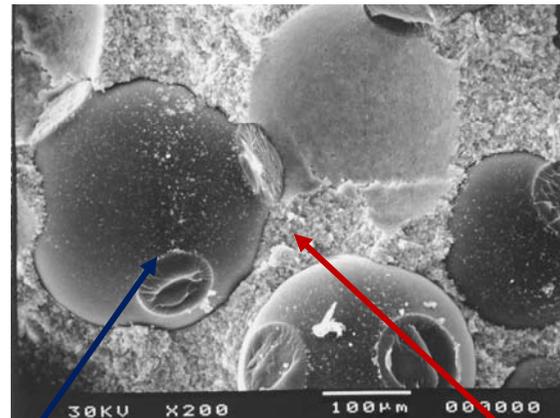
Impregnation



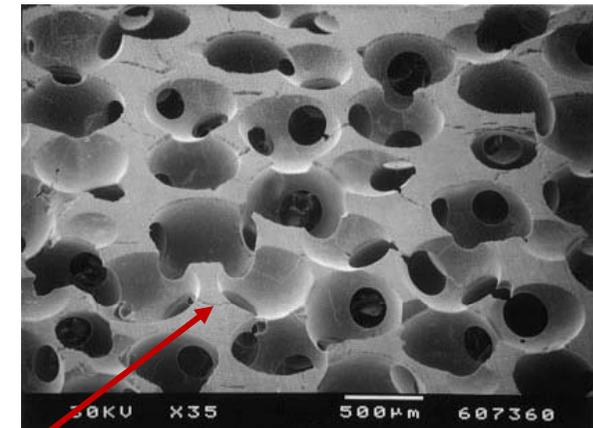
Debinding



PMMA beads



ceramic



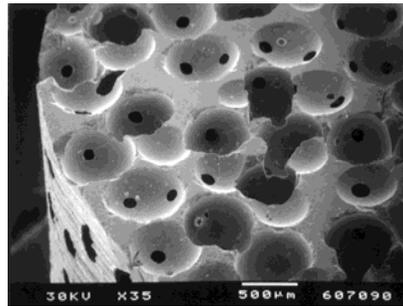
M. Descamps et al., JECS. 28 (2008) 149

Sacrificial templates

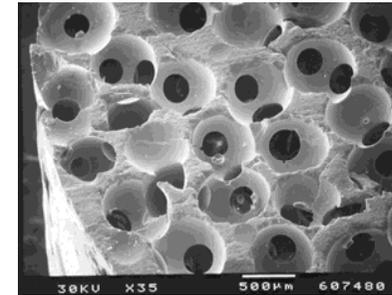
- Control of pore size depending on PMMA beads size
- Control of interconnection diameters: Id
PMMA beads (500 - 600 μm)



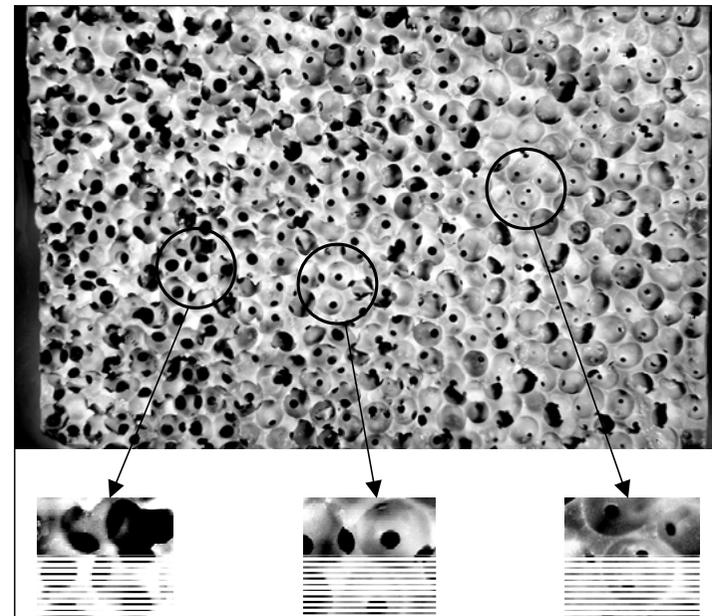
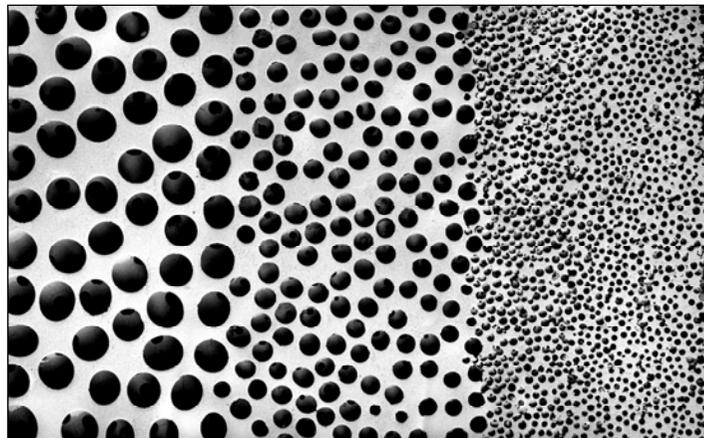
Id : 60 μm



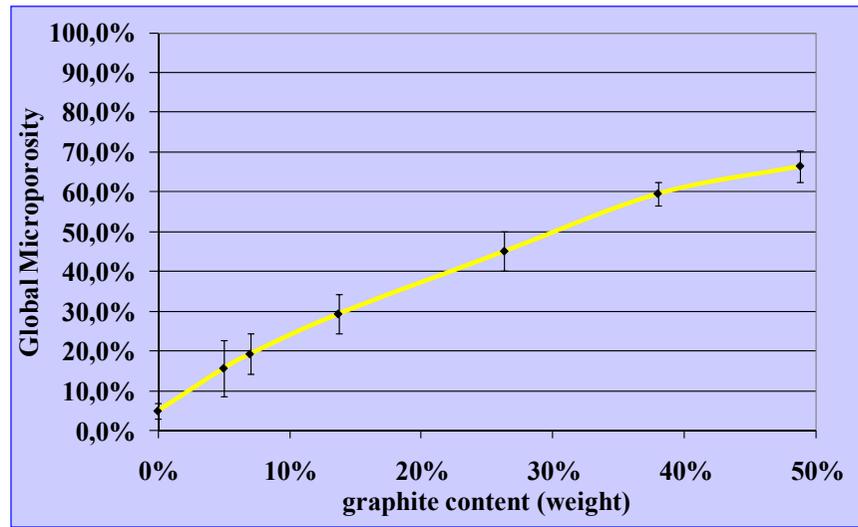
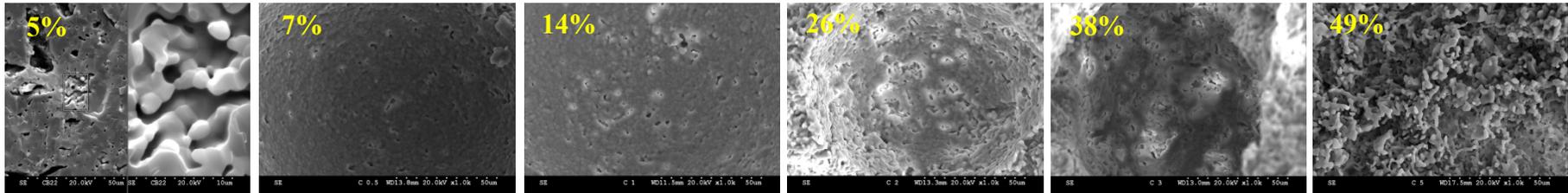
Id: 260 μm



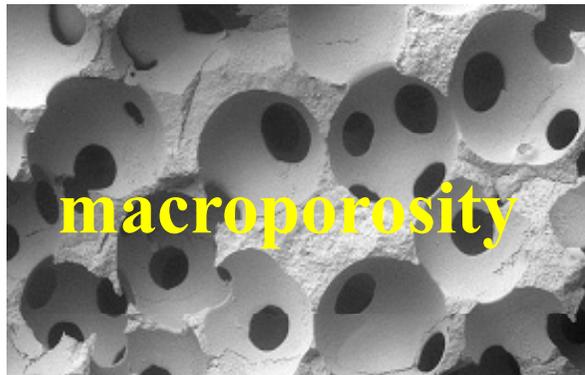
- Control of porosity gradient in pore size and interconnection size



Possibility to add microporosity by mixing graphite as micropore forming agent.

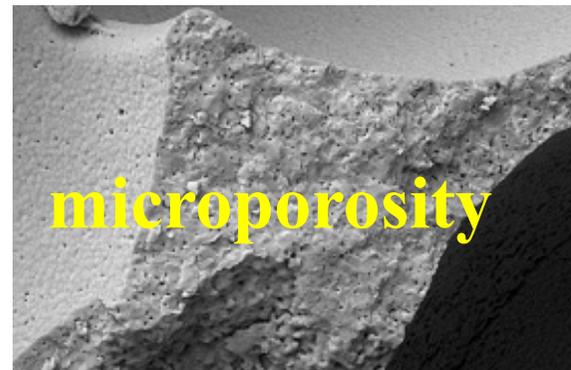


Controlled



macroporosity

and



microporosity

Impregnation of PMMA beads consolidated preforms with CaP powder suspension.

Debinding:

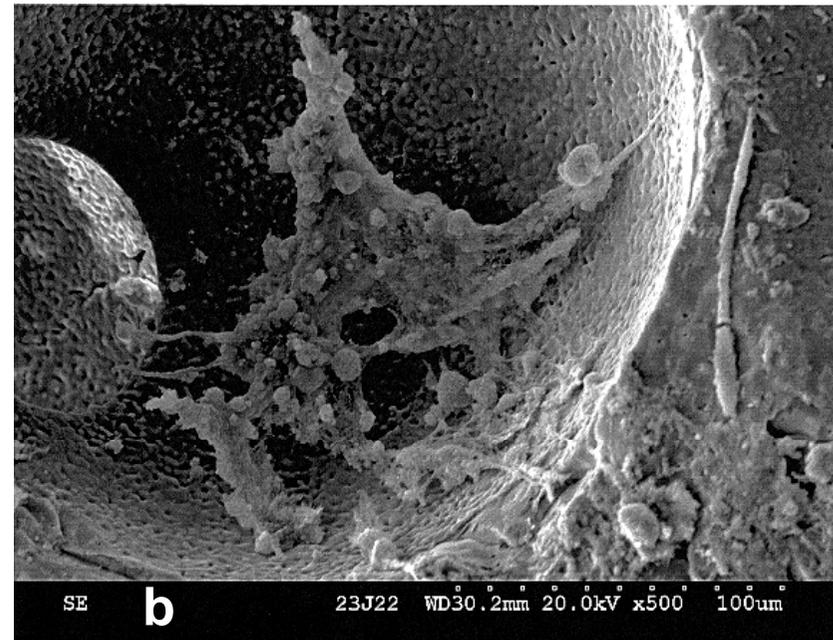
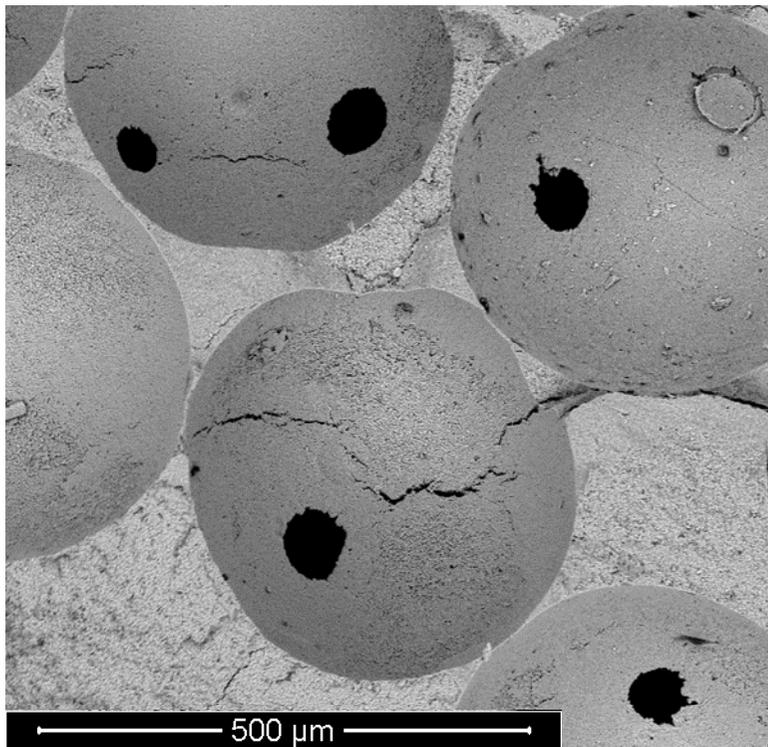
220°C 30 hours + 400°C 5 hours

Sintering: 1115°C 3 hours

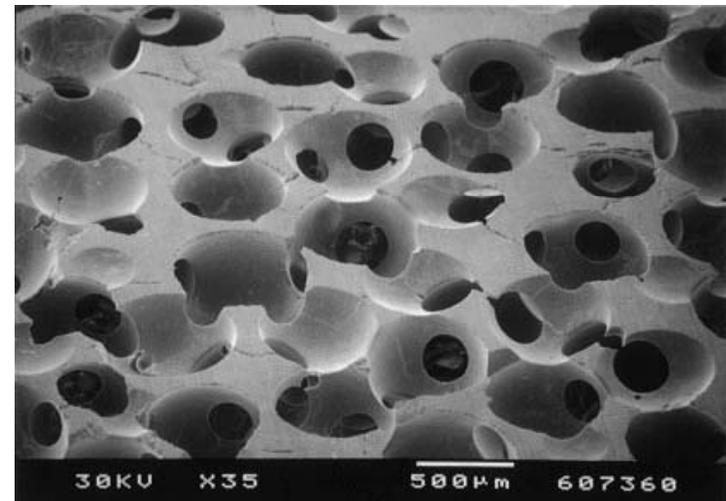
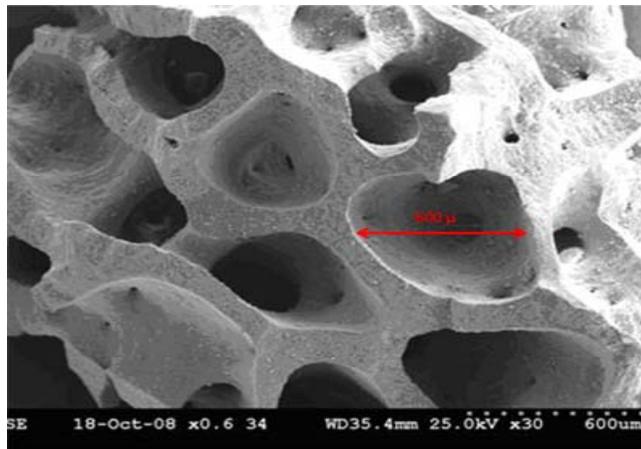
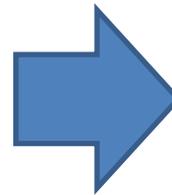
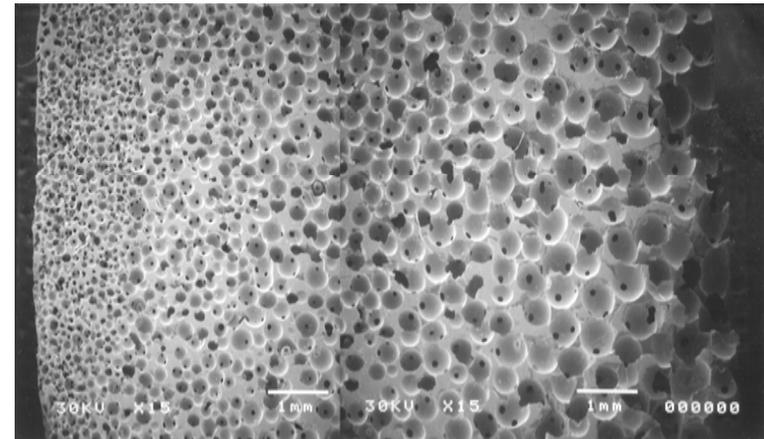
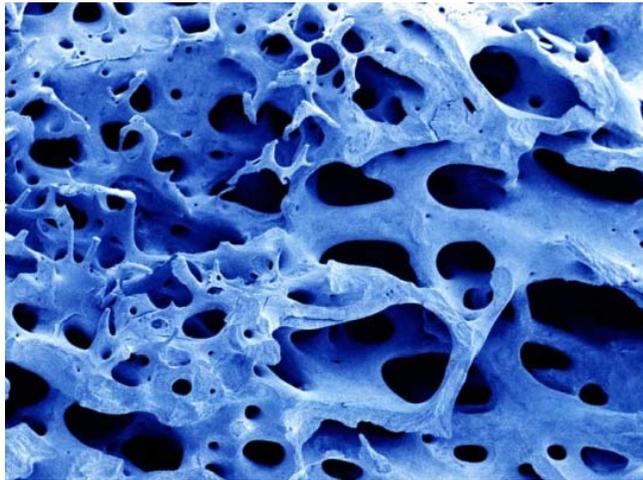
Density of ceramic walls = 99 %

Porosity = 65%

Spherical pores homogeneously distributed
in space with several interconnecting holes.

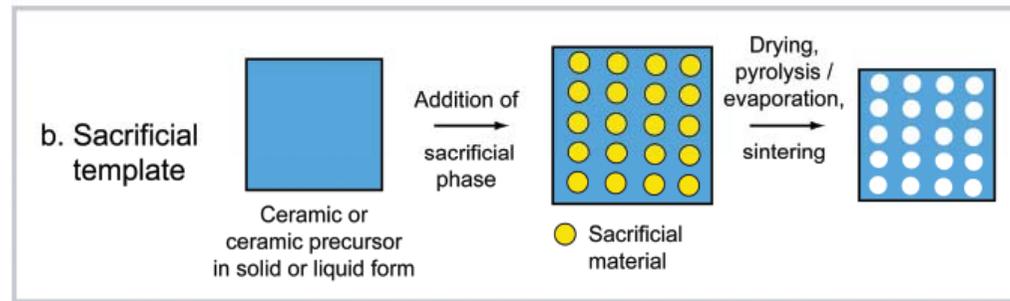


Impregnation of PMMA beads consolidated preforms with CaP powder suspension.



Human bone

*Patent FR2823305, Biocetis SARL,
M. Descamps, P Hardouin, J Lu, F Monchau*



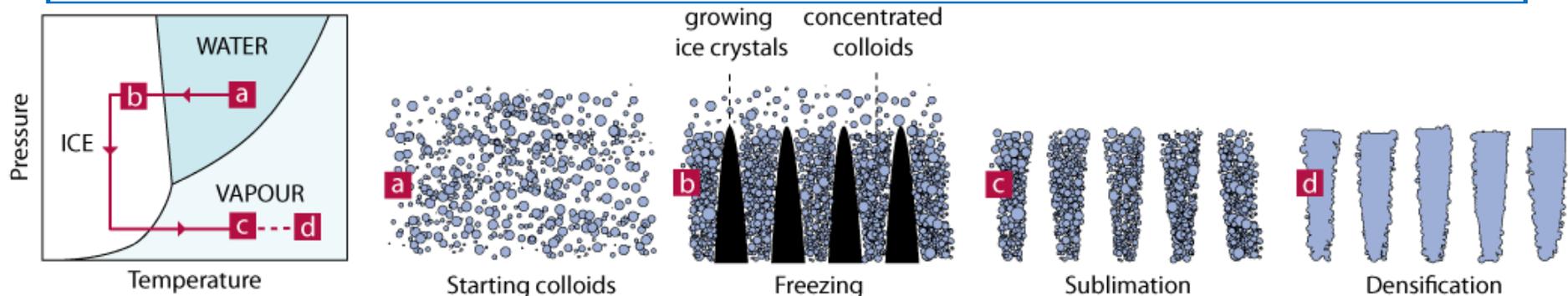
Wide variety of sacrificial materials:

synthetic organics : PVB beads, PMMA or PMMA-PEG beads, ...

natural organics: sucrose, wax, starch...

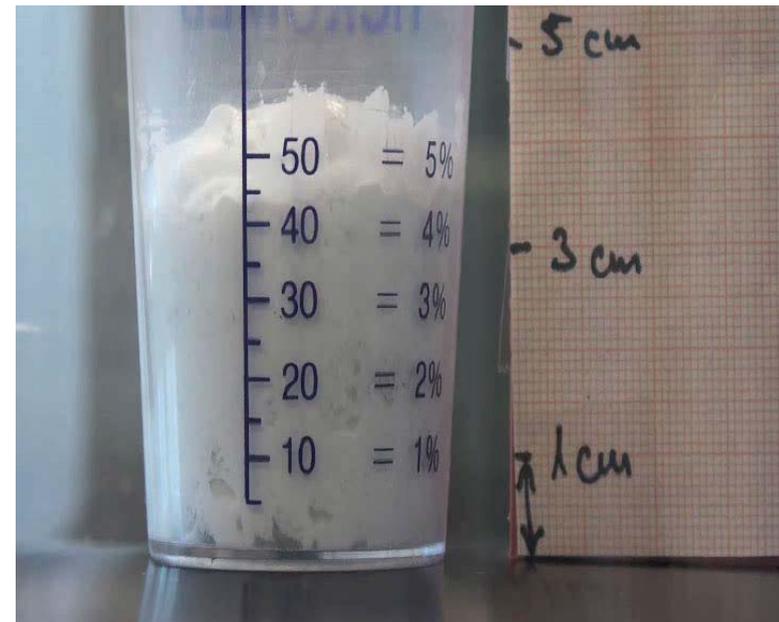
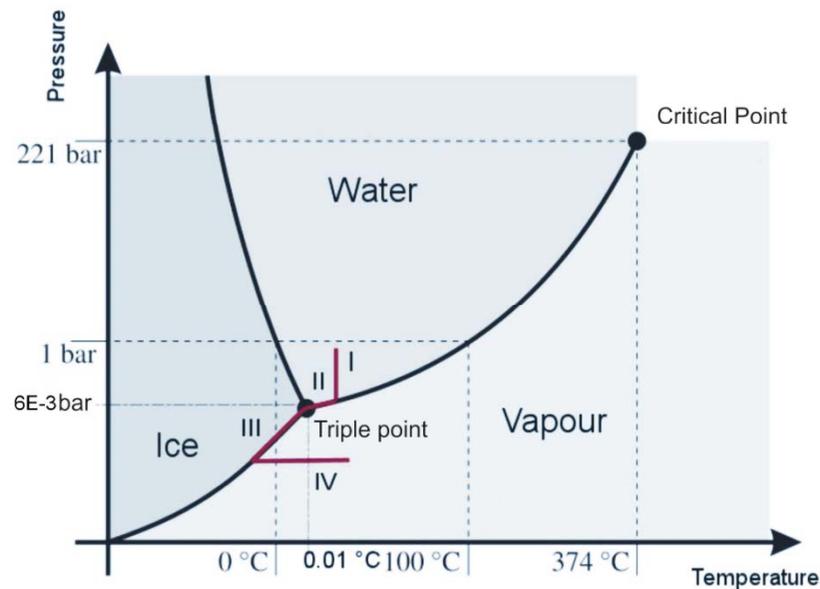
liquids: freeze-drying of water

By using liquid pore formers such as water and oils, liquids and volatile oils can be evaporated or sublimated at milder conditions without generating toxic gases and excessive stresses during pore former removal.

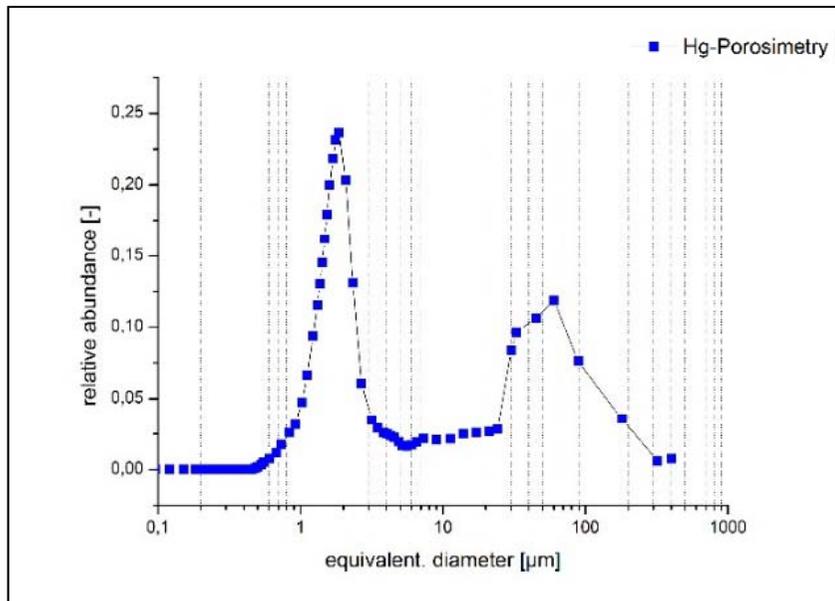
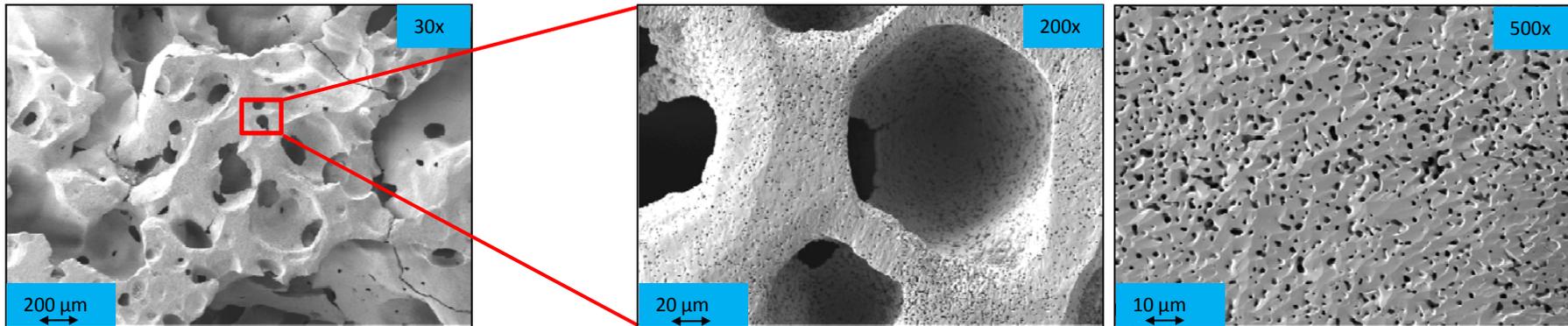


Freeze Foaming

- Foaming process is based on pressure reduction in the vacuum chamber of a freeze dryer
- Pores through rising water vapor, procedural air and later sublimation of frozen water (aqueous suspensions)



Freeze Foaming : Advantages (structural)

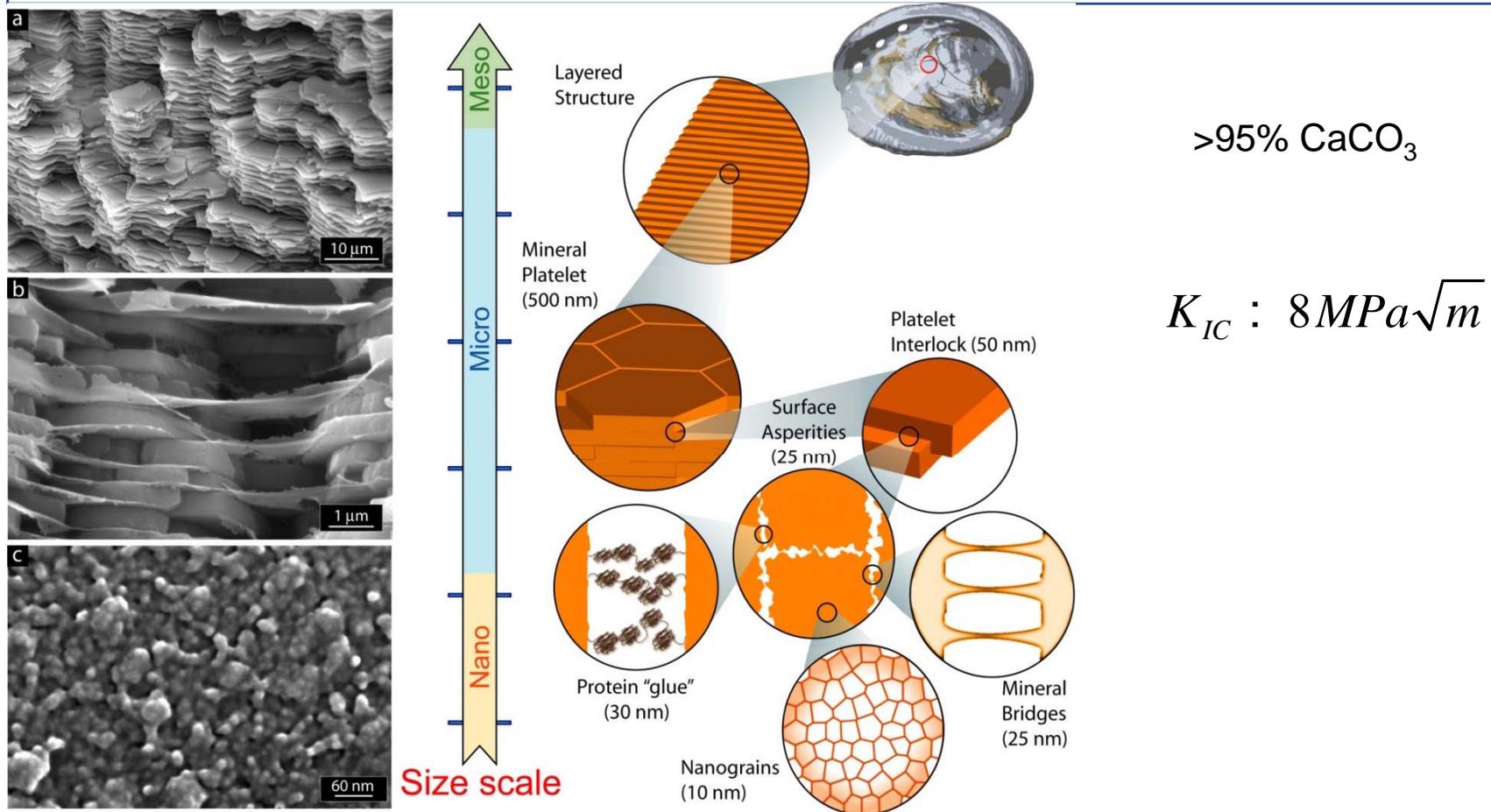


Patent: DE 10 2008 000 100, Tassilo Moritz

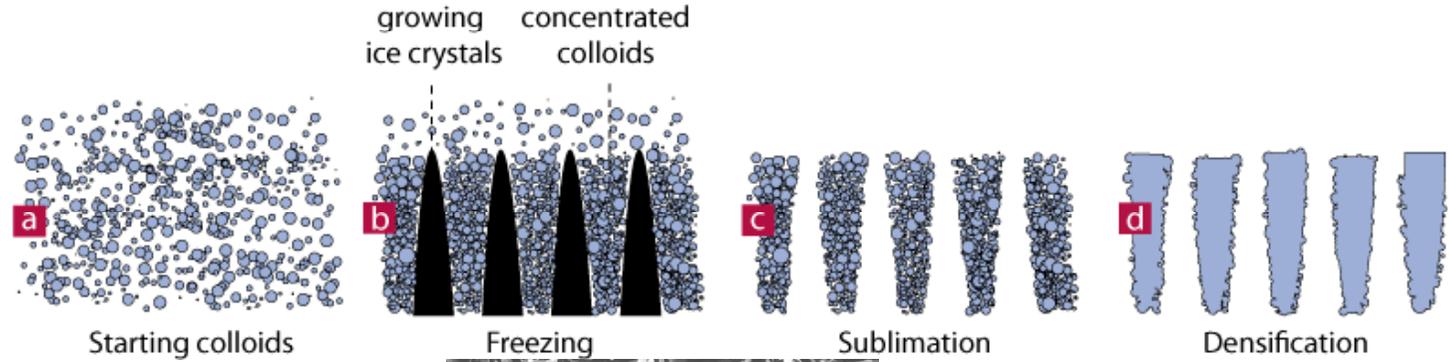
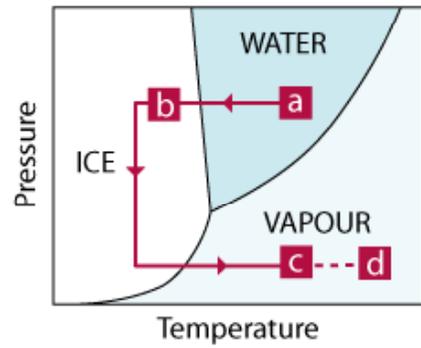
- No pore-forming agents needed (Replica or Placeholder Technique) → environmentally friendly
- Foam with high amount of open porosity (50 - 95%) and bimodal pore size distribution
- Meso- to macropores
- Near-net shaping possibility → personalization
- Different materials → different product lines according to the needs.

Freeze casting – ice templating

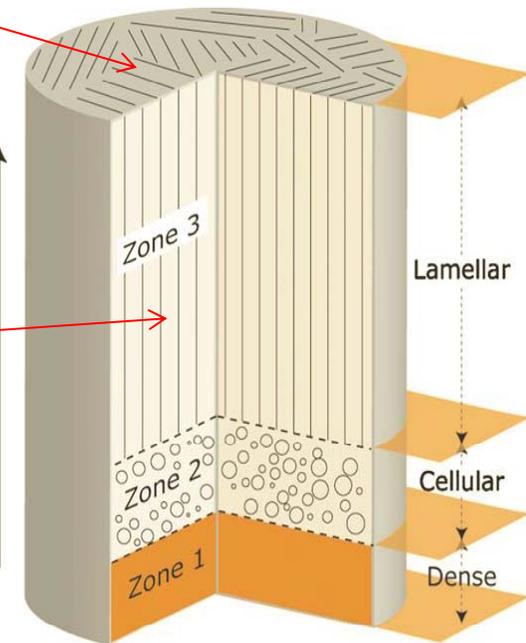
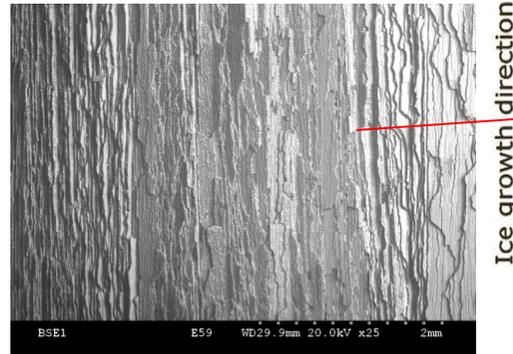
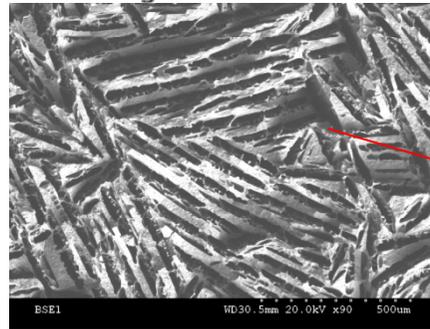
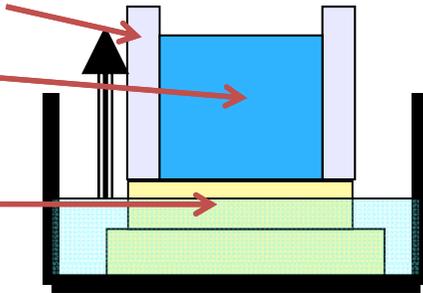
The objective was to mimic the nacre structure by using an oriented freezing process to allow oriented pore development.



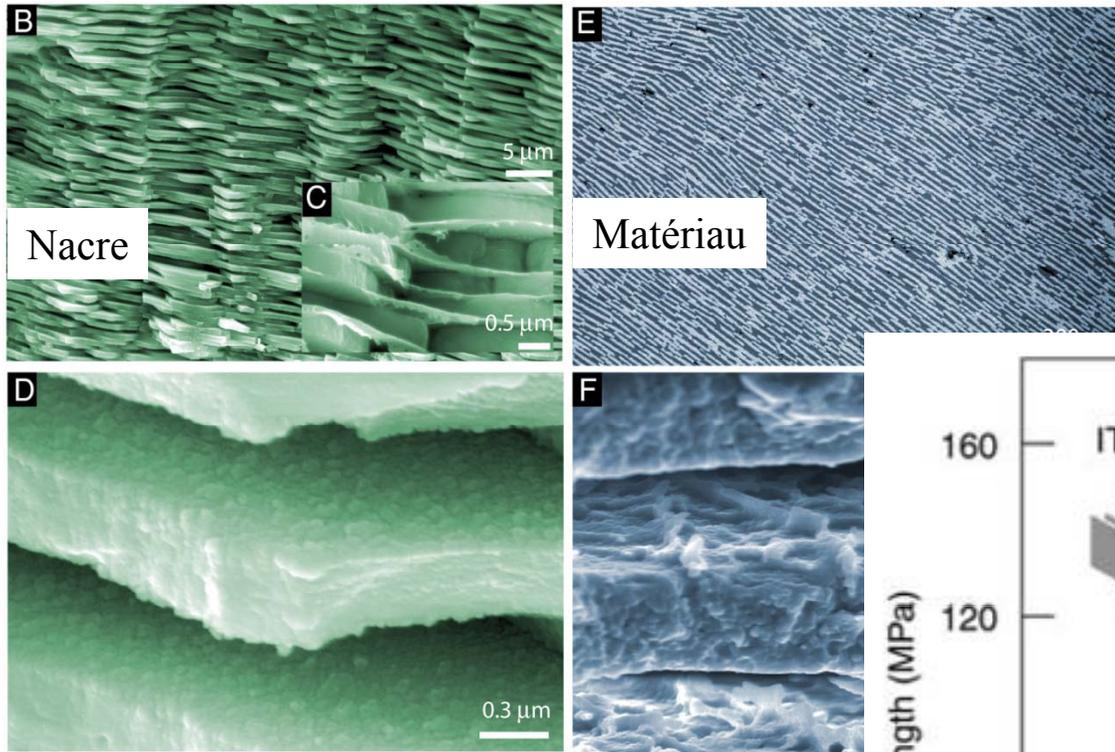
Freeze casting



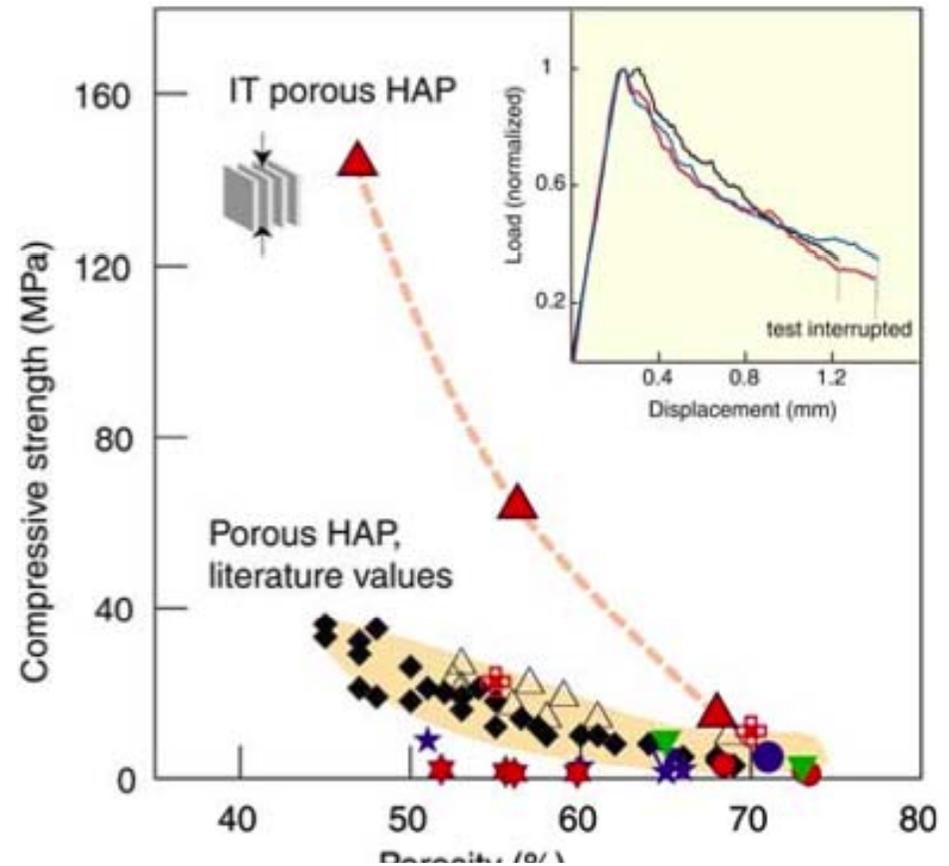
Mold
insulating wall
Slurry
Conductive
material
Cooling liquid



S. Deville et al., *Biomaterials* 27 (2006) 5480–5489

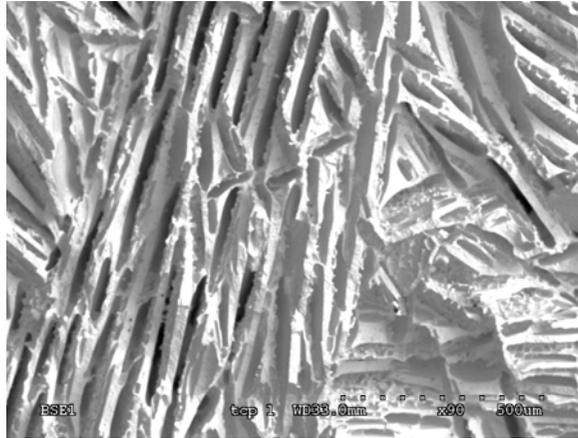


Freeze casting



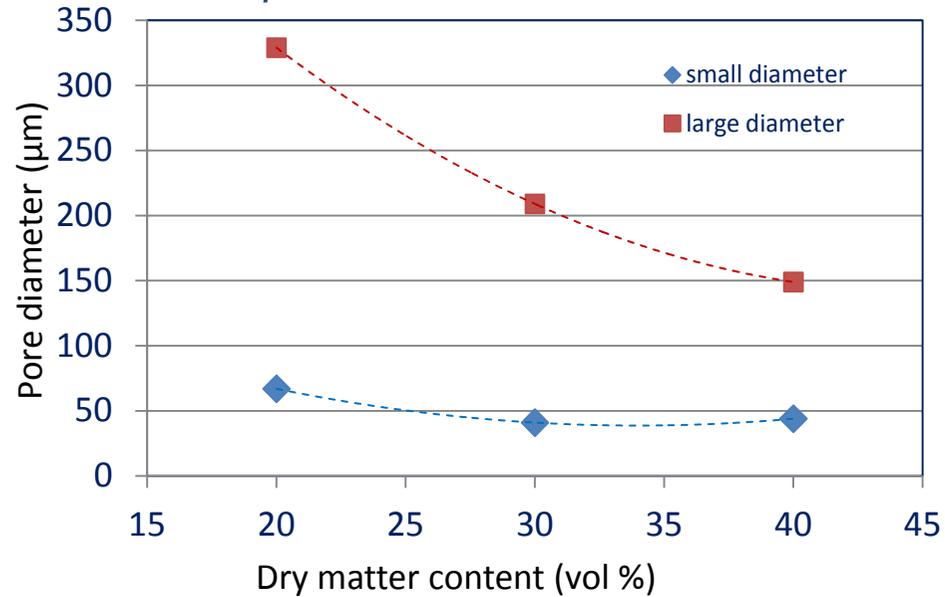
S. Deville et al., Science, 2006

Sacrificial templates



Freeze casting

β -TCP, 1 K/min, 3% binder



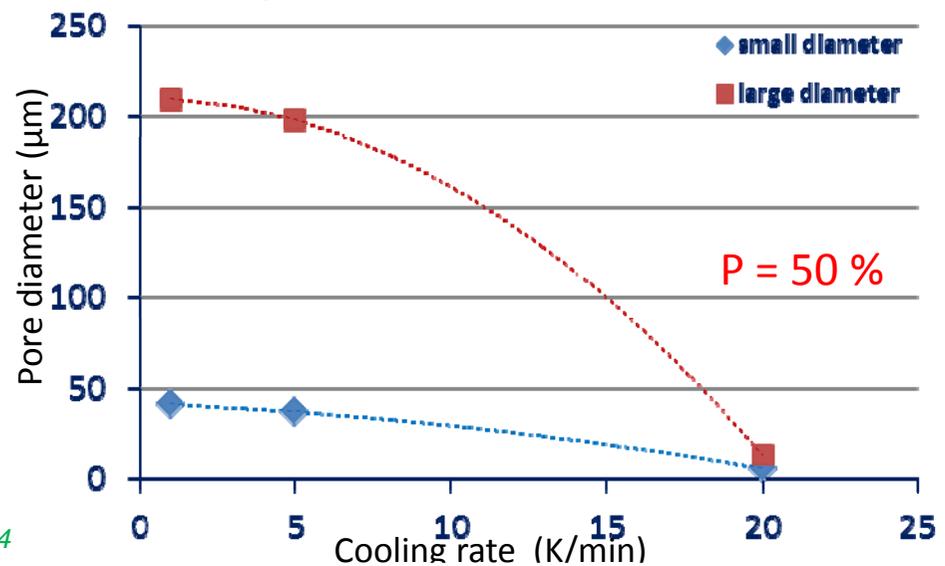
Pore long axis size:

- between 150 and 340 μm versus dry matter content
- between 13 and 210 μm versus cooling rate .

Total porosity:

36 to 67 % versus dry matter %

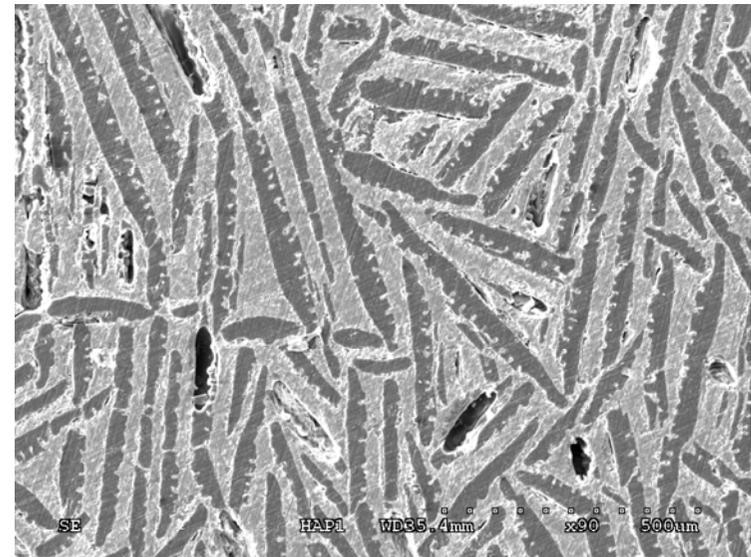
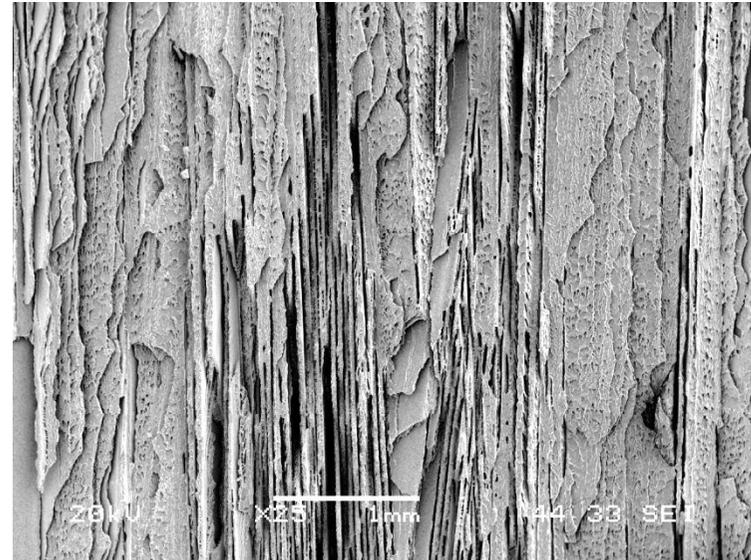
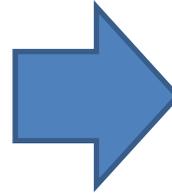
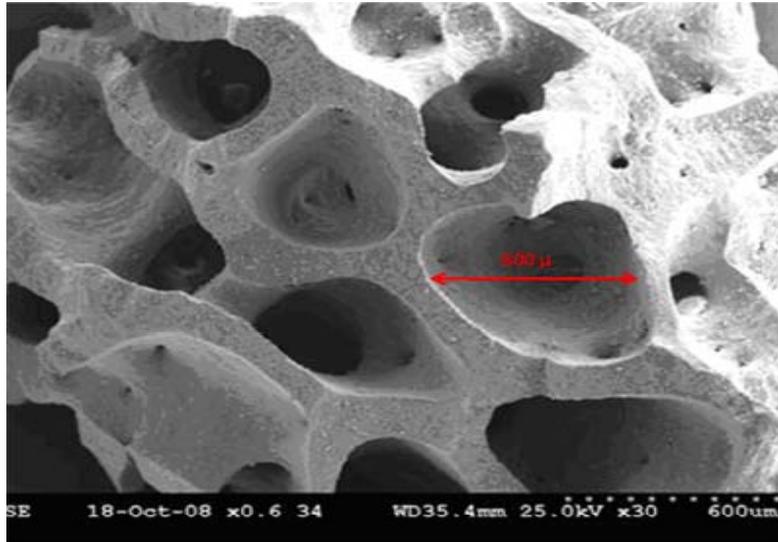
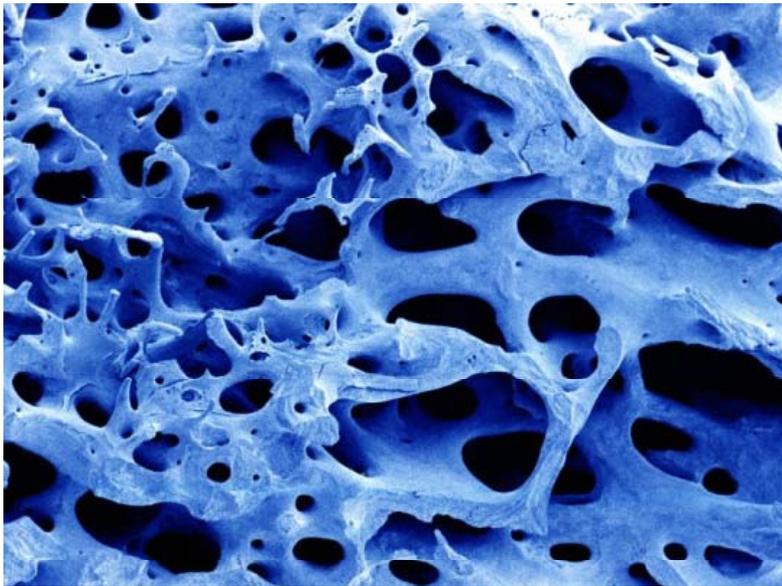
β -TCP, 30 vol % DM, 3% binder



D. Hautcoeur Ph D UMons-BCRC Nov 2014

Human bone

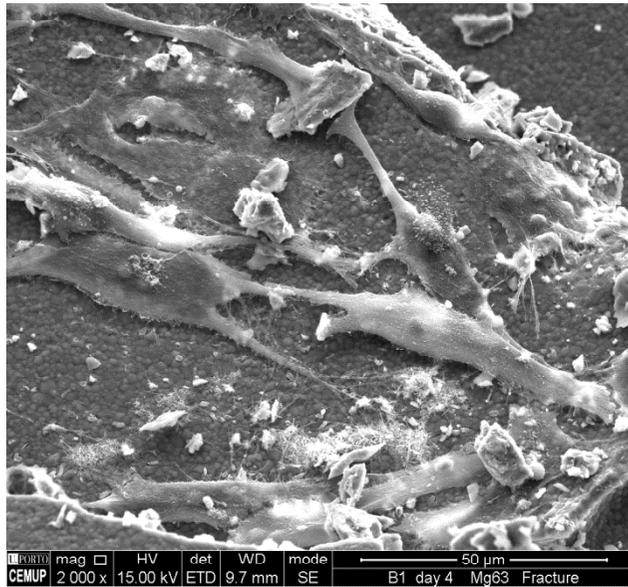
Freeze casting



D. Hautcoeur Ph D I Mons-BCRC Nov 2014

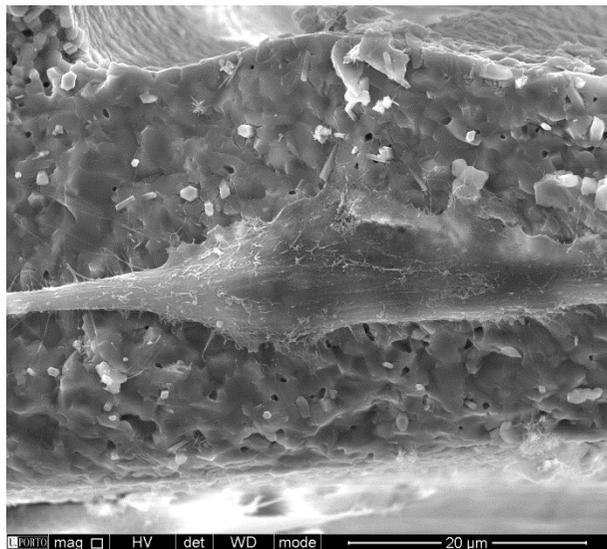
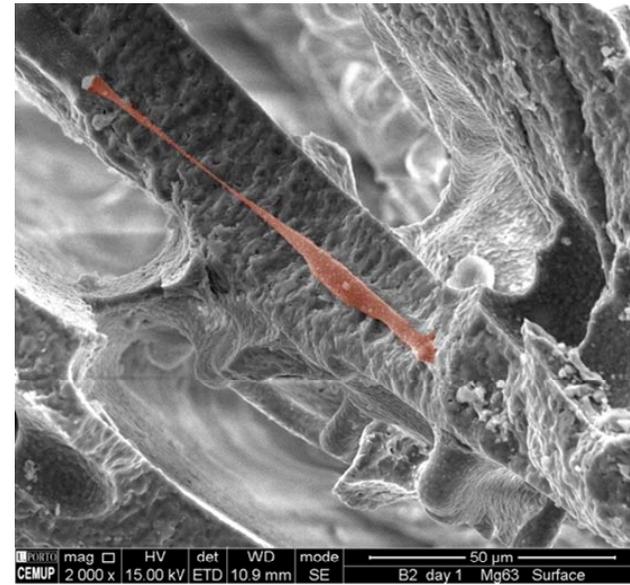
Colonization tests with MG63 osteoblasts

Freeze casting

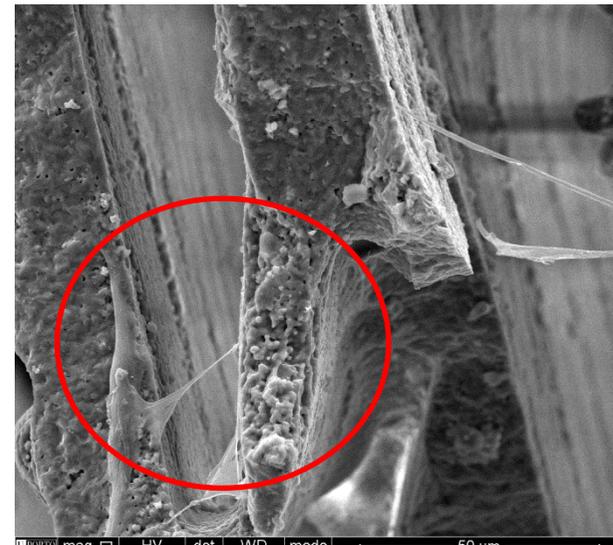


1 day

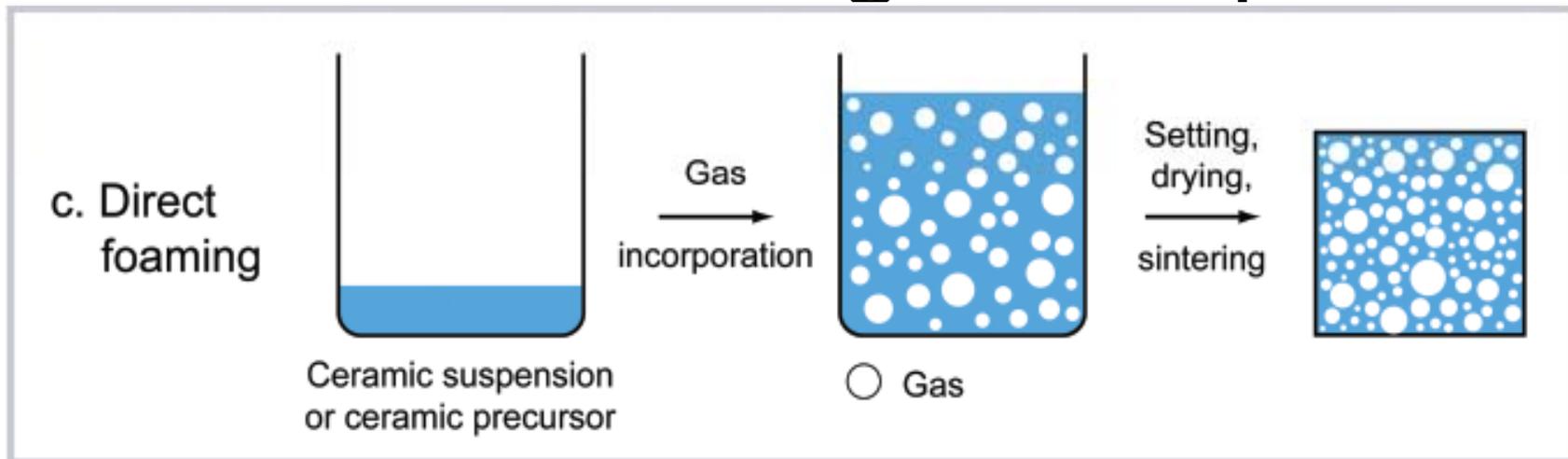
198 μm/37 μm



4 days



3. Direct foaming technique



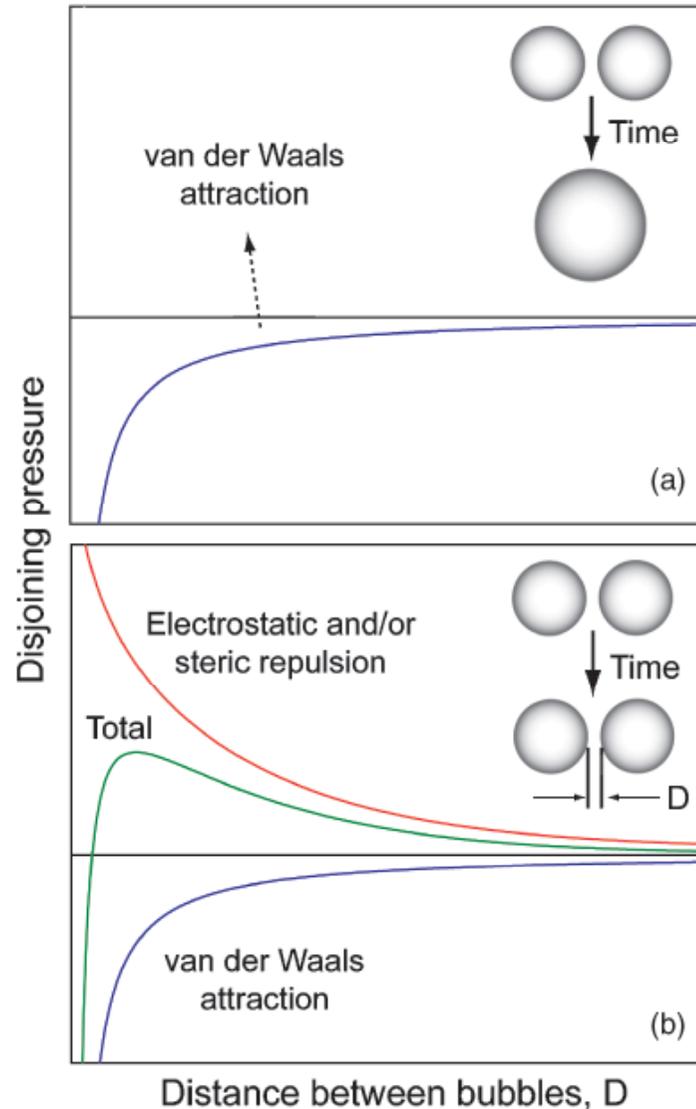
Direct foaming technique consists of the incorporation of air into a suspension to create air bubbles.

The incorporation of bubbles can be carried out by mechanical agitation or by chemical reaction accompanied by degassing.

The total porosity of sintered foamed ceramics is proportional to the amount of gas incorporated into the liquid and is between **40% - 97%**.

The pore size depends on the stability of the wet foam before setting takes place → foam stabilization with surfactant is necessary to control bubble size and final pore size (10 μm - 300 μm).

Schematic dependence of the disjoining pressure among two interacting gas bubbles as a function of their distance D .



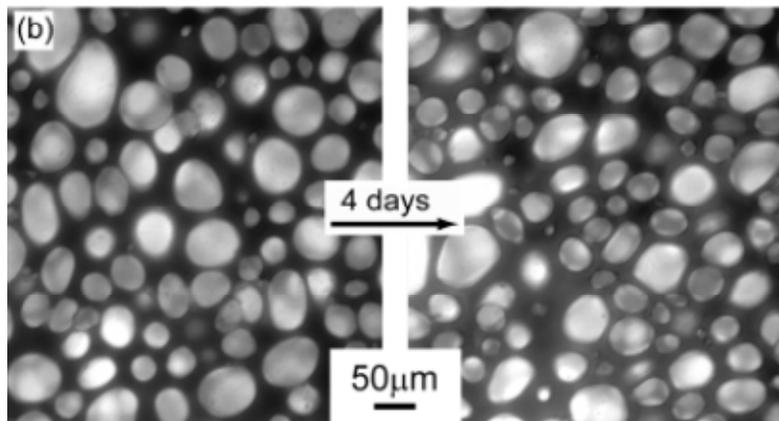
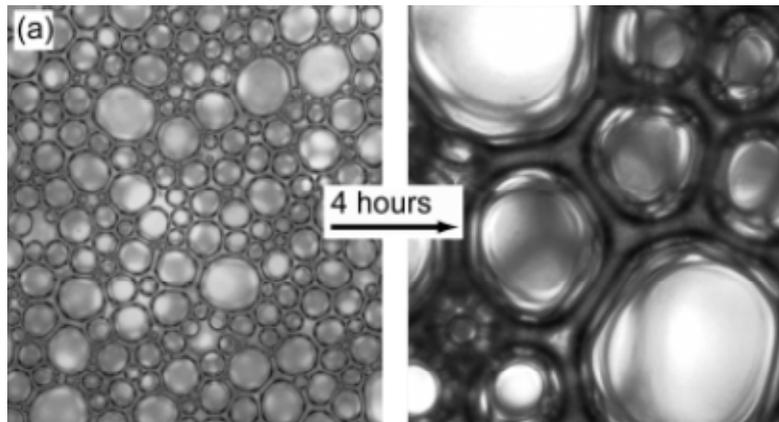
Coalescence is favored by attractive van der Waals forces (a)

and can only be hindered by providing steric and/or electrostatic repulsion among the interacting bubbles (b) by adding long-chain surfactants or proteins or by adding colloidal particles.

A.R.Studart et al JACS 89 [6]1771-1789 (2006)

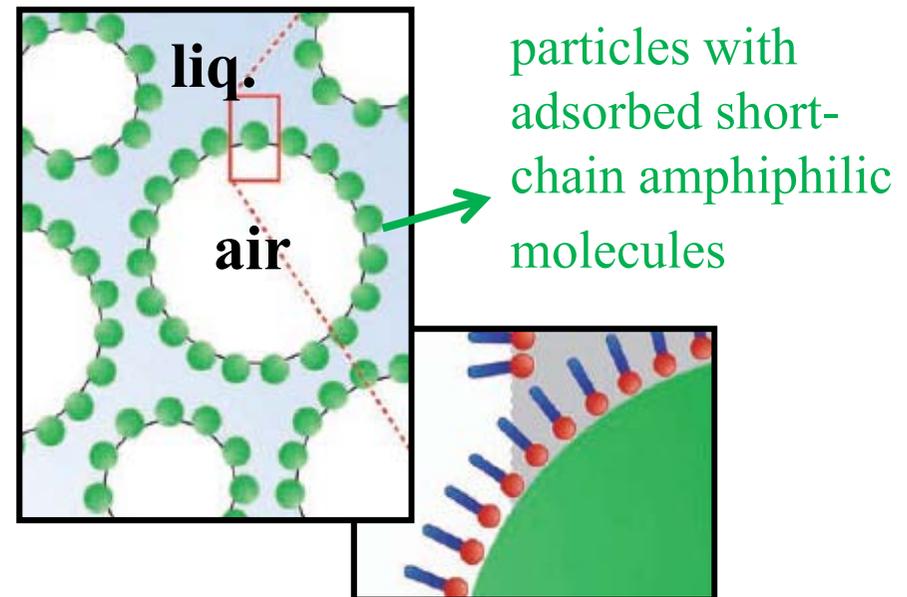
Direct foaming technique

Direct foaming with surfactant



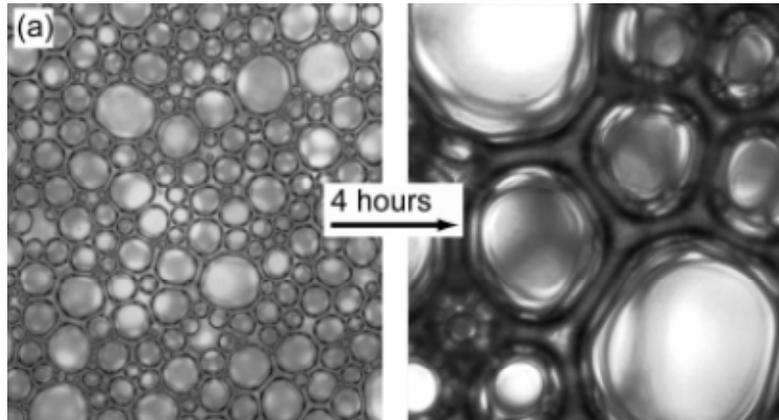
Direct foaming with particles

The stabilisation with colloidal particles produces macroporous ceramics with smaller pore sizes (10 to 100 µm instead of 35 to 1200 µm) .

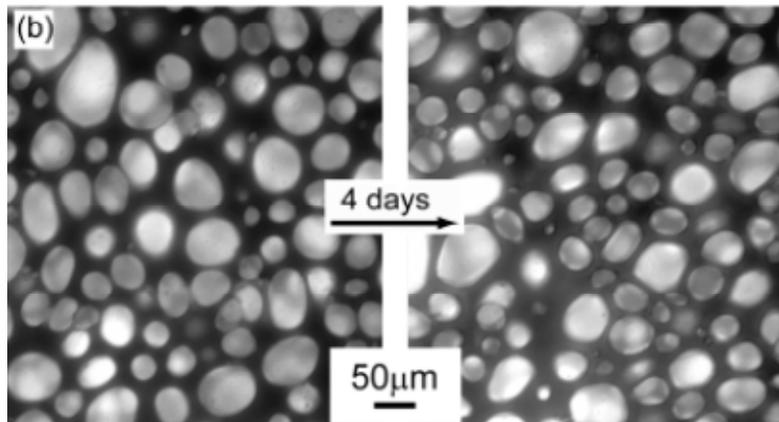


Direct foaming technique

Direct foaming with surfactant

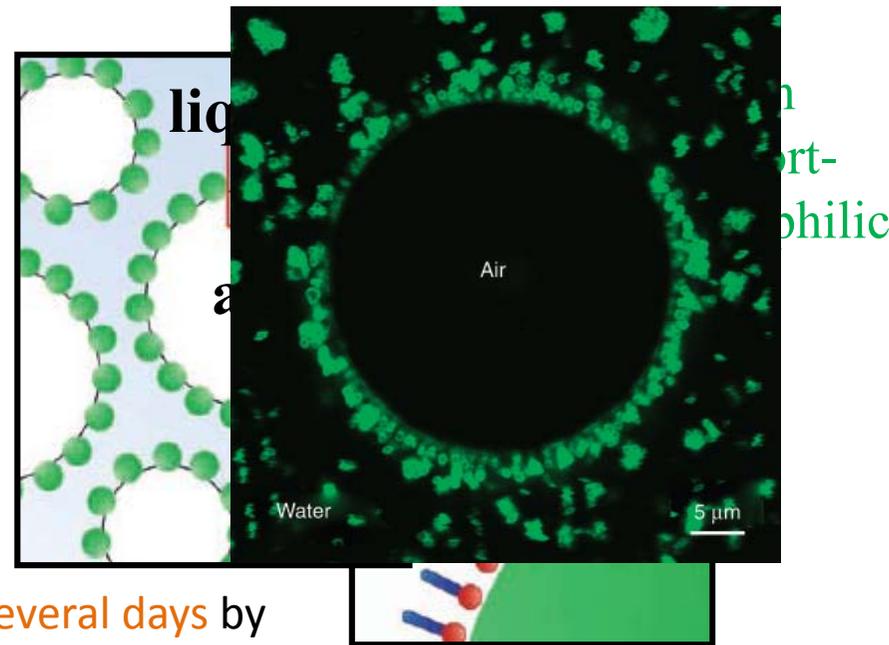


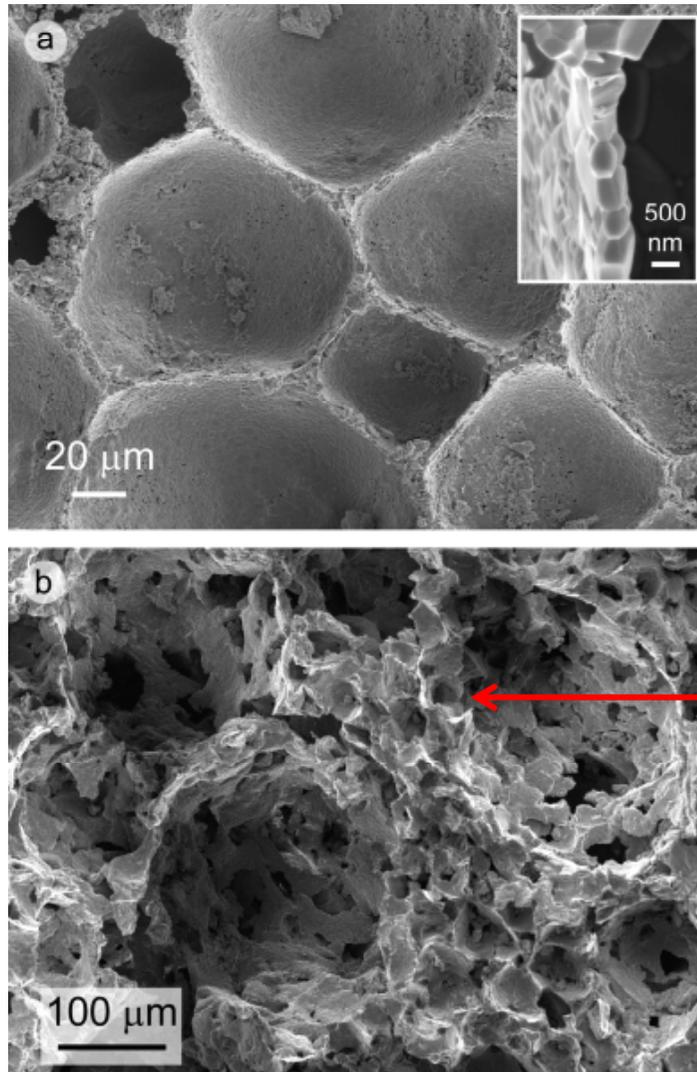
The foam lifetime can be increased to **several hours** by adsorbing long-chain surfactants.



Direct foaming with particles

The foam lifetime can be increased to **several days** by adsorbing colloidal particles in the air bubbles.

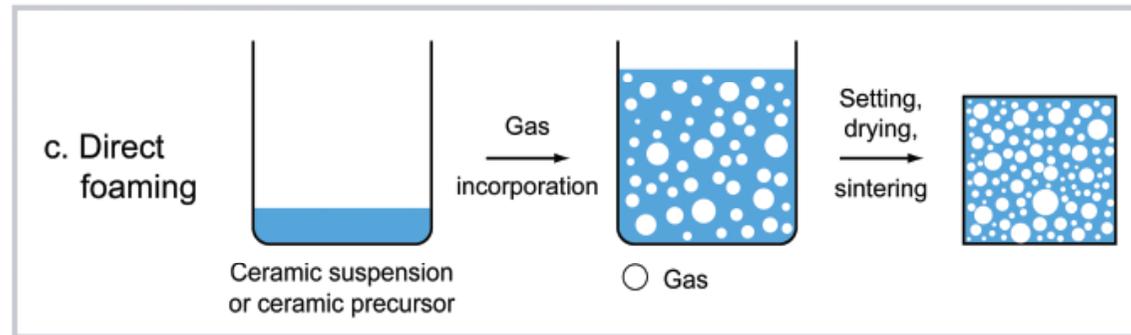




The direct foaming technique leads usually to **close porosity** (Fig a)

but **open porosity** ceramics can be obtained - by decreasing the concentration of stabilizing particles - or by adding minor amounts (<1wt%) of a sacrificial phase (e.g. graphite particles) (Fig b).

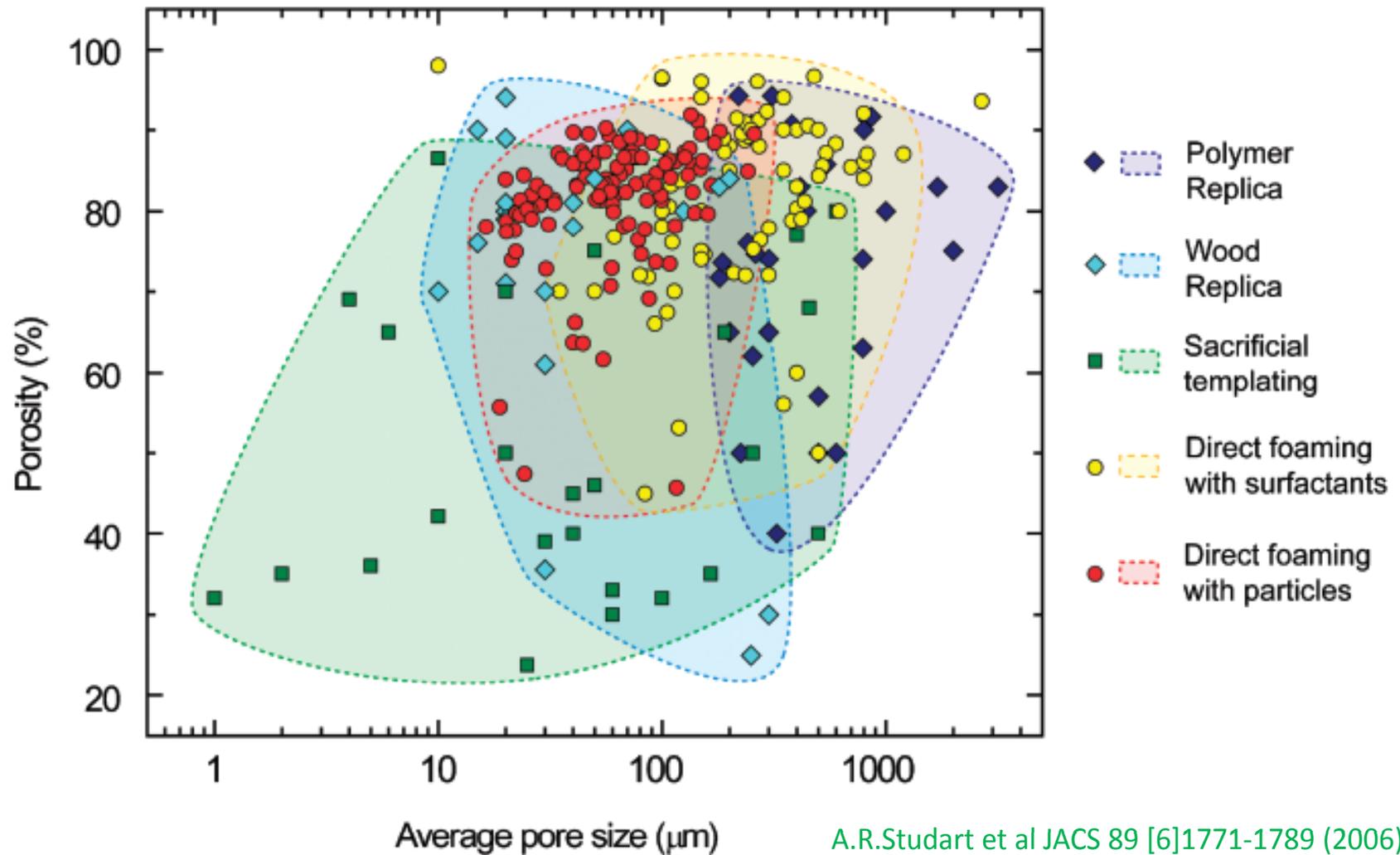
A.R.Studart et al JACS 89 [6]1771-1789 (2006)

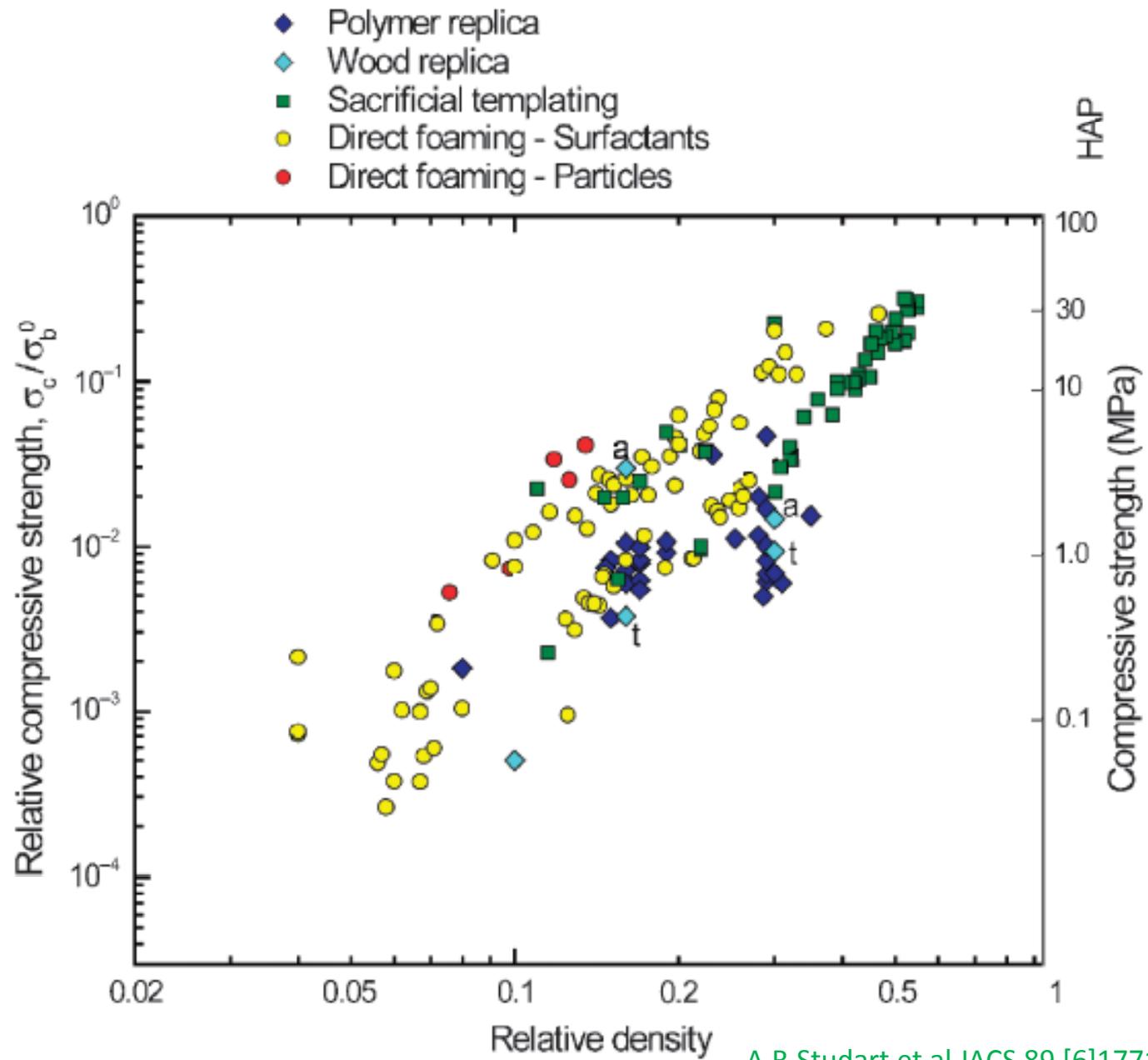


Direct foaming by gel casting technique

Another way to stabilise the bubbles is to gelify the slurry. Suspensions of CaP particles in water with dispersing agents and organic monomers are foamed by agitation with surfactant under a nitrogen atmosphere. In situ polymerisation of the monomers is initiated to provoke cross-linking and form a 3D polymeric network (gel) before casting. Porous samples are sintered. Foam volume (and hence porosity) could be controlled by the surfactant concentration in the slurry, producing pores of maximum diameter of 100–200 μm .

Comparison of porosity between various techniques





	Method	Porosity (%)	Pore size (μm)	Pore size distribution	Pore shape	Space distribution
Replica	PU sponge	40 to 95	150 to 1300	Wide	Random	Anisotropic
	Coral	20 to 50	150 to 500	Wide	Random	Anisotropic
	Wood	25 to 95	10 to 300	Trimodal	Elongated	Columnar
Sacrificial templates	PMMA beads	25 to 90	250 to 1000	Monomodal or multimodal	Spherical	Isotropic
	Freeze foaming	50 to 95	2 to 90	Bimodal	Spherical	Isotropic
	Ice-templating (freeze casting)	30 to 65	5 to 200 width 10 to 500 length	Monomodal	Ellipsoidal	Columnar
Direct foaming	With surfactant	40 to 95	30 to 1000	Wide	Spherical	Isotropic
	With particles	40 to 90	20 to 300	Wide	Spherical	Isotropic
	Gel casting	40 to 90	100 to 1000	Wide	Spherical	Isotropic

4. 3D-Additive manufacturing technique

3D Additive manufacturing technique consists of production of highly complex 3D objects using data generated by computer aided design (CAD) systems.

An image of a defect in a patient can be taken (e.g. by X-ray microtomography, CT scan), which is used to develop 3D CAD computer model. The computer can then reduce the model to slices or layers.

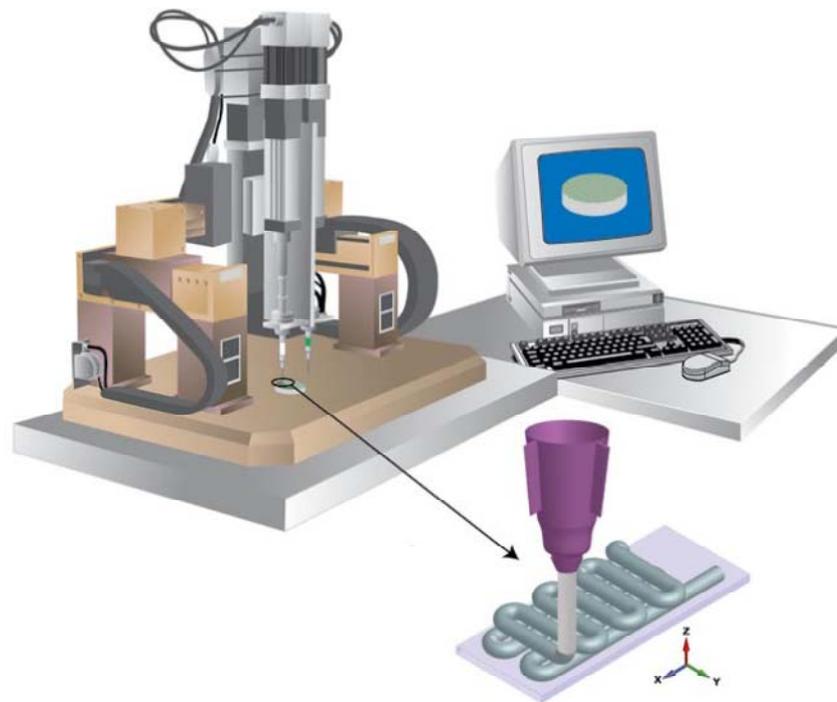
The 3D objects are constructed layer-by-layer using rapid prototyping techniques :

- Paste extrusion techniques,
- Selective laser sintering,
- Binder jetting,
- Stereo lithography.

These techniques are traditionally applied to polymers and recently extended to ceramics.

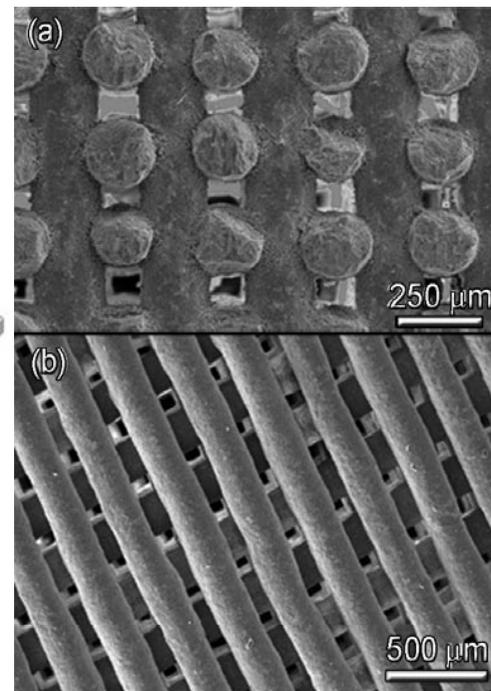
Robocasting

Robotic-assisted deposition consists of the robotic deposition of inks capable to fully supporting their own weight during assembly.

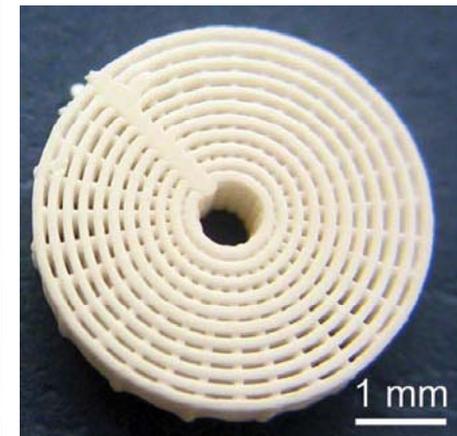


E.Munch et al 2008

Cross section



Surface



HA part with a gradient in porosity after printing and sintering.

Strut thickness : 200 to 500 μm

Line spacing : 75 to 500 μm

P: 45%

$\sigma_c = 25\text{-}40 \text{ MPa}$

Paste extrusion

FDM : fused deposition modeling

- Incandescent material extruded through a nozzle
- The solidification of each layer takes place instantly in contact with the previous one

3DPlot : threedimensional-plotting

Liquid or paste extruded through a mobile head, using compressed air

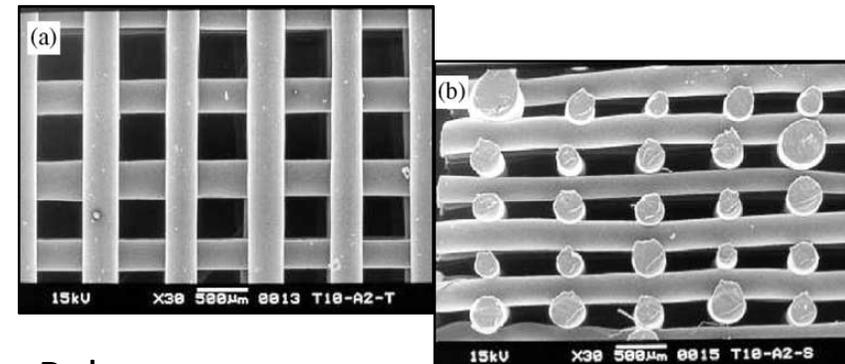
MJS : multiphase jet solidification

- Binder-powder mixture heated and extruded through a nozzle by a pumping system
- The nozzle scans horizontally to deposit the melting loading

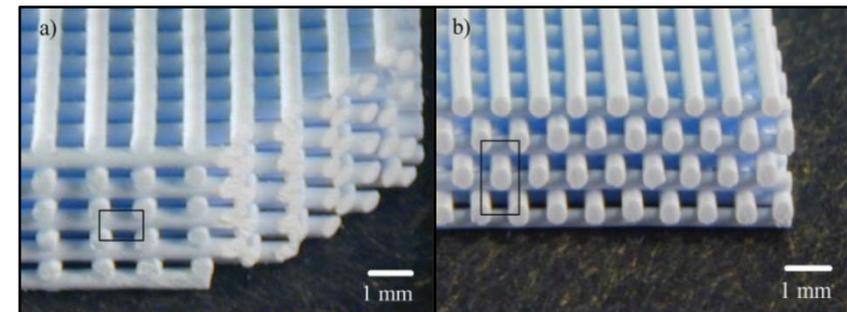
[Kupp et al., Proceedings of the SFF Symposium. 1997]

ROD : robotic dispensing

- Ejection of a slurry in a solvent to induce precipitation
- Freezing and lvonhilizing



Polymer *[Zein et al., Biomaterials. 2002;23:1169–85]*



Hydroxyapatite

[Dellinger et al., J Biomed Mater Res. 2007;82A:383–94]



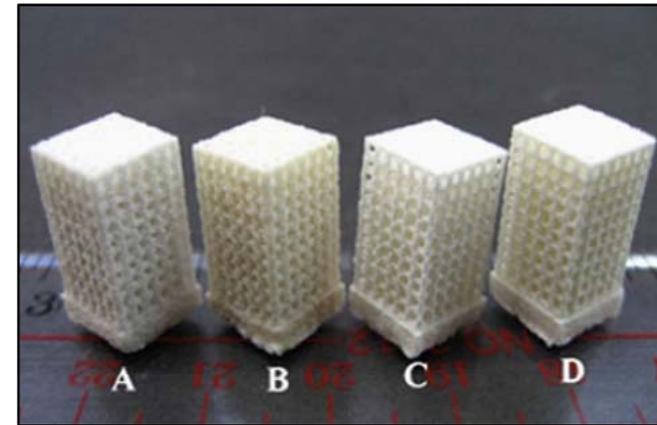
HA/Chitosan

[Ang et al., Mater. Sci. Eng. 2002;20:35–42]

Selective laser consolidation

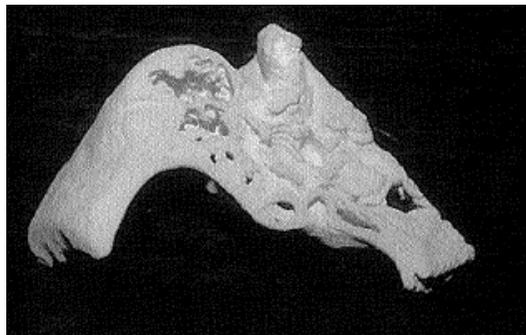
SLS : selective laser sintering

- A laser beam scans the surface of a powder bed, mixed with a binder
 → formation of a layer of material by selective sintering
- The non-sintered powder is then removed by brushing and / or blowing



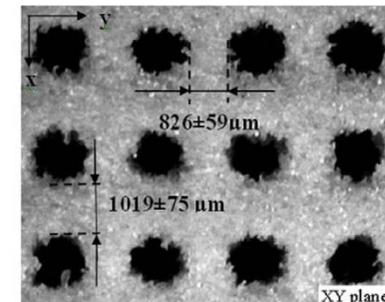
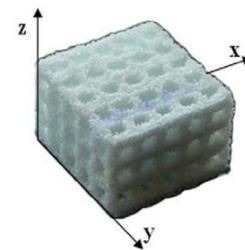
Polymer ; CaP ; polymer/CaP composite

[Duan et al., *Acta Biomater.* 2010;6:4495–505]



CaP craniofacial implant

[Lee et al., *Proc. Solid Free. Fabr. Symp.* 1994;191–7]



Polymer/HA composite

[Eosoly et al., *Acta Biomater.* 2010;6:2511–7]

Selective laser consolidation

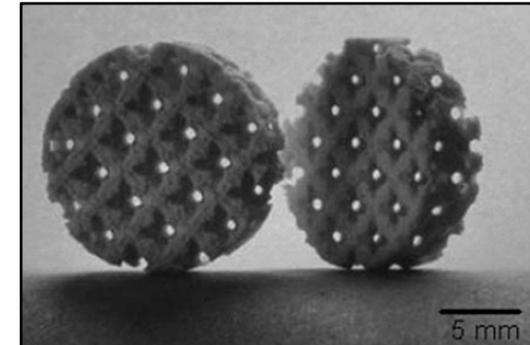
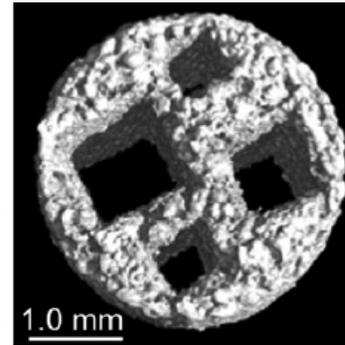
SLM : selective laser melting

The powder is melted under the laser irradiation



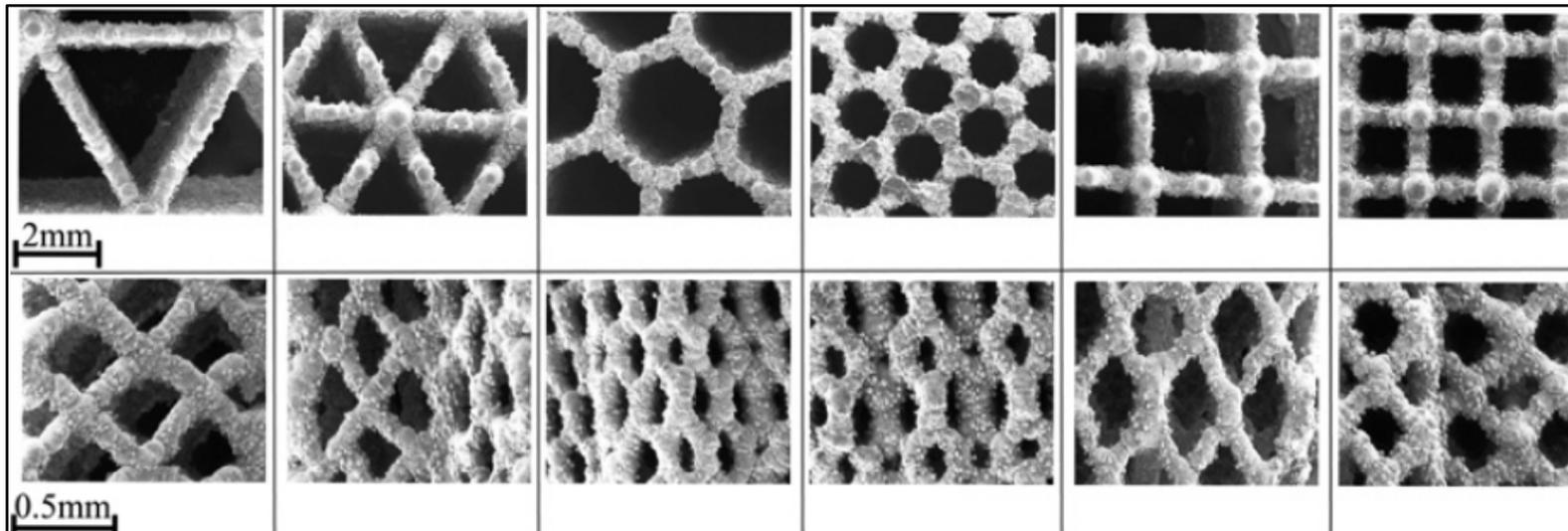
Titanium

[Fukuda et al., *Acta Biomater.* 2011;7:2327–36]



β -TCP / PDLLA composite

[Lindner et al., *J. Biomed. Mater. Res. A.* 2011;97:466–71]



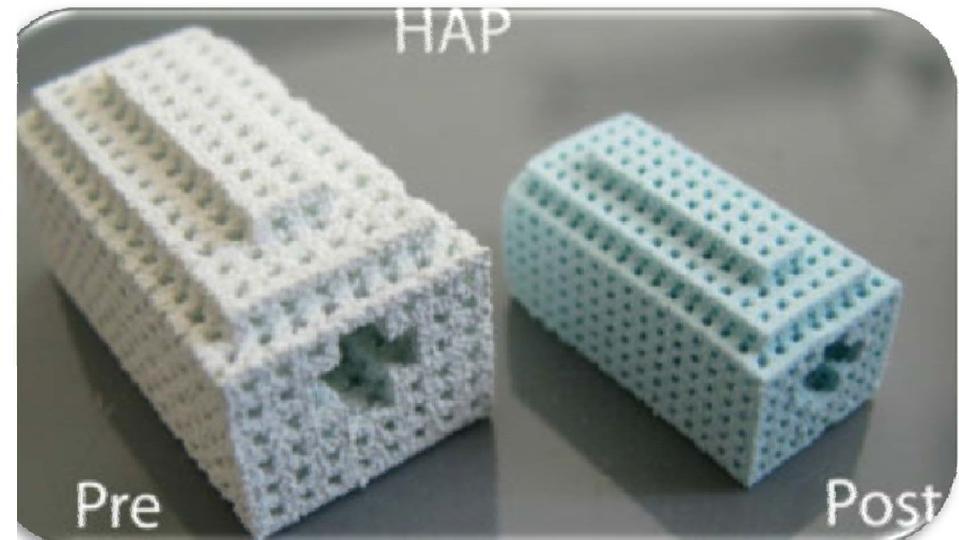
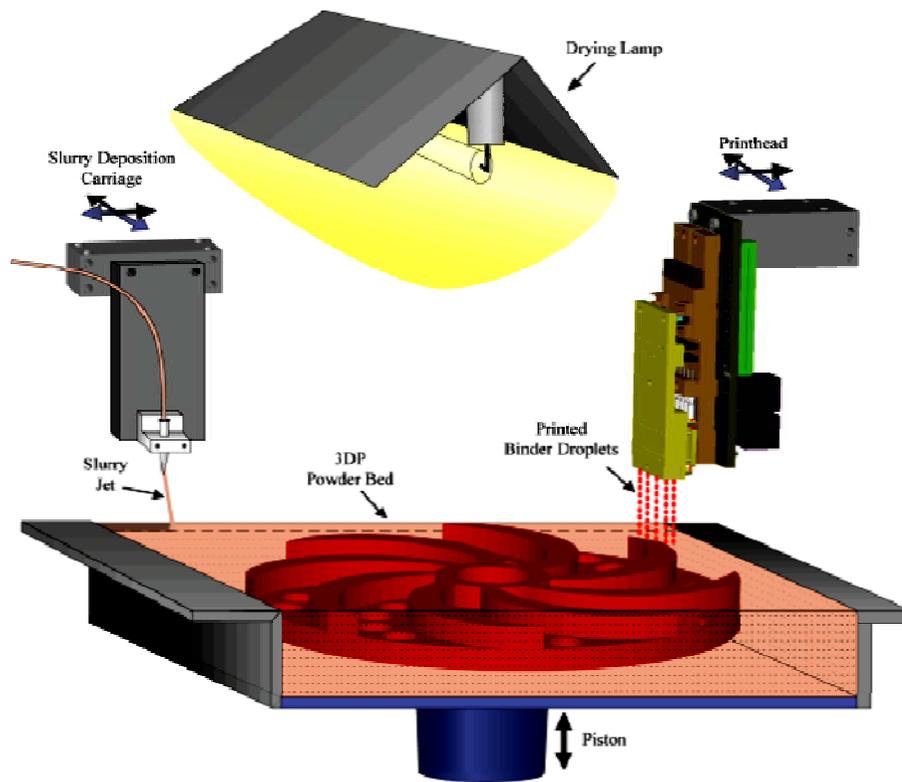
Ti-6Al-4V

[Van Bael et al., *Acta Biomater.* 2012;8:2824–34]

Binder jetting

- Binder jetting – a liquid bonding agent is selectively deposited to consolidate a powder bed

3DP : threedimensional-printing



Before
sintering

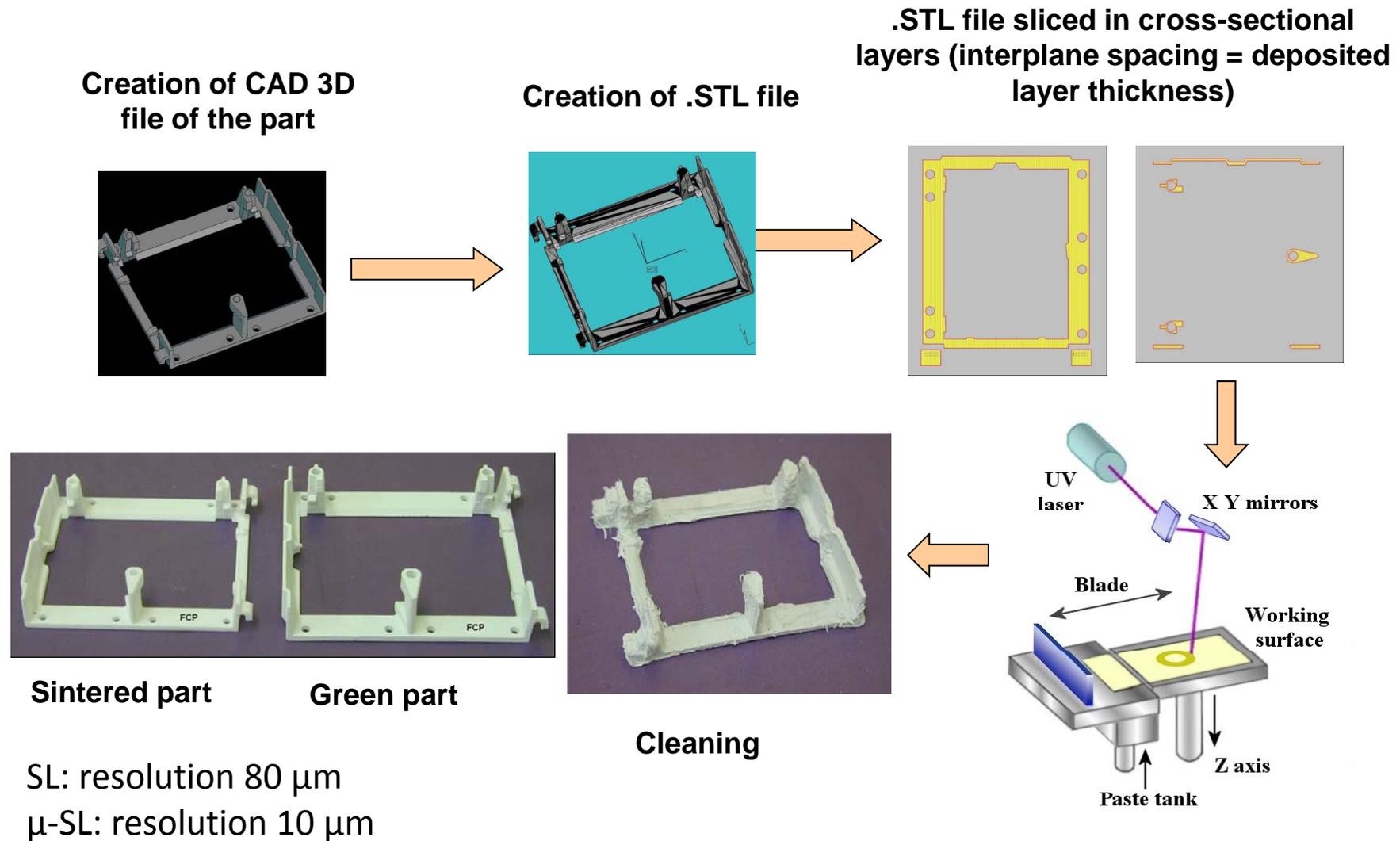
Hydroxyapatite

After
sintering

[Warnke et al., *J. Biomed. Mater. Res. B Appl. Biomater.* 2010;93:212–7]

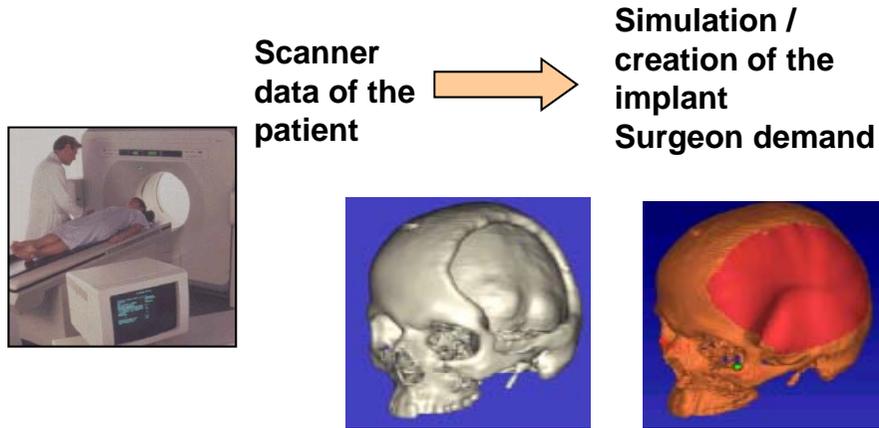
Stereolithography (SLA) and microstereolithography (μ -SLA)

suspension of ceramic particles in UV sensitive monomer/oligomer

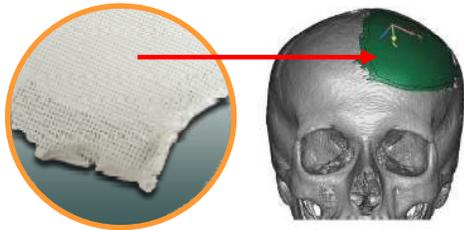


Stereolithography (SLA) and microstereolithography (μ -SLA)

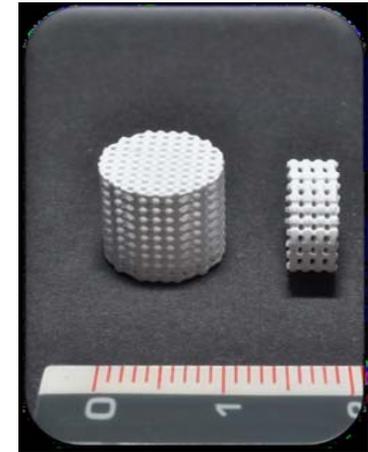
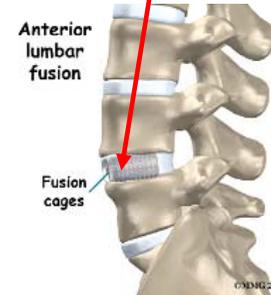
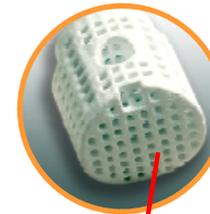
HAP Biactive Implant



3D implant realized from scanner data



Intervertebra bone substitute



Lithoz GmbH

Ocular implant

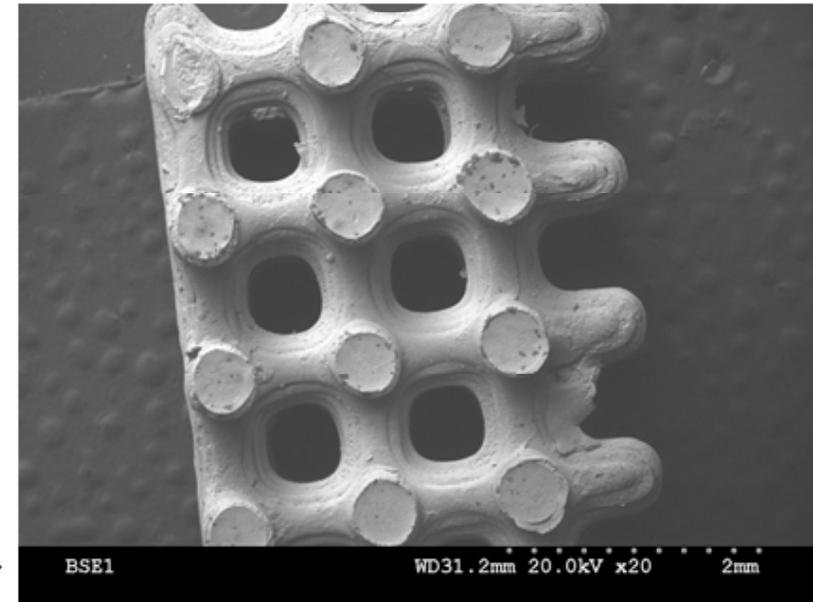
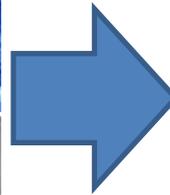
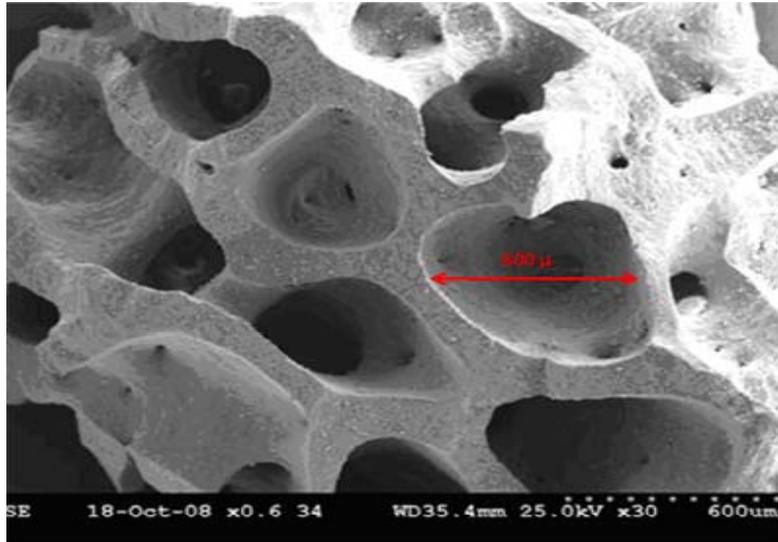
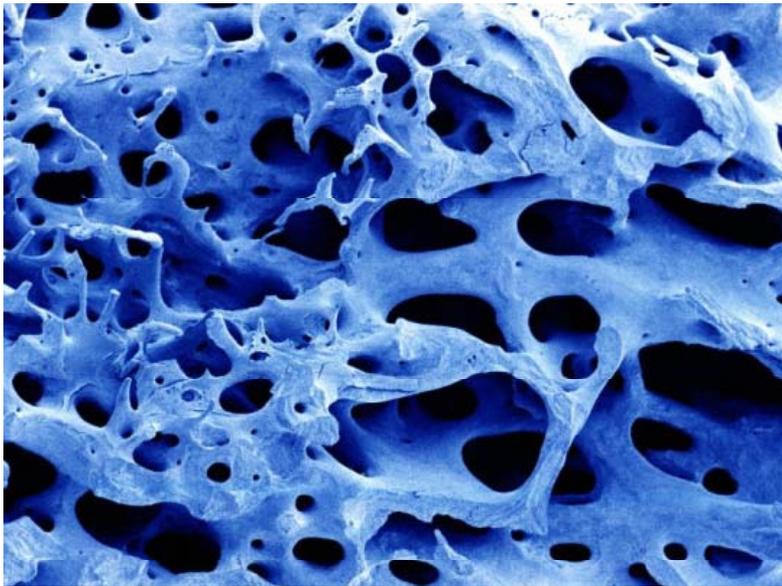


HAP parts implanted at Limoges Hospital

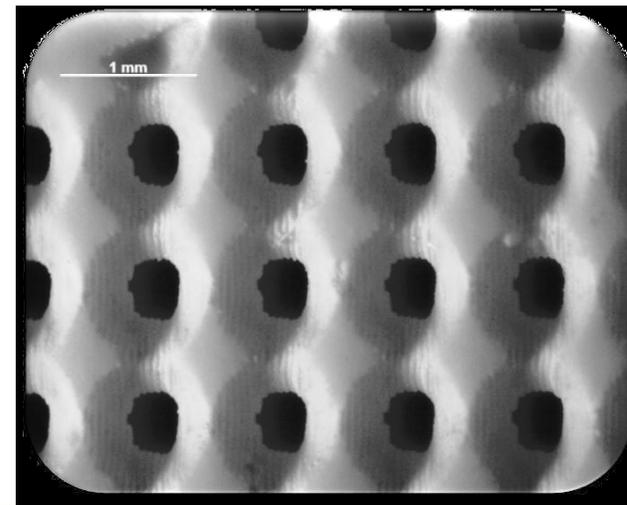


Third method: 3D printing of ceramic slurry

Human bone



JC Hornez LMCPA January 2015



Lithoz

3D AM techniques	Tolerance	Advantages	Limitations
Material extrusion	0.5 to 1mm	<ul style="list-style-type: none"> - Ease of support removal - Good mechanical properties - No material waste 	<ul style="list-style-type: none"> - Precision limited by the filament diameter (about 1mm)
Binder jetting	0.05 to 0.1mm	<ul style="list-style-type: none"> - Wide variety of materials - Simple technology 	<ul style="list-style-type: none"> - High roughness of the surface - Expensive technology - Poor mechanical properties - Use of toxic organic binders
Selective laser consolidation	0.2 to 0.5mm	<ul style="list-style-type: none"> - High production rates possible - Complex designs - Low costs - Good surface finishing 	<ul style="list-style-type: none"> - High roughness of the surface - Poor mechanical properties - Limited to materials which absorb IR light
Stereolithography	0.01 to 0.1mm	<ul style="list-style-type: none"> - Complex designs - Good surface finishing - Good mechanical properties - High accuracy 	<ul style="list-style-type: none"> - Expensive photosensitive resins - Cleaning step necessary - Control of the vertical accuracy

Review: Additive Manufacturing to Produce Complex 3D Ceramic Parts
T. Chartier. C. Dupas.M. Lasgorceix. J. Brie.E. Champion.N. Delhote. Chr. Chaout

J. Ceram. Sci. Tech., xx [xx] xx (2015)
DOI: 10.4416/JCST2014-00040

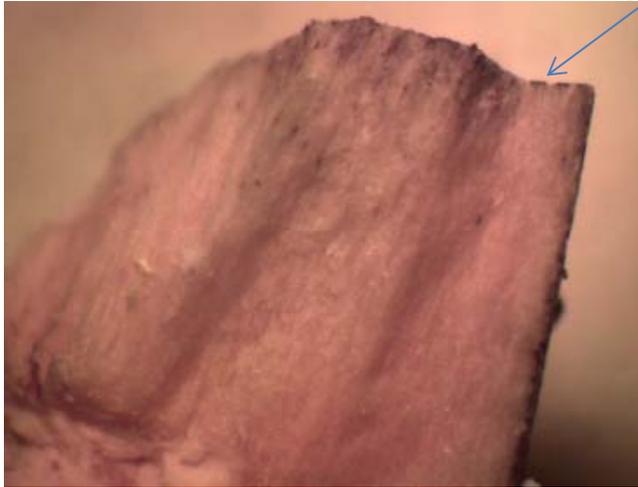
How to mimic natural bone?

Criteria for an ideal scaffold for bone regeneration:

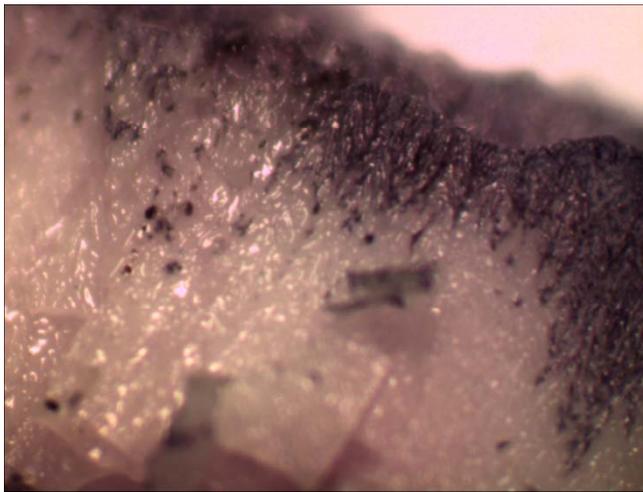
- 1 - Is made from a biocompatible material,
- 2- acts as template for tissue growth in 3 dimensions,
- 3- has an interconnected macro-porous network with diameters > 100µm for cell penetration, tissue ingrowth and vascularisation, and nutrient delivery to the centre.
- 4- bonds to the host tissue
- 5- exhibits a surface texture favorable to cell adhesion
- 6- resorbs at the same rate as the tissue is repaired
- 7- is made from processing technique that can produce irregular shapes to match that of the defect in the bone of the patient,
- 8- exhibits mechanical properties sufficient to be able to regenerate tissue in bone in load bearing sites,
- 9- has the potential to be commercially producible to the required ISO or FDA standards.

J.R.Jones, L.L.Hench Current opinion in solid state and materials science 7 (2003) 301-307

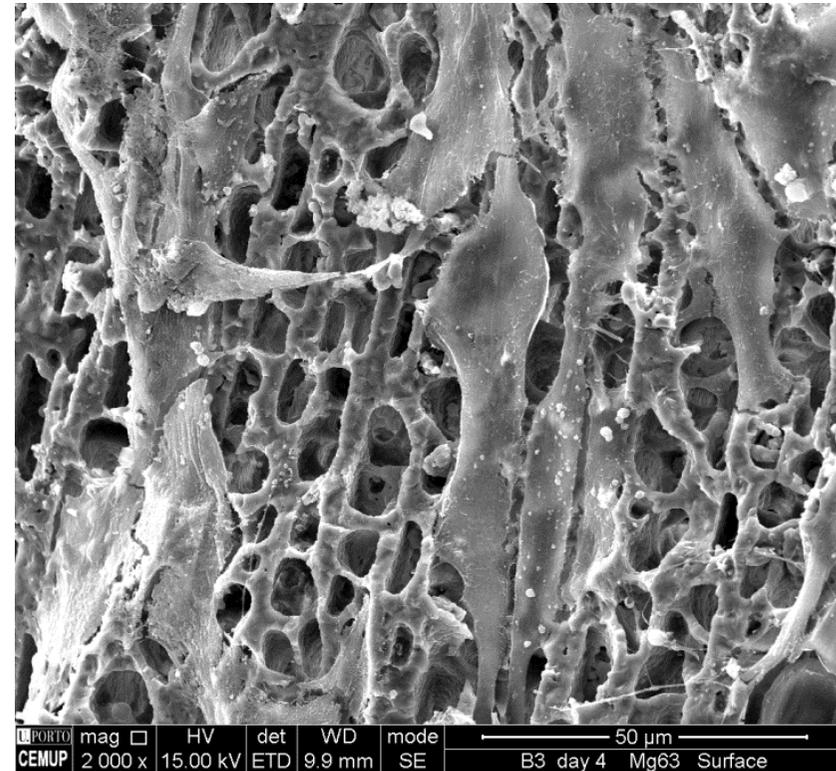
Ice-templating



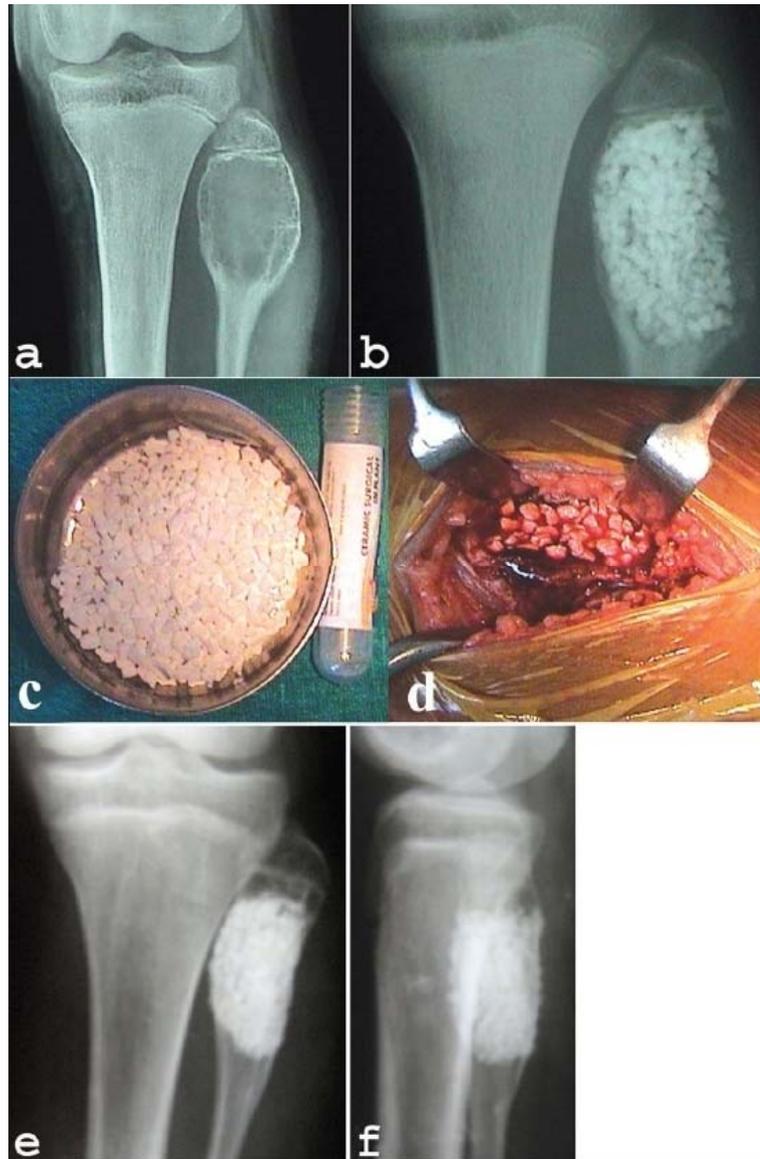
53% porosity $a=6\ \mu\text{m}$ and $b=13\ \mu\text{m}$



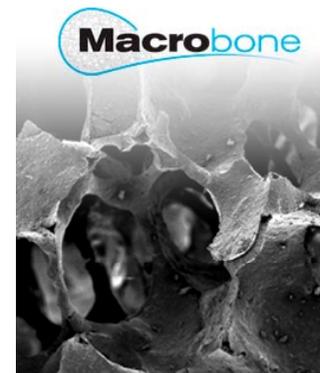
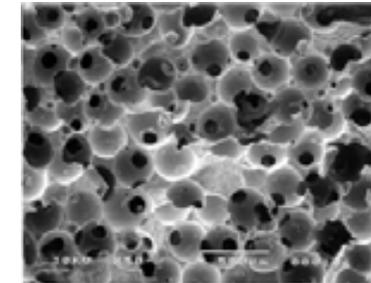
36% porosity $a=44\ \mu\text{m}$ and $b=149\ \mu\text{m}$



MG63 size: $10\ \mu\text{m}$ width, $50\ \mu\text{m}$ length



Vitoss Bone Graft Substitute
Stryker



B 上海贝奥路生物材料有限公司
Shanghai Bio-lu Biomaterials Co., Ltd

Granule form of synthetic β -TCP with pore size of 100-500 μm (Synthes- "ChronOS").

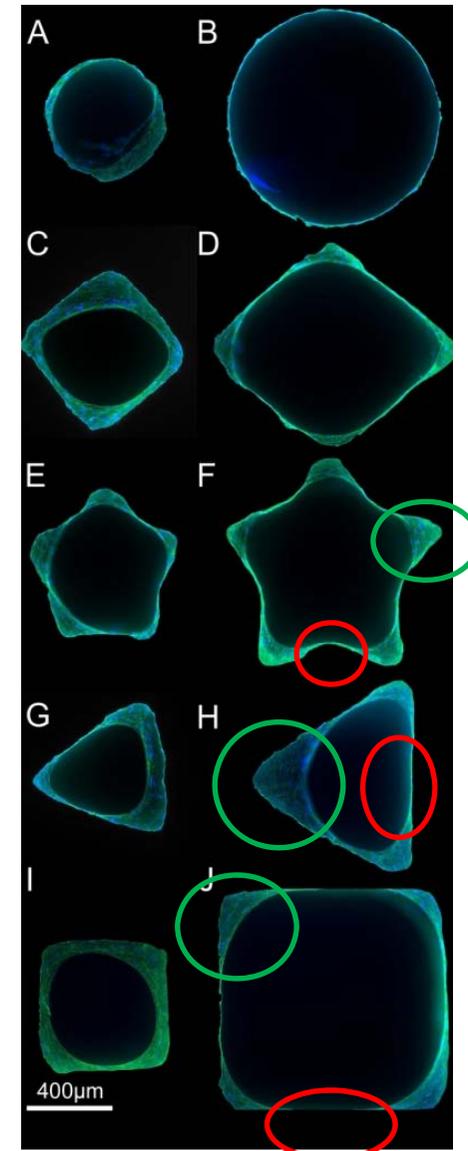
In vitro cell colonisation



7 days

Favoured colonization in salient angles and concave areas

Flat or convexes areas → migration decrease



* collaboration with Dr Urda Rüdric



M.Lasgorceix, Ph.D. SPCTS Limoges 2014

Conclusion

- Many techniques are today employed to produce macroporous bioceramics with varying structural and mechanical properties.
- Most of them are already commercially used.
- The more recent 3D-manufacturing methods are promising to producing specific interconnected scaffold architectures with various pore size and morphologies, not achievable by the usual techniques .
- The choice of the shaping technique has to be done according to the desired pore size range and architecture in relation to the application (implantation site, defect size...)

Acknowledgments

T.Chartier, M.Lasgorceix, *SPCTS Limoges*

A.Tampieri, *ISTEC Faenza*

M.Ahlhelm, *IKTS Fraunhofer*

A.Zocca, P.Colombo, *Dept of Industrial Engineering
University of Padova*

D.Hautcoeur, F.Cambier, *BCRC Mons*

V.Sciamanna, M.Gonon, *University of Mons*

