Glass Processing

Lecture #26. Porous Glass

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Lectures available at:
www.lehigh.edu/imi

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Outline

1. Why porous glass?
2. What is porous glass?
3. Common applications
4. Fabrication methods
   Especially, phase separation
5. Recent progress
   Multi-porous glass for tissue engineering

Why porous glass?

- Glass containers are superior to ceramic vessels due to the lack of porosity!
- Glass-ceramic is better than glass or ceramic because of higher strength that results from lack of porosity – *see lectures by Edgar Zanotto.*
- Glass manufacturers must work hard to eliminate pores – the fining process – *see lectures by Mathieu Hubert*

Following Kelly (1988), consider pores as a second phase i.e. porous glass as a two-phase material. Then design or engineer the second phase for enhanced performance!

A. Kelly, Phil. Trans. R. Soc. A (2006) 364, 5–14

What is porous? Nomenclature

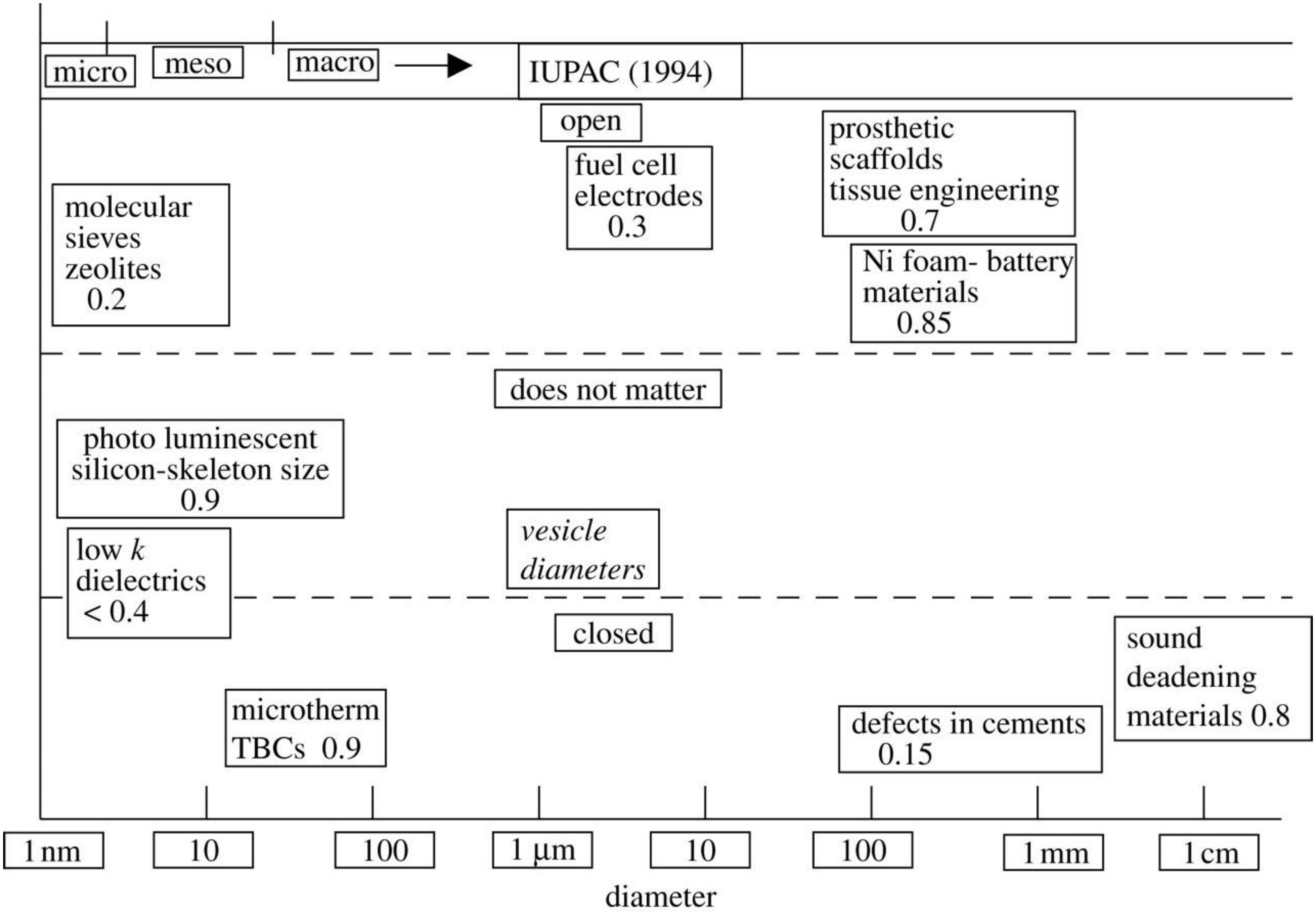
Porous material (broad term), foam, cellular solid, sponge (flexible foam)

Key Parameters

- Closed vs. interconnected pores
- Constitutively (inherent) vs. subtractively (artificial) porous
- Size and size-distribution
- Volume fraction, $V_p/V_{tot.}$
  15-75% for flitration, fluid flow control, self-lubricating bearings, battery electrodes
  80-90% in foams for energy/sound/ absorption, T management, vibration dampening
- Aspect ratio, alignment of pores

IUPAC: Micropores <2nm. Mesopores 2-50 nm. Macropores >50 nm
OK for catalysts, absorbents and membranes, but not other applications
Other: Nanopores <100nm (~mean free path of air at STP). Macropores >10 μm (~size of cells).

Pores for specific applications



A. Kelly, Phil. Trans. R. Soc. A (2006) 364, 5–14

Thermal insulators

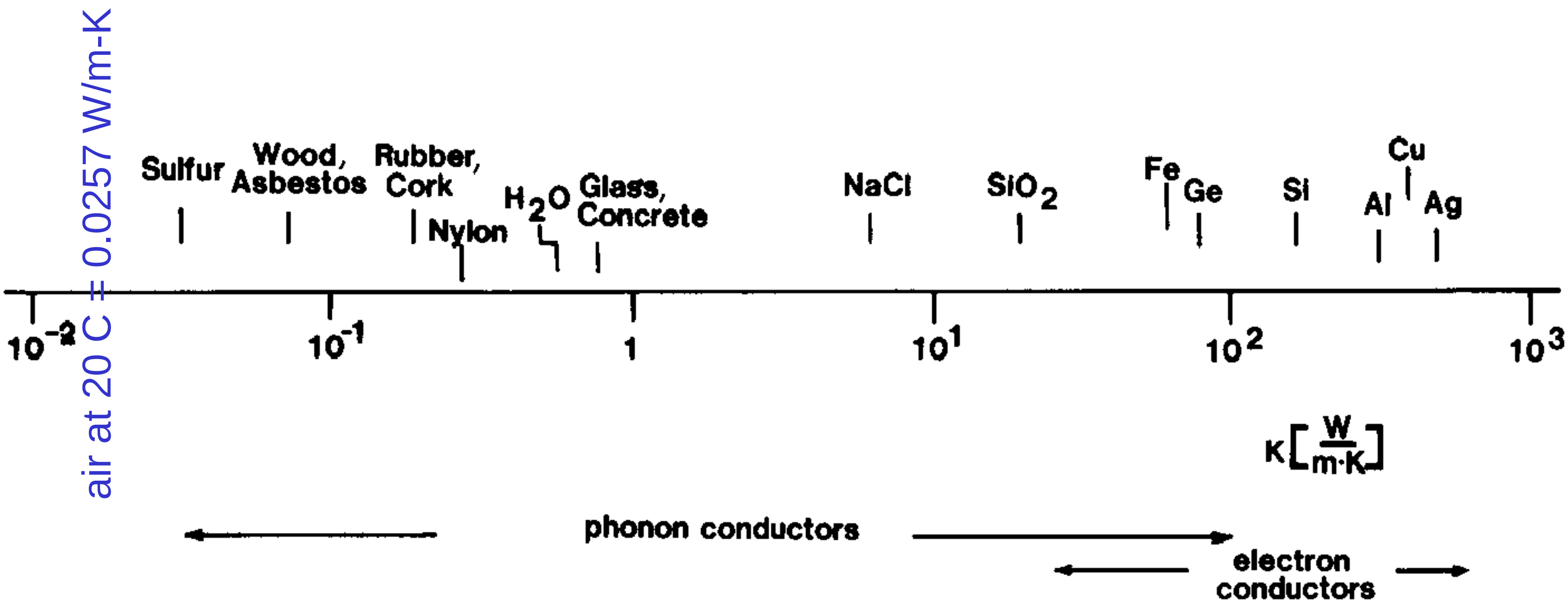


Figure 18.1. Room temperature thermal conductivities for some materials.

Engineering a thermal insulator

Low thermal conductivity of a solid requires minimum:

(i) heat conduction through solid ⇒ use glass / plastic / wood. Use small cross-section of the solid i.e. high vol% of pores

(ii) gaseous convection ⇒ Use vacuum or low pressure gas. Pores should be closed and small

(iii) transmission of infrared radiation (blackbody radiation) ⇒ use opacifiers, scatterers

(iv) gaseous molecular conduction ⇒ The mean free path of still air is ~100 nm at STP

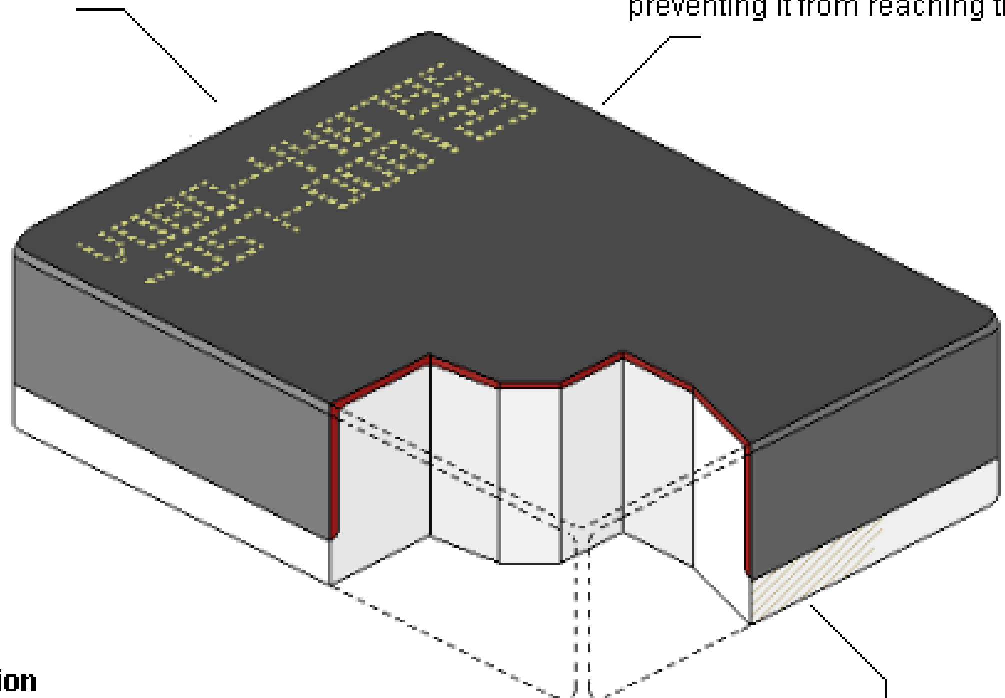
⇒ When temperatures are high, the best thermal insulator is nano-porous silica – for silica aerogel thermal conductivity is 0.003 W/m-K.

Same guidelines apply to insulation from sound and shock waves i.e. for acoustic, vibration damping ⇒ Use foams

Space shuttle tile

Identification number
Each tile has an identification number which tells batch and location. This number can be fed into a computer to produce an identical tile.

Coating
The outer portion of a tile is covered with a black-glazed coating of borosilicate.
These tiles do most of the coating job by shedding about 95% of the heat encountered.
The remaining 5% is absorbed by the tile's interior, preventing it from reaching the orbiter's aluminum skin.



Composition
90% air, 10% silica fibers a few milimeters thick. The tiles feels similar to plastic foam.
The silica fibers are derived from high-quality sand.

Glue
A silicon-rubber glue similar to common bathtub caulking, bonds a tile to a felt pad, that is in turn bonded to the orbiter's skin. The felt absorbs the stresses of airframe bending that could damage the tiles.

Space shuttle tile (sintered silica fiber) demo: https://www.youtube.com/watch?v=Pp9Yax8UNoM

https://en.wikipedia.org/wiki/Space_Shuttle_thermal_protection_system

Filters, sieves, membranes, catalyst substrates

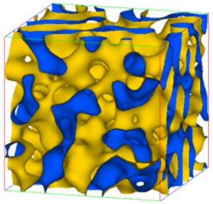
- Natural and synthetic zeolites – crystalline silicates with interconnected pores 1-10 nm diameter ~ 20 vol%.
- Microporous silica membranes with controlled pore size.
- High temperature filters.

Enke, Microporous and Mesoporous Materials 60 (2003) 19–30

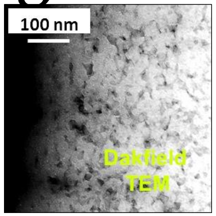
Common approaches for fabricating 3D porous glass structures

1. Dry pressing/sintering

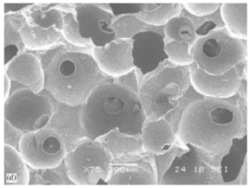
2. Phase separation



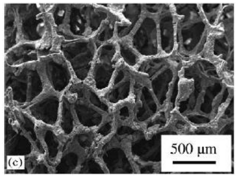
3. Sol-gel based processing



4. Foaming

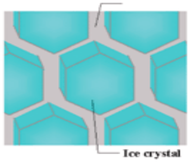


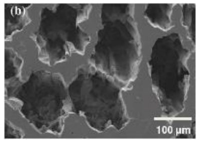
5. Polymer sponge replication



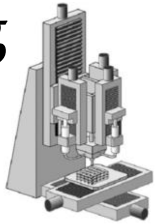
6. Add/remove pore former

7. Freeze casting

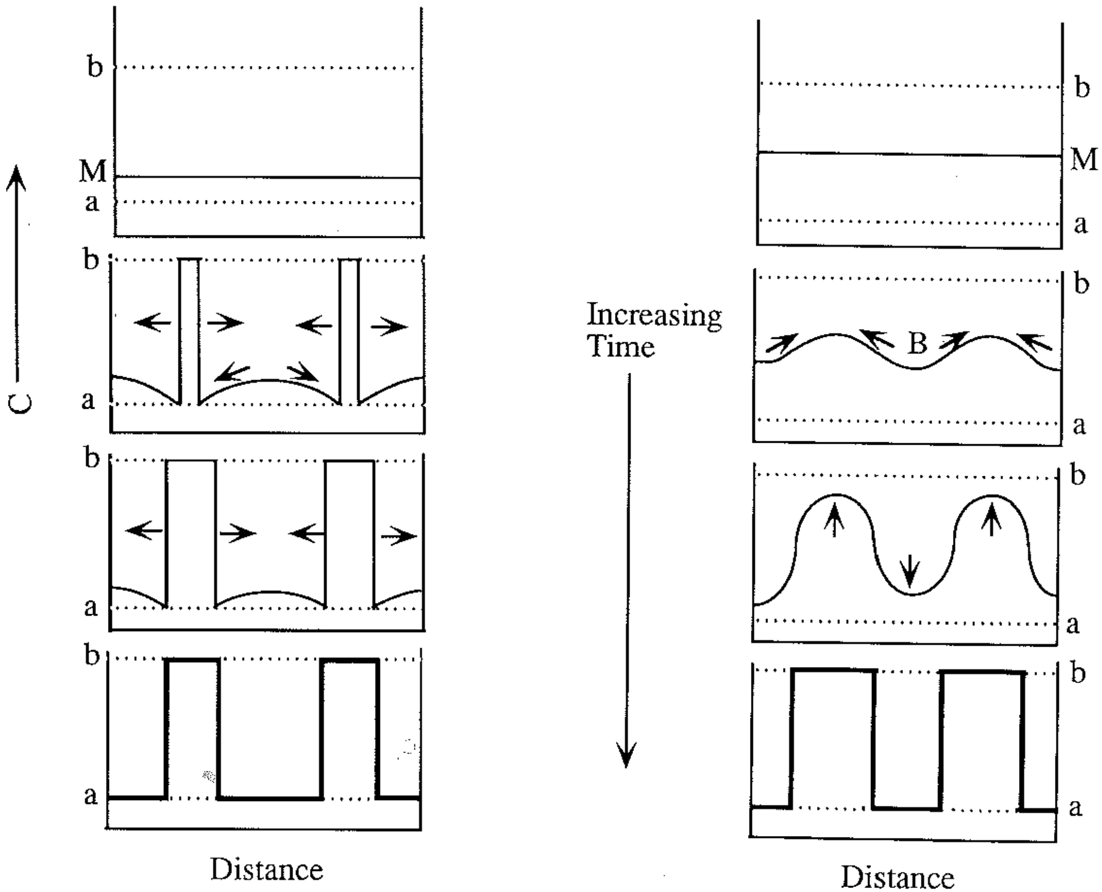




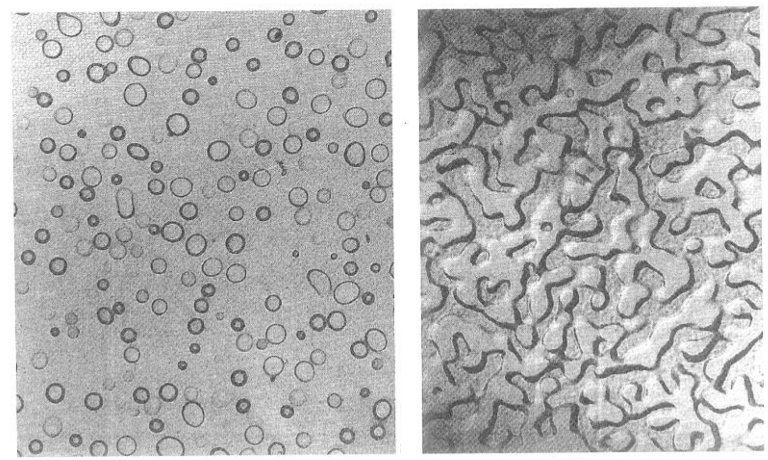
8. 3D printing



Microstructure evolution upon phase separation



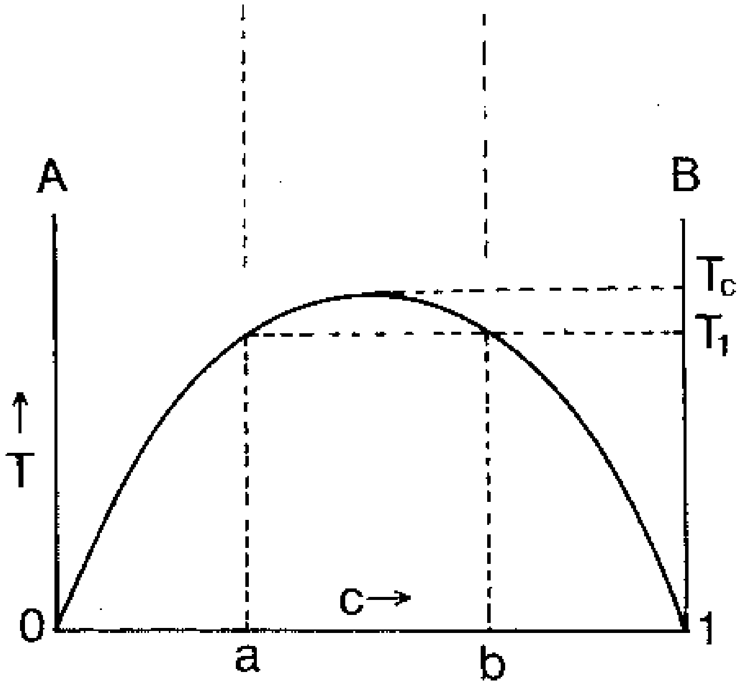
(a) (b)

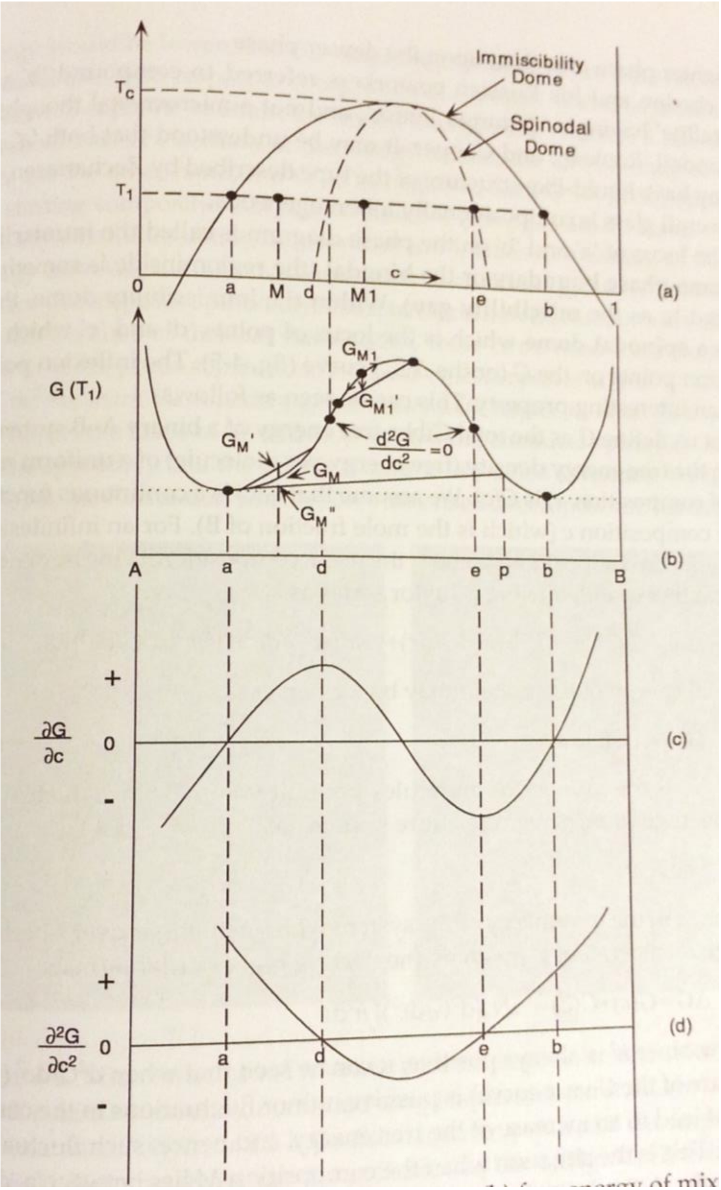


(a) (b)

Cahn and Charles, Phys Chem Glass (1965)

Choice of composition for interconnected porosity





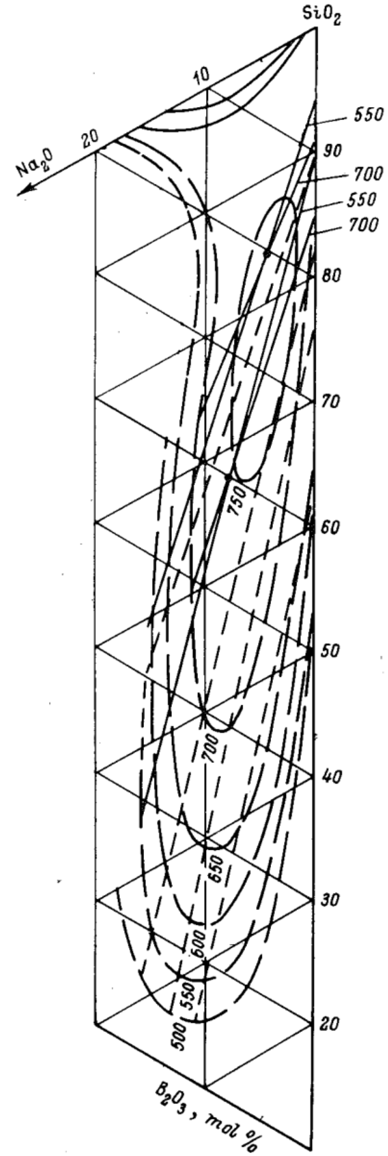
Fundamental of Inorganic Glasses by Varshneya

Phase separation in Na_2O-B_2O_3-SiO_2 system

Vycor Process

- 5-10% Na_2O - 20-35% B_2O_3 - 55-75%SiO_2
- Melt at ~1500C
- Heat treat at 500-600 C spinodal structure – glass is opalescent
- Immerse in H_2SO_4 at 90C to leach sodium borate phase
- Obtain 25-40 % porosity of interconnected 2-5 nm nanopores connected by 96% SiO_2 glass phase.
- (*To obtain solid glass, heat at 1100 C to get transparent Vycor glass*.)

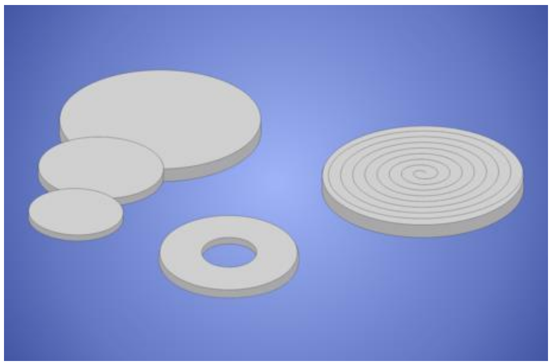
- (*Pyrex is a high silica glass composition in the same system, also phase separated, but with droplet structure for high chemical durability*.)

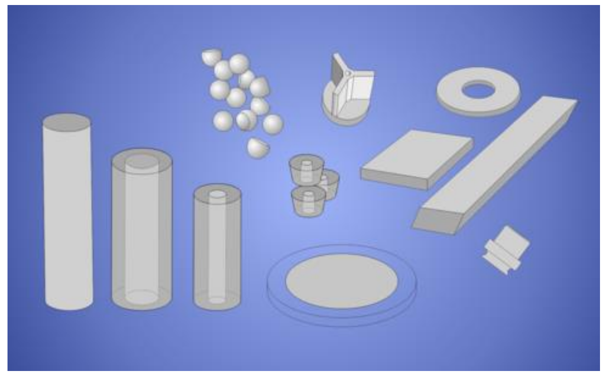


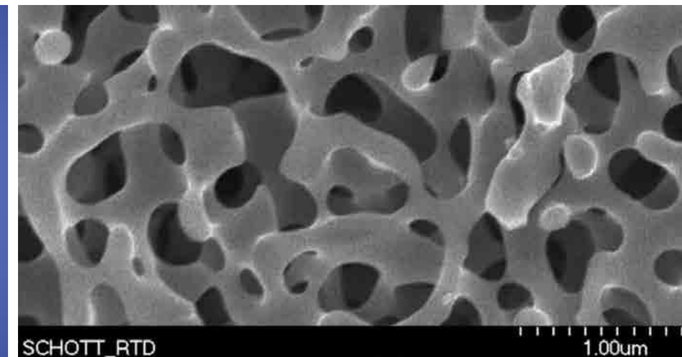
(a)

Examples of commercial products

- Corning Porous Vycor 7930
- VitraPOR® glass filters
- SCHOTT CoralPor® Porous Glass







Product Specification Examples

	CoralPor® 1000	CoralPor® 2000
Average pore dia	4 – 10 nm	40 – 300 nm
Pore dia range	10 – 30 %	7 – 25 %
Surface area	100 – 170 m^2/g	7 – 40 m^2/g
Pore volume	0.2 – 0.3 cc/g	0.4 – 1.0 cc/g

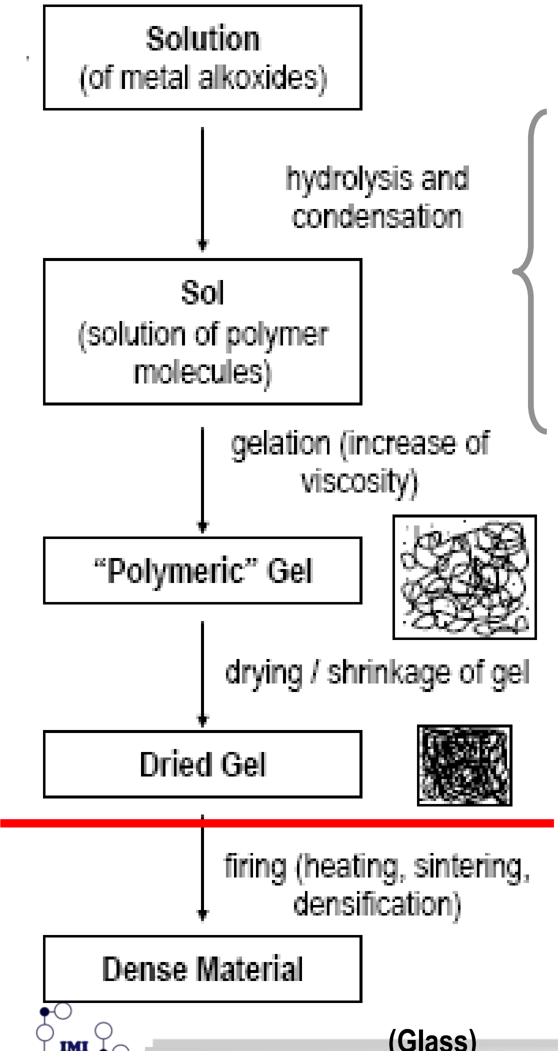
Typical Product Applications

CoralPor® 1000	CoralPor® 2000
• Reference electrode junctions • Desiccants • Coatings • Medical devices	• Chromatography • Synthesis substrate/ catalyst support

http://www.us.schott.com/english/download/06.12.13-final-datasheet-coralpor-porous-glass-new.pdf

Sol-gel Method (see lectures by Dr. Lisa Klein)

Chemical route to synthesize glassy or ceramic materials at relatively **low temperatures**, based on **wet chemistry processing,** which involves the **preparation of a sol**, the **gelation of the sol** and the **removal of the liquid existing in fine interconnected channels within the gel**.



Hydrolysis:

$Si\text{-}(OR)_4 + H_2O \rightarrow Si(OH)(OR)_3 + ROH$

Condensation:

$2\ Si\text{-}OH \rightarrow Si\text{-}O\text{-}Si + H_2O$

$Si\text{-}OH + Si\text{-}OR \rightarrow Si\text{-}O\text{-}Si + ROH$

The hydrolysis of a metal alkoxide (M-OR) produces M-OH, which condenses with other M-OH resulting in M-O-M and water

- Cheap and versatile
- High homogeneity (due to mixing at the molecular level) and purity
- Extended composition ranges
- **Better control of the structure, including porosity and particle size**
- **Intrinsic nanoporosity**

Change in strategy to treat damaged tissue

Replacement → Regeneration

Selection Criteria

- Biocompatible, preferably bioactive for rapid tissue growth
- **Interconnected macro (~200µm) porosity to allow cell migration and proliferation**
- **Resorbable at ~ new tissue growth rate**
- ‘Appropriate’ mechanical properties
- Easy Fabrication in irregular shapes & sizes
- Inexpensive
- Reliable and reproducible performance

Conclusion:

Bioactive glass is one of the most promising material for bone regeneration scaffolds, but it degrades too slowly!

Solution: add nanopores for high surface area!

Hench, Boccaccini, Ducheyne, Jones, Wheeler et al., Hamadouche et al., Zhang et al.,

Nanopores

- Allow independent control of degradation rate
- Provide stronger and faster bonding between the glass and bone cells
- Help in nutrition supply

Ideal solution:

Introduce both nano and macro pores simultaneously

Multi-scale phase separation

- **Typical glass is a homogenous solid**
- **Coexistence of nano and macro pores is thermodynamically unstable**

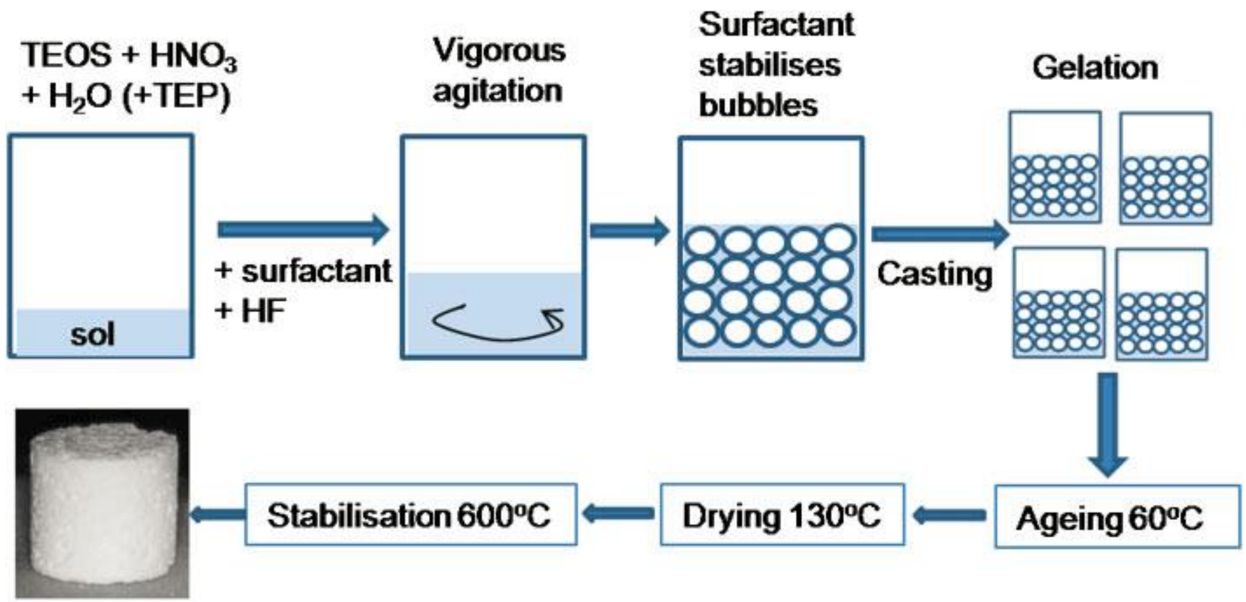
Our solution:

- Create interconnected, **multi-scale** phase separation
- Then remove phases selectively

Foaming

Upon hydrolysis, foam the sol by vigorous agitation with the addition of surfactant (Teepol, a detergent containing surfactants), water (improves foamability of surfactant), and 5 vol% HF as catalyst for polycondensation.

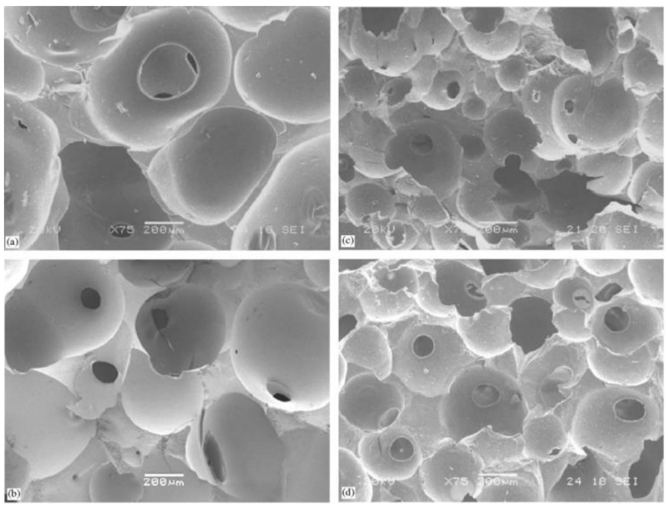
The surfactant stabilizes the bubbles formed by air entrapment during the early stages of foaming by lowering the surface tension of the solution.
As viscosity rapidly increases with gelling the pores are stabilized. Then the gel can be cast into molds.



J.R. Jones, L.L. Hench, J. Biomed Res. 2004

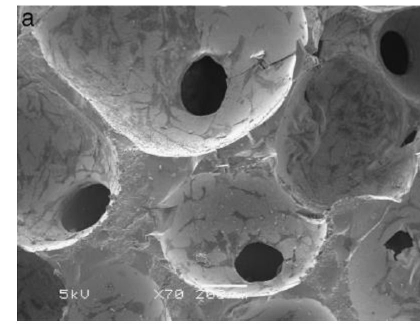
Foam structure

Suitable for porous monolithic samples or coatings on metals, polymers or ceramics



Interconnectivity of pores requires high vol% of pores. Then the mechanical strength is poor.

Also the neck of interconnection is much smaller than the pore size.



Jones et al. 2006, 2007

The Melt-Quench-Heat-Etch Method

Main Steps

(A) ***1st Step:*** Selection of glass composition based on its ability to phase separate; melt and cast.

(B) 2nd Step: Heat treatment to create additional interconnected phase separation/cryst.

(C) 3rd Step: Chemical treatment to dissolve away selected phases

Melt at 1500^oC

⇩

Quenching

⇩

Glass

⇩

Heat Treatment

⇩

Glass-Ceramic

⇩

Chemical Treatment

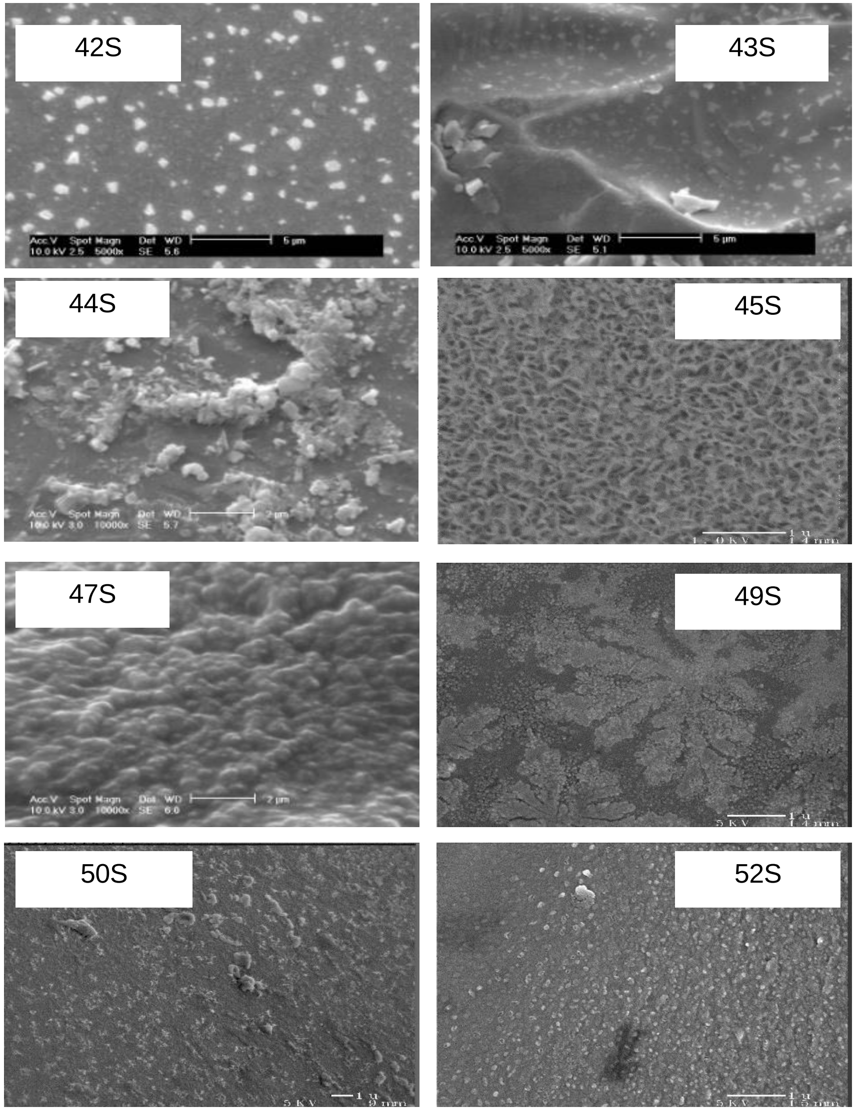
⇩

Interconnected Multi-Modal Porosity

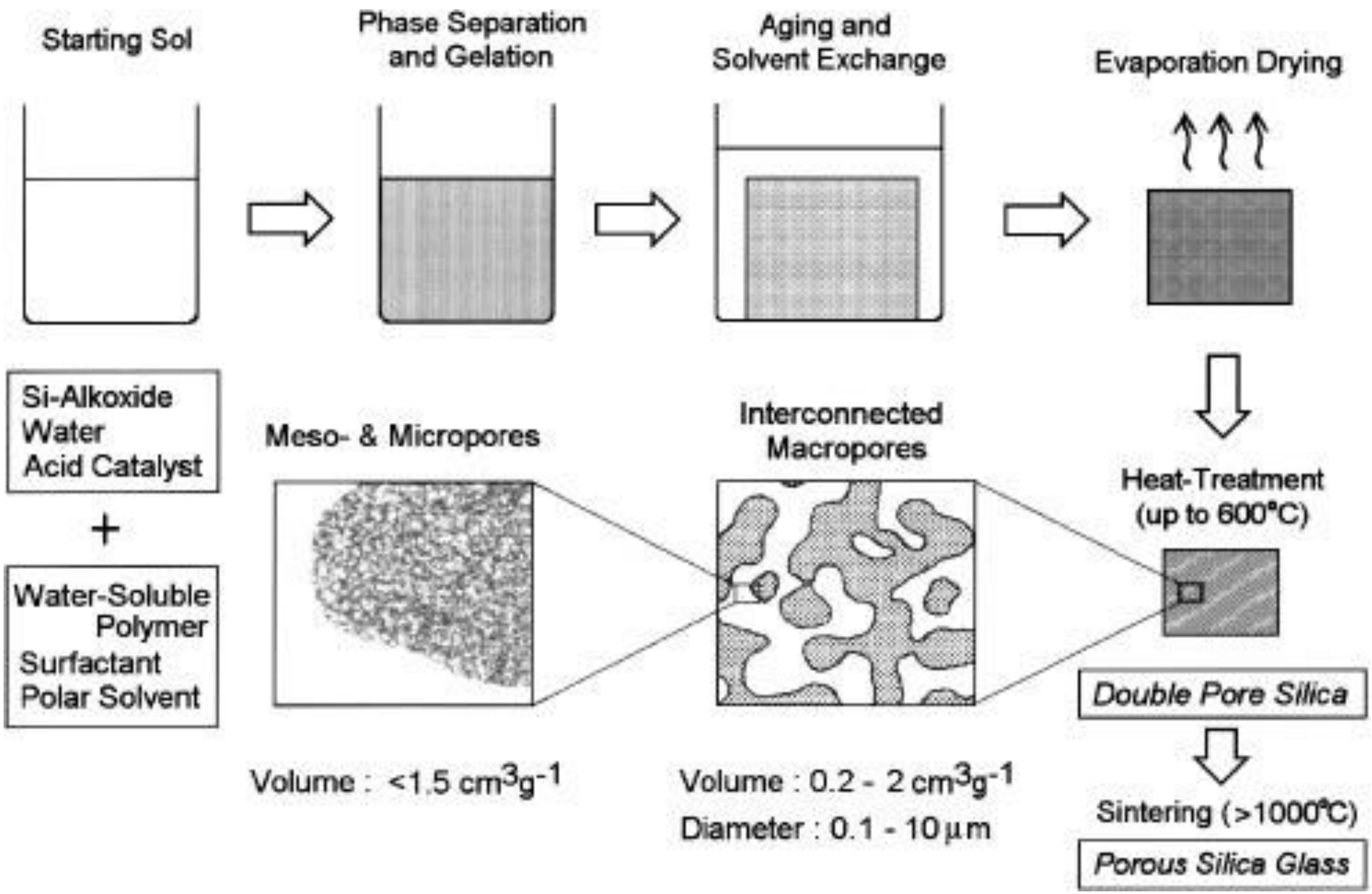
⇩

Composition selection

1st Step (glass is phase separated)



Multi-porous glass



K. Nakanishi, J. Porous Materials 4, 67–112 (1997)

Modified Sol-Gel method

A low temperature, wet chemistry process

Add Poly(ethylene oxide)
as organic polymer

Mixture of DI water, catalyst (CH_3COOH), water-soluble polymer (PEO) and surfactant (urea)

Addition of tetramethoxysilane (TMOS), triethoxyl orthophosphate (TEP, $OP(OC_2H_5)_3$) and calcium nitrate ($Ca(NO_3)_2.4H_2O$)
T=40°C

PHASE SEPARATION AND GELATION

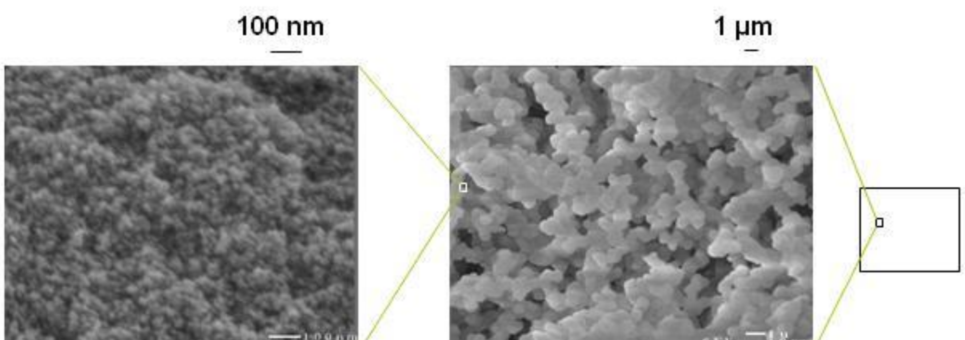
takes place into two phases: one rich in **organic and inorganic polymer**; and other rich in **solvent**

AGING at 40° C

SOLVENT EXCHANGE
0.1 N or 1 M NH_4OH, during 1 or 3 days, at 40° C

EVAPORATION & DRYING AT 60° C

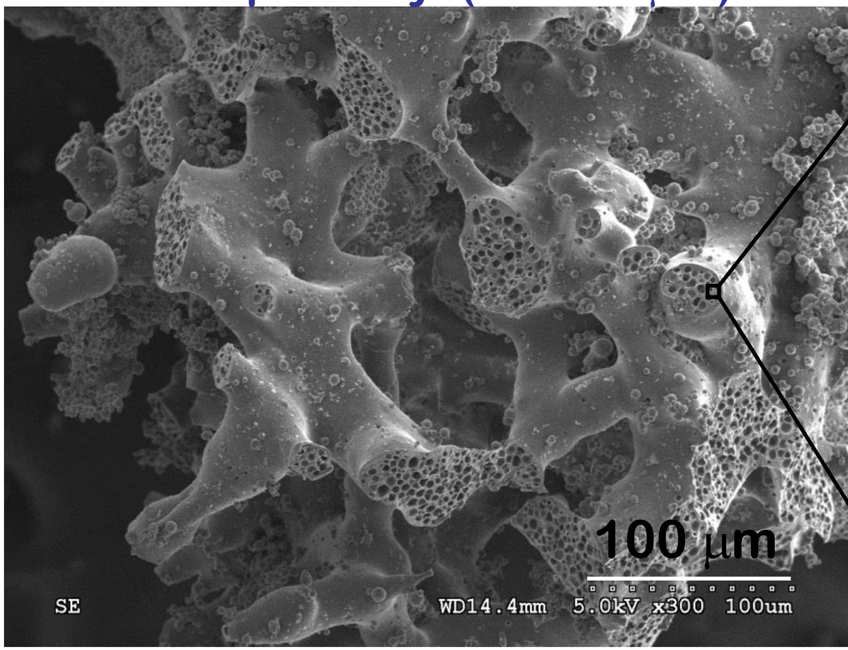
HEAT TREATMENT at 600° C for 1h and 700° C for 2h



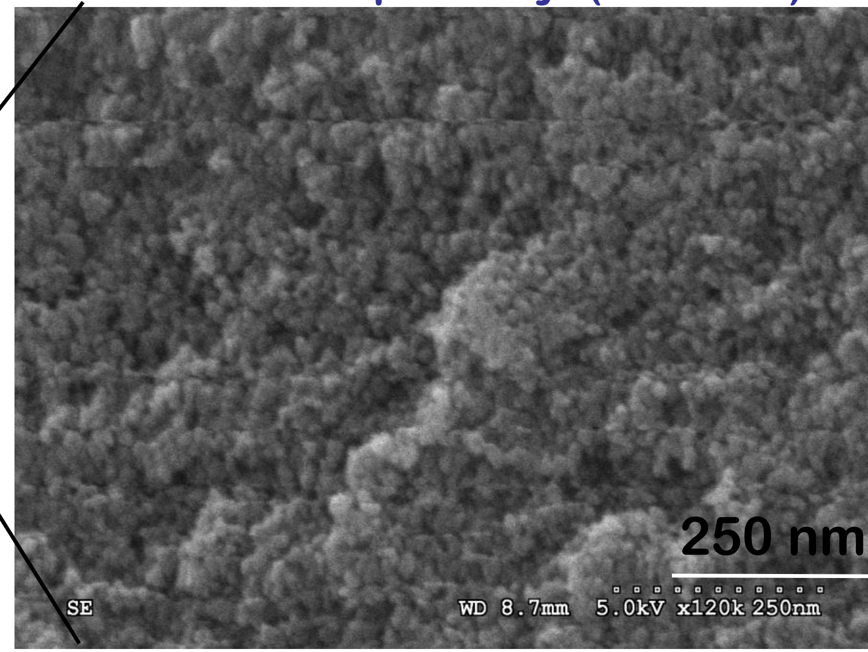
Nakajima et al.

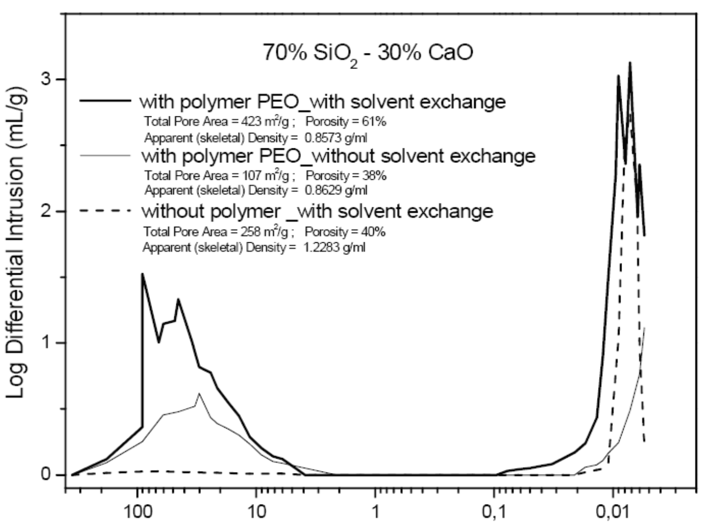
Interconnected, coral-like morphology of modified sol-gel method* developed at Lehigh

Macroporosity (10-200 μm)

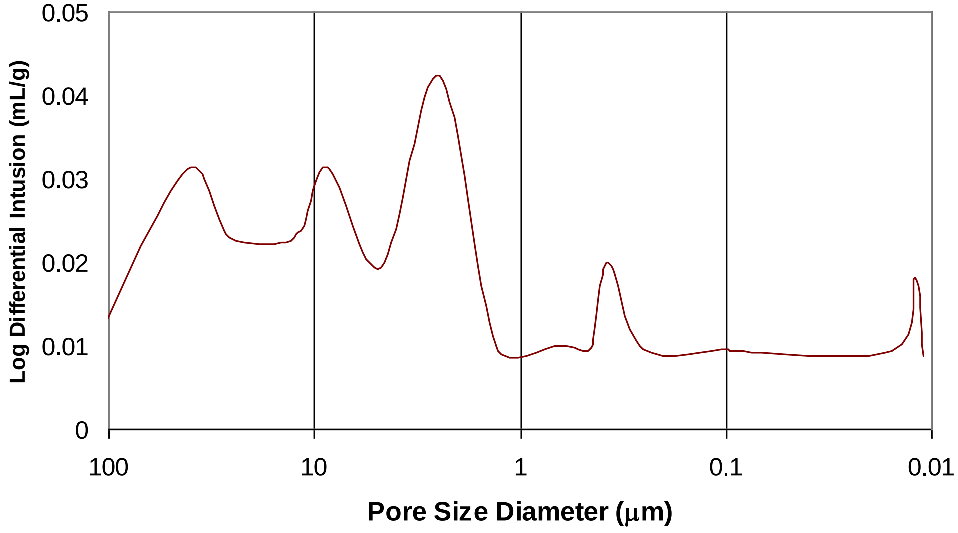


Nanoporosity (5-50 nm)



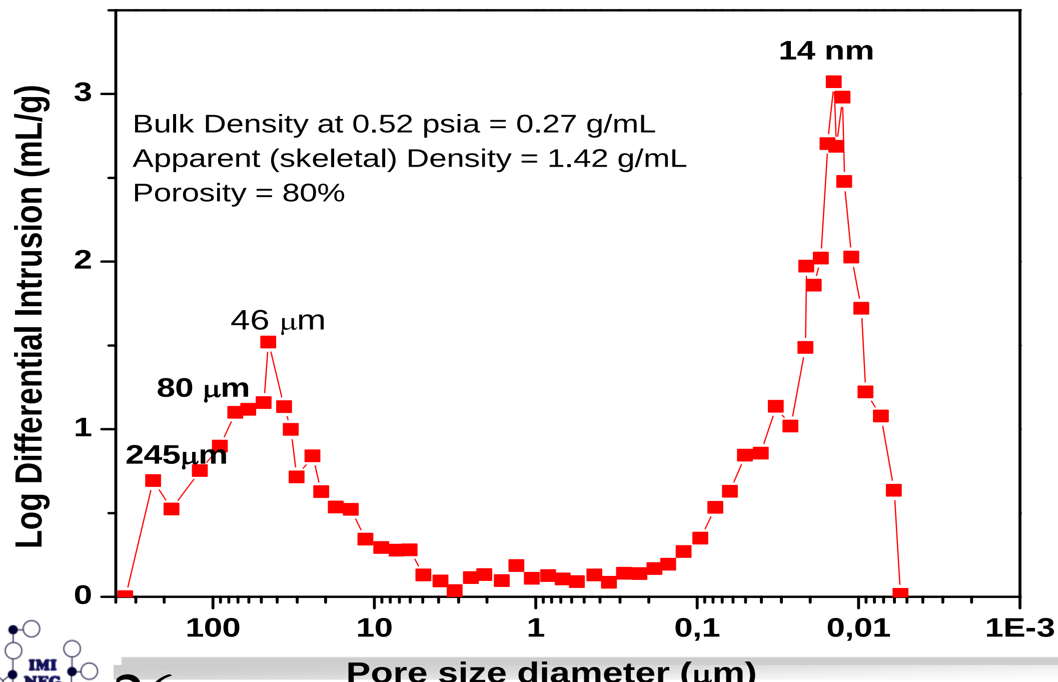


Pore Distribution



Melt-quench nano-macro porous glass

48S4F3ZG specimen after heat treatment + chemical leaching.



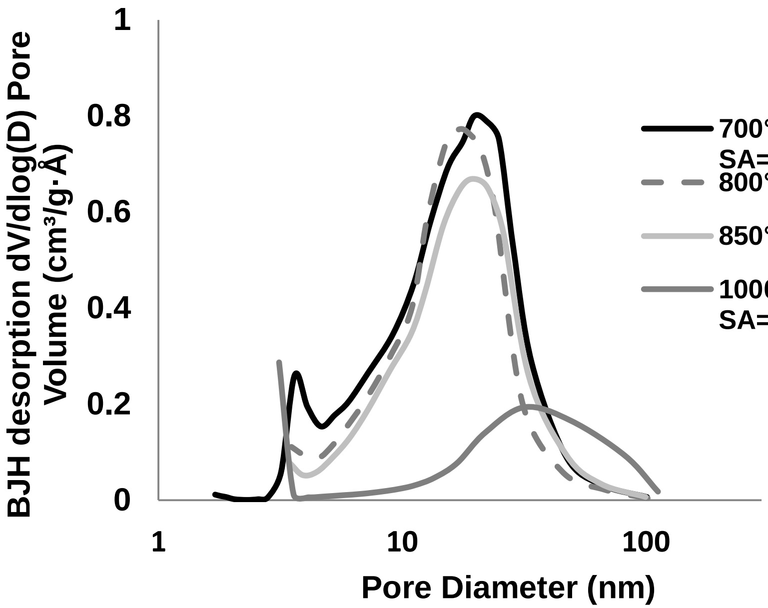
Sol-gel nano-macro porous glass

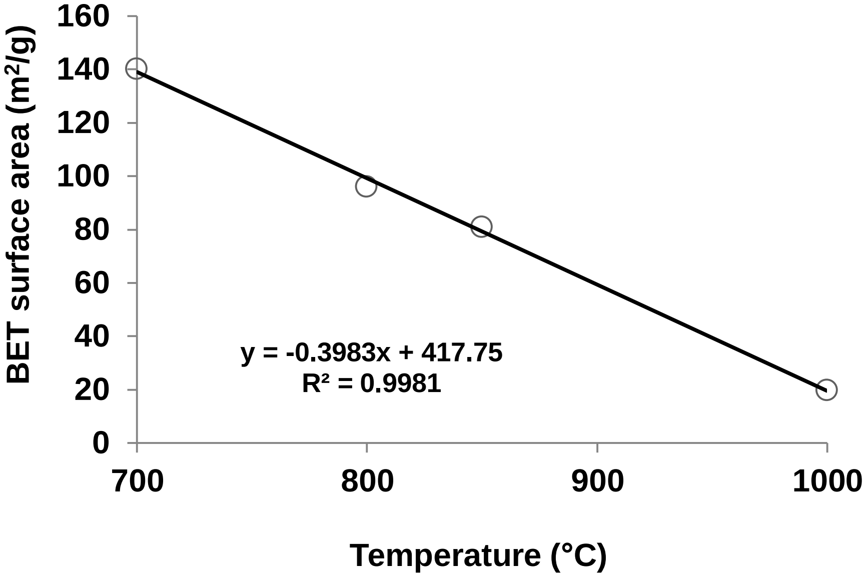
$77SiO_2$-$19CaO$-$4P_2O_5$

Manipulation of nano-pores

How to change nano-porosity?

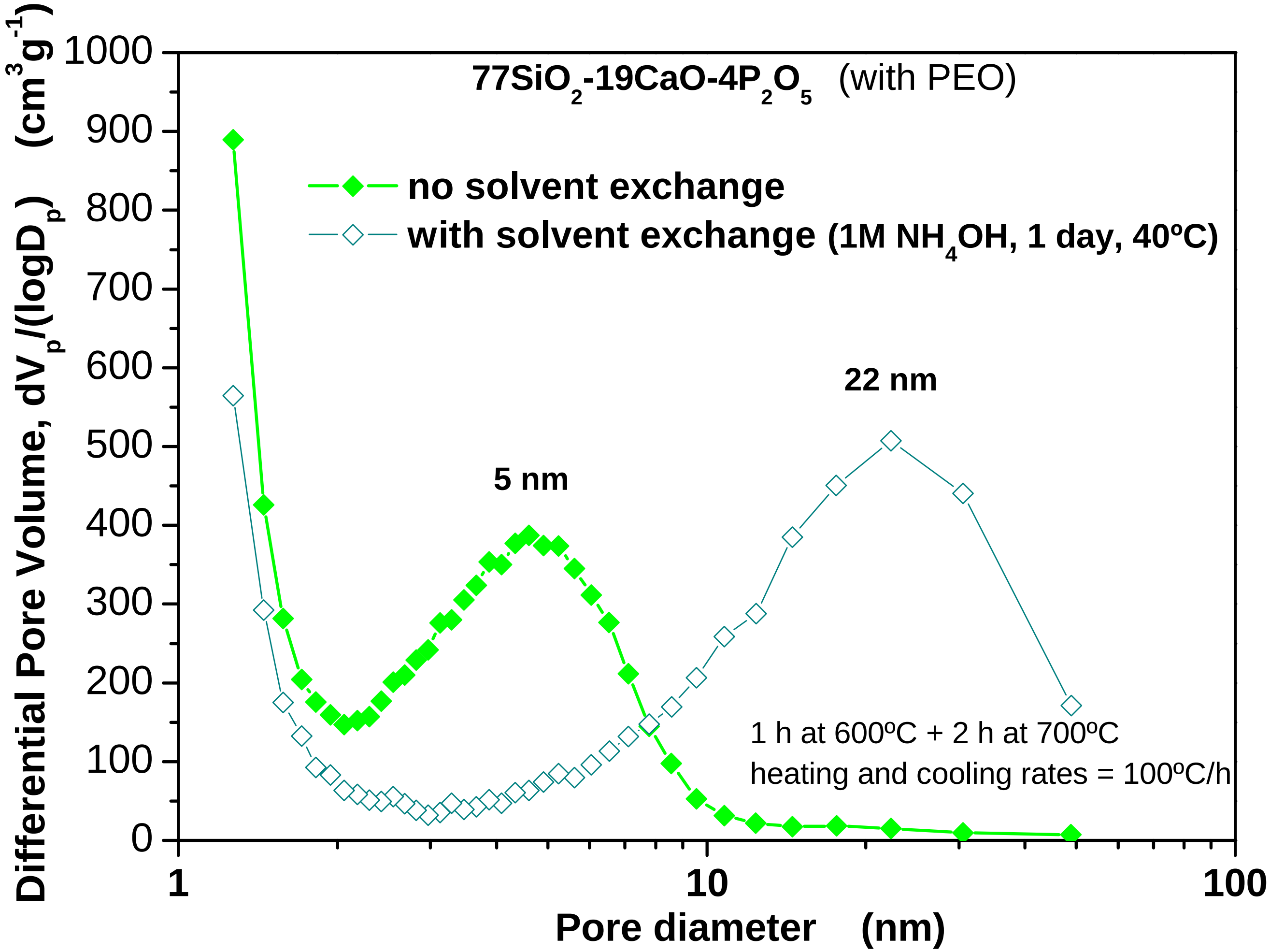
Control of nano-porosity: (a) by heat treatment





The SA can be controlled by adjusting heat-treatment temperature (a linear trend), at 1000°C, majority of the nanopores have been closed.

Control of nano-porosity: (b) solvent exchange with the gel



SiO_2-CaO-(P_2O_5) glass. Polymer: **PEO**

Manipulation of macropores

It is difficult to introduce large macro pores (>200 μm) together with nano-pores by the MQHE or sol-gel methods.

⇓

Need a two-step process

Challenge: How to obtain large (>200 μm) macro pores?

Approach to produce nano-macro porous structure <u>with large macro-pores</u>

Sol-gel process → **Nanoporous structure (Diameter < 100nm)**

Polymer sponge replication → **3D macroporous structure (Diameter > 200μm)**

↓

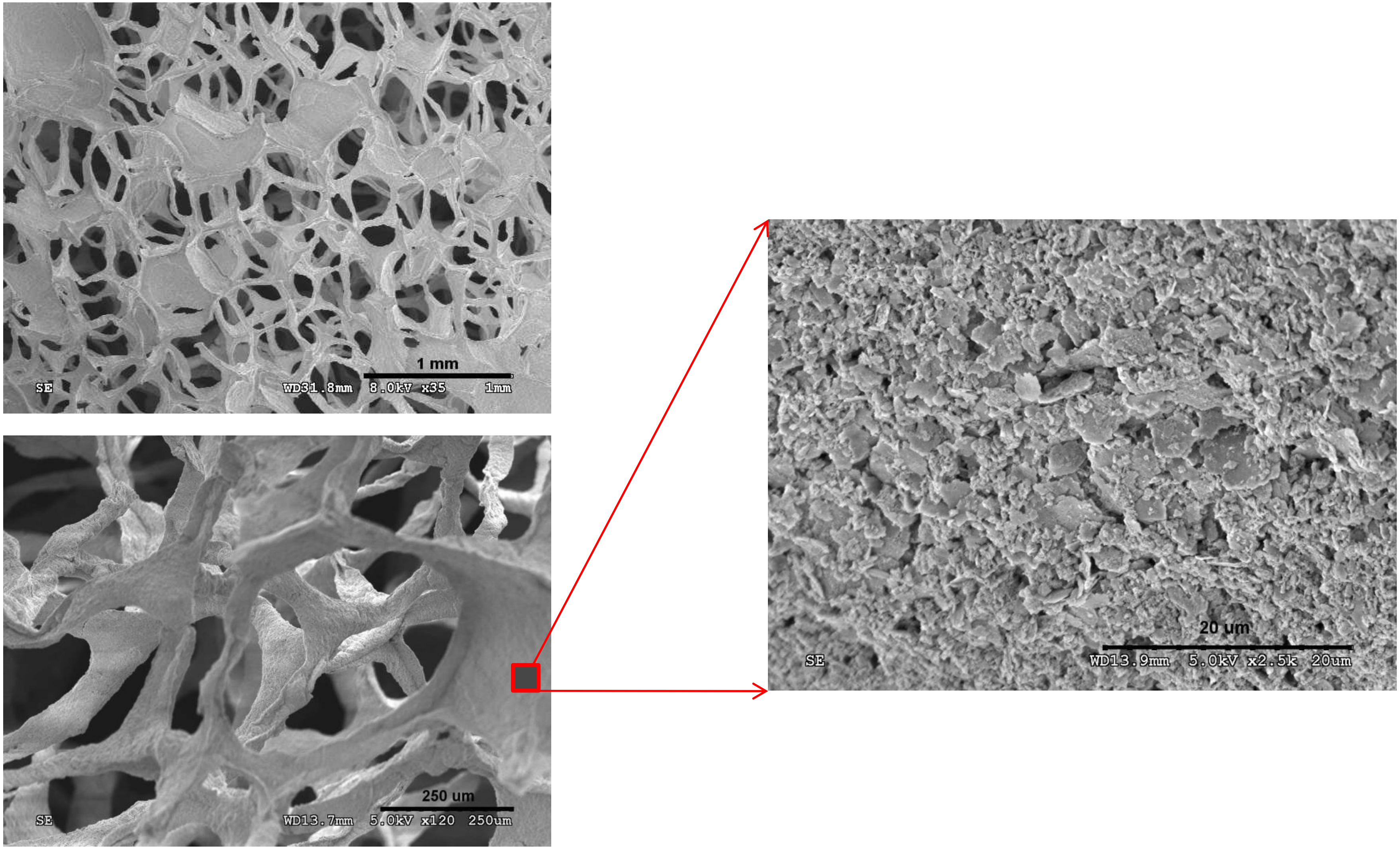
High surface area nano-macro porous bioactive glass scaffold

Foam replication method

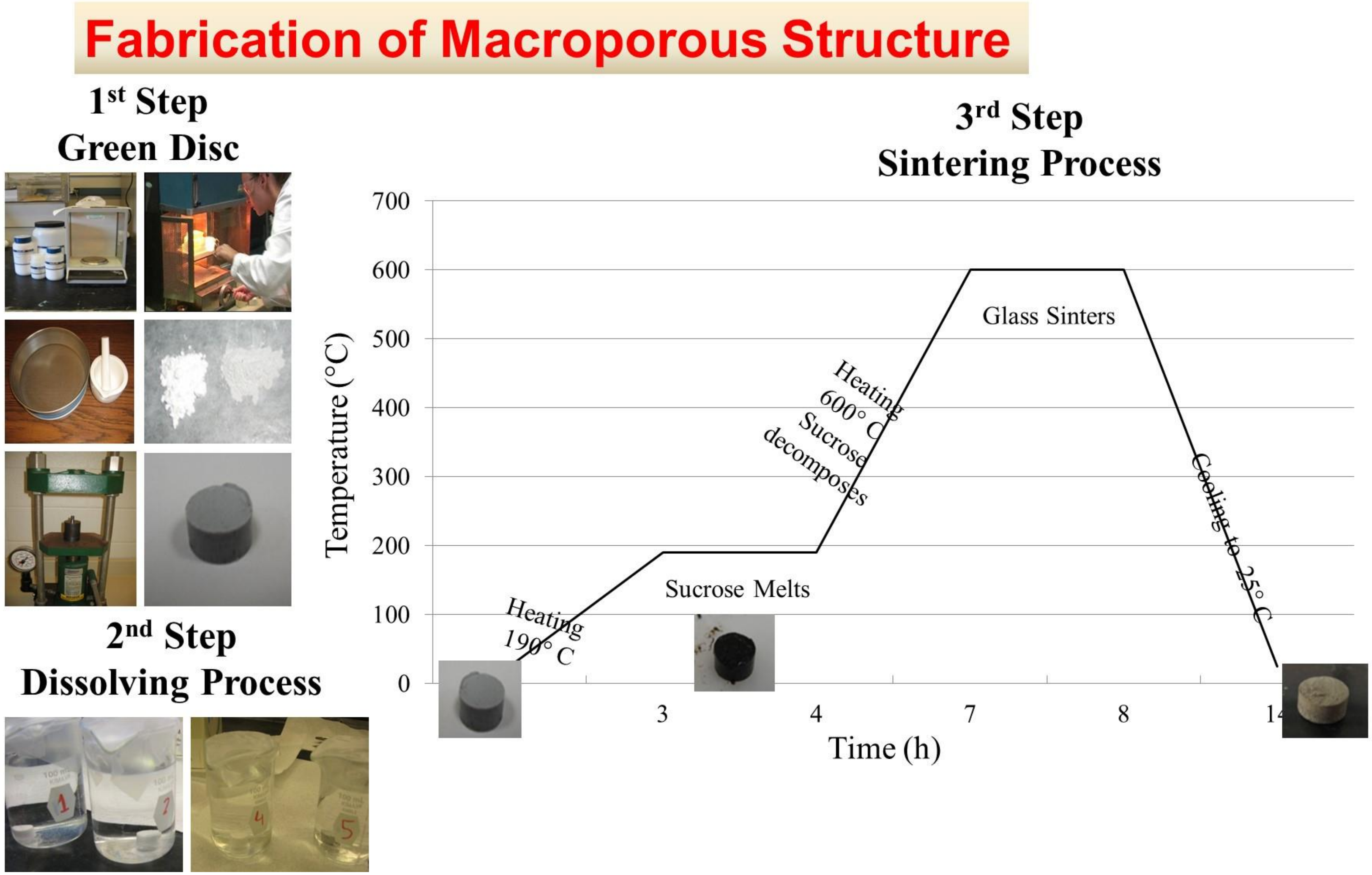
The nano-pores must remain open while the nano-porous skeleton is sintered.

S. J. Wang and H. Jain, J. Am. Ceram. Soc. 93, 3002 (2010).

sol-gel + polymer sponge replication



Water soluble pore former



H. M. Moawad and H. Jain, J. Mater. Sci: Mater. Med. 23 (2012) 307–314.

Results

Photographs of macroporous compact samples (with R = 85/15 wt% and particle size range 38–57 µm) after (a) melting of sucrose at 190C for 1 h followed by sintering at 650C for 1 h, (b) dissolving the sucrose in H_2O at 25C for 48 h, (c) dissolving the sucrose in H_2O at 25C for 48 h followed by sintering at 650C for 1 h

Summary

1. Although porous glasses may not have high tonnage products, they are crucial, even enablers of some applications.
2. A variety of methods exist to introduce and control specific kind of porosity for a given application.
3. New innovative methods are being developed, and old methods are being optimized to meet the needs of emerging applications, most recently in biomedical applications.