Laboratoire MATEIS
Matériaux : Ingénierie et Science
Materials Engineering and Science UMR CNRS 5510

The answer of bioceramics to mechanical demands (towards complex microstructures and architectures)

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SUMMER SCHOOL
CERAMIC & GLASS SCIENCE & TECHNOLOGY,
APPLICATION TO BIOCERAMICS & BIOGLASSES

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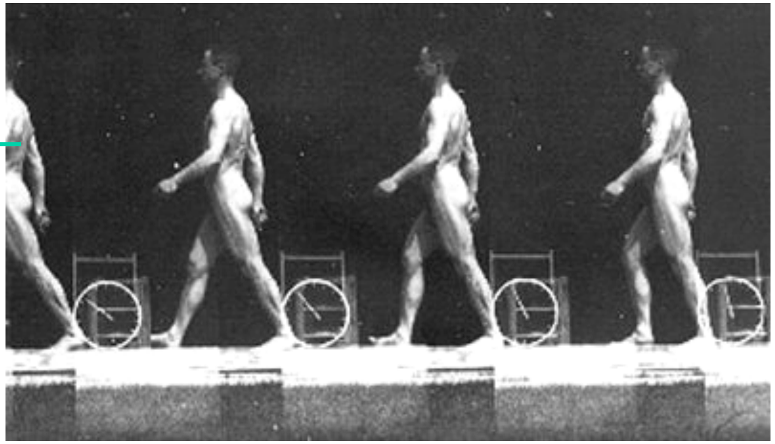
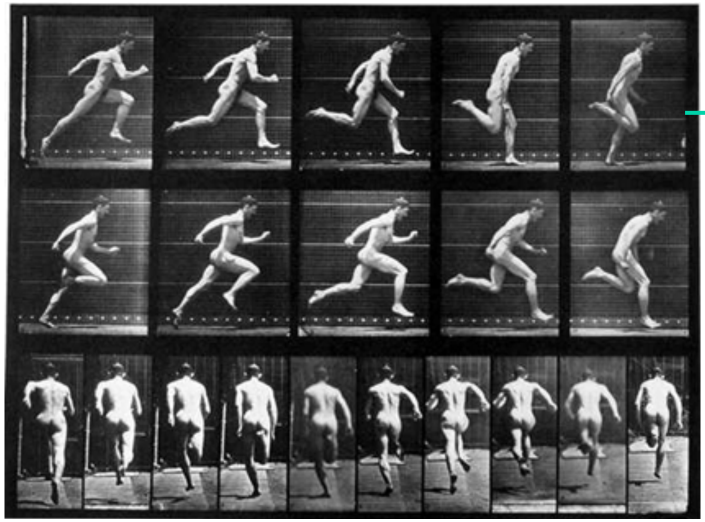
Implants : the quest towards long lasting implants with improved performances

"Neither surgeons nor engineers will ever make an artificial hip-joint which will last thirty years and at the same time in this period enable the patient to play football"

Charnley J., Arthroplasty of the hip. A new operation, Lancet May 27 1961

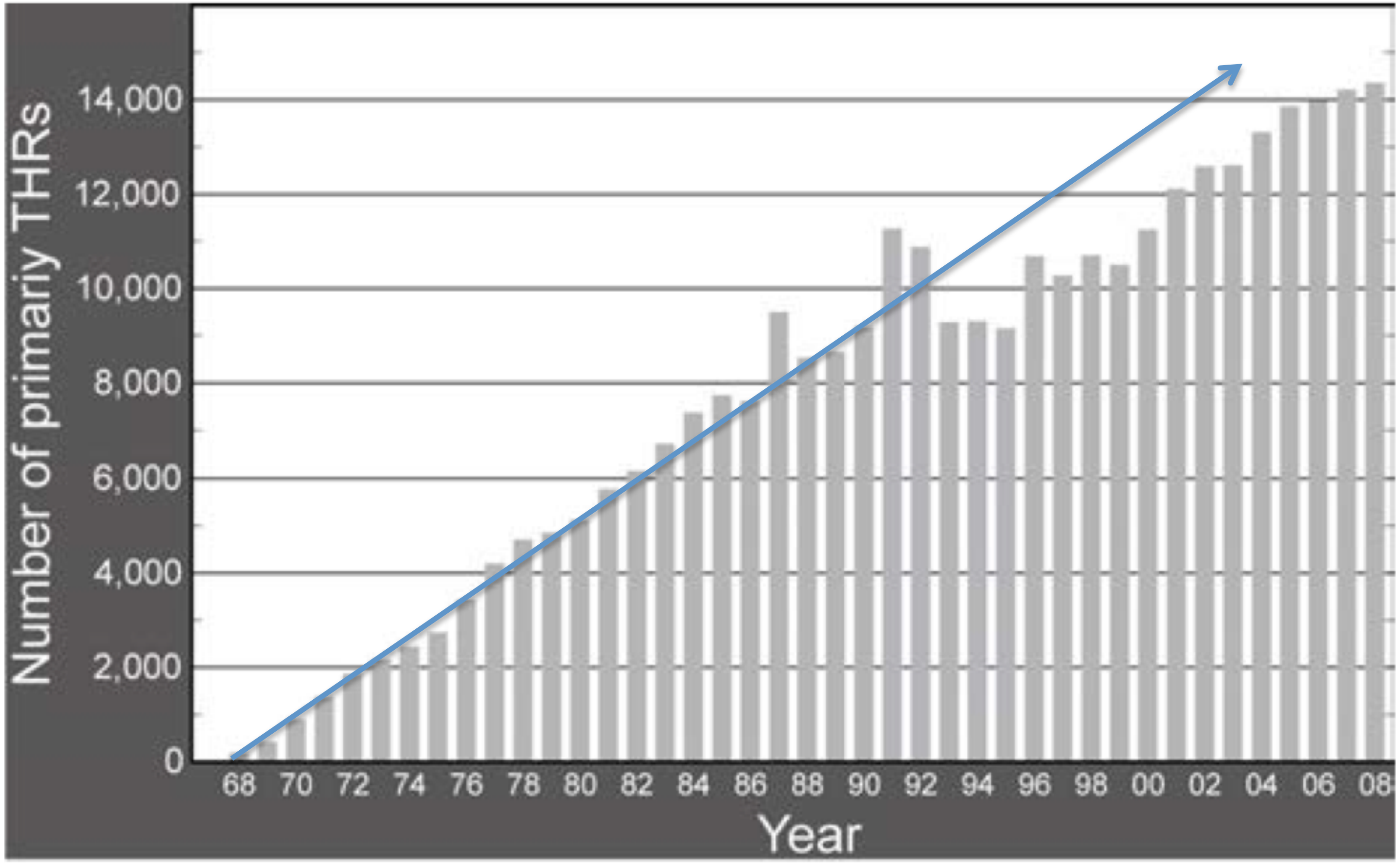




"The challenge today is to develop new bearing surfaces that have the ability to function at a high level for a long time, particularly since THA is now routinely being used in younger, more active patients"

Capello et Al., Ceramic-on Ceramic Total Hip Arthroplasty: Update, *The Journal of Arthroplasty* Vol. 23 n° 1, 2008

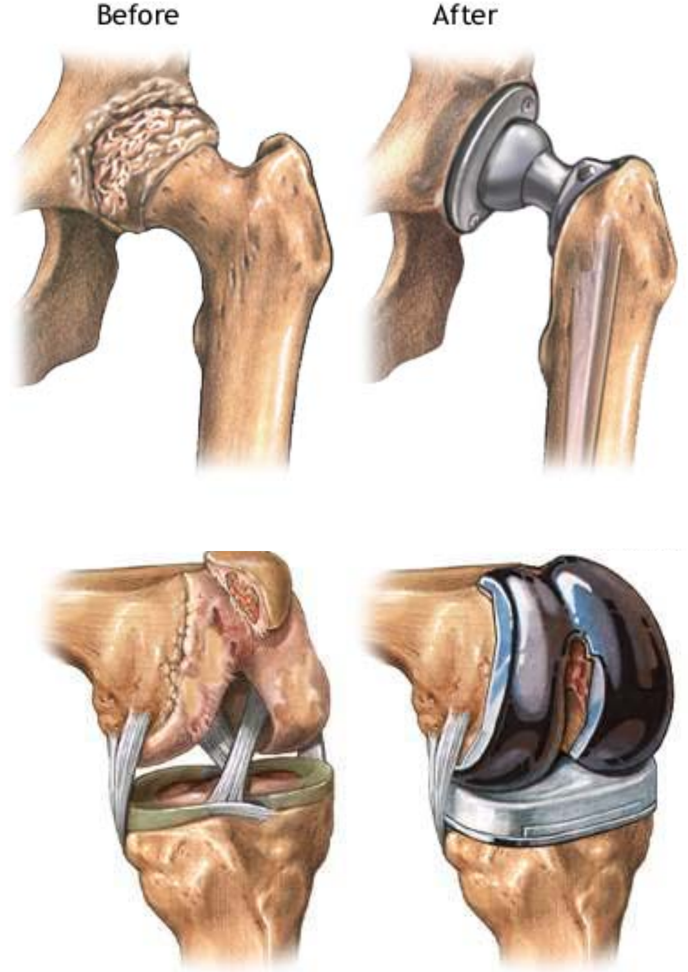
In the future, we will certainly use increasingly tissue engineering strategy but 'traditional' synthetic implants will continue to be widely used

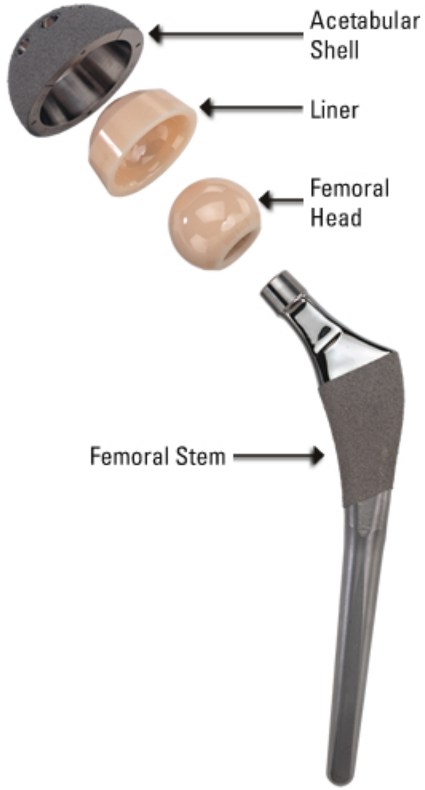


Number of THRs per year in Sweden (adapted from Pezzotti, 2013)

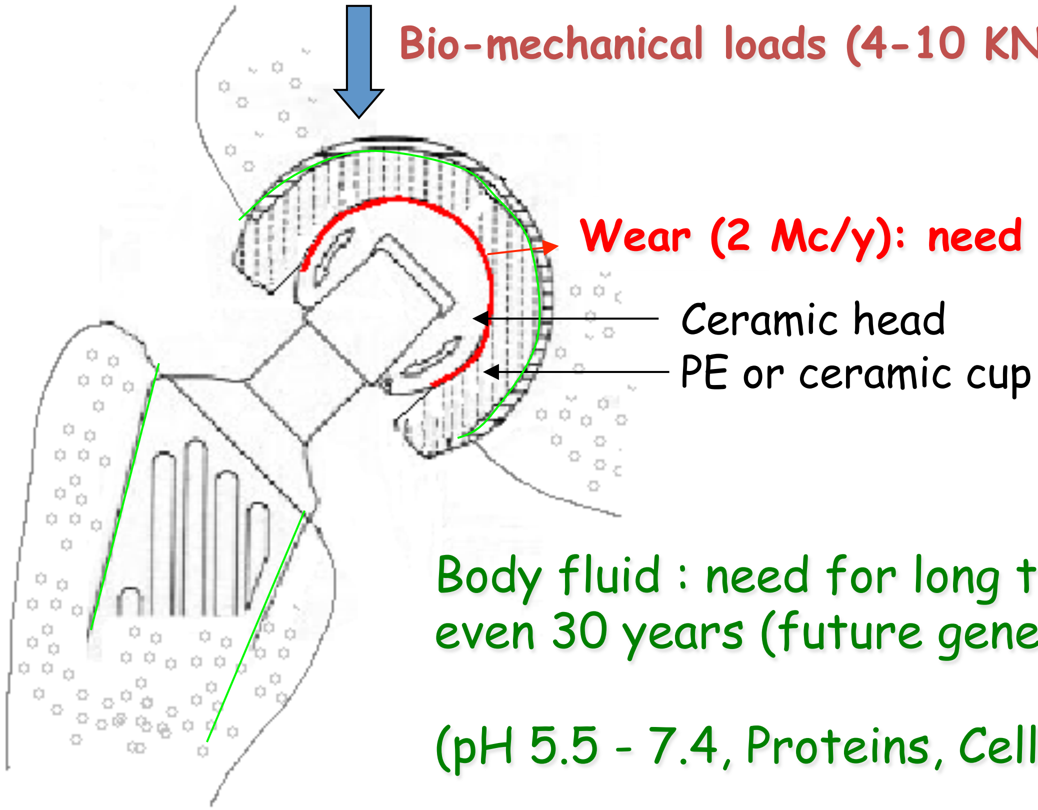
The place of ceramics for biomedical implants

'Bio-inert' ceramics for hip (knee) joint prosthesis applications





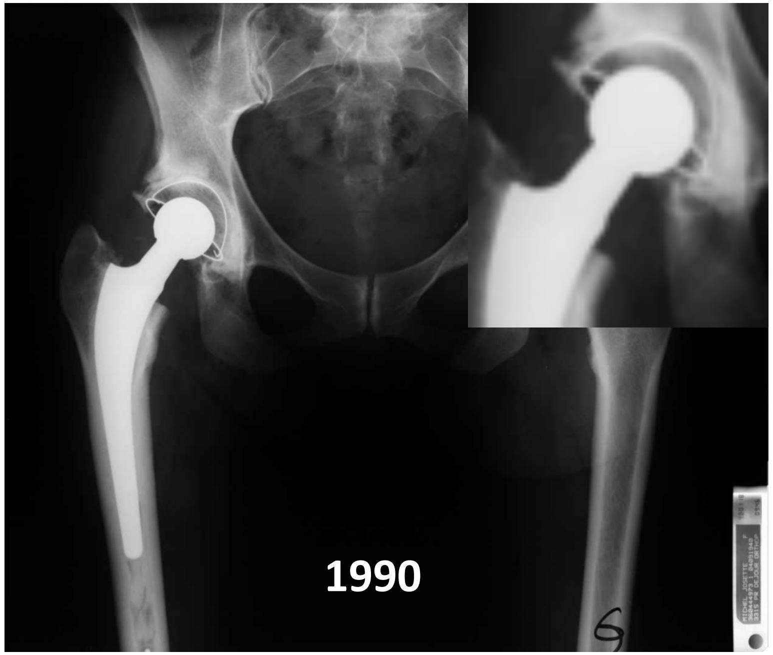
'Bio-inert' ceramics for hip (knee) joint prosthesis applications specifications

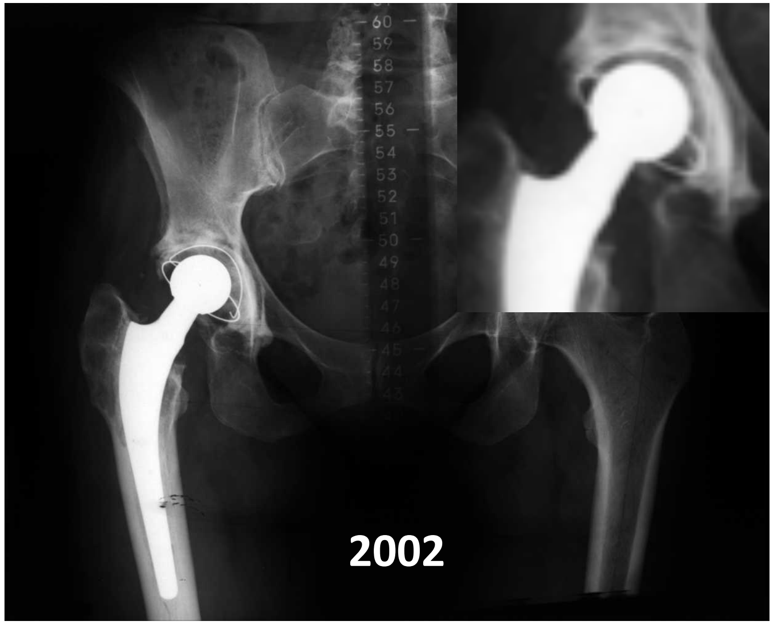


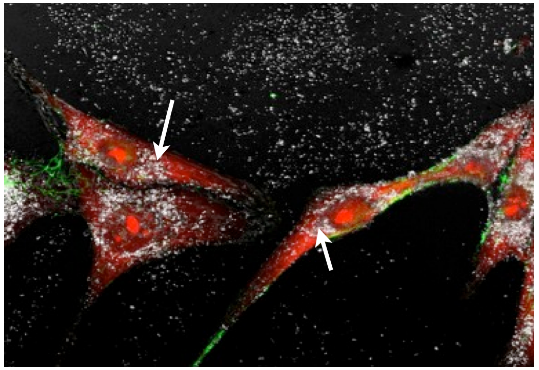
Body fluid : need for long term stability, 15 (today) or even 30 years (future generations, young patients)

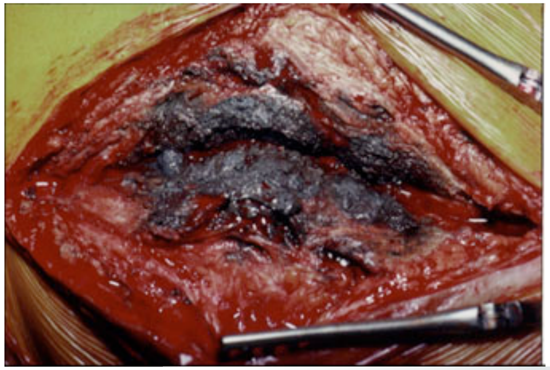
(pH 5.5 - 7.4, Proteins, Cells)

'Bio-inert' ceramics for hip (knee) joint prosthesis applications
Main advantage of ceramics : wear



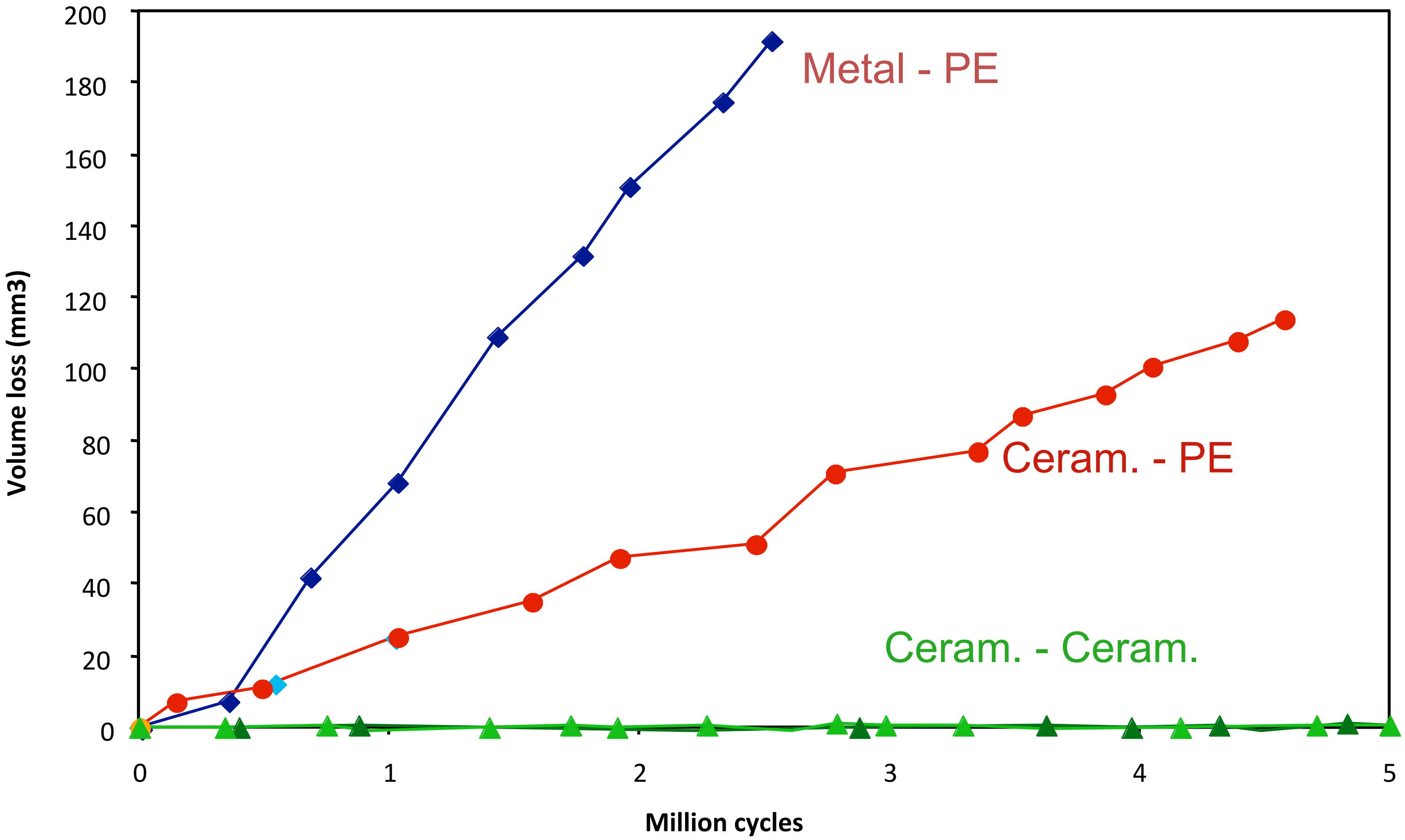






Aseptic Loosening : by far the main cause of revision

'Bio-inert' ceramics for hip (knee) joint prosthesis applications
Main advantage of ceramics : wear



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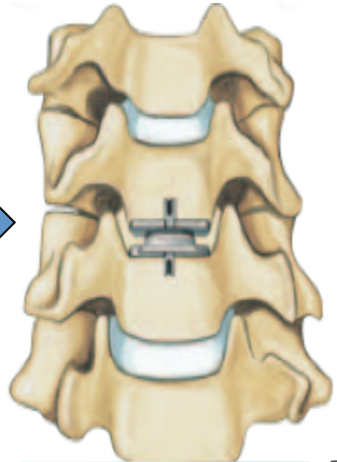
The current need for 'Bio-inert' ceramics in other orthopedic applications

Spine : Intervertebral mobile prostheses, as a new option for surgeons

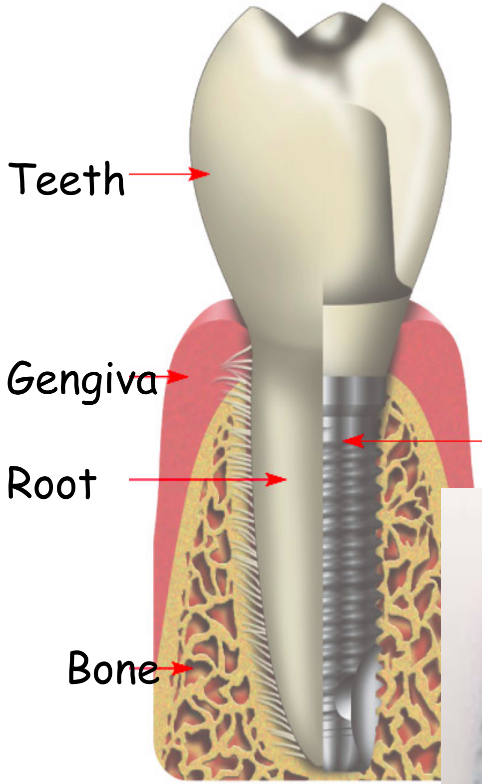


Intervertebral mobile prostheses could answer biomechanical demands, but current solutions (Metal-PE or Metal-Metal) do not work !

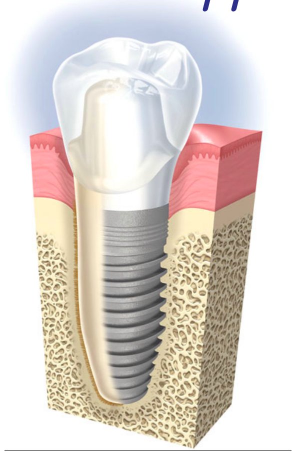
Applied load : up to 10 KN !
(stresses in the implant : more than 500 MPa)

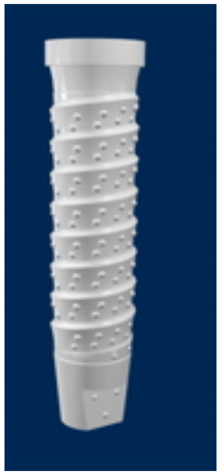
C**<u>urrent situation :</u>** fusion of the two vertebrae remains the standard, even if not fully satisfying. Need for prostheses with a longer lifetime.

The current need for 'Bio-inert' ceramics in dental applications



Zirconia bridge



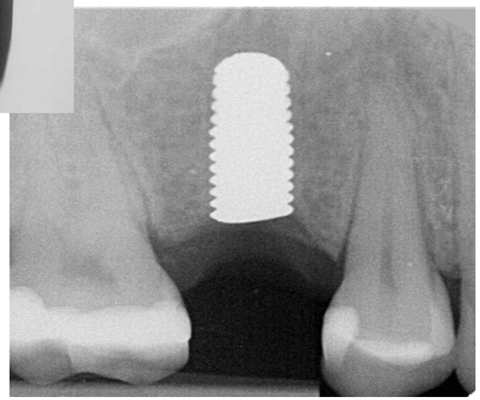


Zirconia implants
(6 large producers
But few % of the market)

Average biting force : 150 N
Max. voluntary biting force : 500 N
Dental implants :
need for strength > 600 MPa

Market : **15.000 to 20.000** zirconia **dental restorations** are made **every day**
Zirconia **dental implants** few % of the market, but forecast **10% in 2020**

Major drawback of ceramics



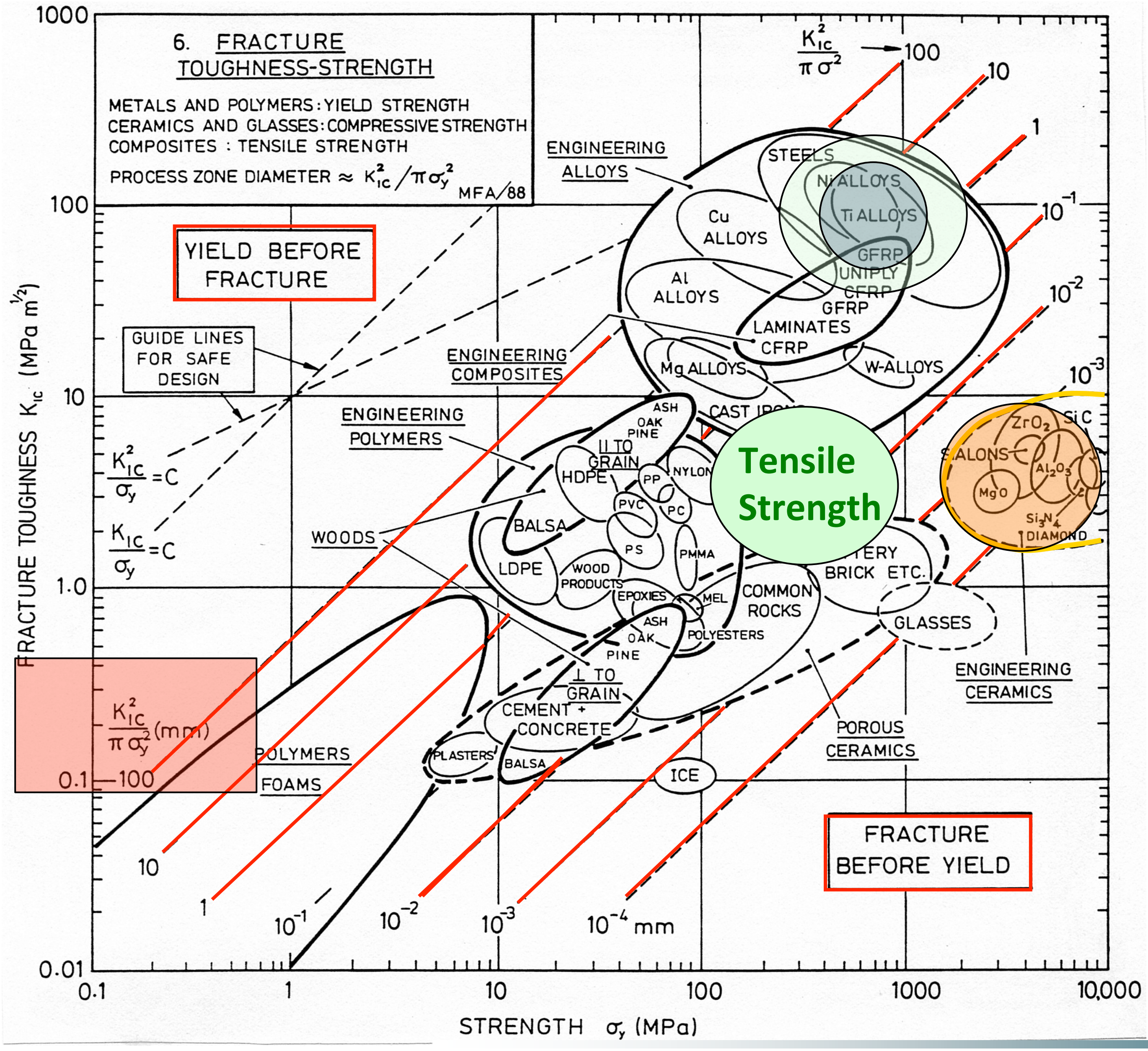
30 years ago : sometimes more than 10%.

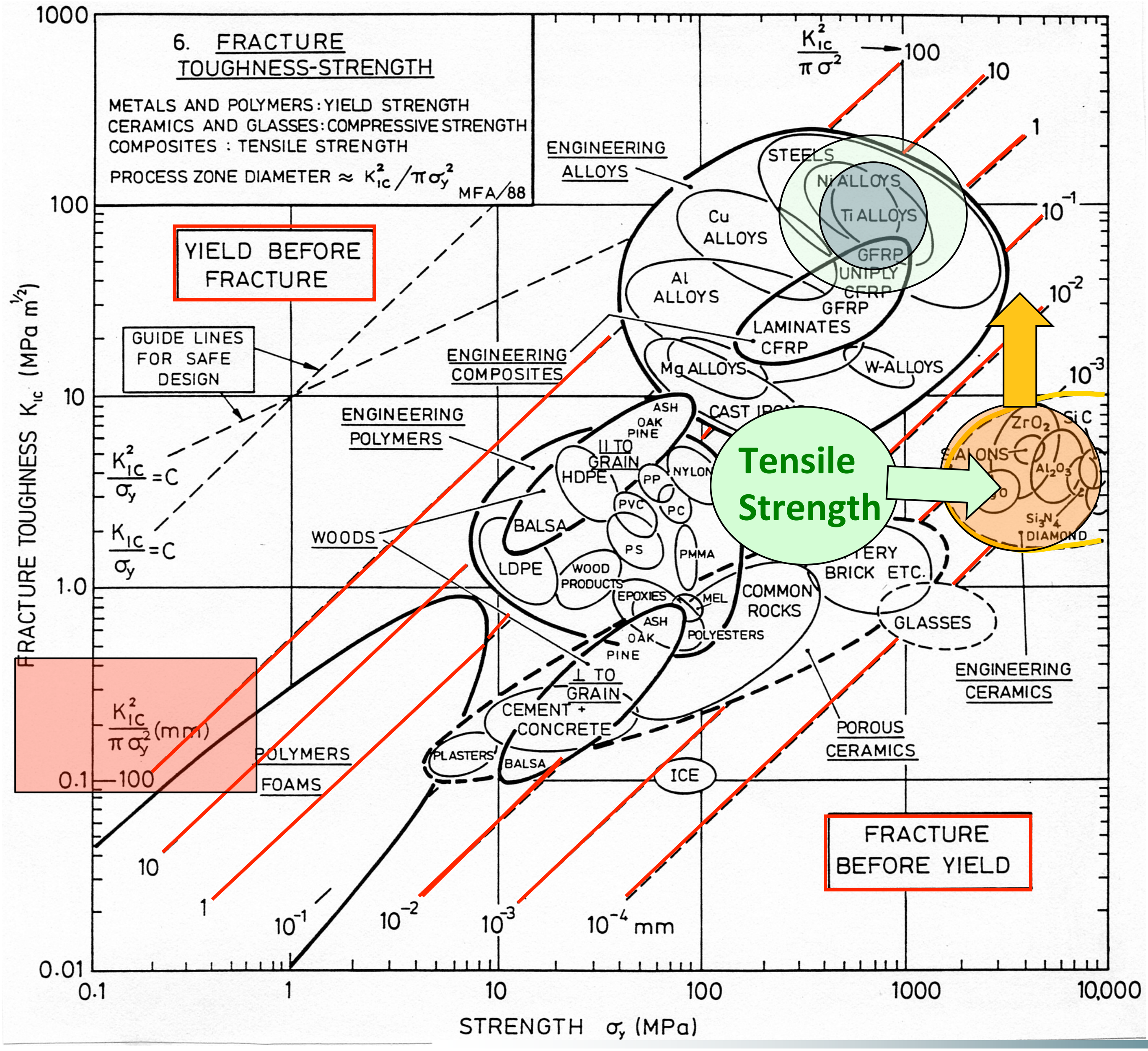
Today : less than 0.1% (much less than metallosis or asceptic loosening due to PE debris). Fatigue of metals also occurs

Today : sometimes more than 10%...

The historical answers of 'bio-inert' ceramics to the mechanical demands

- *From strength improvement to toughness improvement*
- *From materials selection and improvement towards materials by design*


6. FRACTURE TOUGHNESS-STRENGTH
METALS AND POLYMERS: YIELD STRENGTH
CERAMICS AND GLASSES: COMPRESSIVE STRENGTH
COMPOSITES : TENSILE STRENGTH
PROCESS ZONE DIAMETER ≈ $K_{Ic}^2/\pi\sigma_y^2$
MFA/88
YIELD BEFORE FRACTURE
FRACTURE BEFORE YIELD
GUIDE LINES FOR SAFE DESIGN
$\frac{K_{Ic}^2}{\sigma_y}$ = C
$\frac{K_{Ic}}{\sigma_y}$ = C
$\frac{K_{Ic}^2}{\pi\sigma^2}$ → 100
10
1
10^{-1}
10^{-2}
10^{-3}
$\frac{K_{Ic}^2}{\pi\sigma_y^2}$ (mm)
100
10
1
10^{-1}
10^{-2}
10^{-3}
10^{-4} mm
ENGINEERING ALLOYS
STEELS
Ni ALLOYS
Ti ALLOYS
Cu ALLOYS
Al ALLOYS
GFRP
UNIPLY
CFRP
GFRP
LAMINATES
CFRP
Mg ALLOYS
W-ALLOYS
CAST IRONS
ENGINEERING COMPOSITES
ENGINEERING POLYMERS
ASH
OAK
PINE
II TO GRAIN
HDPE
PP
NYLON
PVC
PC
PS
PMMA
BALSA
LDPE
WOOD PRODUCTS
EPOXIES
MEL
ASH
OAK
PINE
POLYESTERS
⊥ TO GRAIN
WOODS
CEMENT + CONCRETE
PLASTERS
BALSA
ICE
POLYMERS
FOAMS
COMMON ROCKS
POTTERY
BRICK ETC.
GLASSES
POROUS CERAMICS
ENGINEERING CERAMICS
SiC
ZrO_2
SIALONS
Al_2O_3
MgO
Si_3N_4
DIAMOND
Tensile Strength
FRACTURE TOUGHNESS K_{Ic} (MPa $m^{1/2}$)
1000
100
10
1.0
0.1
0.01
0.1
1
10
100
1000
10,000
STRENGTH σ_y (MPa)



6. FRACTURE TOUGHNESS-STRENGTH
METALS AND POLYMERS: YIELD STRENGTH
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COMPOSITES : TENSILE STRENGTH
PROCESS ZONE DIAMETER ≈ $K_{IC}^2/\pi\sigma_y^2$
MFA/88
YIELD BEFORE FRACTURE
FRACTURE BEFORE YIELD
GUIDE LINES FOR SAFE DESIGN
$\frac{K_{IC}^2}{\sigma_y}$ = C
$\frac{K_{IC}}{\sigma_y}$ = C
$\frac{K_{IC}^2}{\pi\sigma_y^2}$ (mm)
ENGINEERING ALLOYS
ENGINEERING COMPOSITES
ENGINEERING POLYMERS
ENGINEERING CERAMICS
POROUS CERAMICS
POLYMERS FOAMS
WOODS
STEELS
Ni ALLOYS
Ti ALLOYS
Cu ALLOYS
Al ALLOYS
Mg ALLOYS
W-ALLOYS
CAST IRON
GFRP
UNIPLY CFRP
LAMINATES
CFRP
HDPE
LDPE
PP
PVC
PC
PS
PMMA
NYLON
BALSA
ASH OAK PINE
II TO GRAIN
⊥ TO GRAIN
WOOD PRODUCTS
EPOXIES
MEL
POLYESTERS
COMMON ROCKS
POTTERY BRICK ETC.
GLASSES
CEMENT + CONCRETE
PLASTERS
ICE
ZrO2
SiC
SIALONS
Al2O3
Si3N4
DIAMOND
Tensile Strength
FRACTURE TOUGHNESS K_{IC} (MPa $m^{1/2}$)
STRENGTH σ_y (MPa)

The two paradigms of improving (Bio)-ceramics mechanical performances

Two paradigms based on the same equation :

$$\sigma_R = \frac{K_{IC}}{\sqrt{\pi \times a}}$$

Increasing tensile strength :

- Decreasing the processing/machining defect size for a given ceramic (alumina : approach of the 80's)

Increasing the fracture toughness :

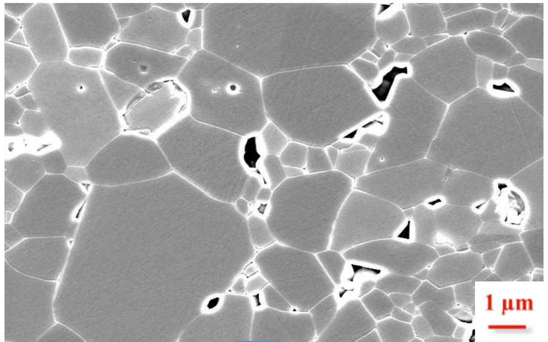
- Zirconia based materials : approach of the 90's

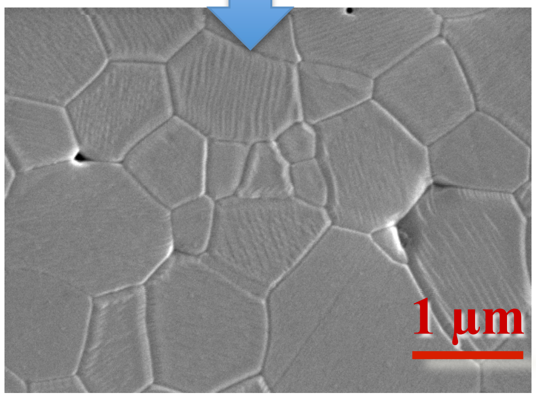
Bridging the gap between the two strategies :
- Improving both strength and toughness with complex microstructures : approaches of today

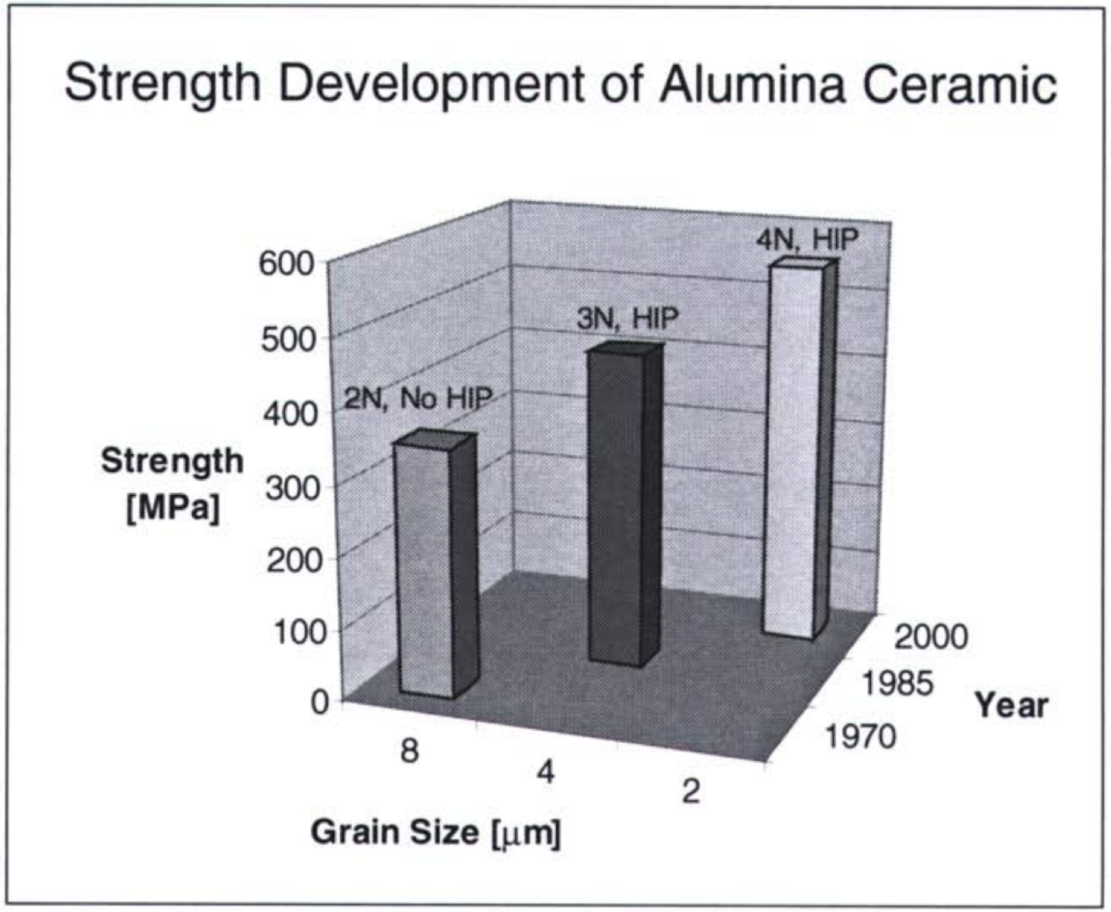
*The 80's : The quest towards strong **alumina** ceramics*

Decreasing the grain size and microstructure heterogeneity

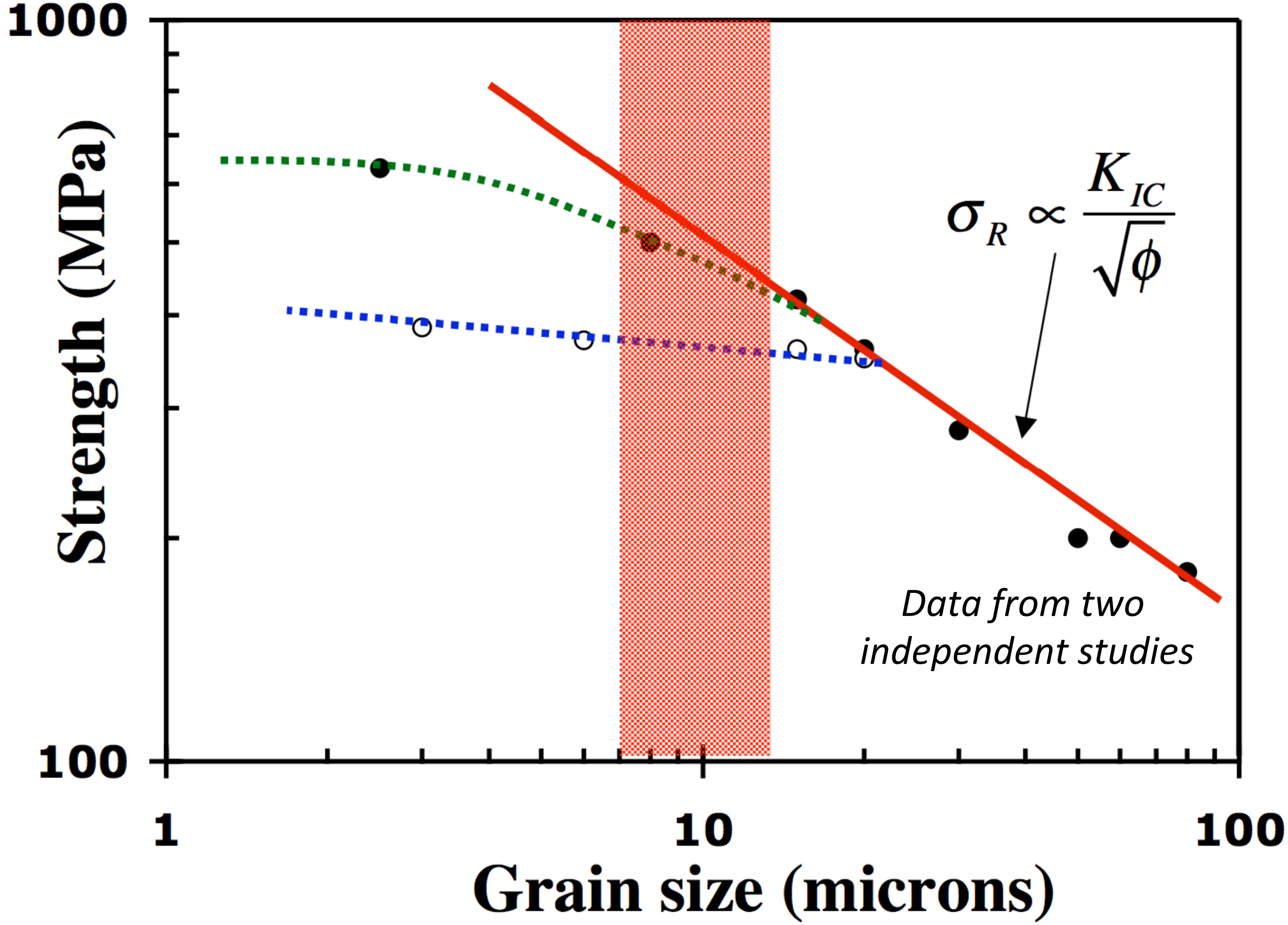
Increase of strength





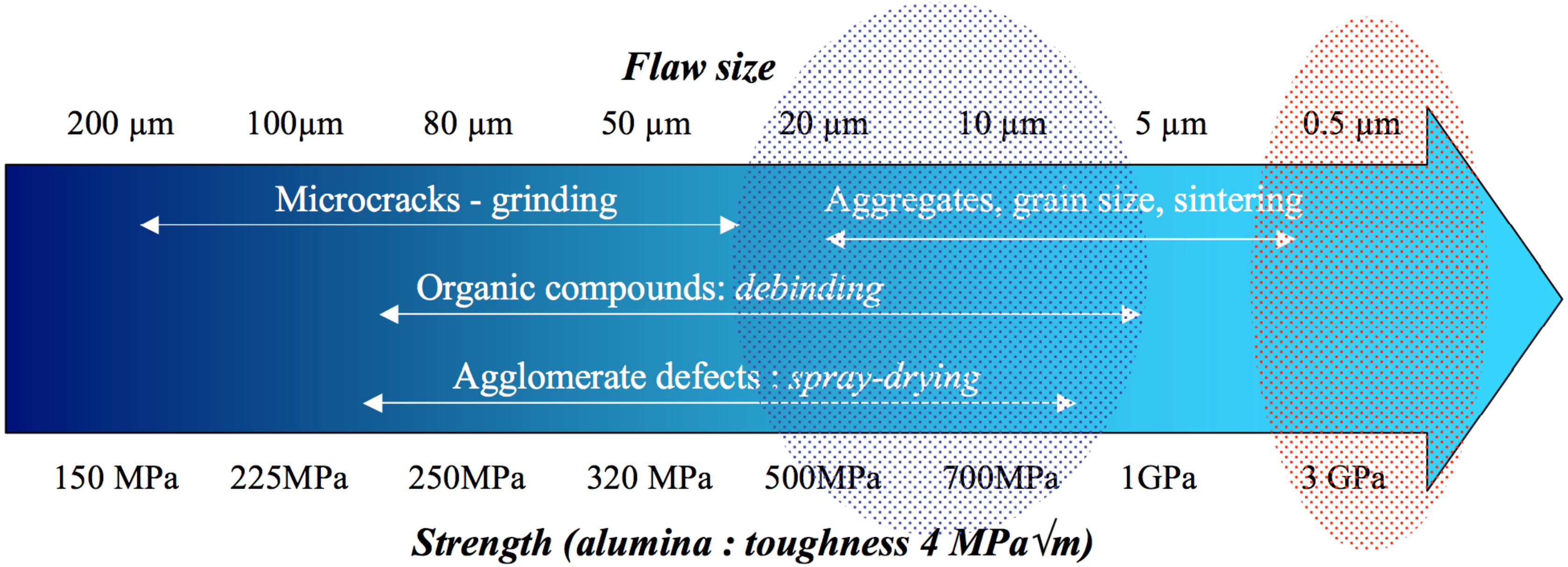


The limits of strengthening strategy



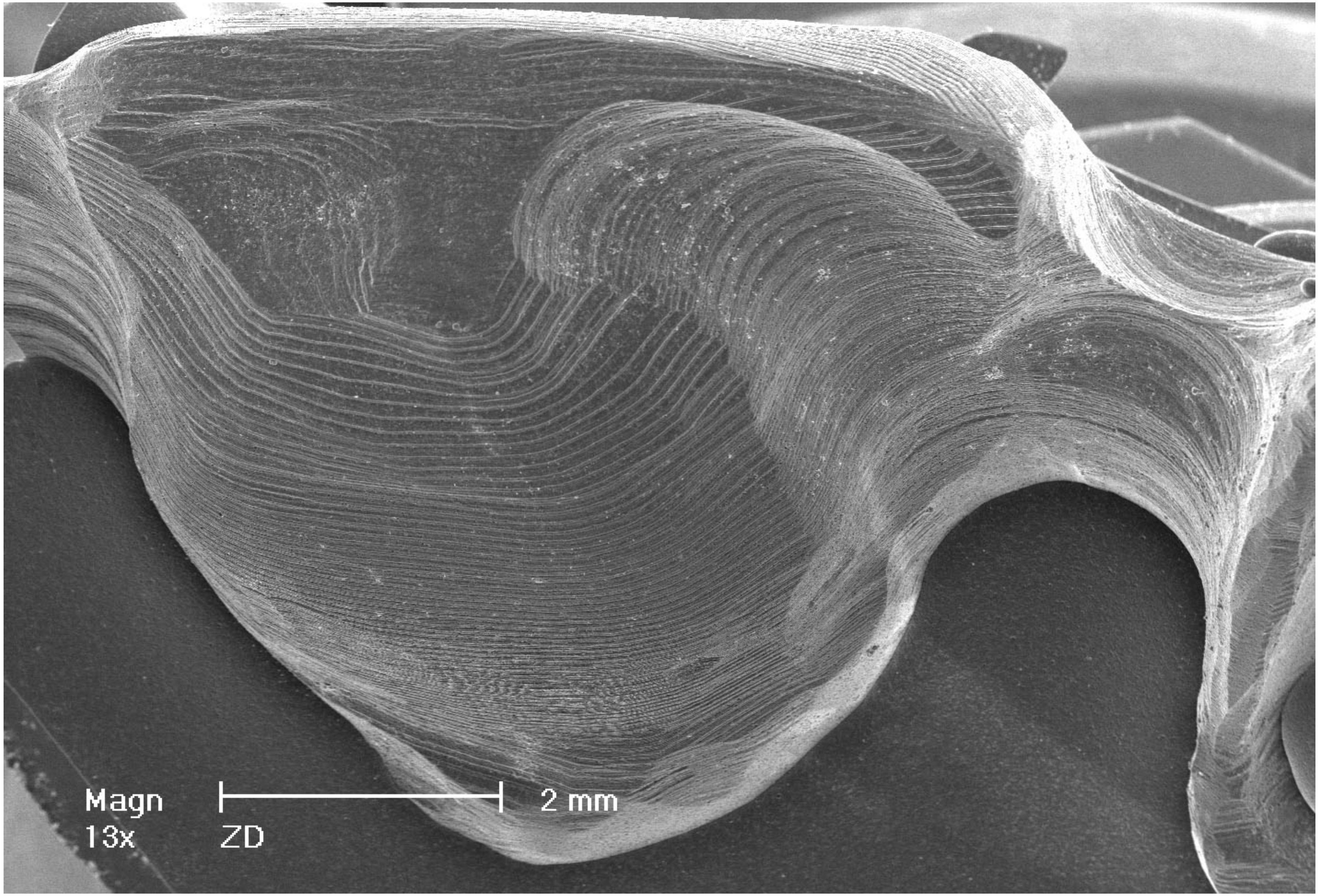
Below some microns, decreasing the grain size does not provide significant strengthening

The limits of strengthening strategy



Flaws in ceramics : generally (much) larger than the grain size !!!

Limit of the strengthening by grain size reduction (other defects relevant)



Crédit : Susanne Scherrer, Université de Genève

*The 90's : The quest **towards tough ceramics – zirconia***
Phase transformation toughening

1980 | 1990 | 2000 | 2010

Alumina
K_{IC} = 4 $MPam^{1/2}$

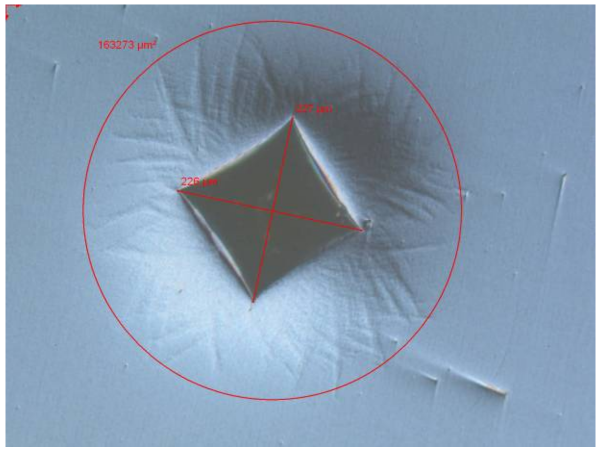
Mg-PSZ

3Y-TZP
K_{IC} = 6 $MPam^{1/2}$

Al_2O_3-ZrO_2
K_{IC} = 8 $MPam^{1/2}$

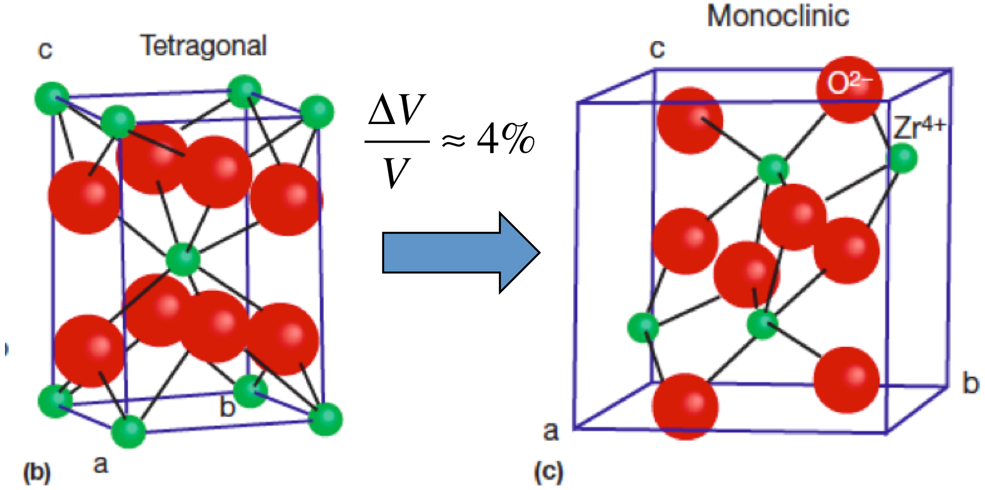
Ce-TZP (-Al_2O_3)
K_{IC} > 10 $MPam^{1/2}$

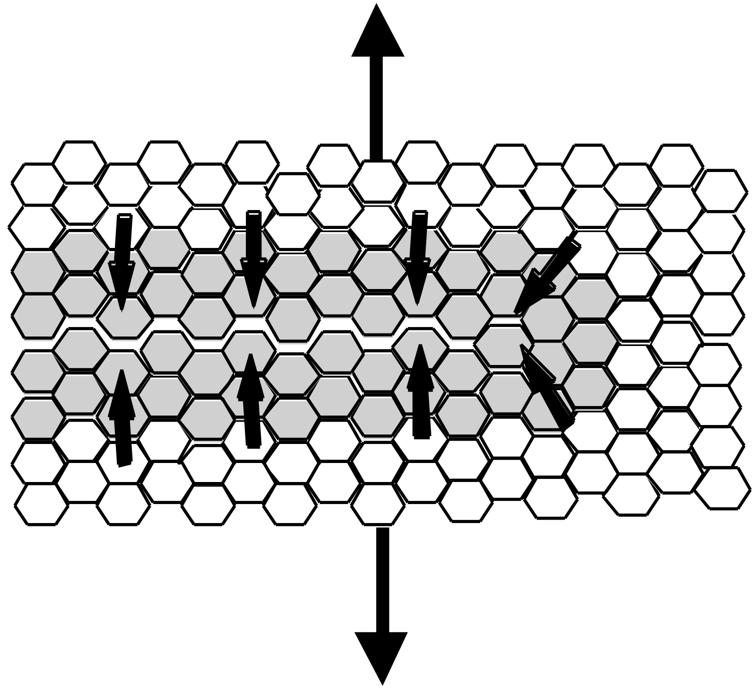
Garvie
(1975)



Transformation autour d'une indentation Vickers réalisée avec une charge de 30kg

*The quest towards tough ceramics : **zirconia***





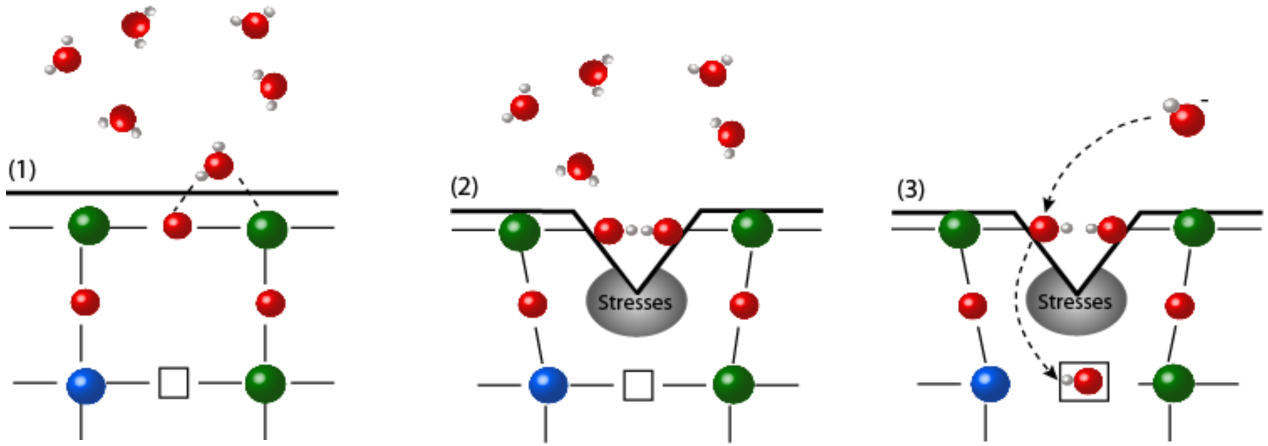
'The ceramic steel' (Garvie, 1975) : t-m transformation at the crack tip (discovered fortunately)

Consequence: Increased toughness (strength) and load to failure of implants

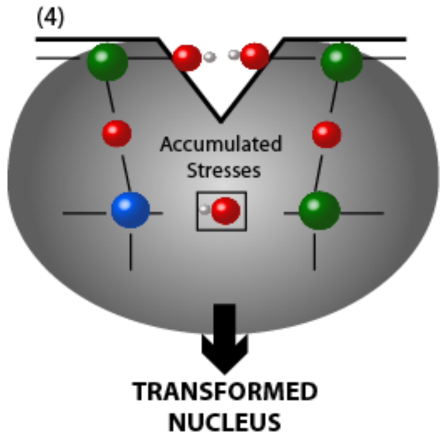
before 2001 : failure rates lower than 0,1% (alumina : 0.2 to 13,4%)
Small diameter heads (22 mm), knee joints (japan) (UCL twice that of alumina)

The Achilles Heel: aging of zirconia (Y-TZP) ceramics

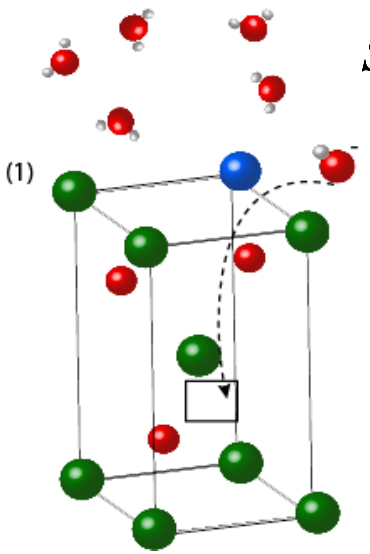
Aging: Slow tranformation at the surface of zirconia, initiated by water diffusion and stress accumulation

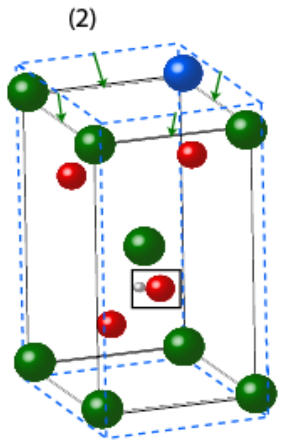


Yoshimura et al. 1987



Schubert and Frey 2004

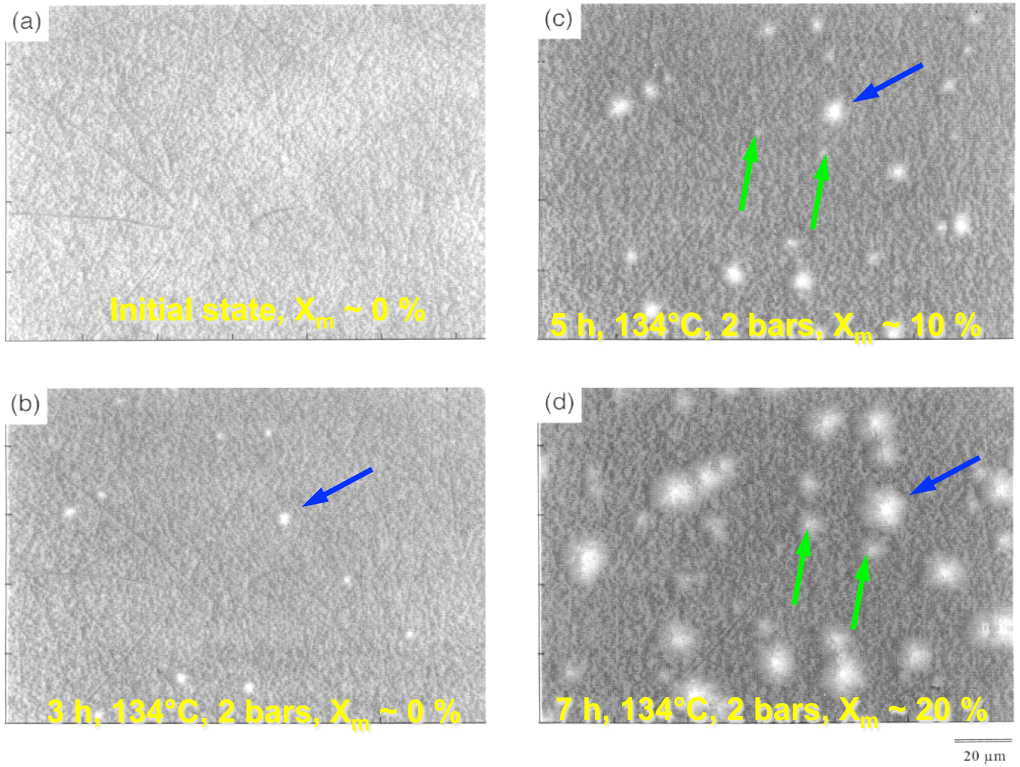




- accumulation of tensile stresses
- t-m transformation

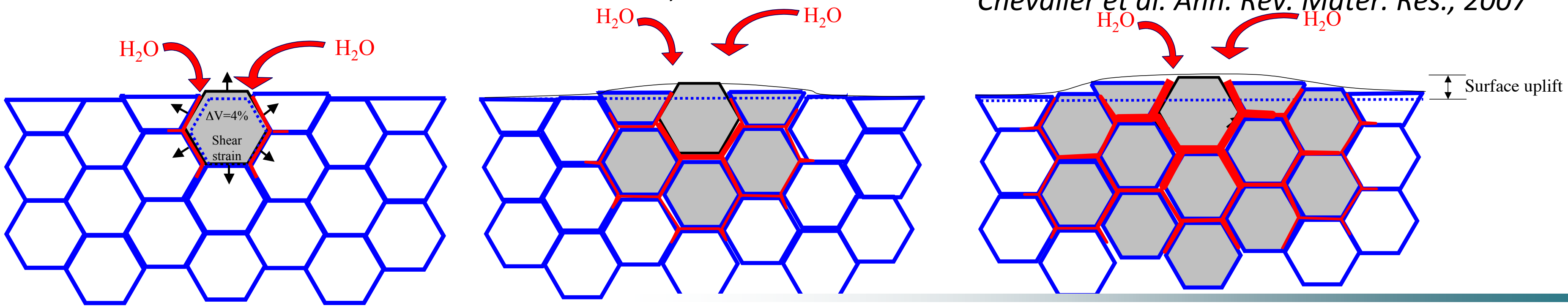
Localized to the grains at the surface in contact with water

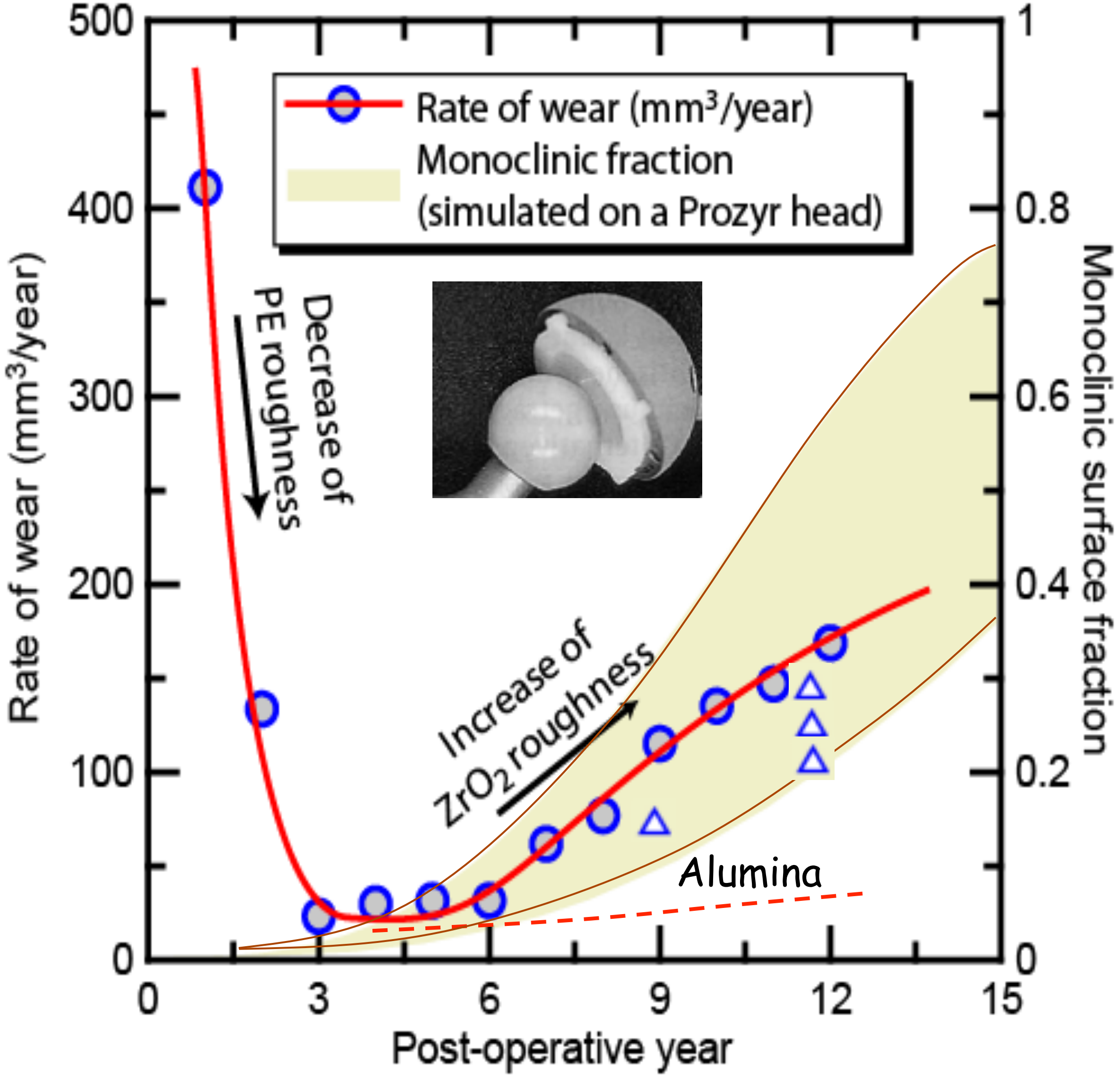
Aging of zirconia, or a 'Slow Surface Degradation'

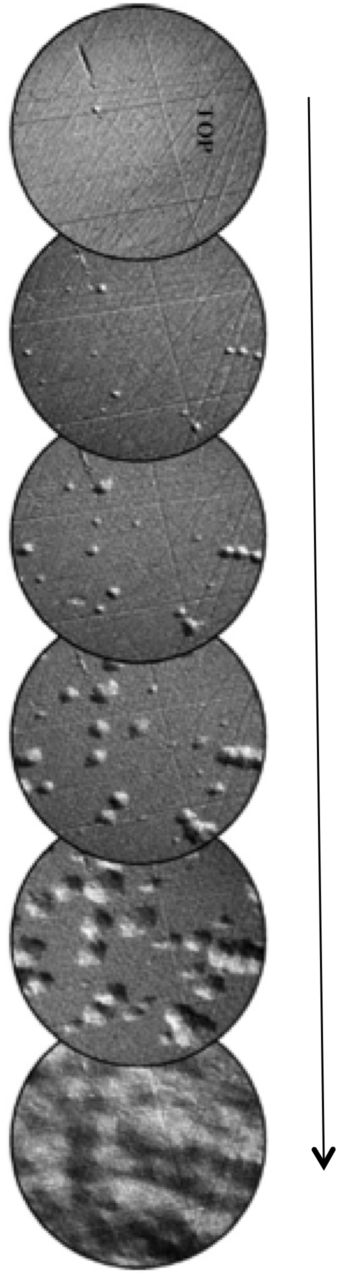


Chevalier et al. J. Am. Ceram. Soc., 1999

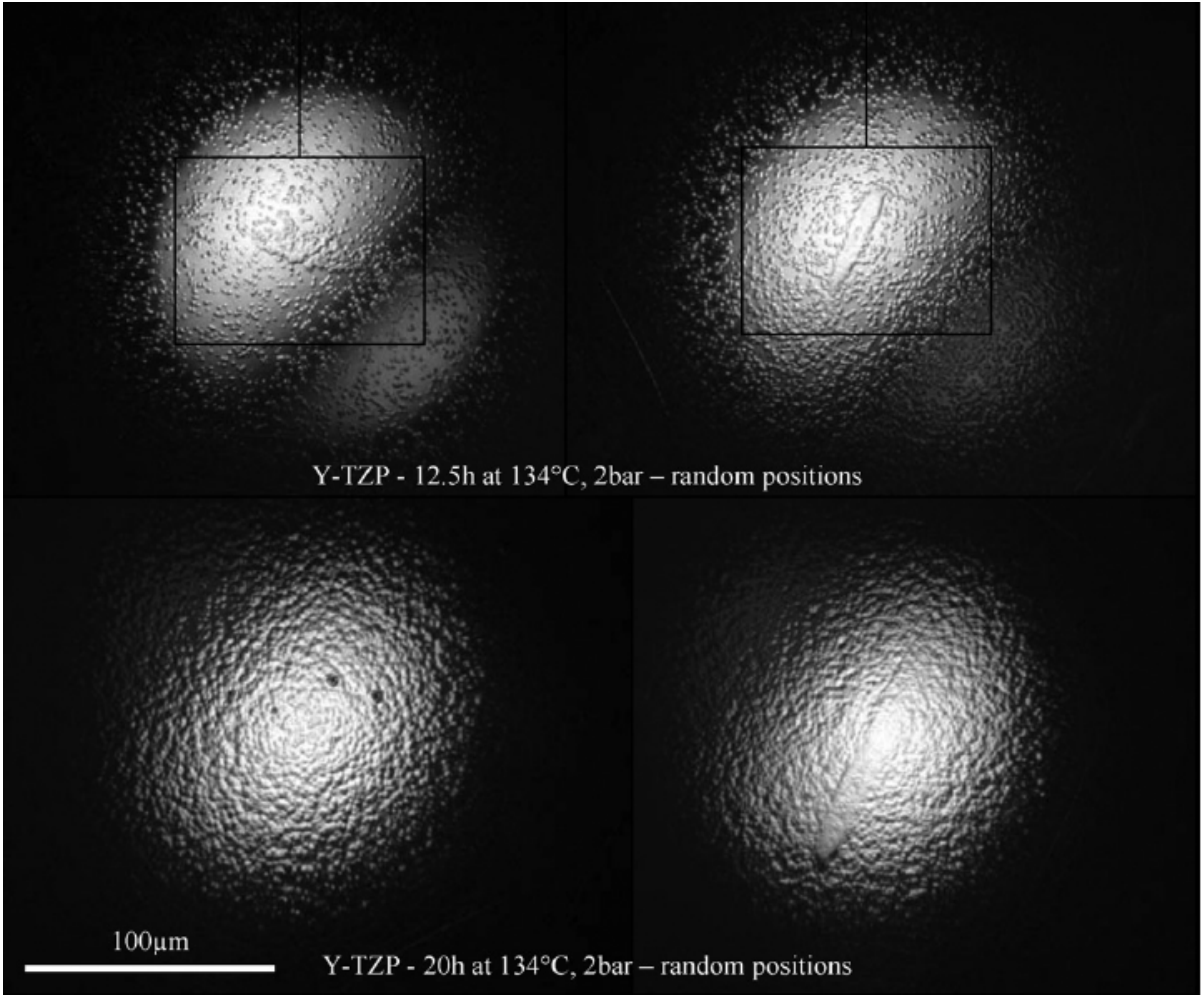
Chevalier et al. Ann. Rev. Mater. Res., 2007



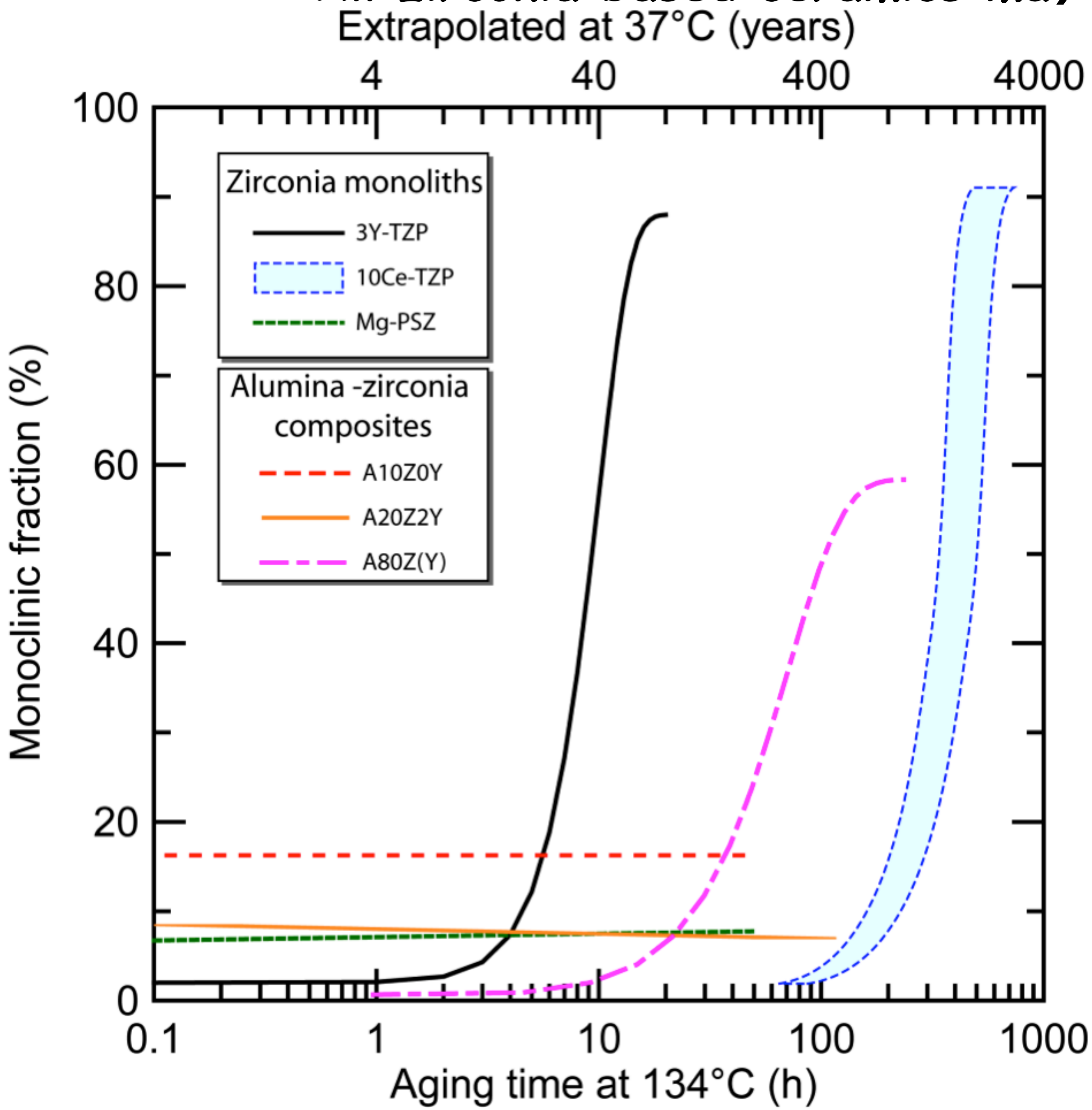




After Hernigou et al. J. Bone Joint Surg Br 2003
and Chevalier et al. Ann. Rev. Mat. Res. 2007

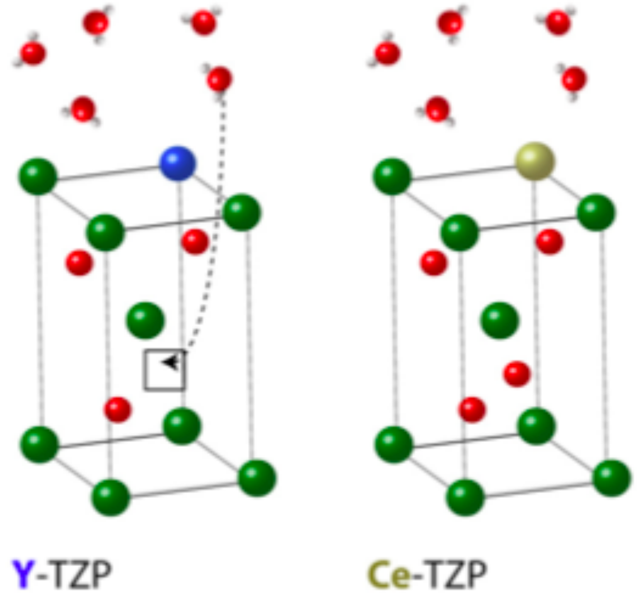

Y-TZP - 12.5h at 134°C, 2bar – random positions
100µm
Y-TZP - 20h at 134°C, 2bar – random positions

All zirconia based ceramics may degrade in vivo ?

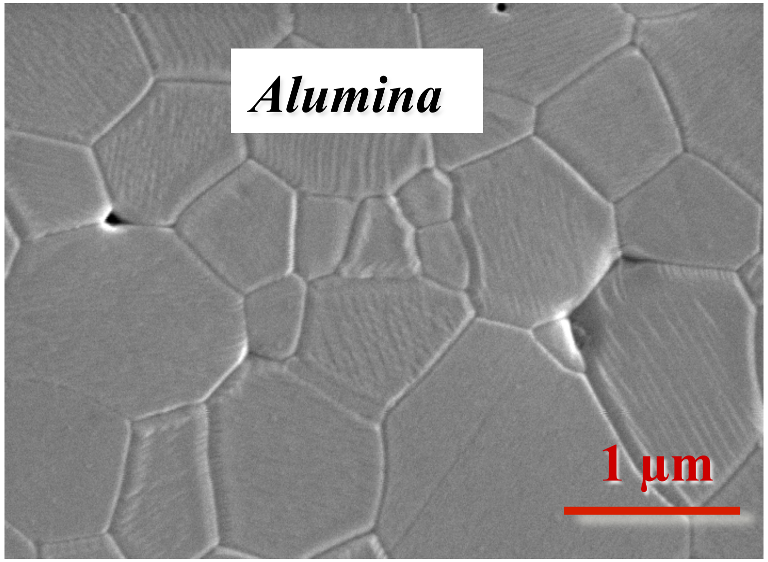


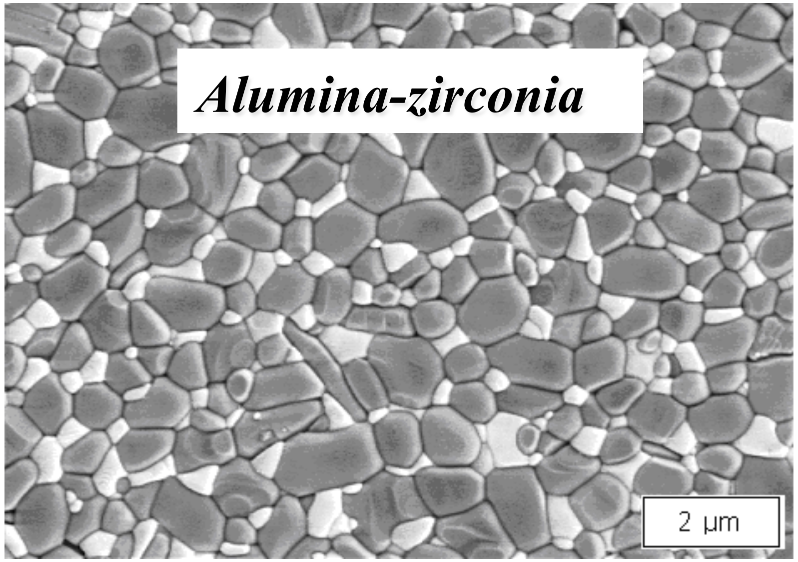
- **Ce-TZP** and Mg-PSZ
- **Alumina rich ZTA**

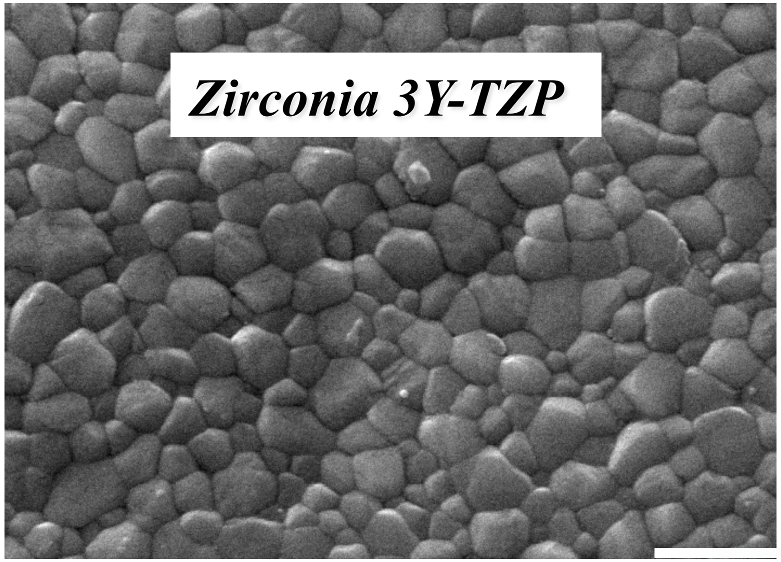
(in which zirconia is not stabilized by yttria)

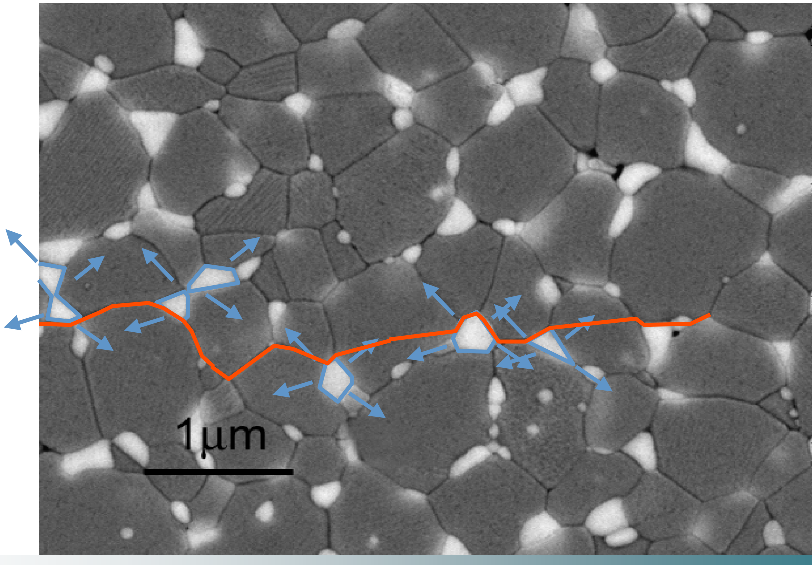


A step further in efficiency (and microstructure complexity) : alumina – zirconia
Strategy of composites : benefit from advantages without the drawbacks

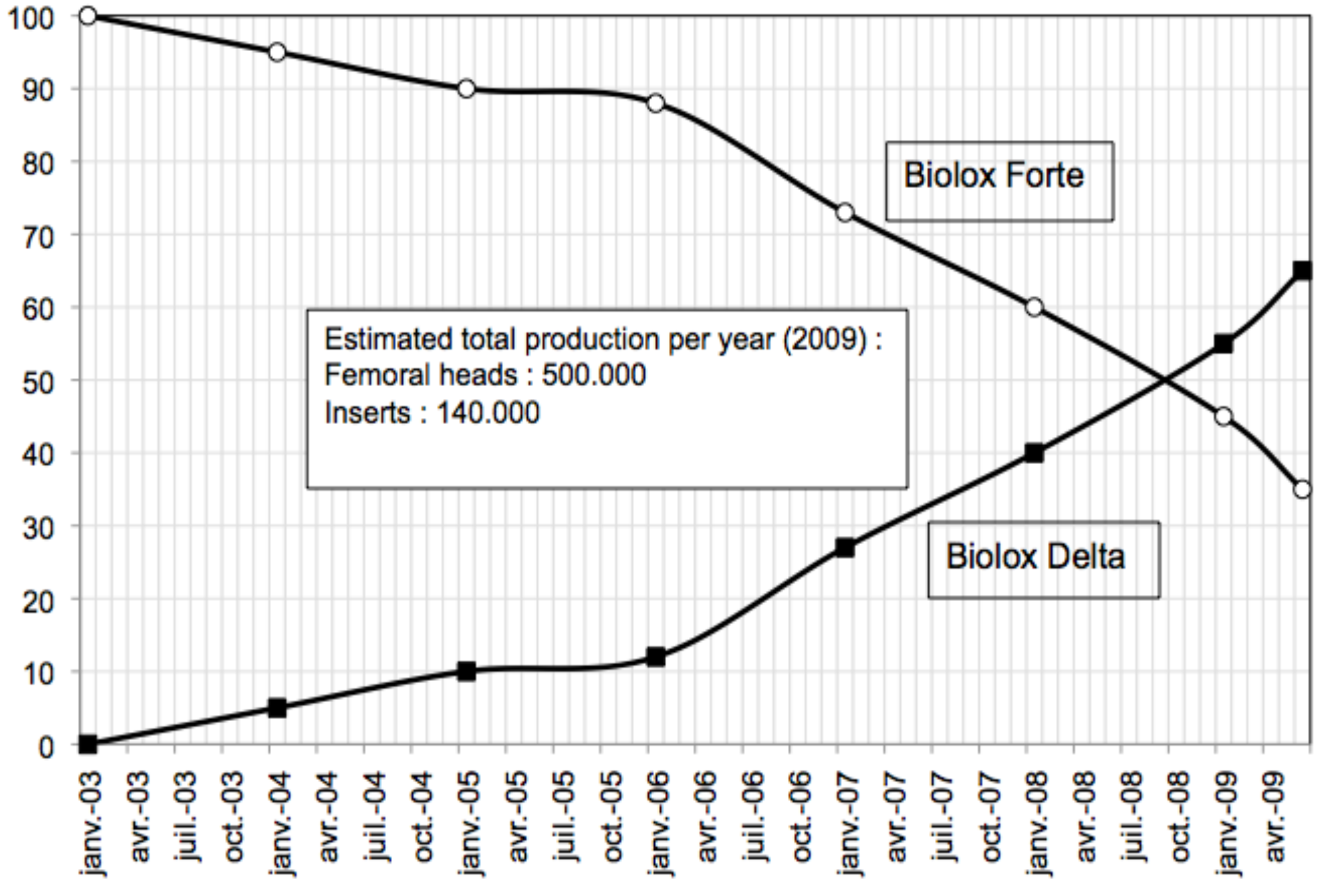








Orthopaedics : Alumina-zirconia as the new standard

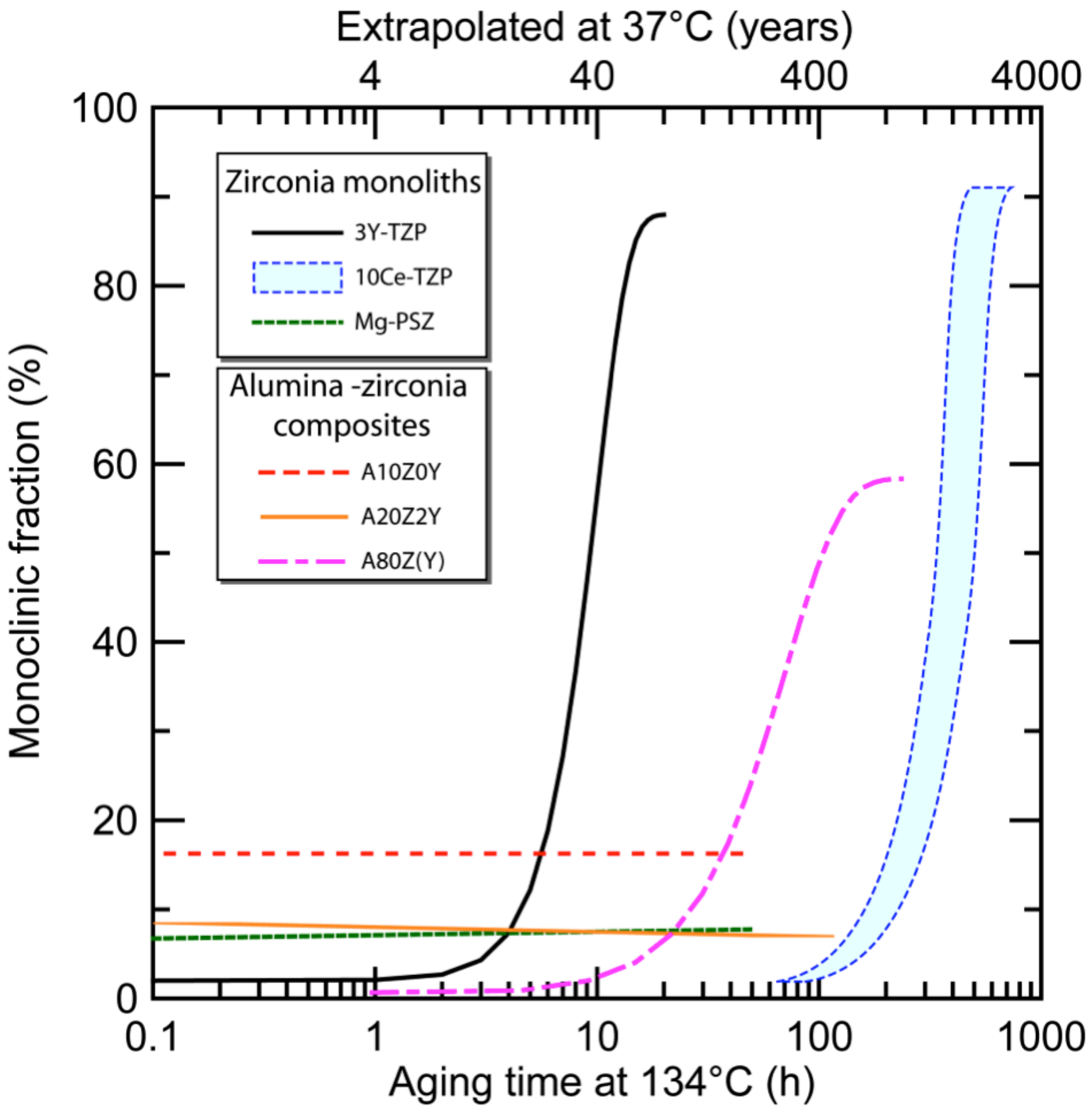


Market : <u>**more than 600.000 zirconia heads implanted between 1990 and 2002**</u>

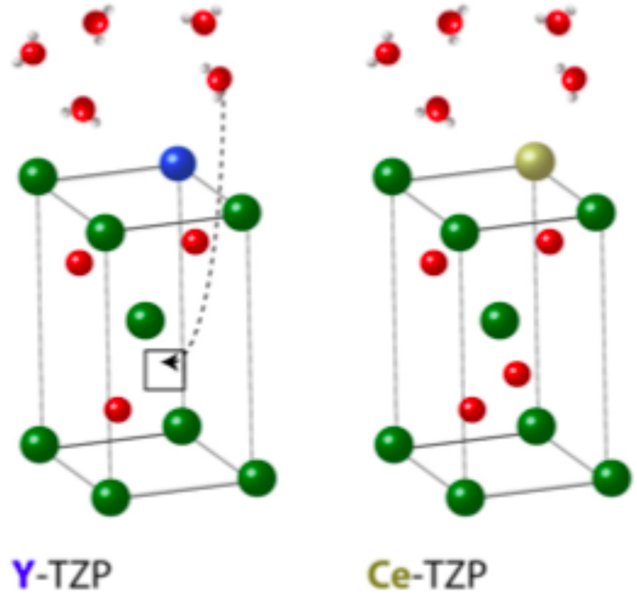
No more zirconia (3Y-TZP) in the market (Saint Gobain Prozyr® story)

ZTA (Biolox Delta®) represents more than 70% of the market

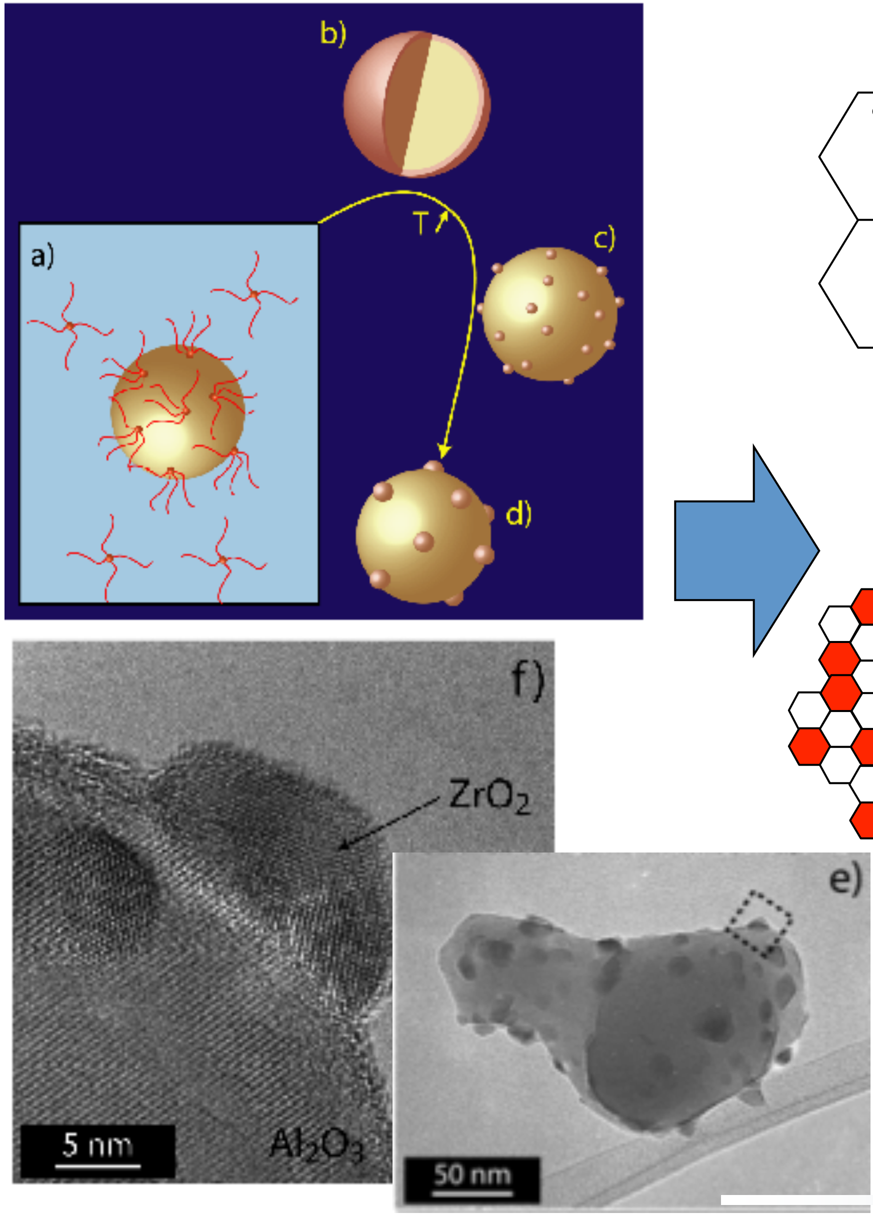
Not all zirconia degrade in vivo !

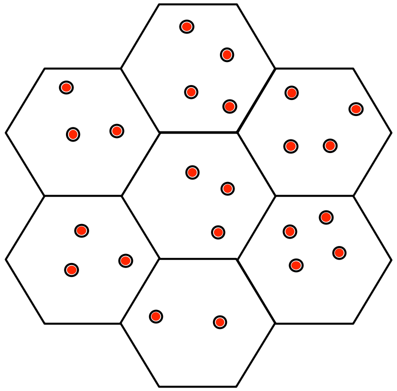


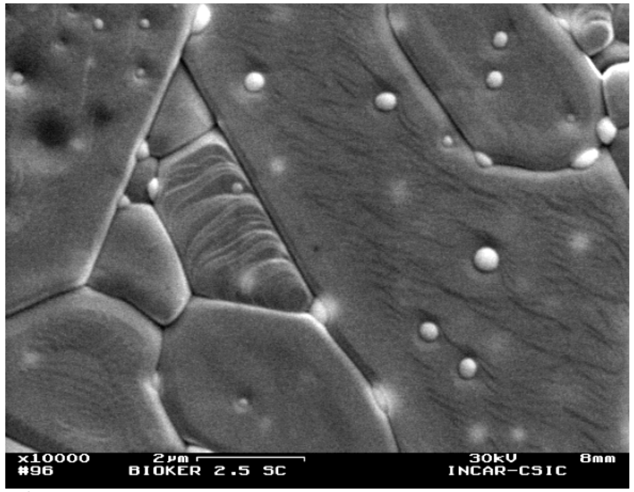
- **Ce-TZP** and Mg-PSZ
- **Alumina rich ZTA (better if no Yttria)**



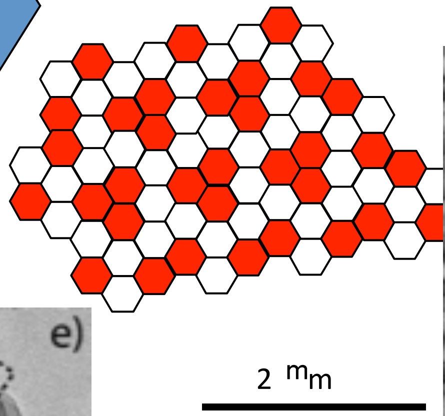
Improving toughness and strength : Towards complex micro- and nano-structures

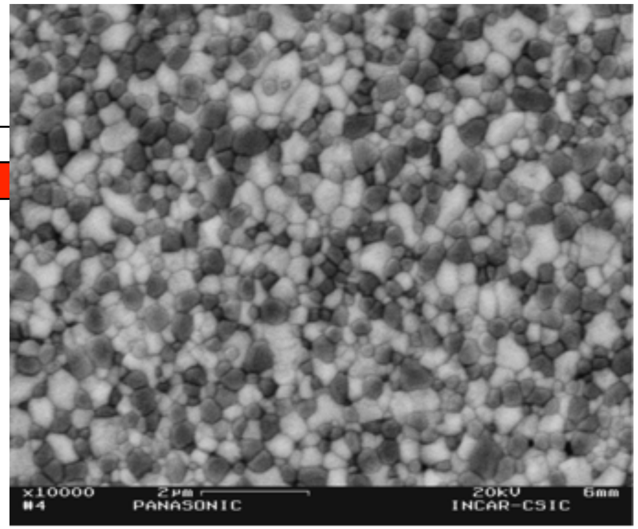






*Alumina - **pure zirconia** composite*

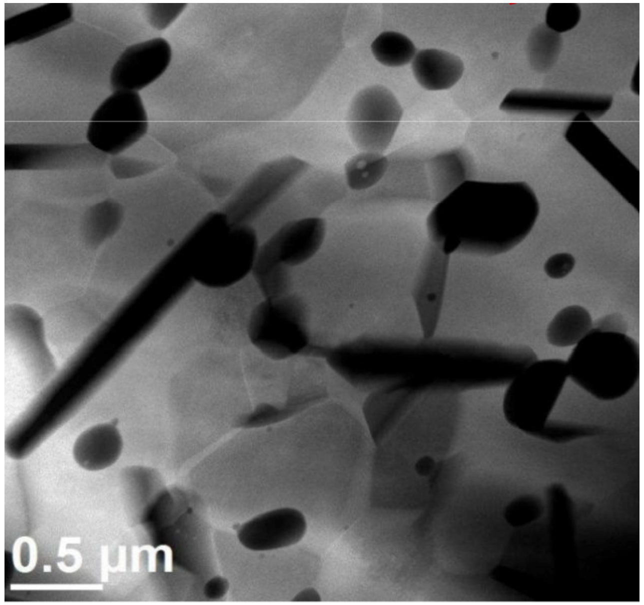


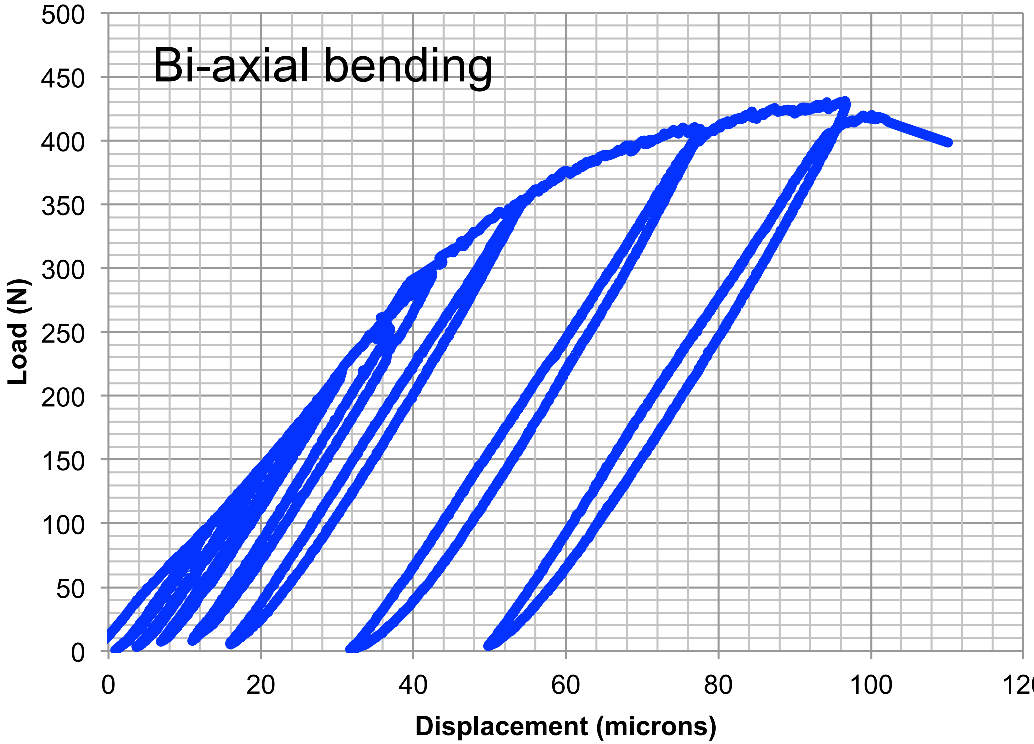


***Ce TZP** - alumina composite*

INSA Institut National des Sciences Appliquées Lyon · CNRS · Mateis · Université Claude Bernard Lyon 1 · membre de Université de Lyon

Complex bio-ceramics at the nano-scale : Example of a tri-phasic system zirconia-alumina-aluminate

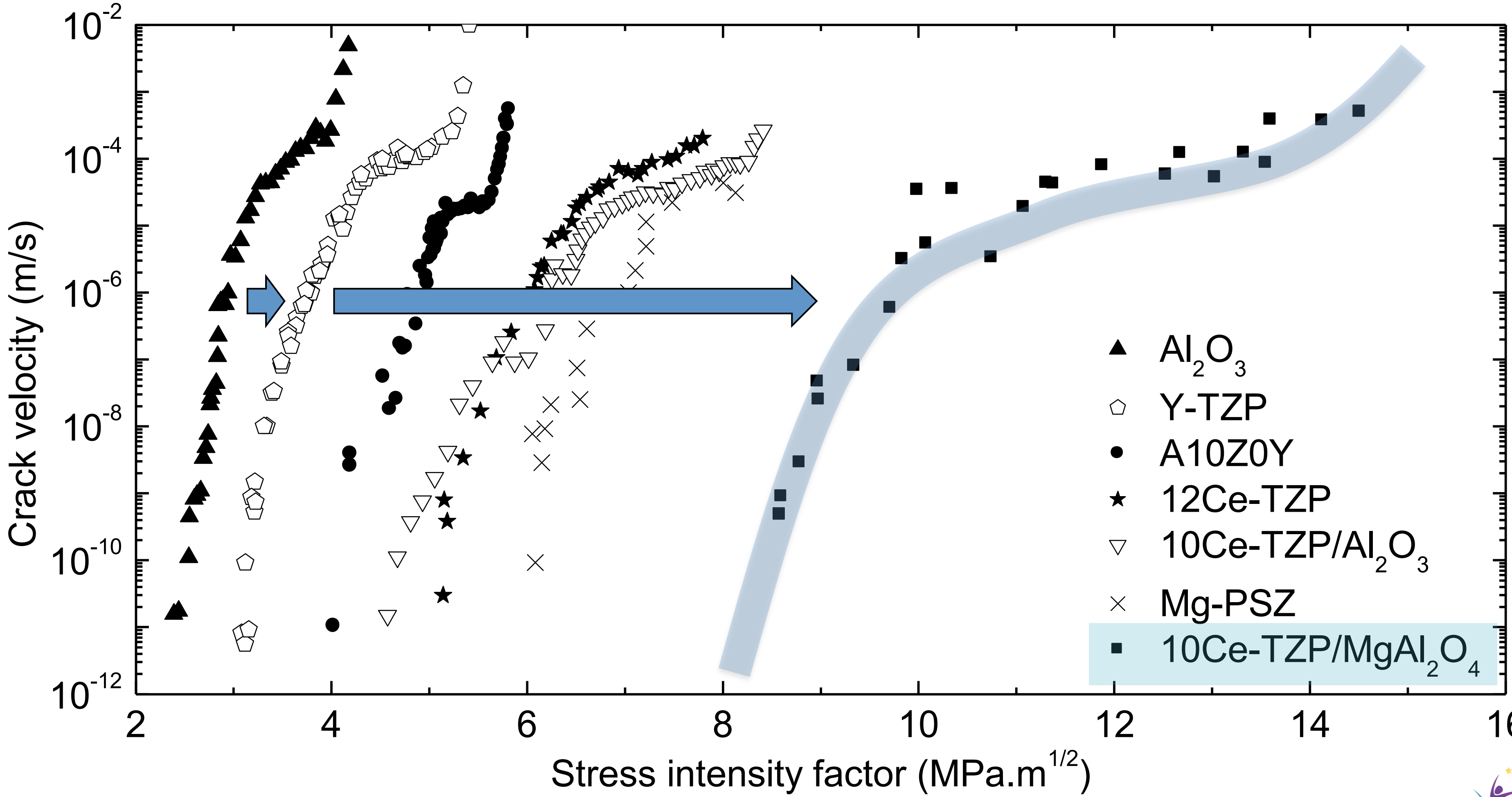




- Strengthening (1000 Mpa) by : Decrease of grain size

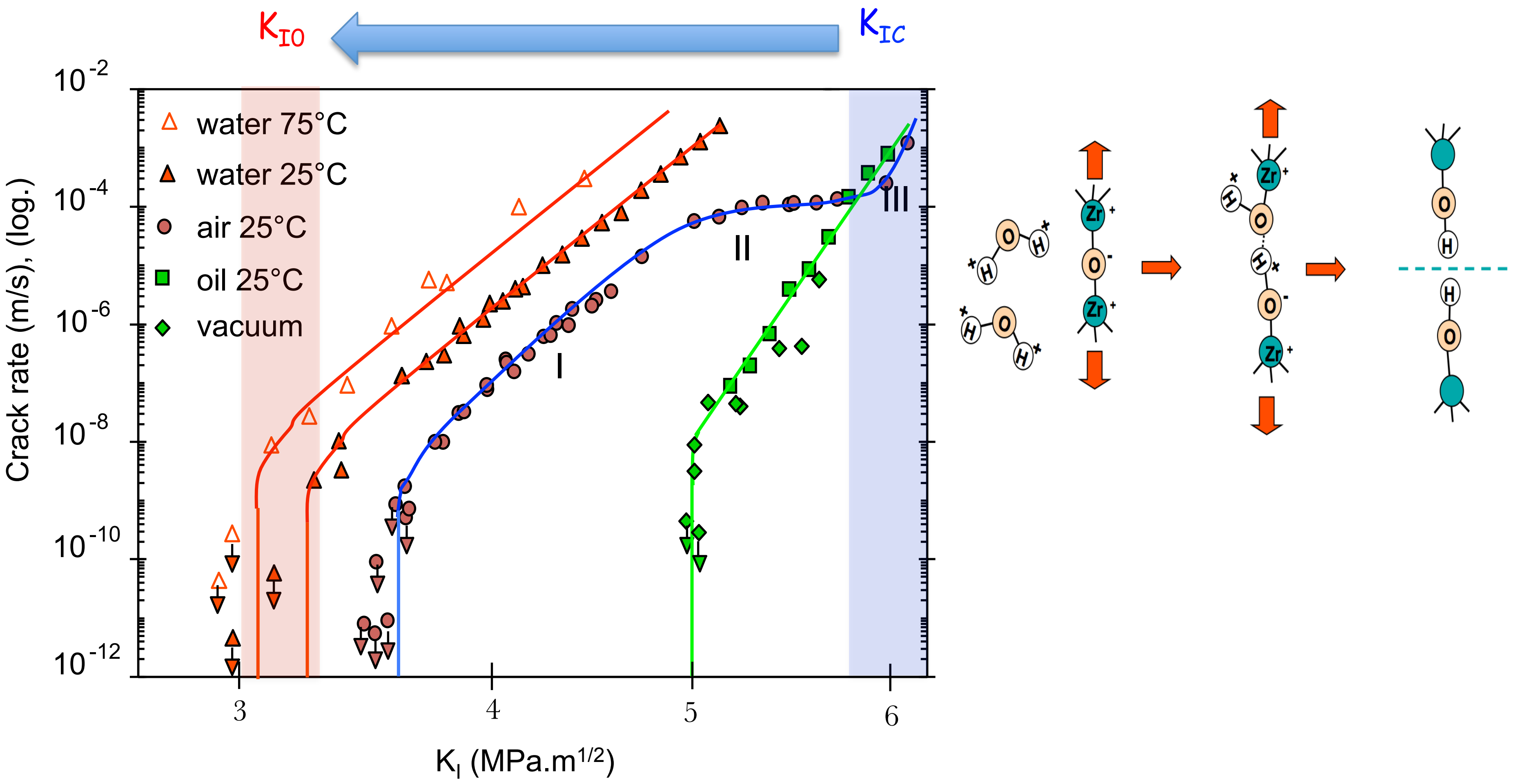
- Toughening (20 $MPa.m^{1/2}$) by : Phase transformation toughening Crack deflection and bridging

Crack resistance of nano-structured complex ceramic composites

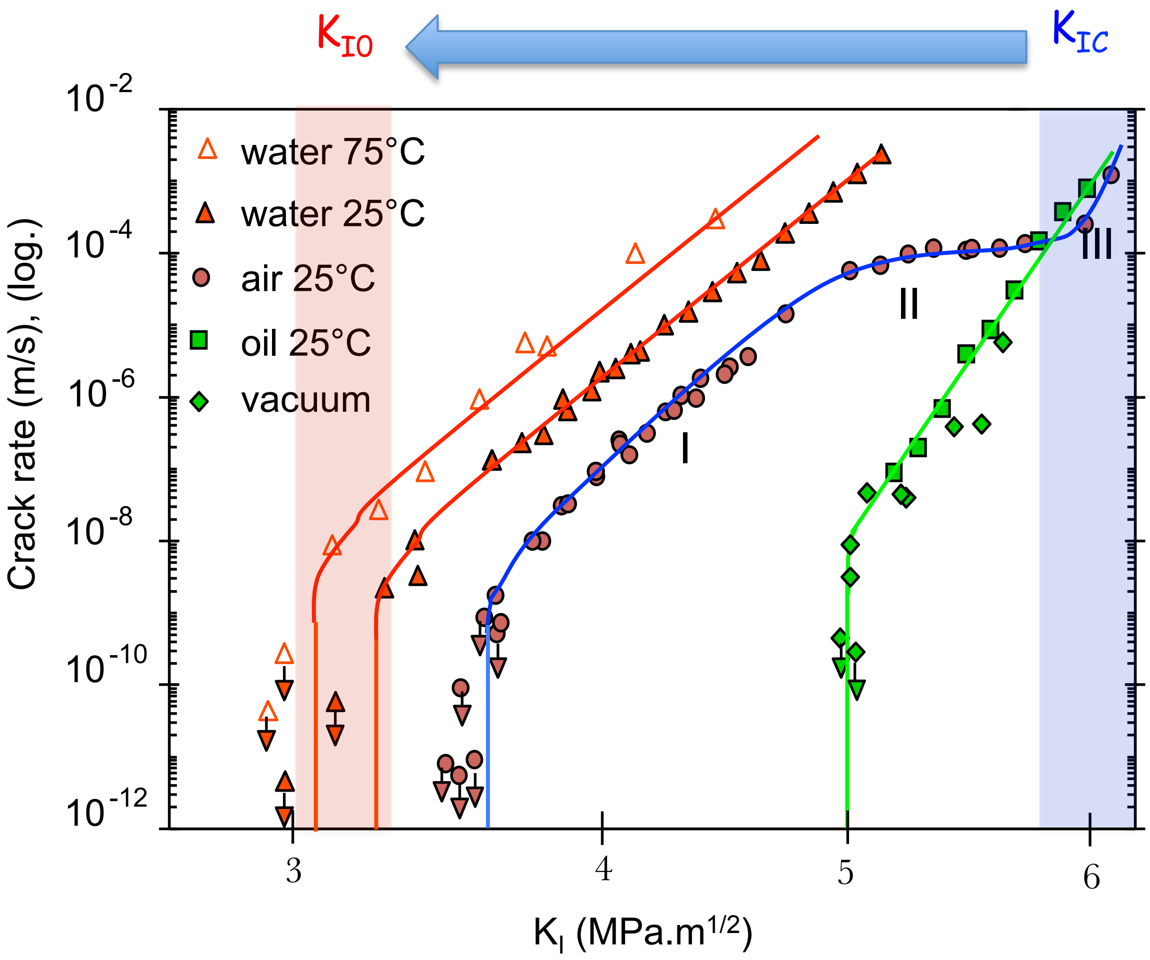


AND NO AGING ! → Tough, strong and stable ceramics !

Susceptibility to Slow Crack Growth (Stress Corrosion Cracking), in all oxides



V – K_I curves of Y-TZP in different environments



K_{IC} : fast fracture (vacuum conditions)

K_{I0} : delayed failure

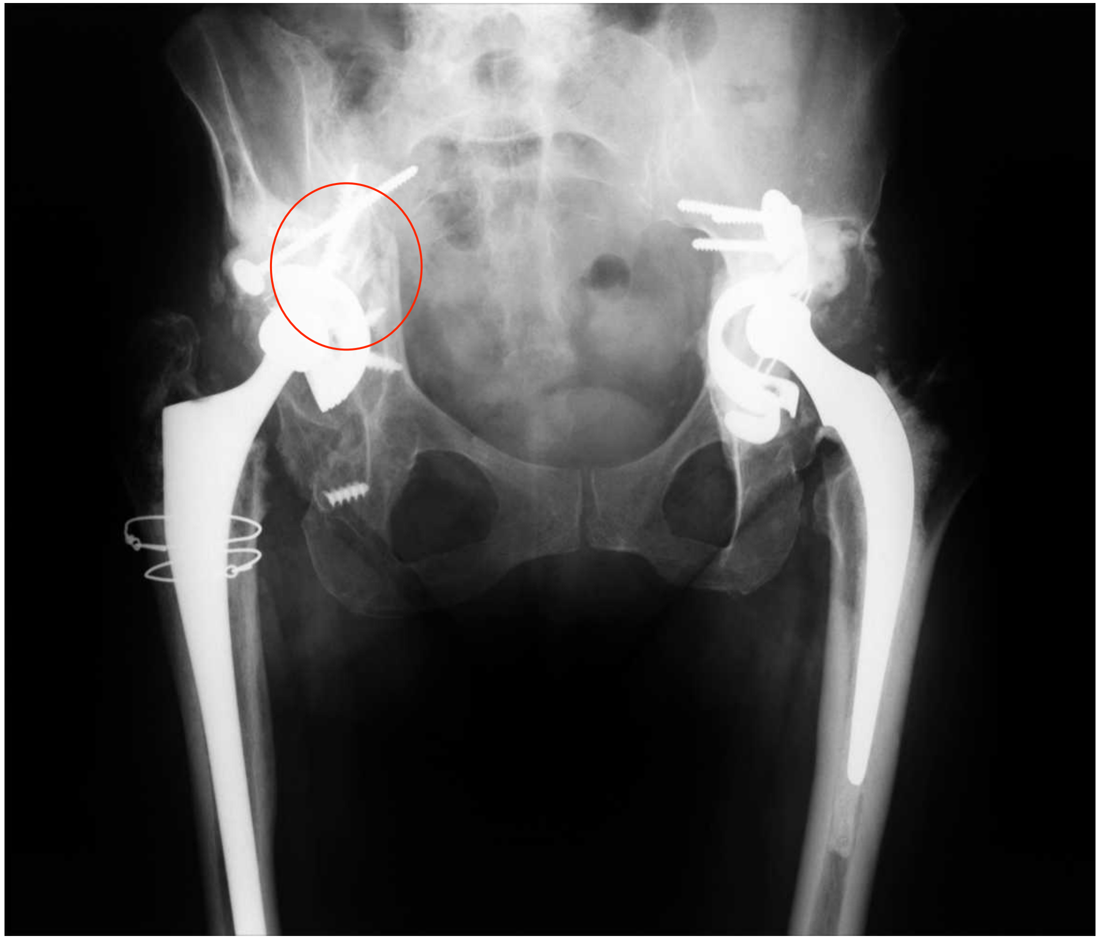
In practical terms :

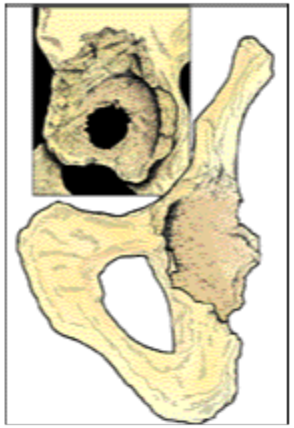
*Load necessary for delayed failure **is half** of the load to failure under fast conditions*

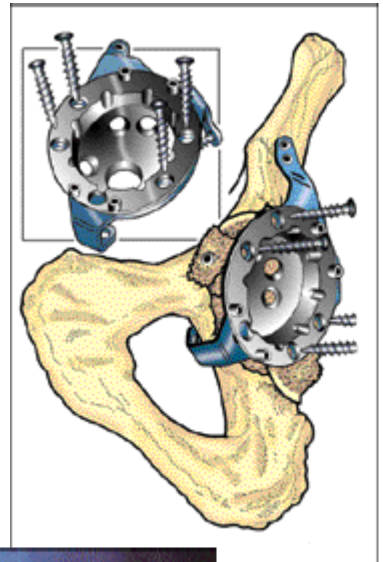
V – K_I curves of Y-TZP in different environments

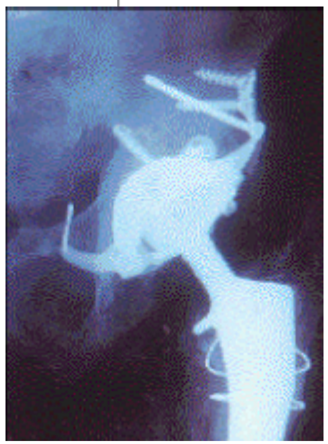
The place of ceramics for bone substitute applications

Clinical use of bone substitutes : revision surgery



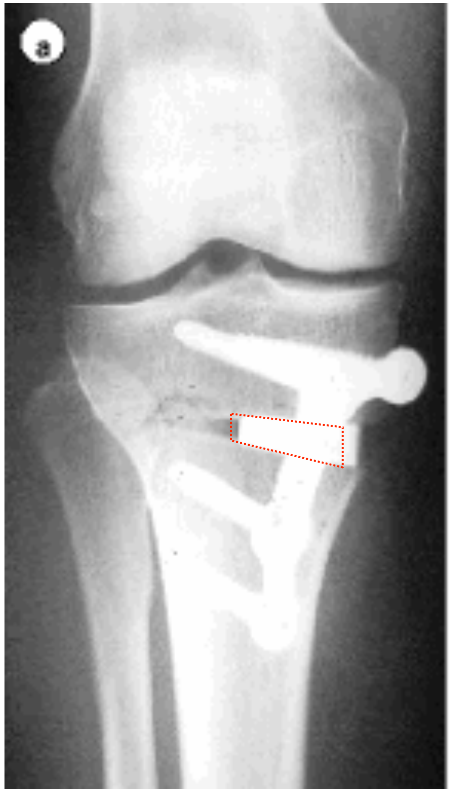






Clinical use of bone substitutes : other

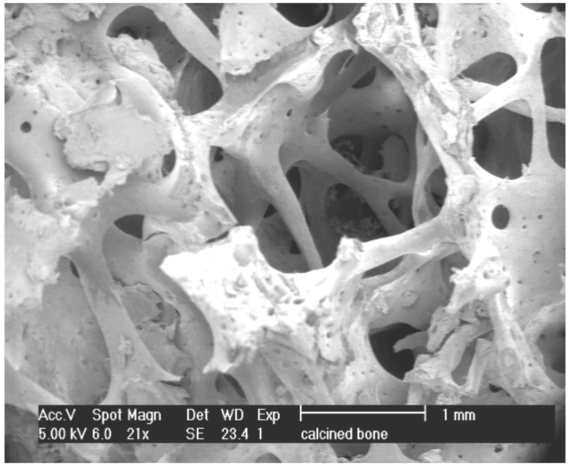
Tumor resection
(image RMN)



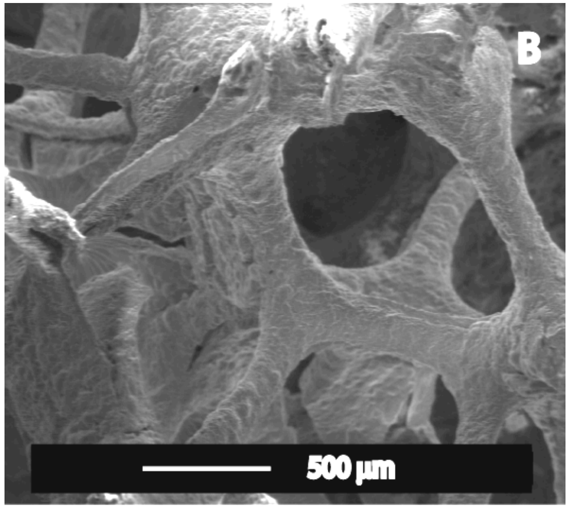
Tibial osteotomy

Maxillo-facial reconstruction
(Biom'up MATRI-BONE®)

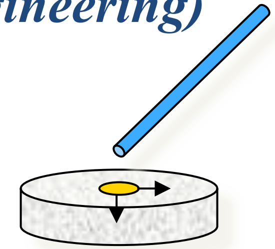
'Bio-active' ceramics for bone substitutes applications (tissue engineering)
***Current clinical use** of calcium phosphate ceramics*

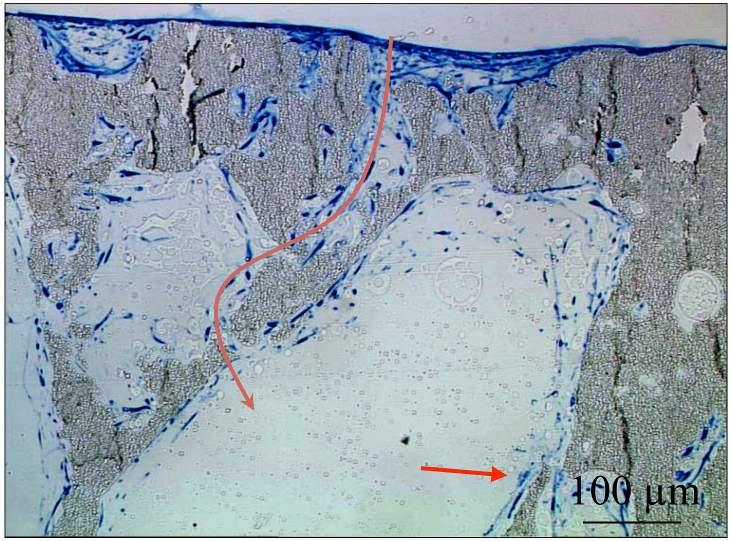


Natural bone (calcined)



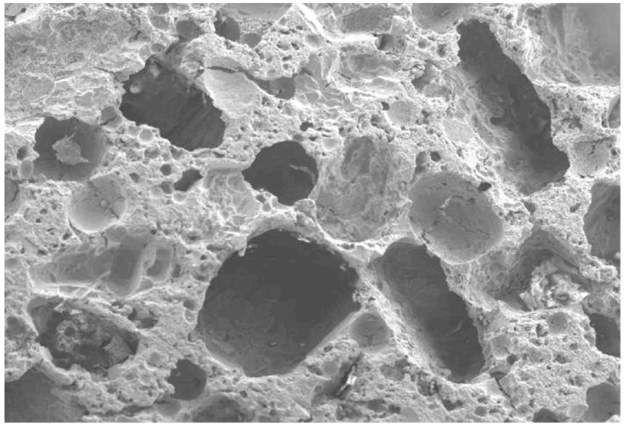
Synthetic calcium phosphate bone substitute (Foam impregnation)



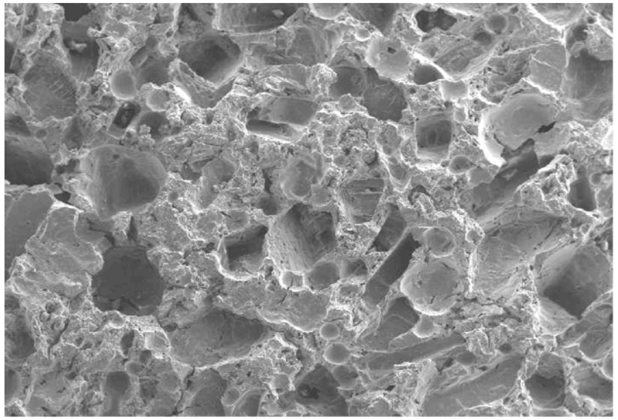


HAP : Hydroxyapatite - $\mathbf{Ca_{10}(PO_4)_6OH_2}$

HAP : Tri-calcium phosphate - $\mathbf{Ca_3(PO_4)_2}$

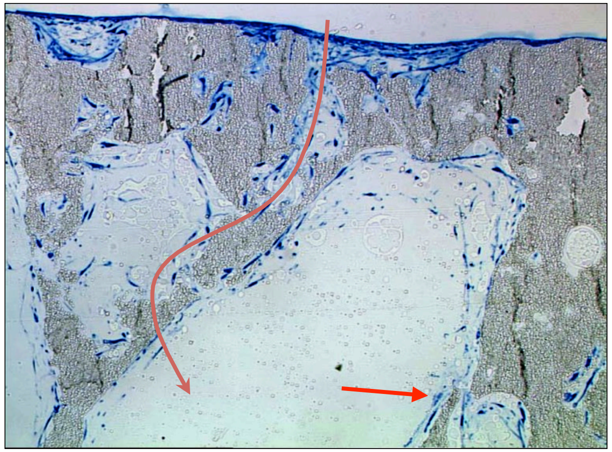


macro-interconnections



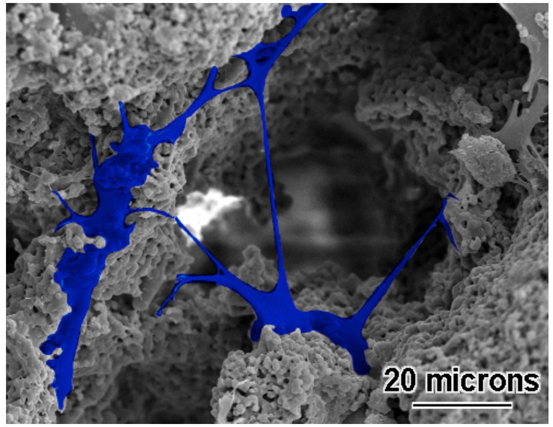
Synthetic calcium phosphate

bone substitute (Porogen addition, sintering)

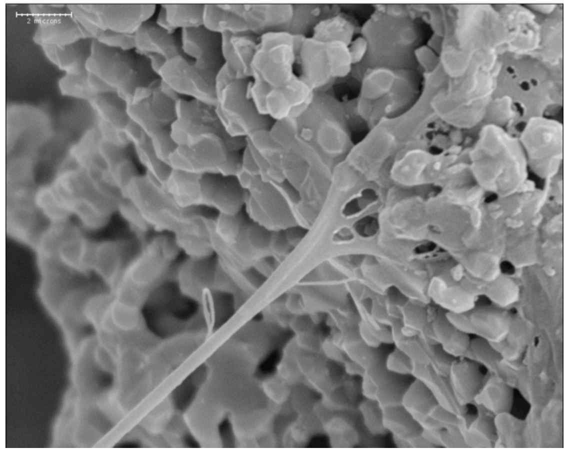


100 µm

Growth of a bone cell on a porous ceramic bone substitute



micro-porosity



Atlantik® bone substitutes
Bignon, Chevalier et al. ,
J. Biomed. Mater. Res. 2002

Current limitations of calcium phosphate ceramics

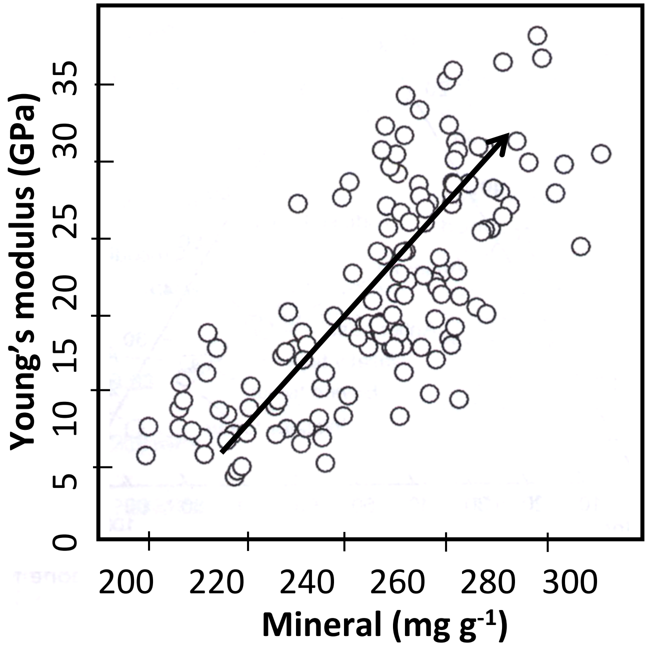
***Mechanical properties of CaP** ceramics versus structural ceramics and composites*

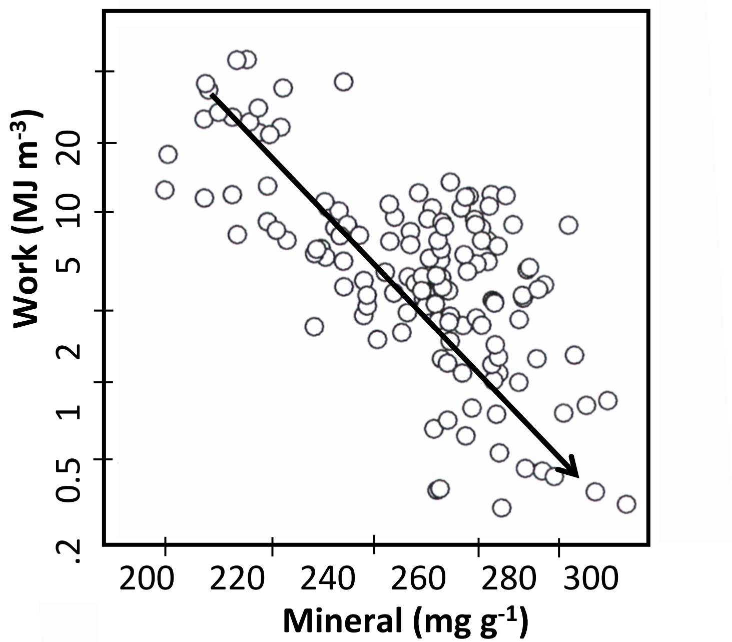
MATERIAL	**Toughness** (K_{IC}, MPa√m)	**Threshold** (K_{I0}, MPa√m)	**Strength** (MPa)	**Vickers Hardness**
Alumina	4.2	2.4	400-600	1800-2000
Zirconia	5.4	3.5	1000	1200-1300
A10Z0Y	5.8	4	700-900	1800
Hydroxyapatite	0.9	0.6	50-60	500
Tricalcium phosphate	1.3	0.8	50-60	900
Mg-PSZ	8	6	600	1000
12Ce-TZP	7.8	5.1	700	1000-1100
Micro-Nano Alumina-Zirconia	6	5	600	1800
Nano-Nano Ce-TZP-alumina	8.4	4.6	900	1300
Silicon Nitride	10 (*)	?	1000 (*)	2500

Towards tougher bone substitutes ?
Processing of organic-inorganic scaffolds

Towards tougher bone substitutes ?
Processing of organic-inorganic scaffolds

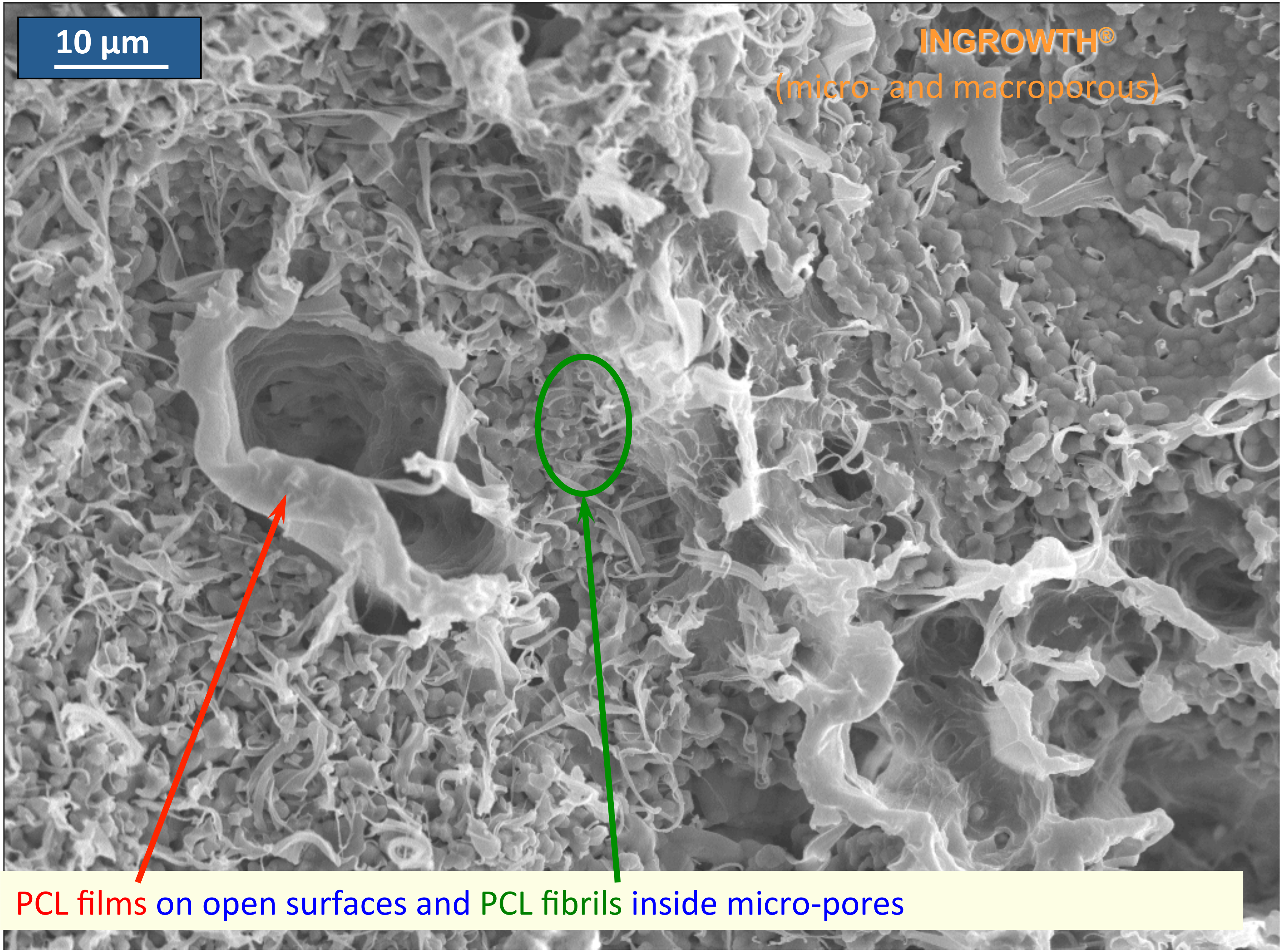
- Motivation : Bone is a hybrid material: its mechanical behavior can be matched only by another organic-inorganic composite

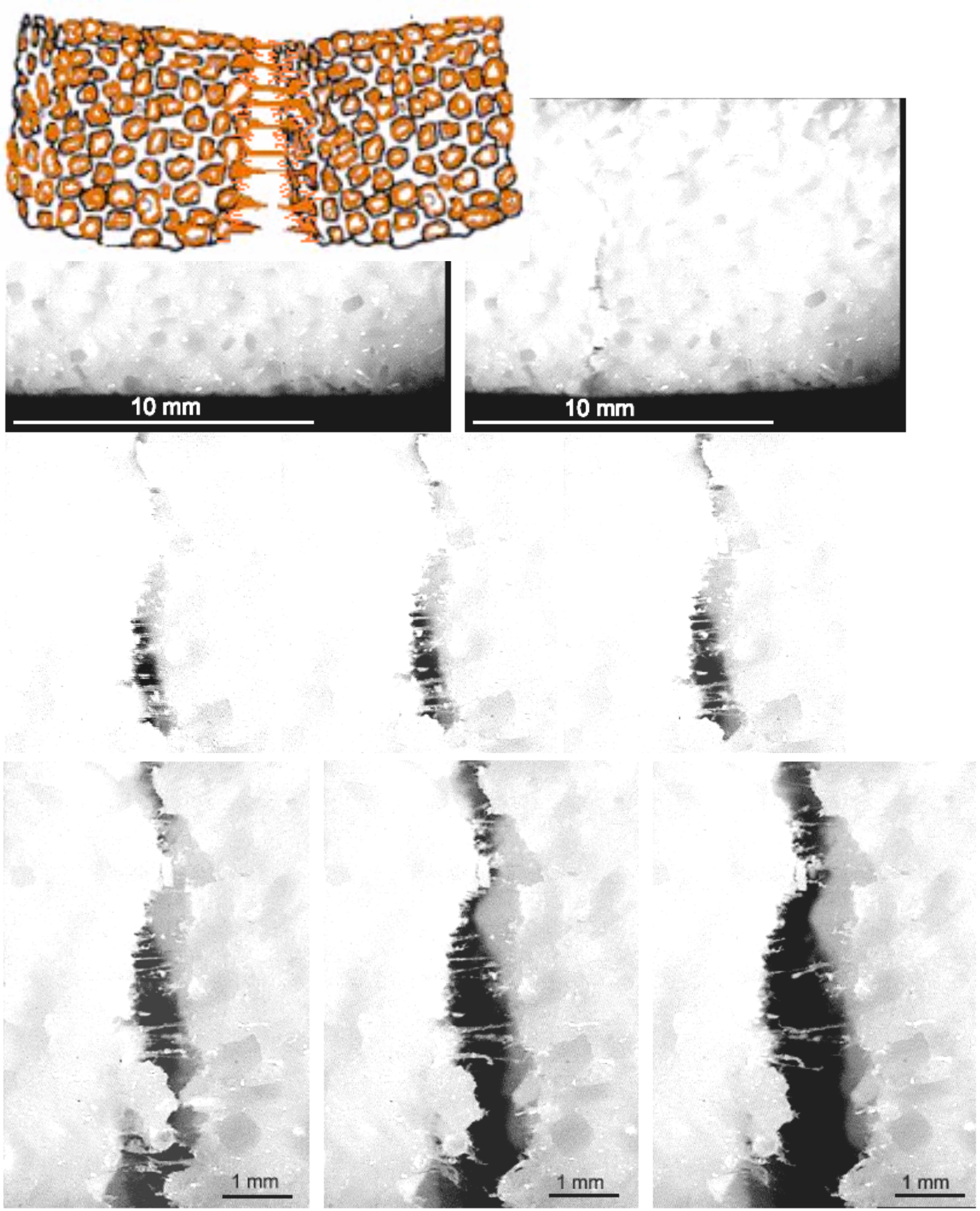


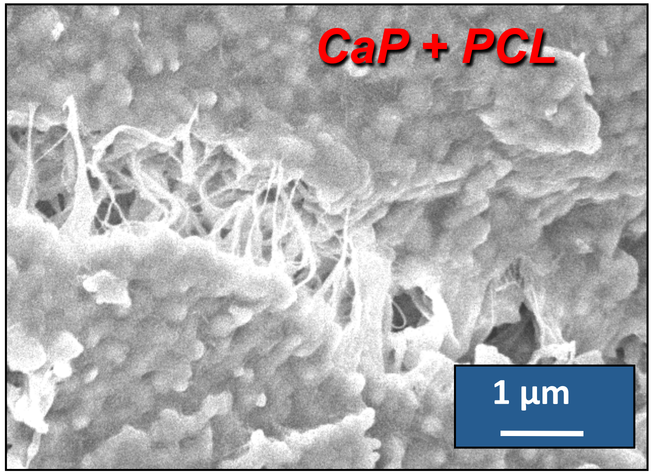


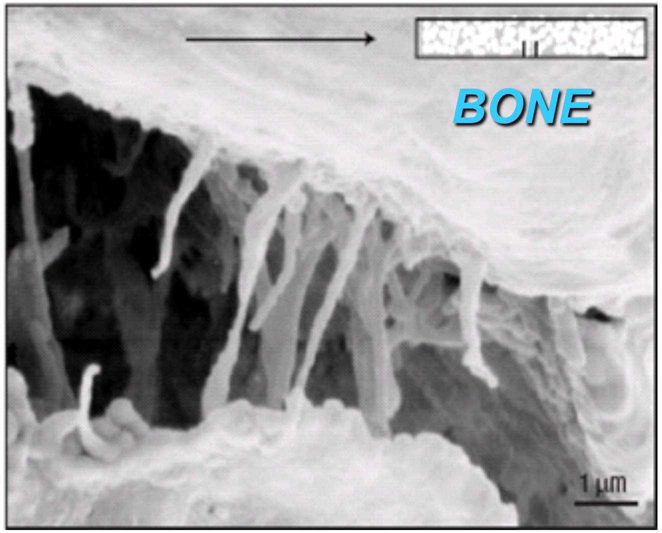
  – Need of stronger substitutes that can (at least) withstand more easily the surgeon manipulations.

Organic - inorganic composites for bone substitutes :
An example of sintered micro-porous ceramics scaffolds impregnated by a bio-polymer

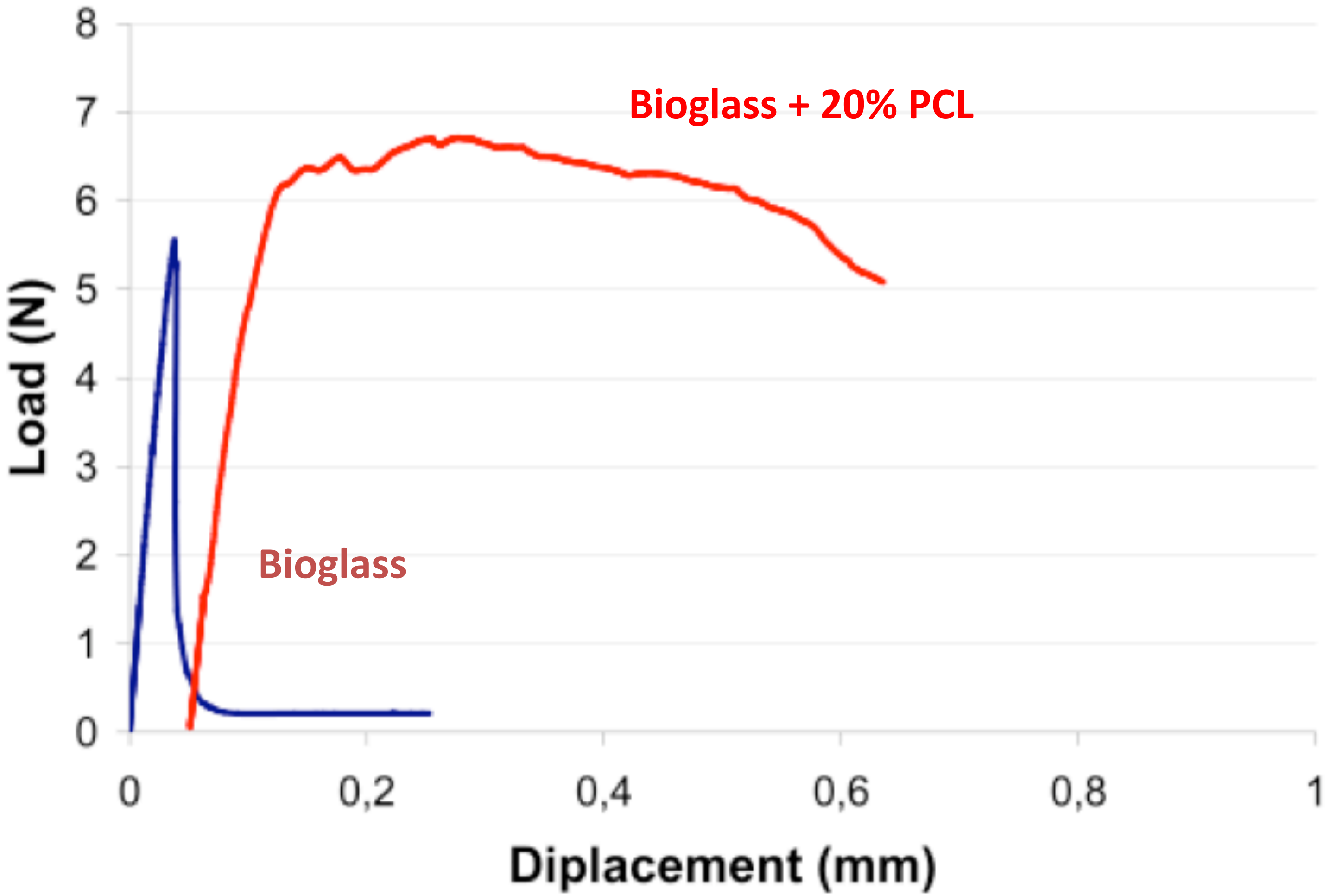




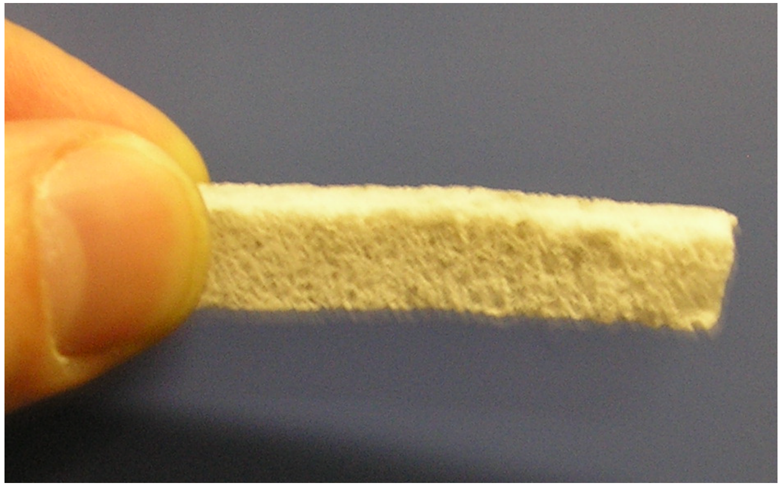




Nalla RK et al. Nat Mater 2003; 2: 64-168



Peroglio, Gremillard, Chevalier et al., J. Europ. Ceram. Soc. 2007




b)


a)
~2 cm

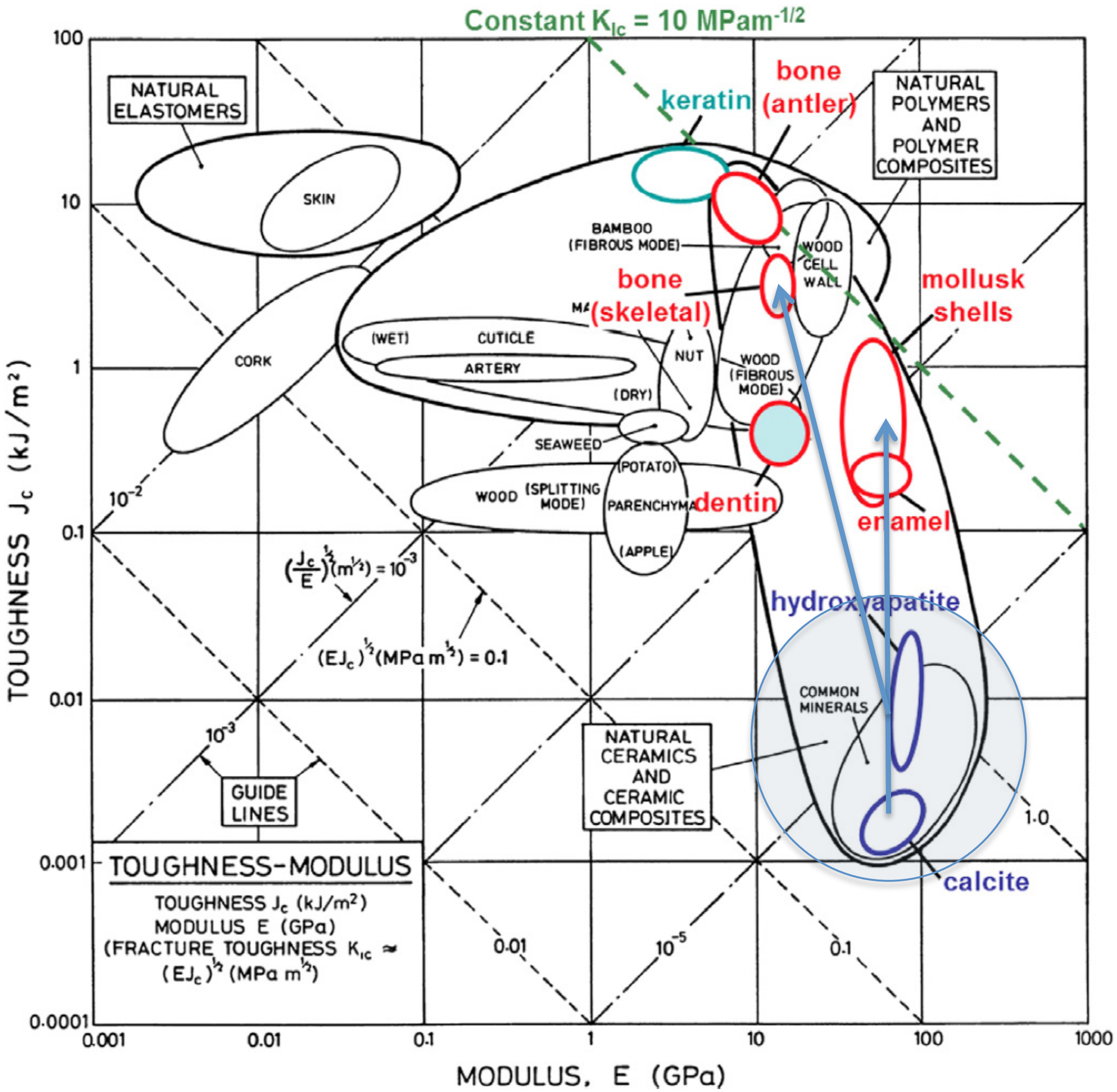
Towards still tougher bone substitutes ?
Bio-inspired strategies

Towards still tougher bone substitutes ?
Bio-inspired strategies

- Motivation : Mimicking natural tissues should lead to different sources of reinforcements

- Interesting thoughts (at least for me) :
  - Bone does not exhibit high strength ! (less that materials currently used as implants) BUT crack resistance (and an ability to heal). It needs flexibility (high organic content)
  - Only enamel who has not the ability to recover (heal) exhibits high strength (high wear resistance), and high toughness with a very high inorganic content.

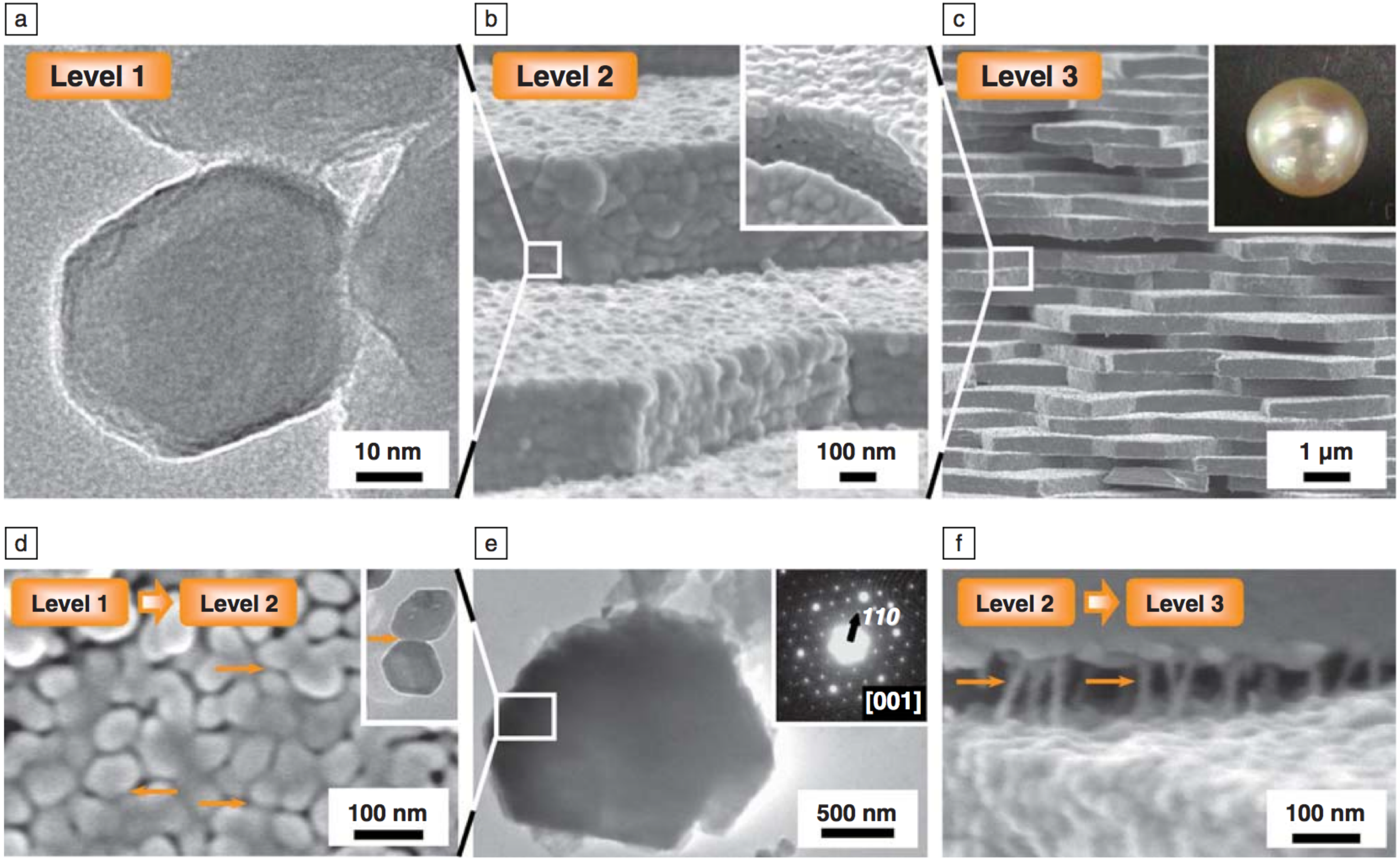
  - All hard tissues exhibit multi-scale reinforcement mechanisms, with architectures from the nano- to the micro- and macro-scale.



Biological materials exhibit a **toughness 2 orders of magnitude** higher than their constitutive inorganic crystals !

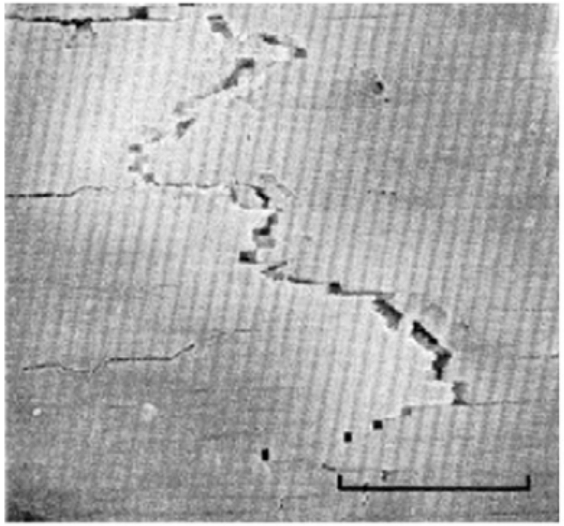
Starting with materials of low intrinsic toughness, how is it possible to exhibit high toughness ?

The case of Nacre : multi-scale architectured materials

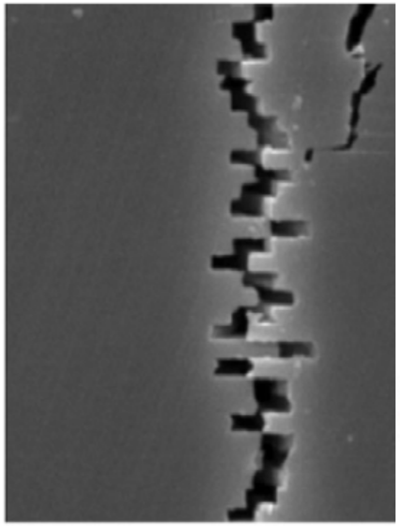


IMAI and OAKI• MRS BULLETIN • VOLUME 35 • FEBRUARY 2010

The different sources of toughening in Nacre

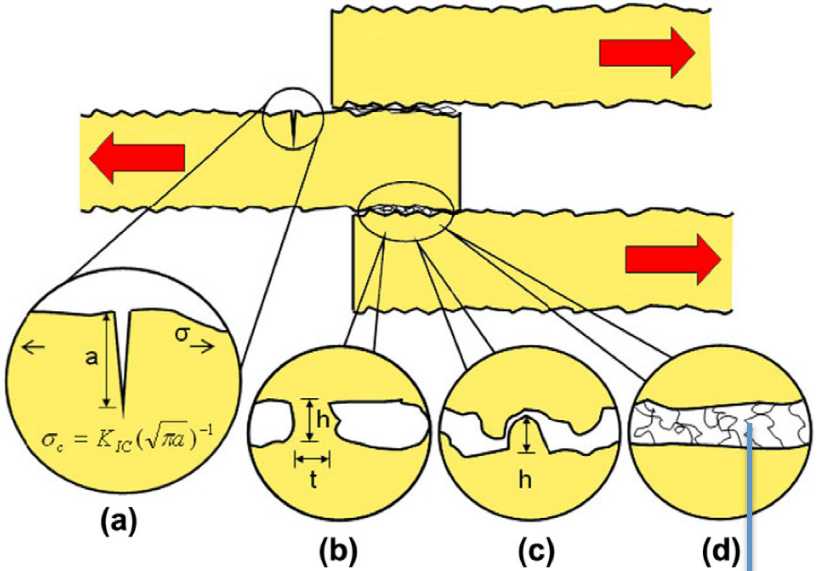


Crack tortuosity
Crack blunting

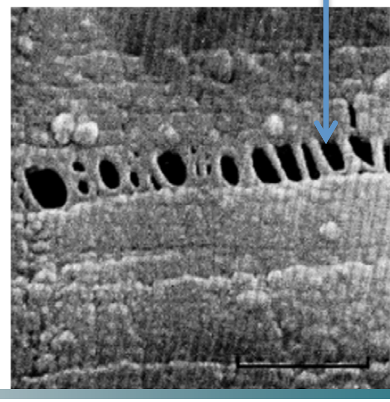


Tiles pull-out
Crack bridging

Chen et al. Progress in Materials Science 57 (2012)



Tiles sliding, mineral bridges
Organic visco-elastic layer

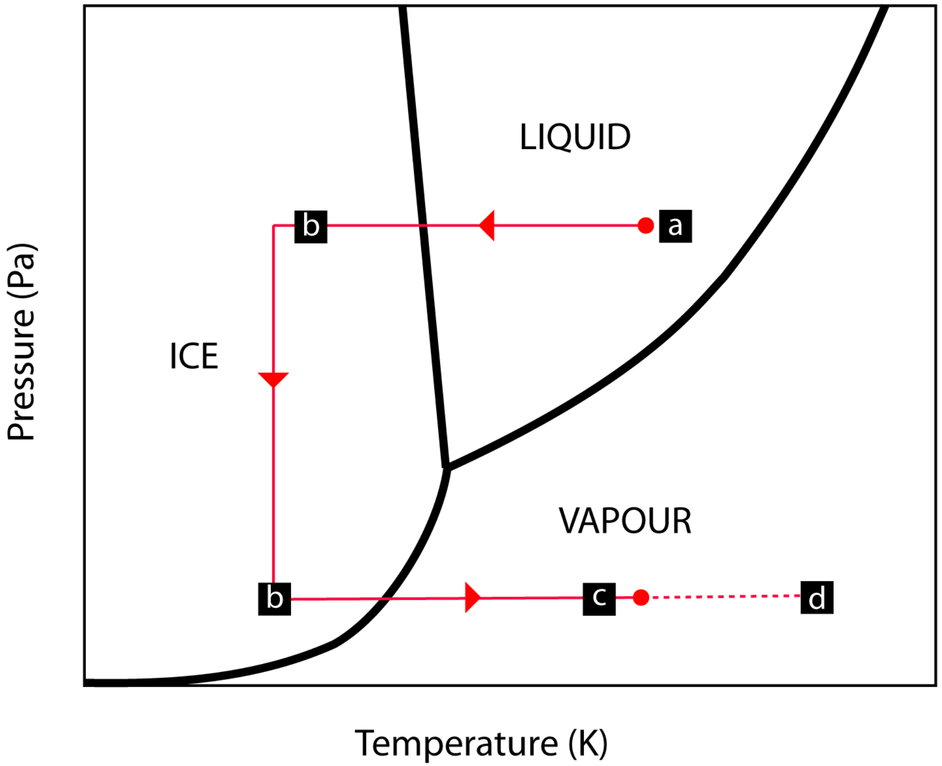


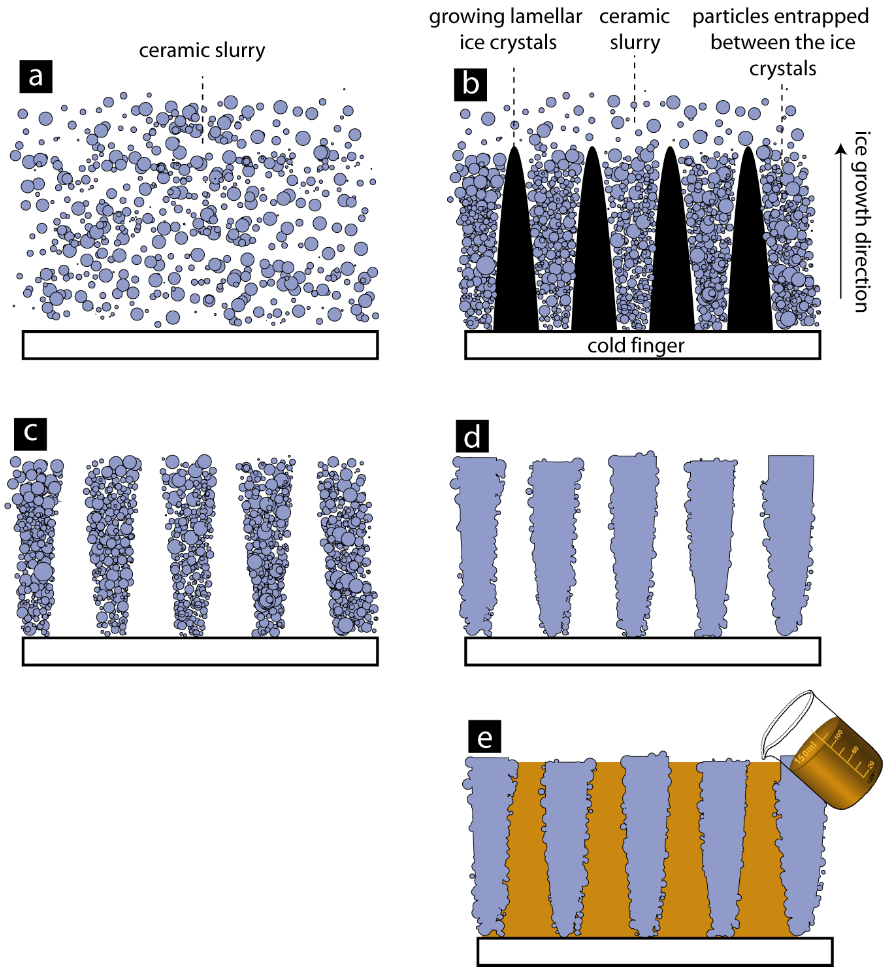
Mineral (>95%): $CaCO_3$ (Aragonite)
organic (<5%): proteins and polysaccharides

$$K_{IC} \sim 8\,MPa\sqrt{m}$$

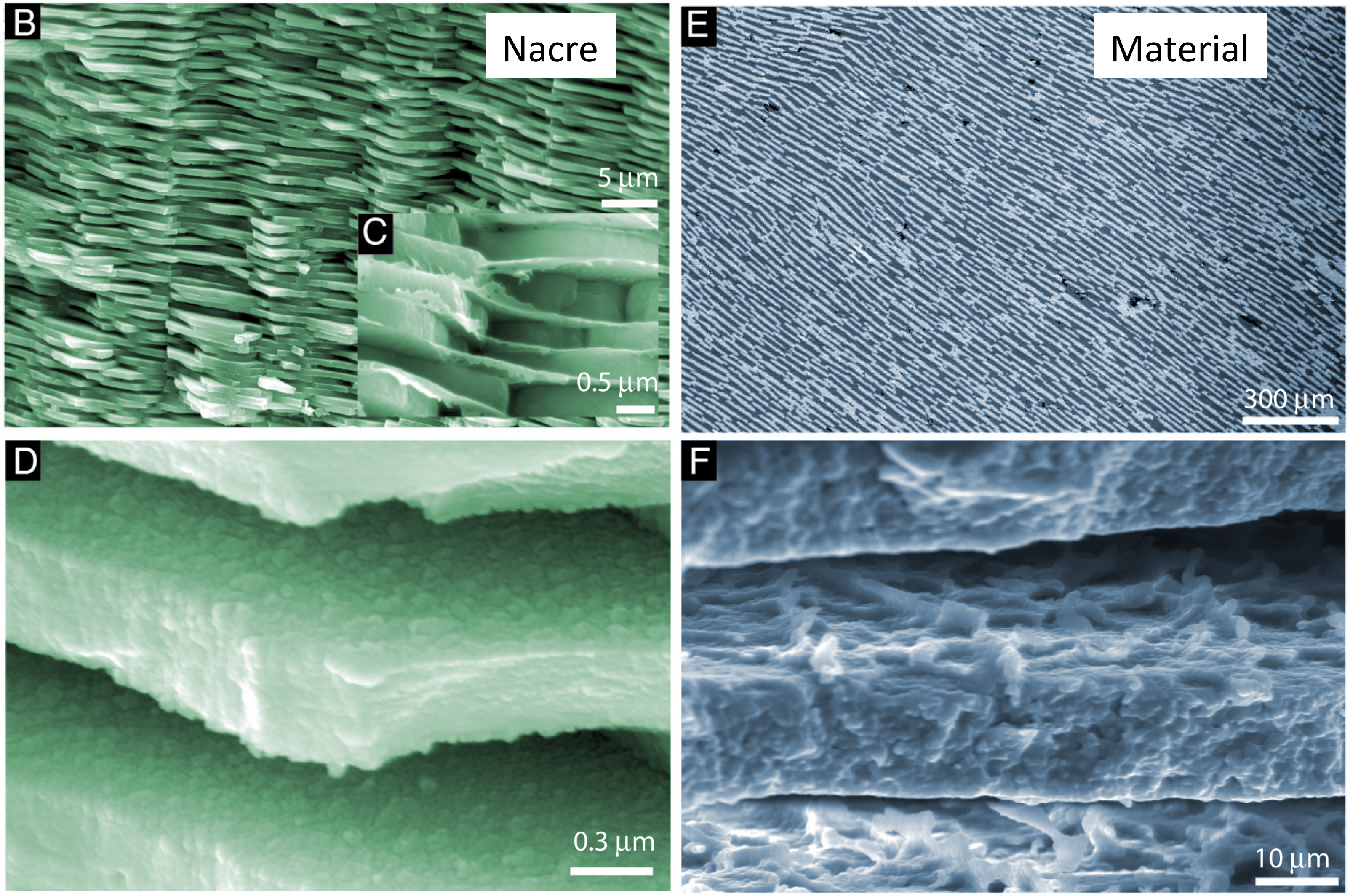
Multi-scale reinforcement, influence of organic content

Can we process nacre-like structures ?





Deville et al. (Science 2006)

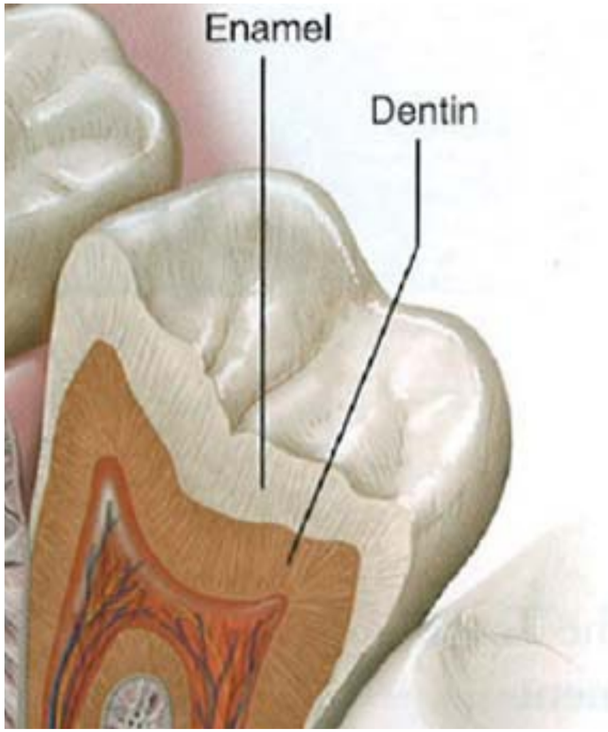


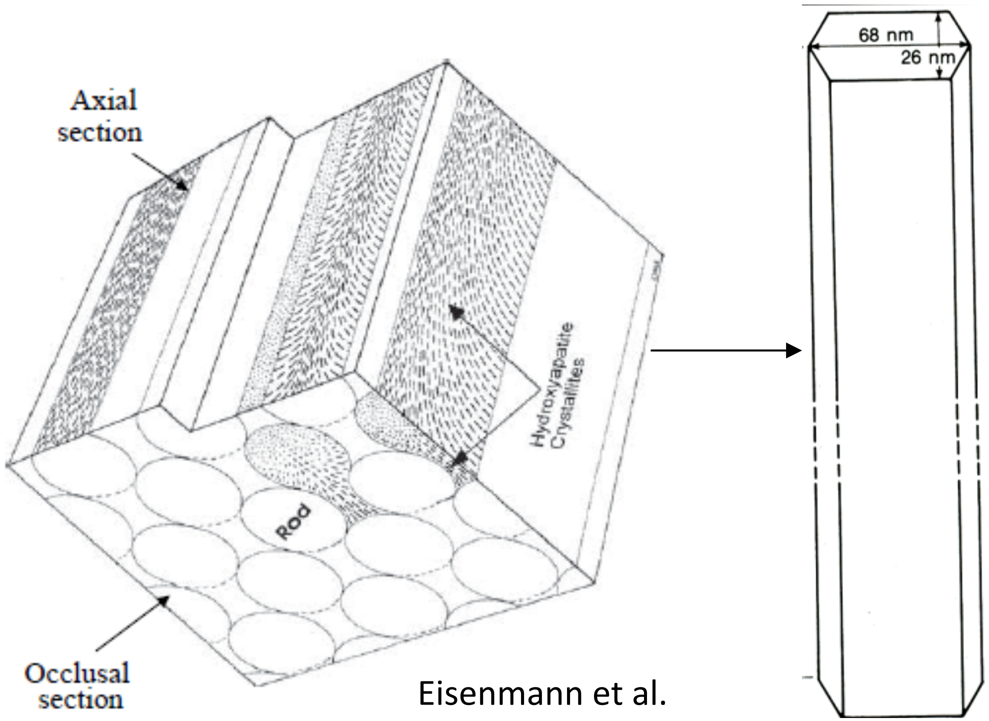
Deville et al., Science 2006

The case of Dental enamel

Strength : 400 MPa
Toughness : 8-10 MPa.m$^{1/2}$

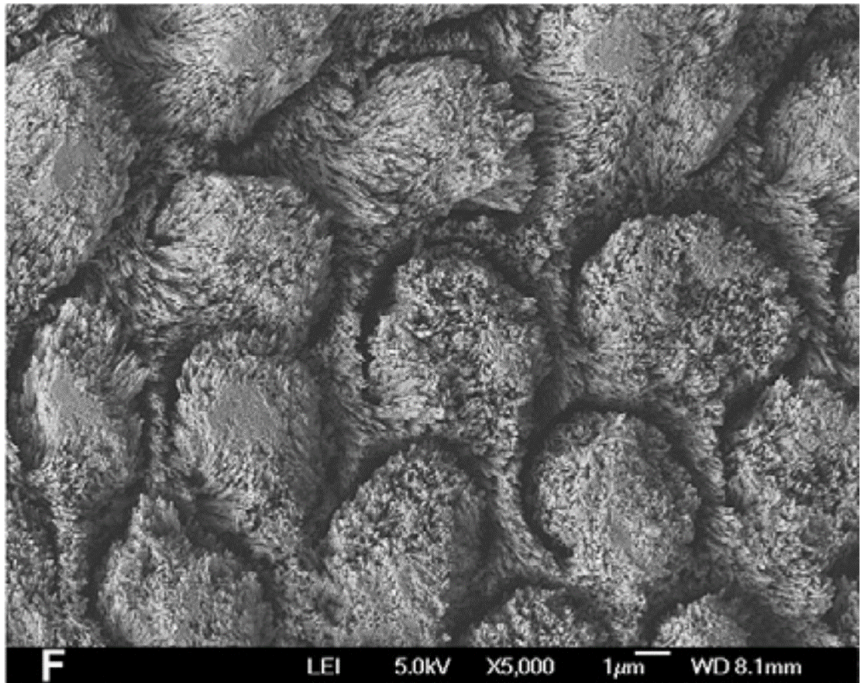
Inorganic content : 98wt.% (apatite)
Organic content (proteins) : 2 wt.%

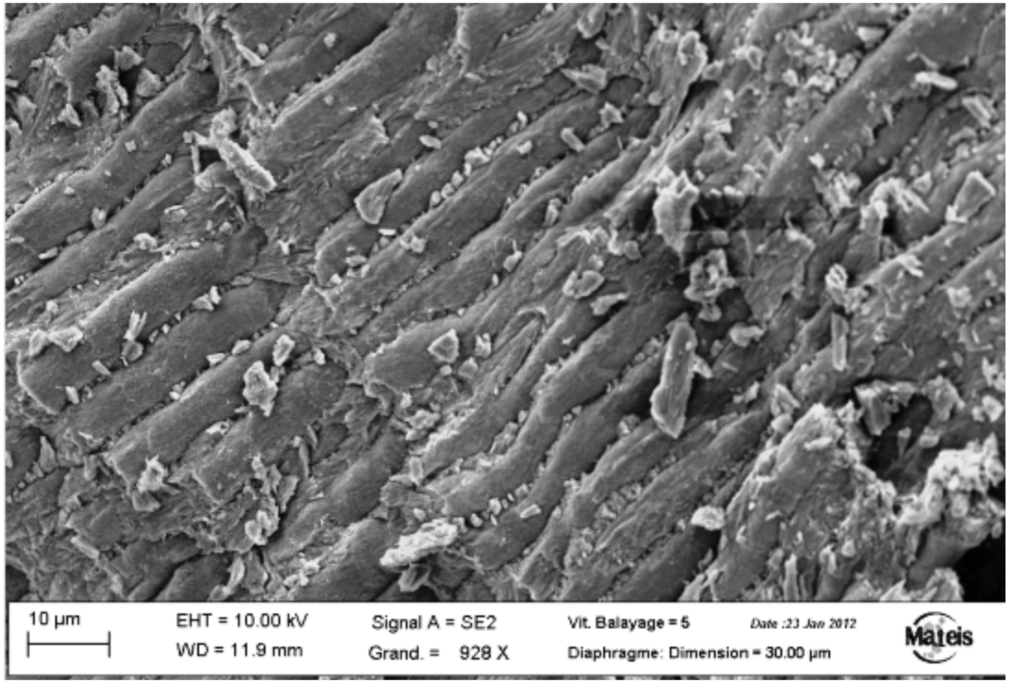




Eisenmann et al. 1998

The case of Dental enamel

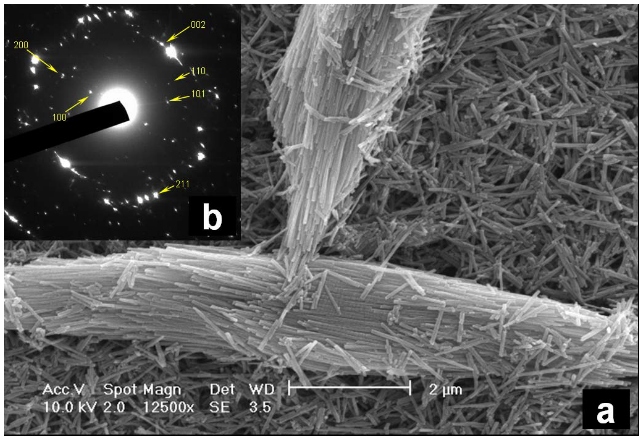




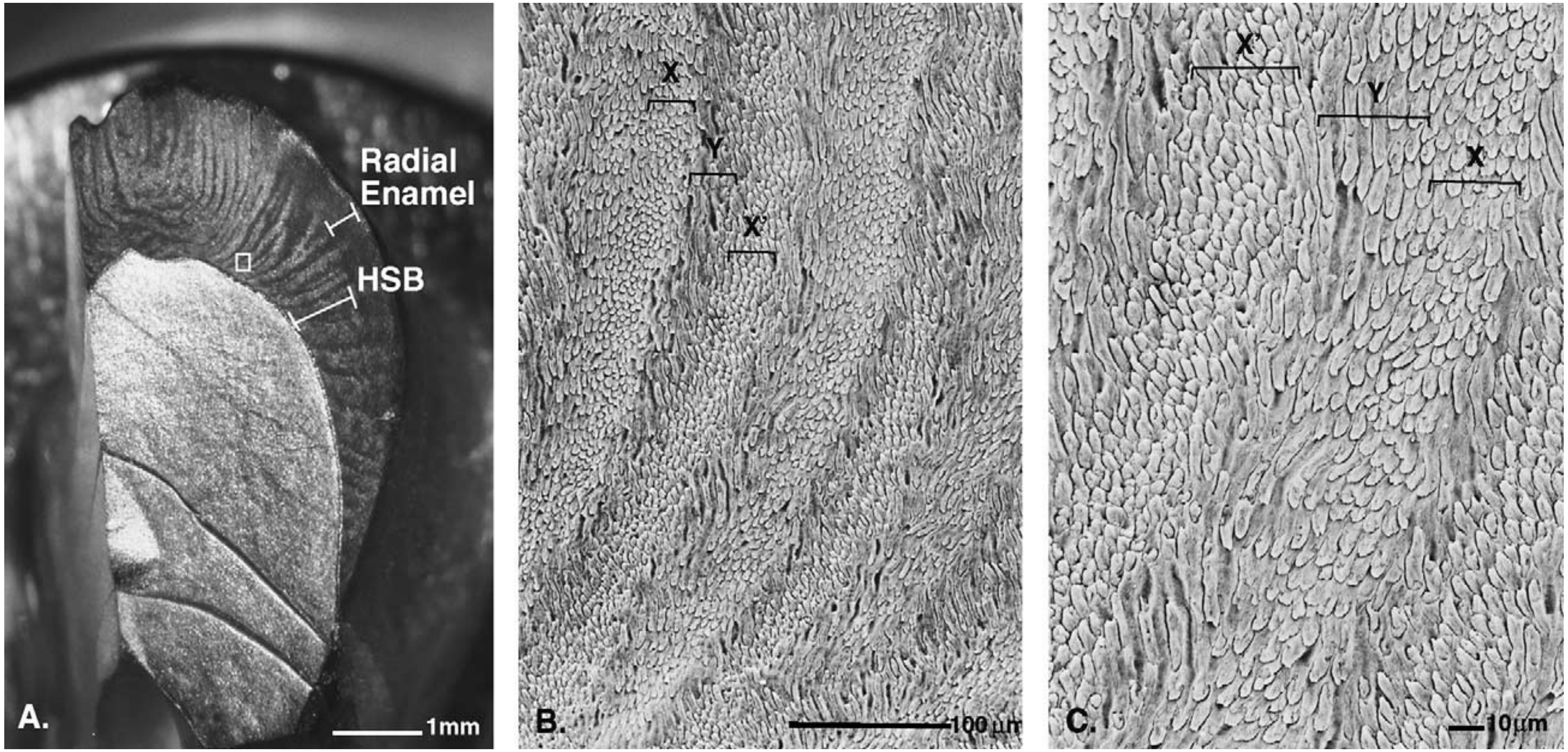
Transversal or occlusal section

Axial section

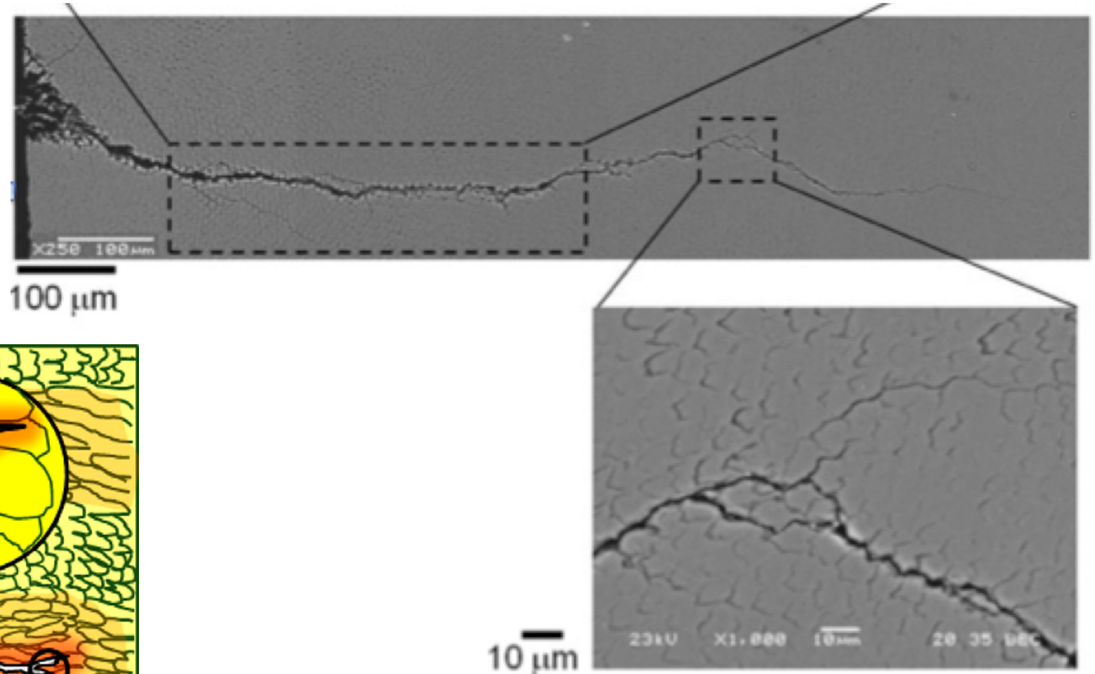
L.-H. He et al. (2013)

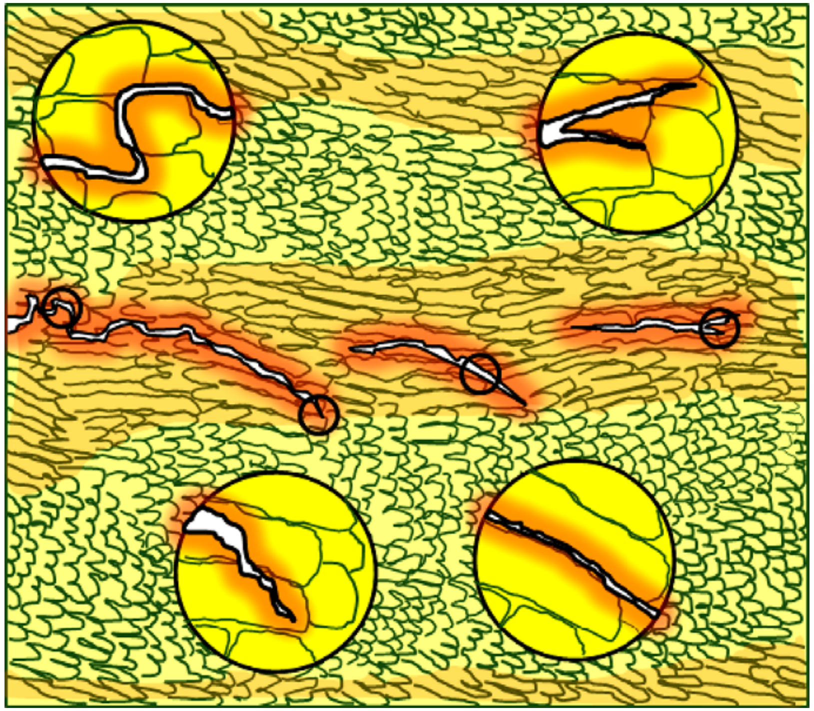


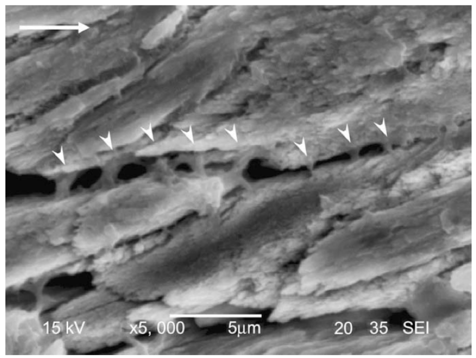
The case of Dental enamel



The different sources of toughening in Dental enamel







Conclusion

The answer of bioceramics to mechanical demands
(towards complex microstructures and architectures)

- From their inception and first clinical development as implant materials, ceramics have been improved in terms of strength and toughness.

- From a materials selection and improvement approach, engineers and researchers have shifted towards a 'material by design' approach.

- New ceramic materials are built with the aim of combining different toughening mechanisms (phase transformation, crack deflection, bridging, etc…)

- A new Bio-inspired class of biomaterials could emerge in the near future, provided new processes unable to build hierarchical architectures.

- Biological tissues can serve as models to build such complex structures, since they exhibit high crack resistance thanks to multi-scale reinforcement mechanisms.