

生醫材料導論

生醫陶瓷 Bioceramics

曾靖嬪
Ching-Li Tseng

Professor
Graduate Institute of Biomedical Materials & Tissue Engineering
Taipei Medical University

Ceramics

製陶業

- an inorganic, non-metallic solid material comprising metal, nonmetal or metalloid atoms primarily **held in ionic and covalent bonds**.
- are those things made from materials which are **permanently changed when heated**.

Clay

Clay has chemically bonded water in it which will cause it to slake down (disintegrate) when a dried clay object is put in water. Once **heated (fired)** to between 660° and 1470 °F (350 and 800 °C), the **clay is converted to ceramic** and will never dissolve again (**pottery**).



Ceramics

- ❑ Polycrystalline compounds
- ❑ Refractory (*hard, brittle*)
- ❑ High compressive strength

拉伸不 $\gamma\gamma$

壓 $\gamma\gamma$



Bioceramics

The class of ceramics used for repair and replacement of diseased and damaged parts of the **living organ/tissue** such as **musculoskeletal system** referred to as bioceramics.

- Silicates SiO_4^{-4}
- Metallic oxides: Al_2O_3 , MgO , SiO_2
- Carbides: Diamond, graphite , pyrolyzed carbons
- Sulfides S^{2-}

Atomic Bonding and Arrangement

Two parameters to effect ceramic crystal

- Magnitude of the **electrical charge** on the constituent ions
relative electronegativity
- The **physical size** of these ions
radius ratios

NaCl

CaF₂



Table 6-1. Atomic and Ionic Radii of Some Elements

Group I		Group II			Group IV			Group VI			
Element	Atomic radius ^a	Ionic radius	Ele.	Atomic radius ^a	Ionic radius	Ele.	Atomic radius ^a	Ionic radius	Ele.	Atomic radius ^a	Ionic radius
Li ⁺	0.152	0.068	Be ⁺⁺	0.111	0.031	O ⁻	0.074	1.40	O ₆ ²⁻	0.071	0.130
Na ⁺	0.186	0.095	Mg ⁺⁺	0.160	0.065	S ⁻⁻	0.102	1.84	Cl ⁻	0.099	0.181
K ⁺	0.227	0.133	Ca ⁺⁺	0.197	0.099	Se ⁻⁻	0.116	1.98	Br ⁻	0.114	0.195

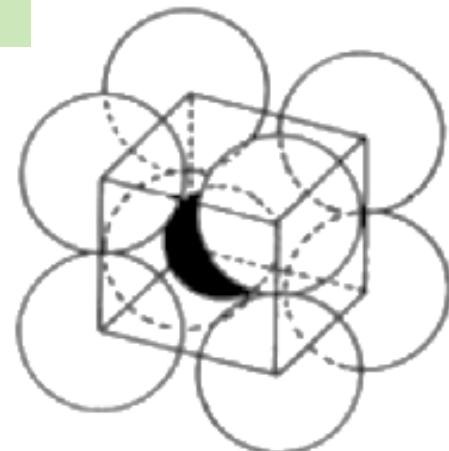
cation

anion

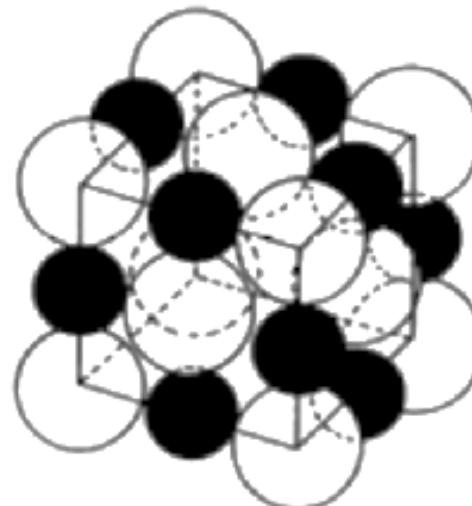
Atomic Bonding and Arrangement

AmX_n

(a) $CsCl$



(b) $NaCl$



(c) Al_2O_3

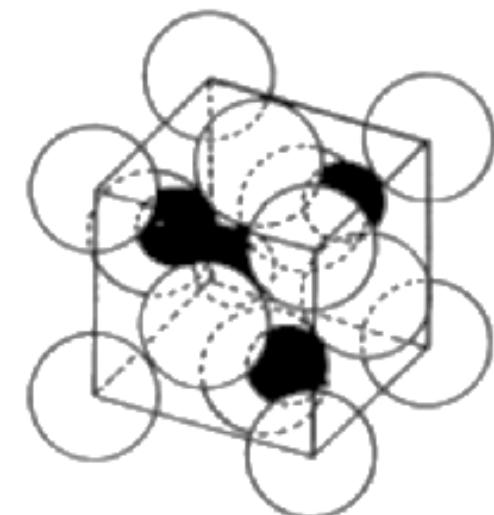


Table 6-2. Selected A_mX_n Structures

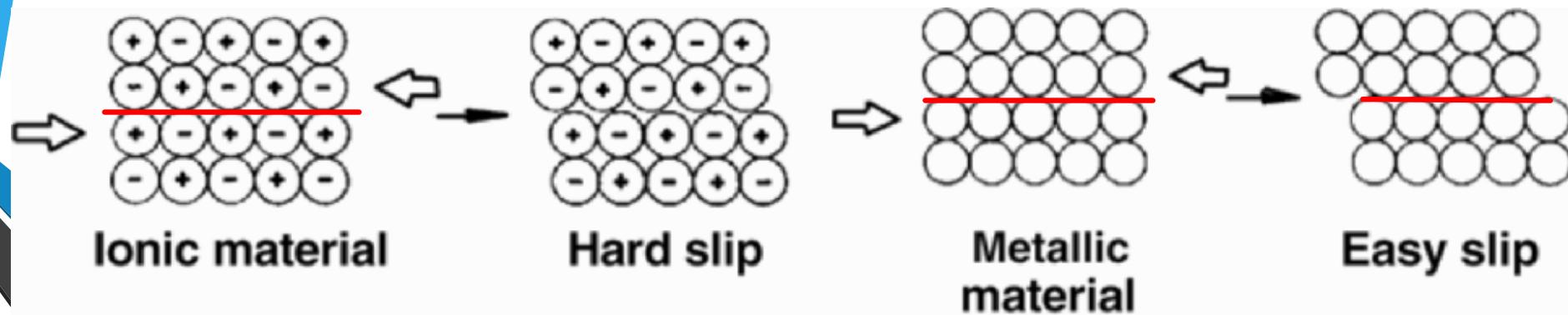
Prototype compound	Lattice of A (or X)	CN of A (or X) sites	Available sites filled	Minimum r_A/R_x	Other compounds
$CsCl$	Simple cubic	8	All	0.732	CsI
$NaCl$	fcc	6	All	0.414	MgP , MnS , LiF
ZnS	fcc	4	1/2	0.225	β - SiC , CdS , AlP
Al_2O_3	hcp	6	2/3	0.414	Cr_2O_3 , Fe_2O_3

Physical Properties

- Hardness
- High melting temperatures
- Low conductivity of electricity and heat
- Brittle, (*difficult to shear plastically change*)

Diamond: Mohs scale of 10

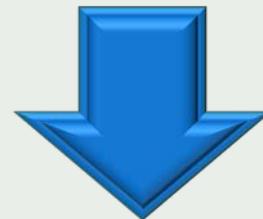
Talc ($Mg_3Si_4O_{10}COH$) is the softest
(Moh's hardness 1)



Bioceramics

Applications

- Orthopedic load-bearing coatings
- Dental implants
- Bone graft substitutes
- Bone cements



- Biocompatible
- Wear resistant
- Light weight



- Low tensile strength
- Difficult to fabricate
- Low toughness
- Not resilient

Ceramics in medical application

Interaction with surround tissue

- **Bioinert Ceramics:**

Al_2O_3 , ZrO_2 , SiC , Si_3N_4

- **Bioactive Ceramics:**

氫氧基磷灰石

Surface Active → Hydroxyapatite, Bioglass ,
Glass-ceramic

- **Biodegradable Ceramics**

Tricalcium phosphate (TCP)

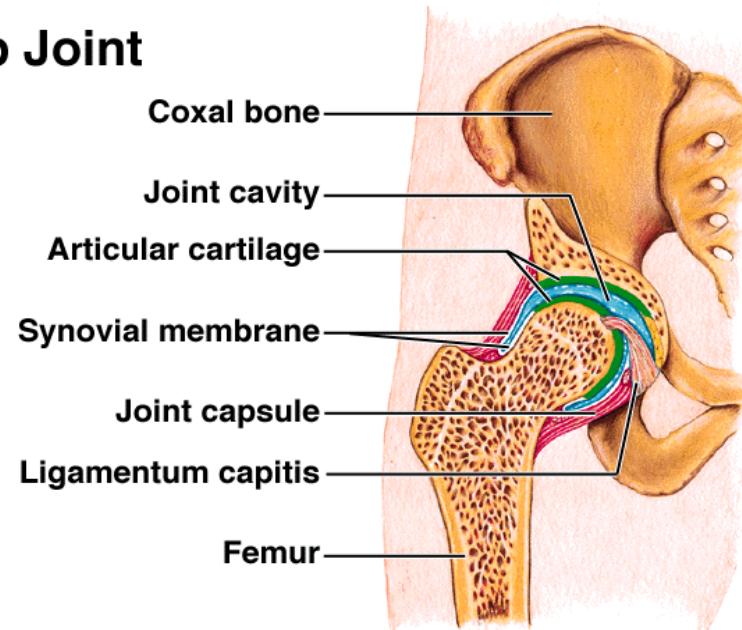
三鈣磷酸鹽

Calcium phosphate with $\text{Ca}/\text{P} < 1$

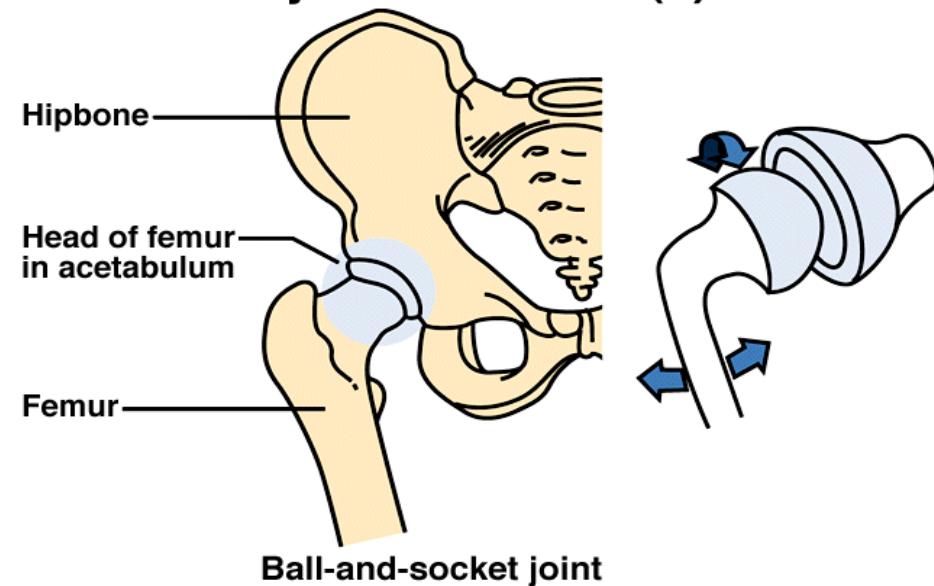
TABLE 10.1. Overview of Applications for Bioceramics

Bioceramic	Function	Tissue reaction
Zirconia	Artificial total hip, knee, bone screws and plates, dental crowns and bridges	Bioinert
Alumina	Artificial total hip, shoulder, elbow, wrist, bone screws, porous coatings for femoral stems	Bioinert
Carbon	Coatings on heart valves, blood vessel grafts, surfaces in dentistry	Bioinert
Calcium phosphates	Drug delivery, bone substitute, coatings for metal implants, stems, ocular implants	Bioactive, Bioresorbable
Bioactive glass	Bone cement filler, bioactive coating on implants	Bioactive, Bioresorbable
TiN	Coating on implants like artificial hip, dental and shoulder implants	Bioactive

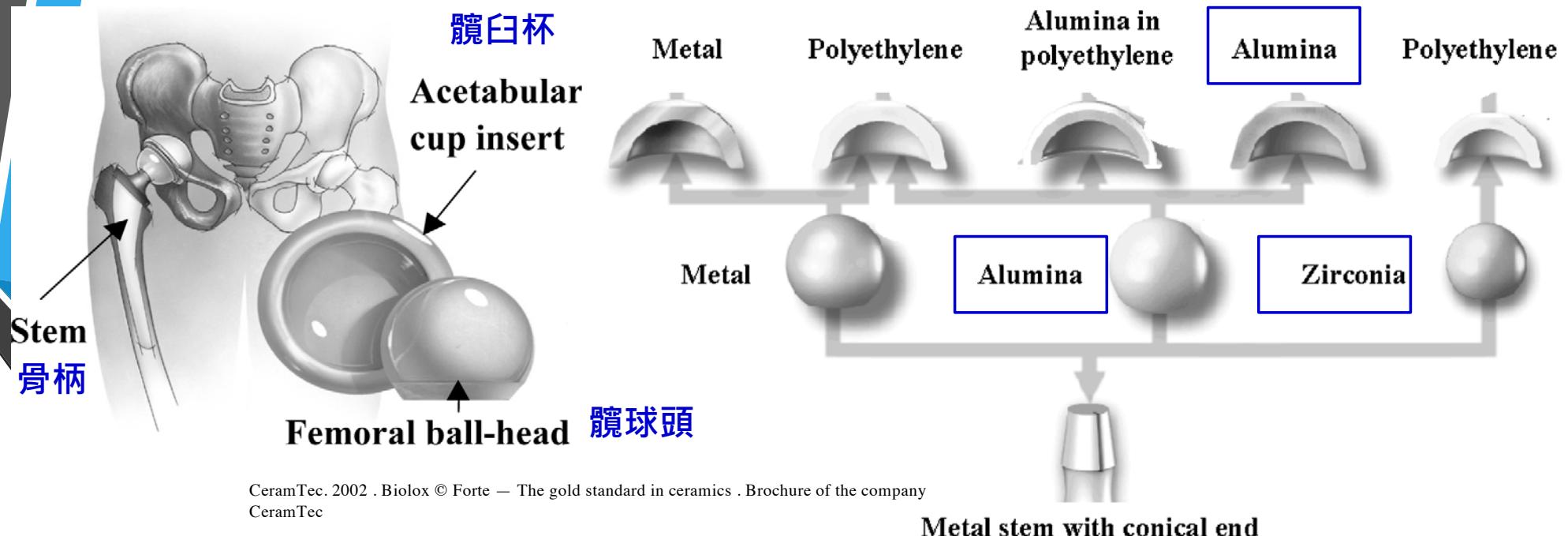
Hip Joint



Synovial Joints (1)



Components for total hip replacement and current material combinations for total hip replacement



Bioinert ceramics

Aluminum Oxide (Alumina)



- Hexagonal close-packed structure ($a = 0.4758 \text{ nm}$ and $c = 1.2991 \text{ nm}$)
- It's very **inert** and **resistant to corrosion *in vivo*.**
- Minimal response from the tissues
- Hardness, resulted in low wear rate (wear resistant) 抗摩耗

Low friction coefficient

Surface rough $< 0.02 \mu\text{m}$

Grain size $< 4.00 \mu\text{m}$



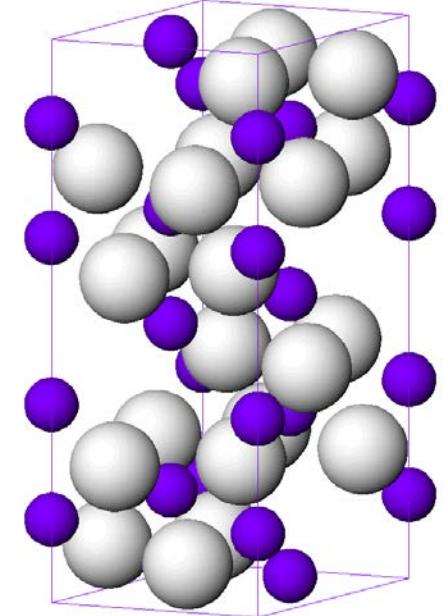
Alumina particles formed by **wear** of the implant can induce **a foreign-body reaction**, or **osteolysis** for long-term failure of the implant

Schematic drawing of the first layer in the alpha alumina structure

Bioinert ceramics

$\alpha\text{-Al}_2\text{O}_3$

- Natural alumina is known as sapphire or ruby.
- The main source of high-purity alumina (aluminum oxide) is bauxite(鐵鋁氧化石)and native corundum (金剛砂).
- The commonly available alumina can be prepared by calcining alumina trihydrate resulting in calcined alumina.



Sapphire



Ruby



Bayer process

1. $\text{Al}(\text{OH})_3 + 4\text{Na}^+\text{OH}^- \rightarrow \text{Al}(\text{OH})_4^- + 4\text{Na}^+$ - Extraction
2. $\text{Al}(\text{OH})_4^- + 4\text{Na}^+ \rightarrow \text{Al}(\text{OH})_3 + \text{Na}^+ + \text{OH}^-$ - Precipitation
3. $2\text{Al}(\text{OH})_3 \rightarrow \text{Al}_2\text{O}_3 + 3\text{H}_2\text{O}$ - Calcination

Bioinert ceramics

$\alpha\text{-Al}_2\text{O}_3$

Young's modulus		
Alumina	380 -420	GPa
Cancellous bone	0.05-0.5	GPa
Cortical bone	7-25	GPa

Table 6-4. Physical Property Requirements of Alumina Implants (ASTM, 2000)

Properties	Values
Flexural strength	> 400 MPa (58,000 psi)
Elastic modulus	380 GPa (55.1×10^6 psi)
Density (g/cm ³)	3.8–3.9

Table 6-3. Chemical Composition of Calcined Aluminas

Chemicals	Composition (weight %)
Al ₂ O ₃	99.6
SiO ₂	0.12
Fe ₂ O ₃	0.03
Na ₂ O	0.04

Aluminum Company of America. Reprinted with permission from Gitzen (1970). Copyright © 1970, American Ceramic Society.



BIOLOX® delta ceramic femoral head

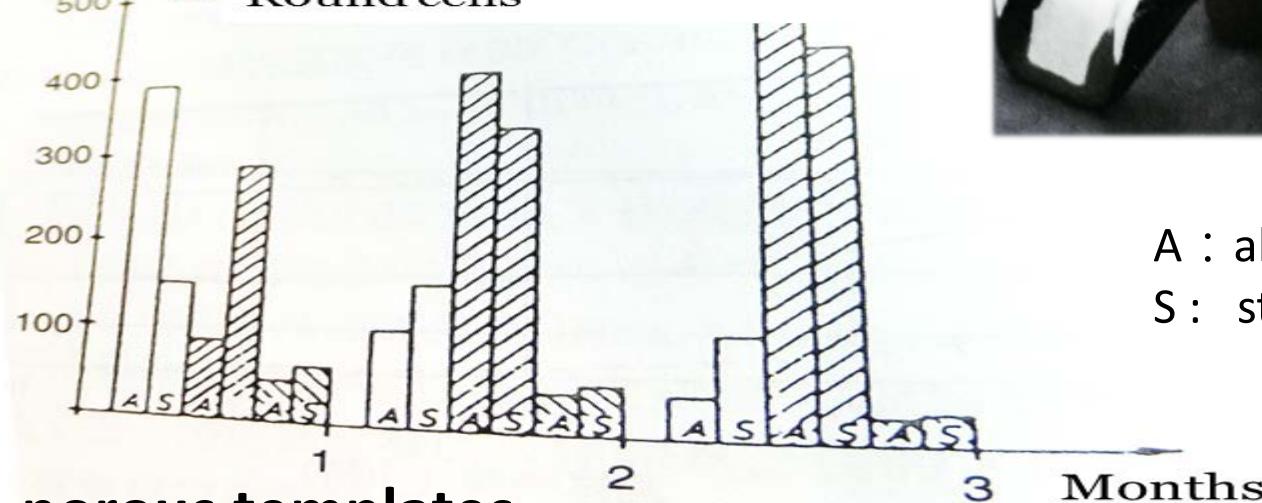
- The American Society for Testing and Materials (ASTM)
99.5% pure alumina and less than 0.1% of combined SiO₂ and alkali oxides (mostly Na₂O) for implant use.

Bioinert ceramics

$\alpha\text{-Al}_2\text{O}_3$

Counted cells/unit

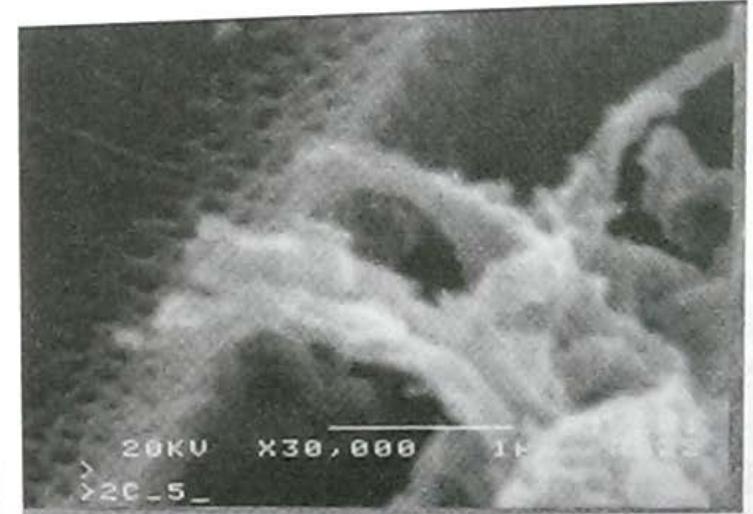
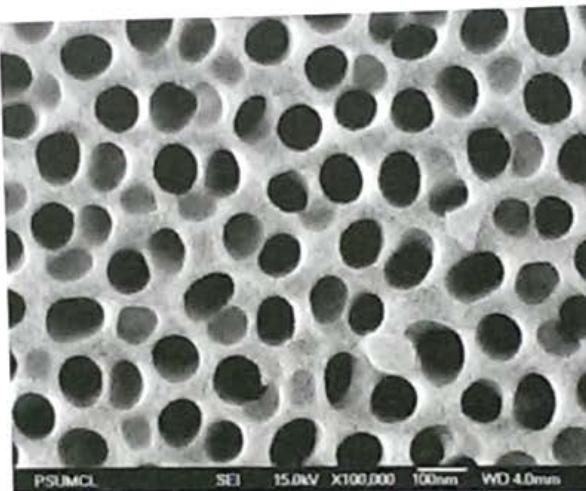
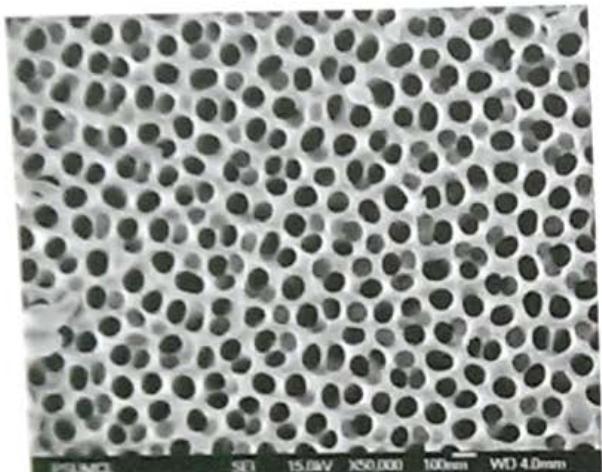
- Fibroblasts/Histiocytes
- ▨ Fibrocytes
- ▨ Round cells

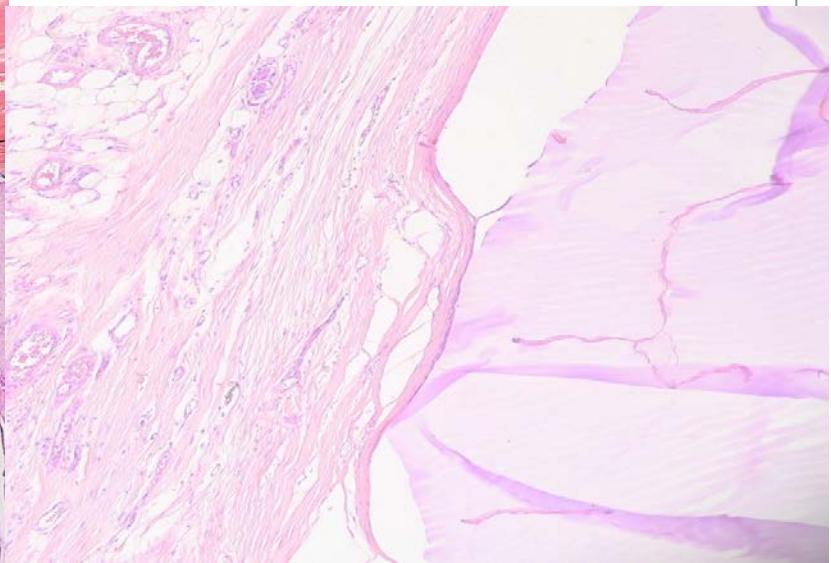
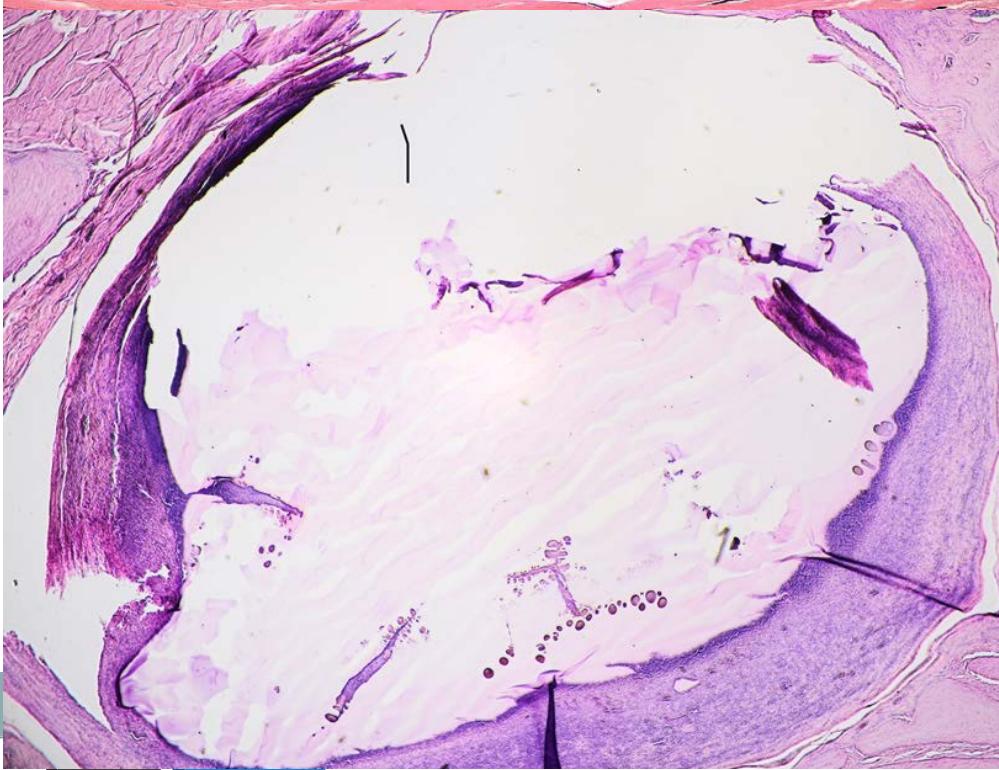
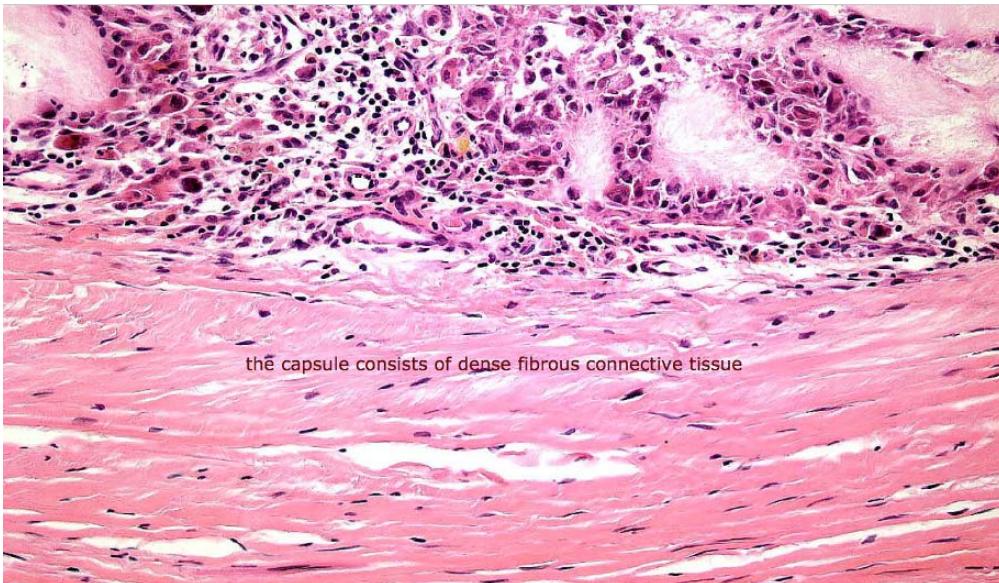


A : alumina
S : steel

Al_2O_3 nano-porous templates

Different pore diameter





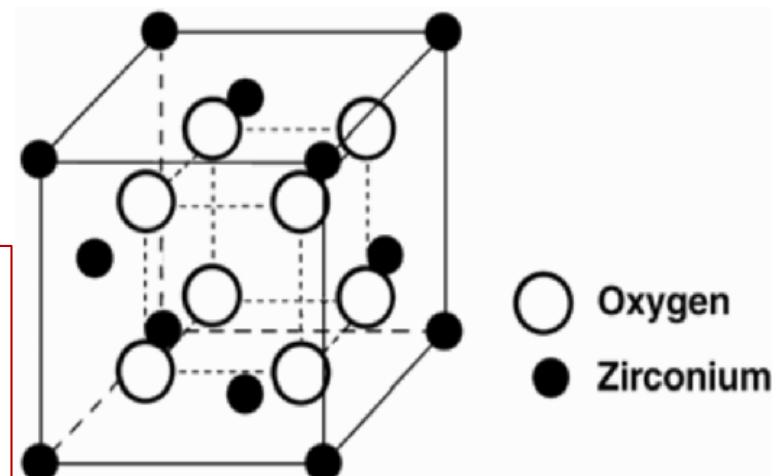
Bioinert ceramics

Zirconium oxides (Zirconia)



氧化鋯

- Highly biocompatible
- Implants such as the **femoral head** and **acetabular cup in total hip joint replacement** (1988)
- A major drawback is that they may be **weakened significantly under stress in the presence of moisture**; this weakening occurs at a much faster rate at elevated temperature such as occurs during steam sterilization (autoclaving).



Cubic structure of zirconia that belongs to the fluorite structure

monoclinic ($a \neq b \neq c, \alpha = \gamma = 90^\circ \neq \beta$)

tetragonal ($a = b \neq c, \alpha = \gamma = \beta = 90^\circ$) at $1000\text{--}1200^\circ\text{C}$

tetragonal to cubic ($a = b = c, \alpha =$

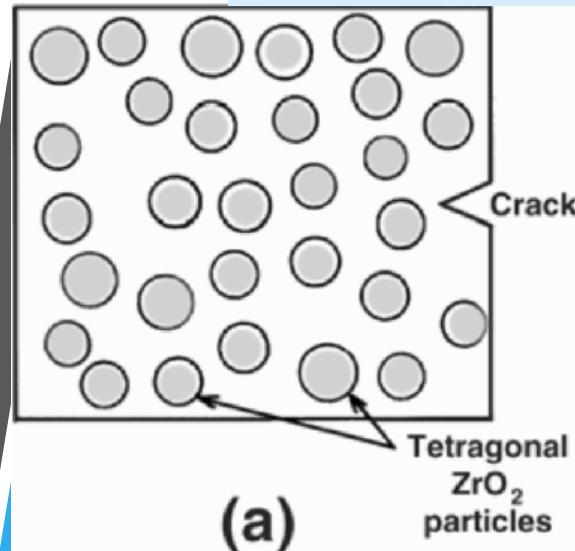
$\gamma = \beta = 90^\circ$) structure at 2370°C .

Properties of Zirconia

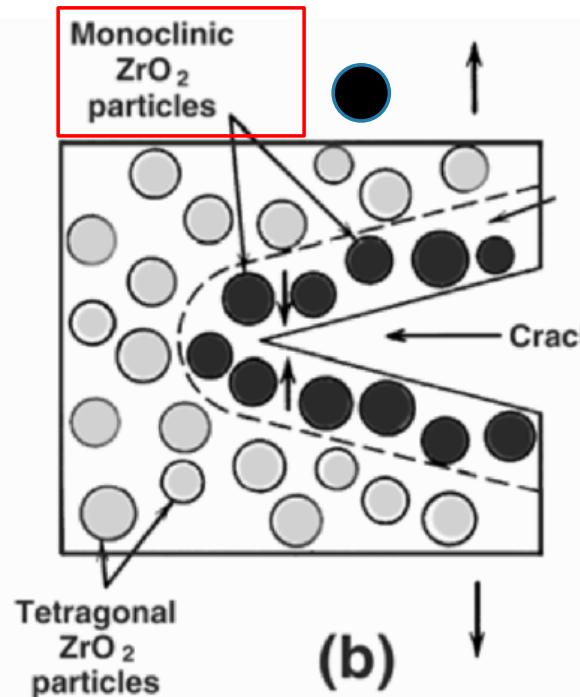
tetragonal zirconia polycrystalline (TZP)

ZrO_2

crack before phase transformation



(a)



(b)

Crack arrestment due to phase transformation of the dispersed PSZ particles

Table 6-5. Physical Properties of Zirconia

Polymorphism^{a,b}

Monoclinic tetragonal	1273–1473 (K)
Tetragonal cubic	2643 (K)
Cubic liquid	2953 (K)

Crystallography

Monoclinic

a	5.1454 Å
b	5.2075 Å
c	5.3107 Å

Space group

Tetragonal

99°14'

P2₁/c

a

3.64 Å^c

c

5.27 Å

- This partial stabilization enables the retention of a metastable tetragonal structure at ambient temperature.
- During crack propagation, the tetragonal particles in the crack tip region undergo phase transformation become **monoclinic ZrO_2** , increasing its volume, which ***sets up a compressive field surrounding the particles and closes the crack opening, resulting in a stronger material.***
- The process is similar to the precipitation of a tetragonal structure in cubic grains.

Properties of Zirconia ZrO_2

The friction and wear properties of zirconia, alumina, and 316L stainless steel against ultra-high-molecular weight polyethylene (UHMWPE)

Tribology
摩擦學

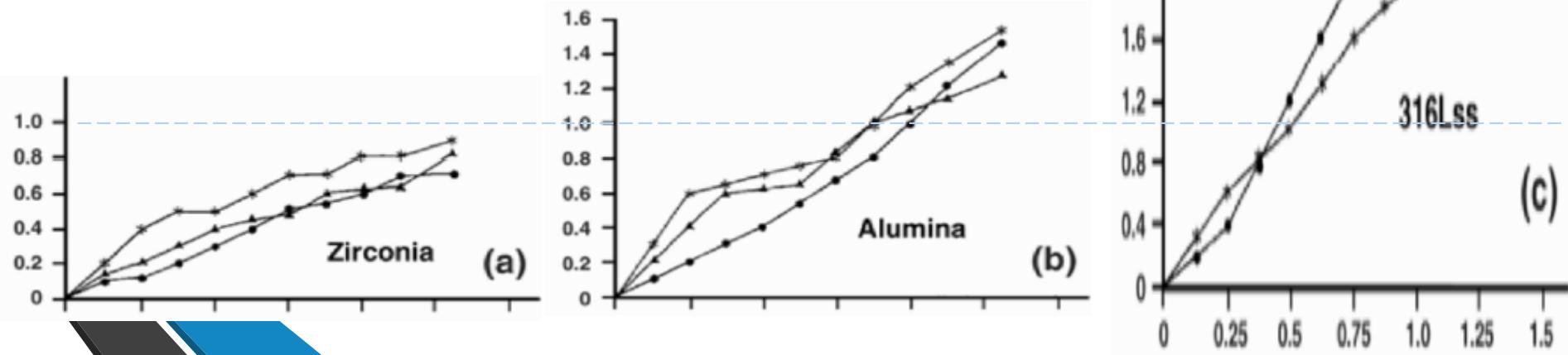
Table 6-8. Wear of UHMWPE on Two Different Wear Devices

Medium	*Wear factor ($\text{mm}^3/\text{N}\cdot\text{m}$) $\times 10^{-9}$					
	Bovine serum		Saline		Distilled water	
Counterfaces	Unidirectional	Reciprocate	Unidirectional	Reciprocate	Unidirectional	Reciprocate
Zirconia (3)	10.7 ± 12	0.56 ± 14	7.5 ± 3	0.45 ± 5	8.61 ± 11	0.38 ± 6
Alumina (3)	18.2 ± 6	1.01 ± 8	32.7 ± 7	0.57 ± 2	11.8 ± 4	0.68 ± 4
316L SS (2)	27.7 ± 30	1.81 ± 4	90.5 ± 40	3.89 ± 8	37.1 ± 10	1.12 ± 10

() = number of specimens tested. *Average and range.

Reprinted with permission from Kumar et al. (1991). Copyright © 1991, Wiley.

Yttrium-stabilized zirconia (6% Y_2O_3 in ZrO_2)



Properties of Zirconia

Table 6-7. Comparison of Properties of Alumina and Zirconia

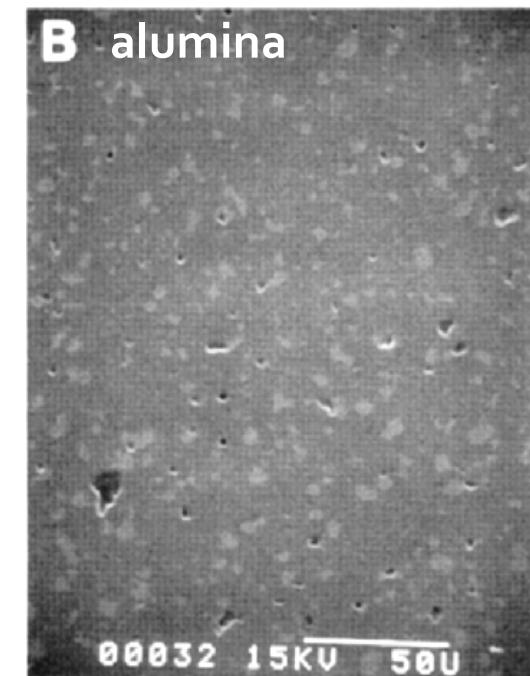
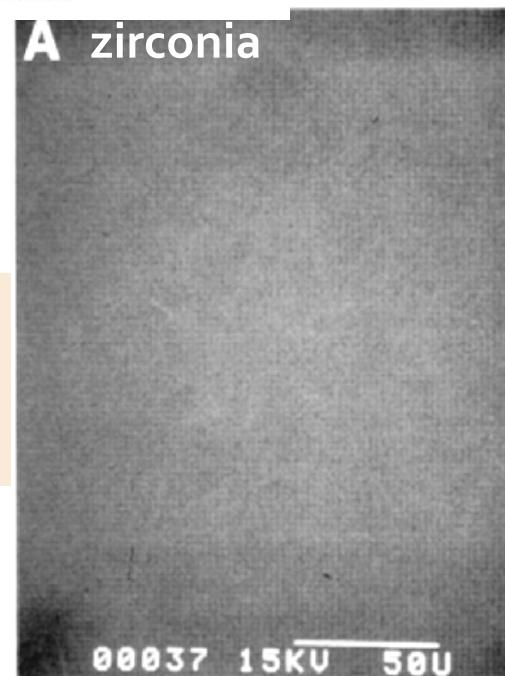
Property	Alumina	Zirconia
Chemical composition	$\text{Al}_2\text{O}_3 + \text{MgO}$	$\text{ZrO}_2 + \text{MgO} + \text{Y}_2\text{O}_3$
Purity (%)	99.9	95~97
Density (g/cm^3)	> 3.97	5.74~6.0
Porosity (%)	< 0.1	< 0.1
Bending strength (MPa)	> 500	500~1 000
Compression strength (MPa)	4100	2000
Young's modulus (GPa)	380	210
Poisson's ratio	0.23	0.3
Fracture toughness (MPa $\text{m}^{1/2}$)	4	up to 10
Thermal expansion coefficient ($\times 10^{-6}/\text{K}$)	8	11
Thermal conductivity (W/m/K)	30	2
Hardness (HV0.1)	up to 2200	1200
Contact angle (°)	10	50

Reprinted with permission from Willmann (1993). Copyright © 1993, Pergamon.

ZrO_2

Tribology
摩擦學

One reason for the excellent wear and friction characteristic of the **zirconia** is attributed to the fact that **zirconia has less porosity**.



Bioinert ceramics

ZrO_2

Fabrication:

- Obtained from the mineral zircon
- Addition of MgO , CaO or Y_2O_3 stabilize tetragonal crystal structure (97 mol% ZrO_2 and 3 mole% Y_2O_3)
- Usually hot-pressed or hot isostatically pressed

Applications:

- Orthopedics: femoral head, artificial knee ,
bone screws and plates,
- Favored cover UHMWPE due to superior wear resistance
- Dental: crown and bridges



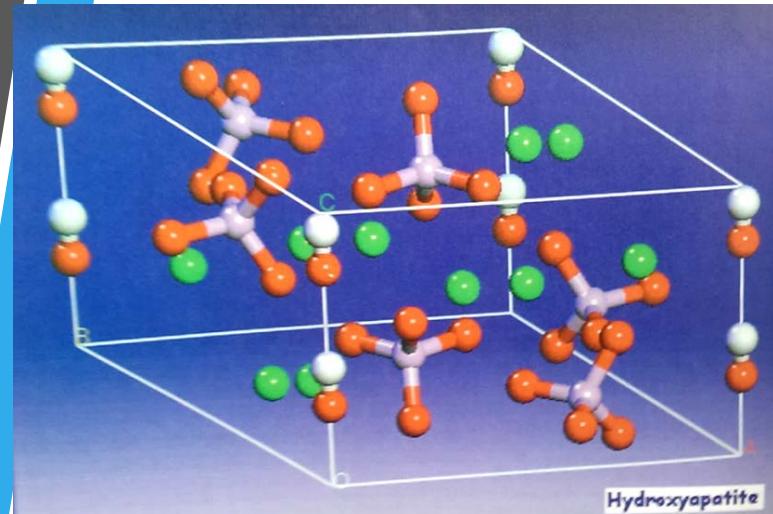
Surface Active ceramics

- Aluminum-calcium phosphorous oxides
- Glass fiber and their composites
- Corals
- Calcium sulfates, including plaster of pairs
- Ferric-calcium –phosphorous oxides
- **Hydroxyapatites**
- **Tricalcium phosphate**
- Zinc-calcium-phosphorous oxides
- Zinc sulfate-calcium-phosphorous oxides

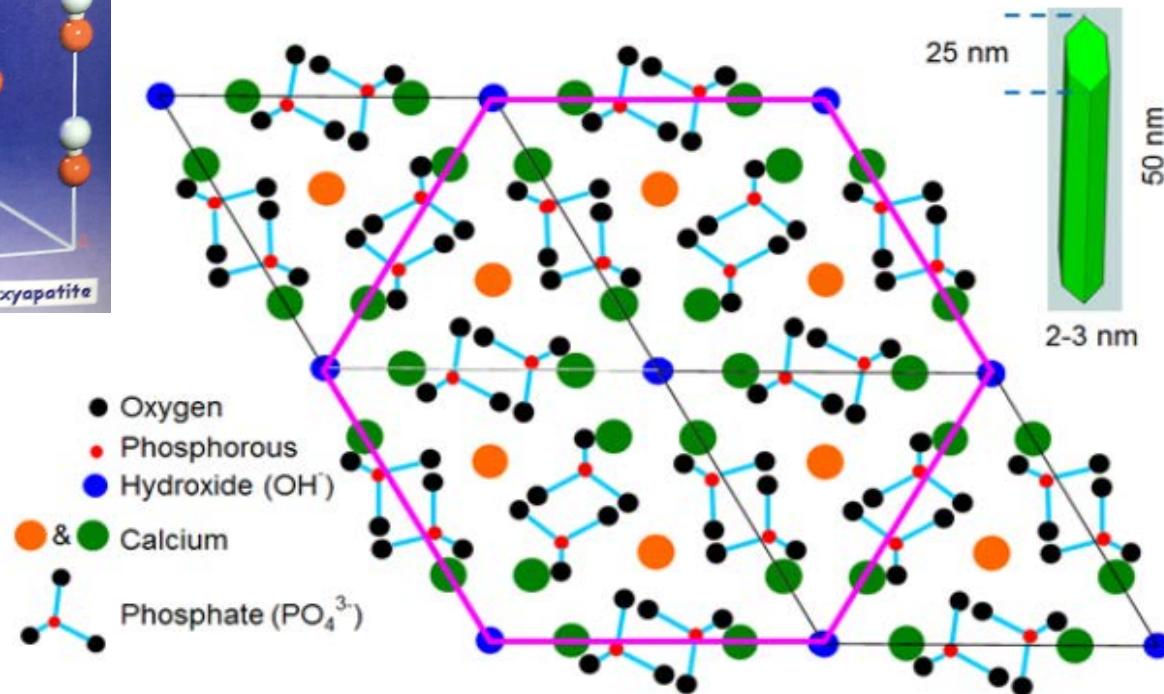
Surface Active ceramics

氢氧基磷灰石

Calcium Phosphate



Hydroxyapatite (HAP)



<http://engr.iupui.edu/bme/bbml/boneintro.shtml>

Hydroxyapatite structure projected down the c -axis on the basal plane.

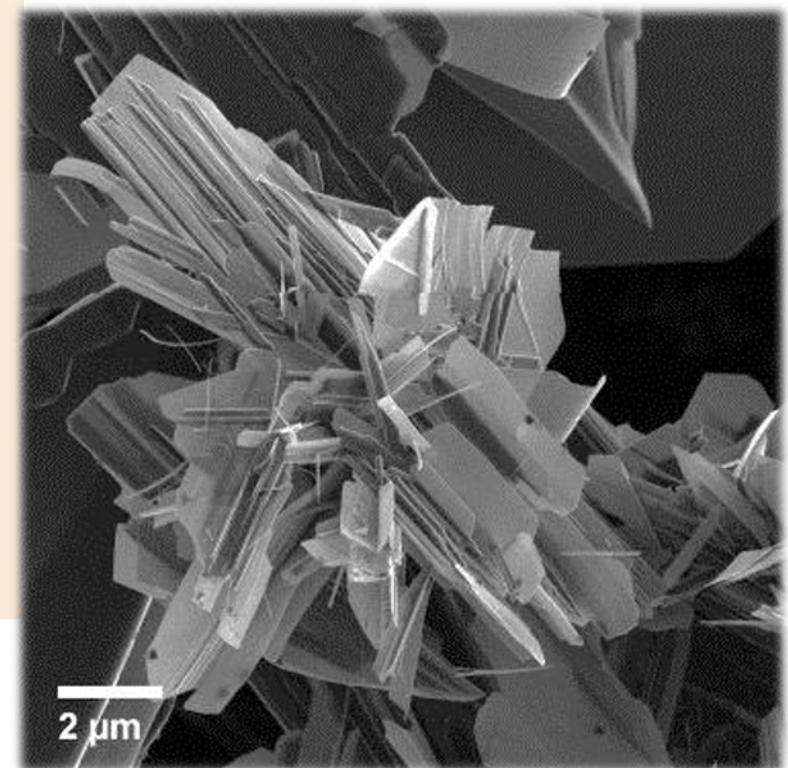
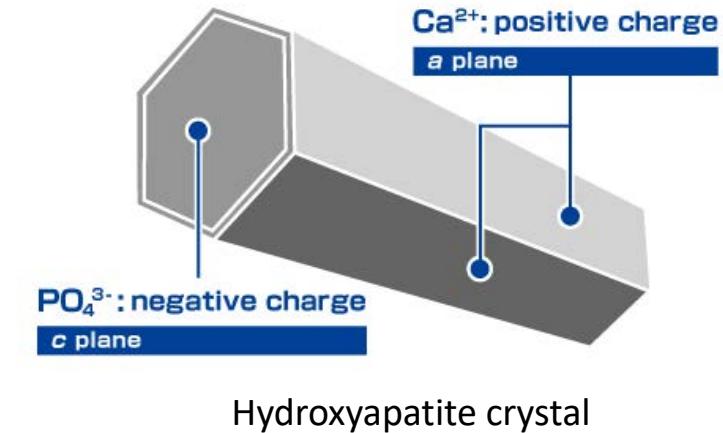
Surface Active ceramics

http://sofsera.co.jp/hap_e.html

Hydroxyapatite (HAP)



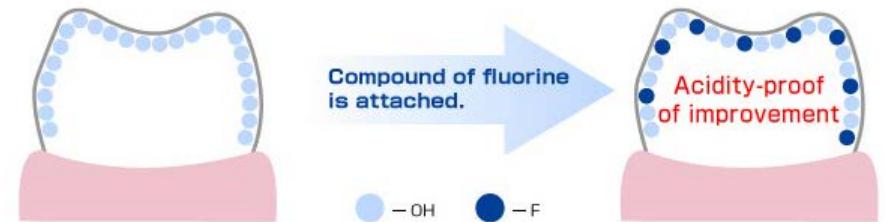
- Existing as main material of **bones, teeth** and mineral naturally with high bioaffinity.
- Hexagonal rhombic prisms
- $a = b = 9.432 \text{ \AA}$; $c = 6.881 \text{ \AA}$
- $\text{Ca}/\text{P}=1.6$; Density: 3.129 g/cm^3
- Excellent ion-exchange performance,
 - Ca^{2+} site with cation and phosphate group
 - OH^- site with anion



Biodegradable ceramics

Ion replacement in the HAP crystal

- OH^- was replaced by F^-



- OH^- or PO_4^{3-} was replaced by CO_3^{2-}

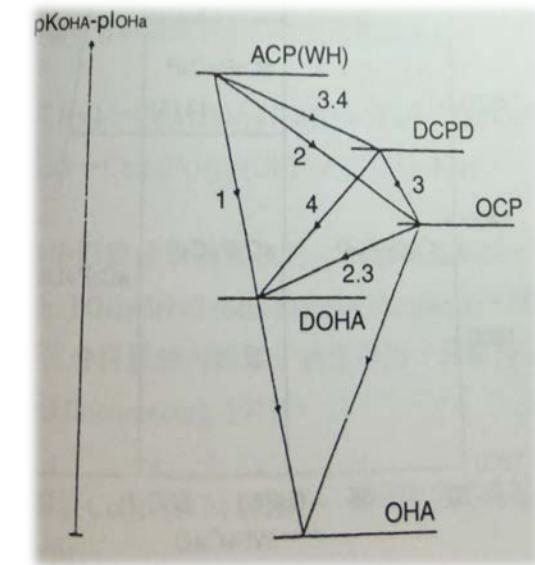
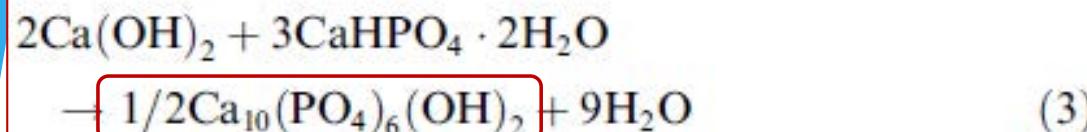
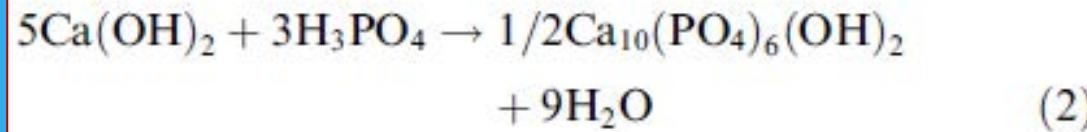


- Ca^{2+} was replaced by Mg^{2+}



Biodegradable ceramics

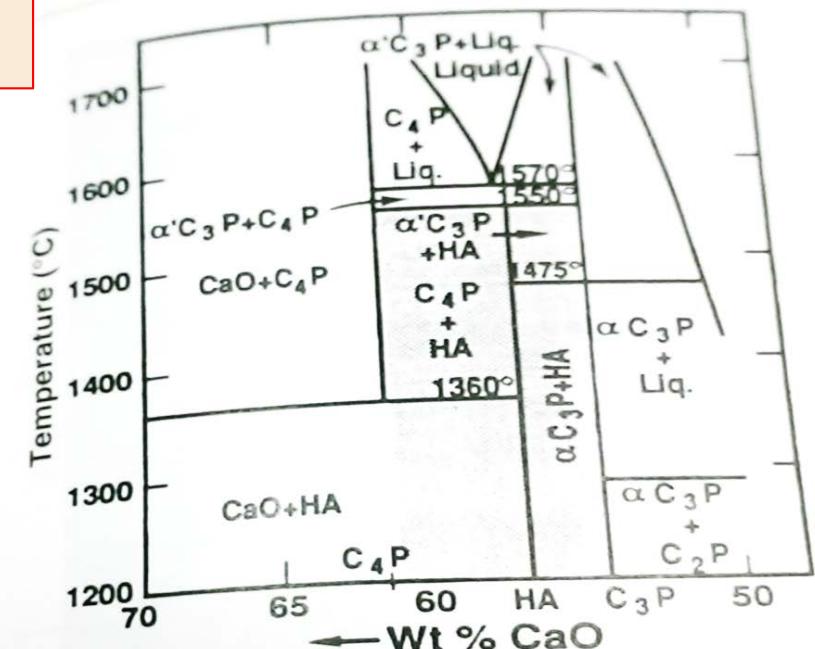
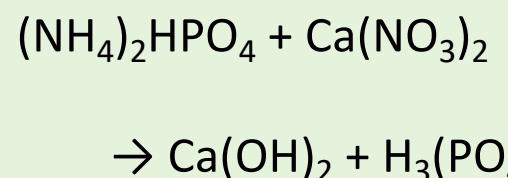
Wet chemical reaction



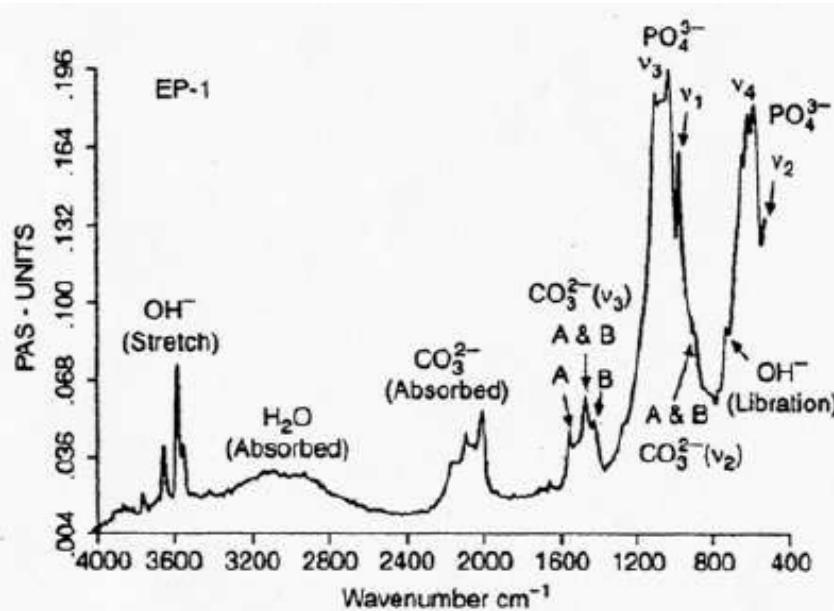
OHA: octacalcium phosphate
 $\text{Ca}_8\text{H}_2(\text{PO}_4)_6 \cdot 5\text{H}_2\text{O}$

Parameters to influence HAP preparation

- pH Value
- Calcium concentration
- Temperature
- Stirred time
- Impurities

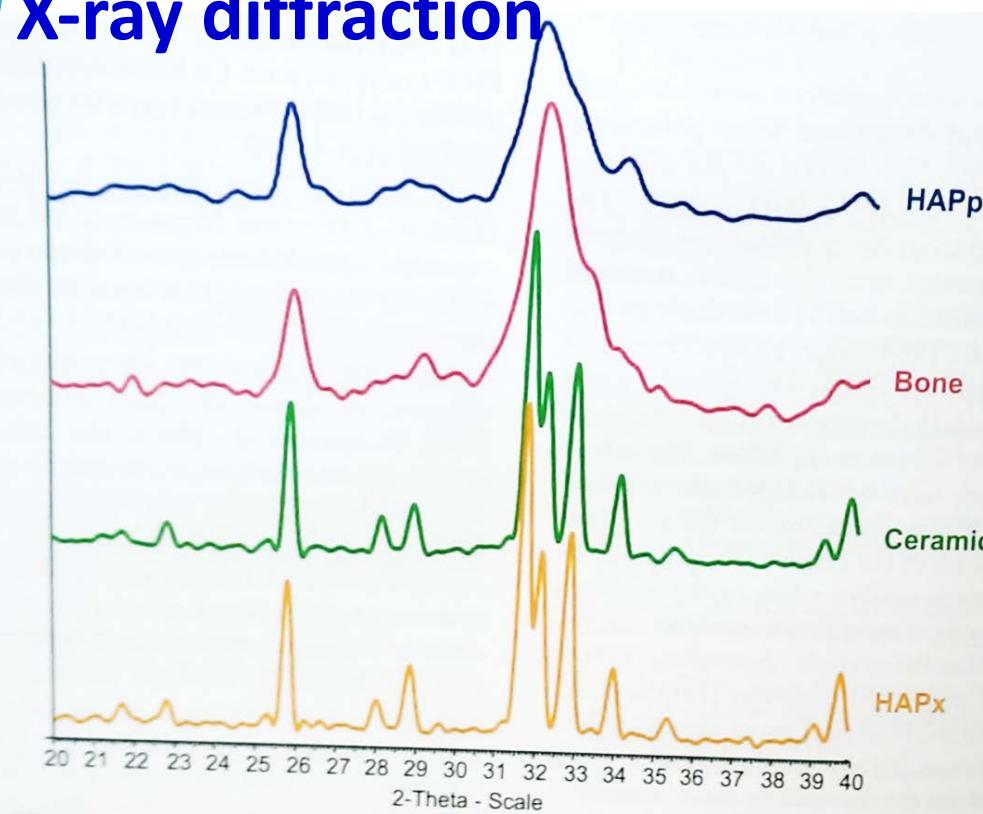


FT-IR



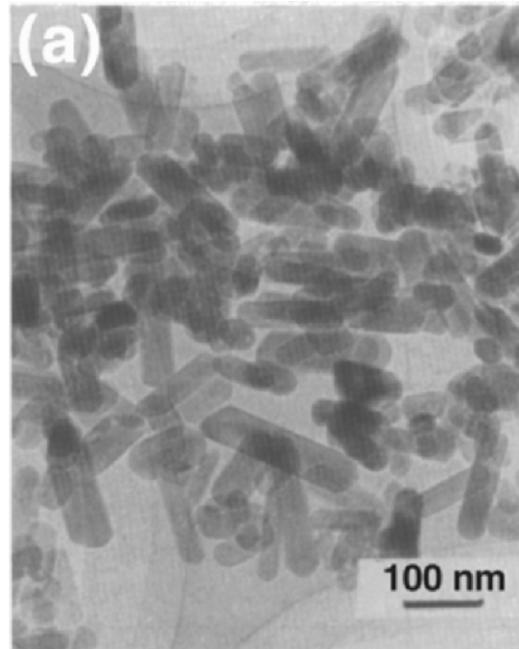
Chemical groups	Absorption bands, (cm ⁻¹)
CO ₃ ²⁻	873; 1450; 1640 (Meejoo, et al., 2006); 1650 (Raynaud, et al., 2002); 870 and 880; 1460 and 1530 (Ratner, 2004)
OH ⁻	3500 (Meejoo, et al., 2006); 630 and 3540 (Destainville, et al., 2003), (Raynaud, et al., 2002); 3570 and 3420 (Han J-K., et al., 2006); 1650 (Raynaud, et al., 2002)
Adsorbed water	2600 – 3600 (Meejoo, et al., 2006)
HPO ₄ ²⁻	875 (Destainville, et al., 2003), (Raynaud, et al., 2002); 880 (Kwon, et al., 2003)
PO ₄ ³⁻	460 (Destainville, et al., 2003); (Raynaud, et al., 2002); 560 - 600 (Destainville, et al., 2003), (Raynaud, et al., 2002), (Mobasherpour & Heshajin, 2007); 602 un 555 (Han J-K., et al., 2006); 960 (Destainville, et al., 2003), (Raynaud, et al., 2002); 1020 -1120 (Destainville, et al., 2003), (Raynaud, et al., 2002); 1040 (Han J-K., et al., 2006); 1000 - 1100 (Mobasherpour & Heshajin, 2007);
NO ₃ ⁻	820 and 1380 (Destainville, et al., 2003); (Raynaud, et al., 2002)

X-ray diffraction

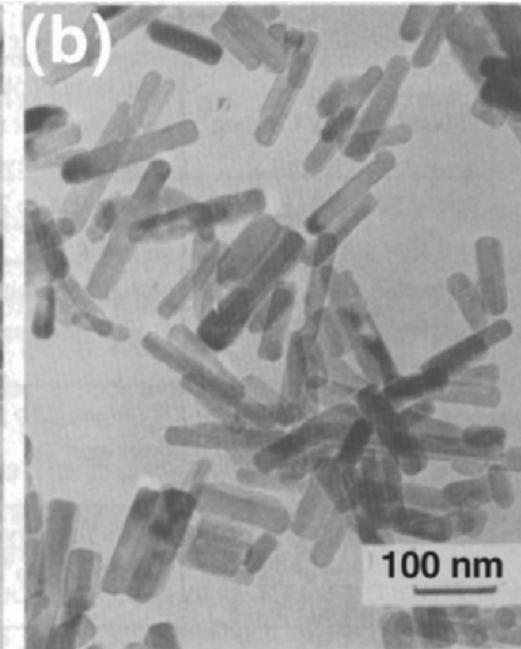


TEM photographs of hydroxyapatite crystals

without additives

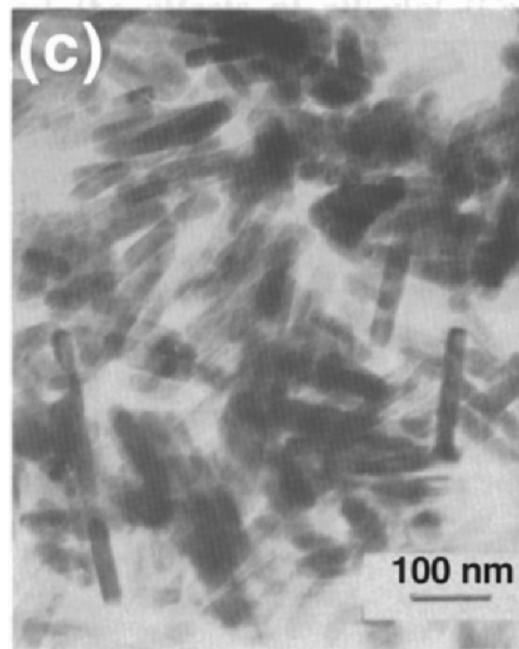


$\text{CaHPO}_4 + \text{NaOH}$

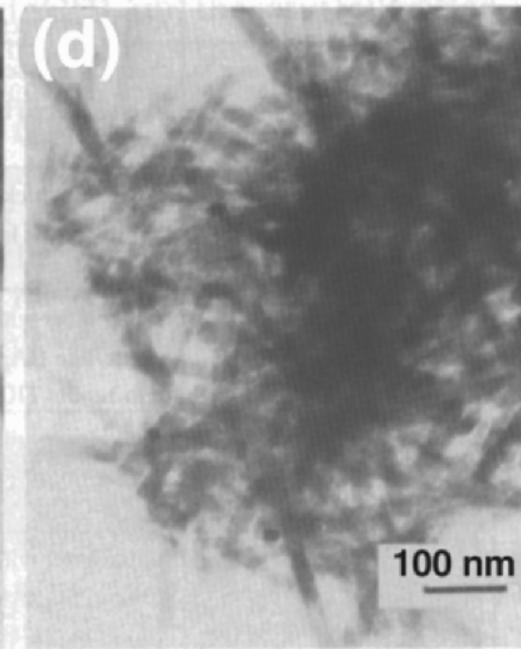


KOH (10 wt%) added

K_3PO_4 (10 wt%) added

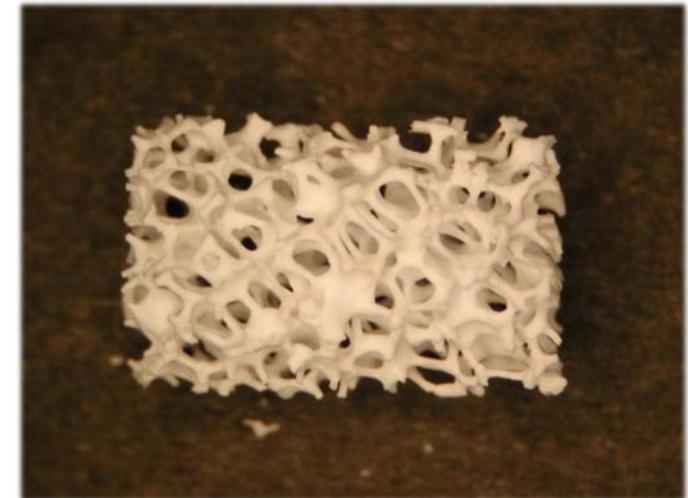
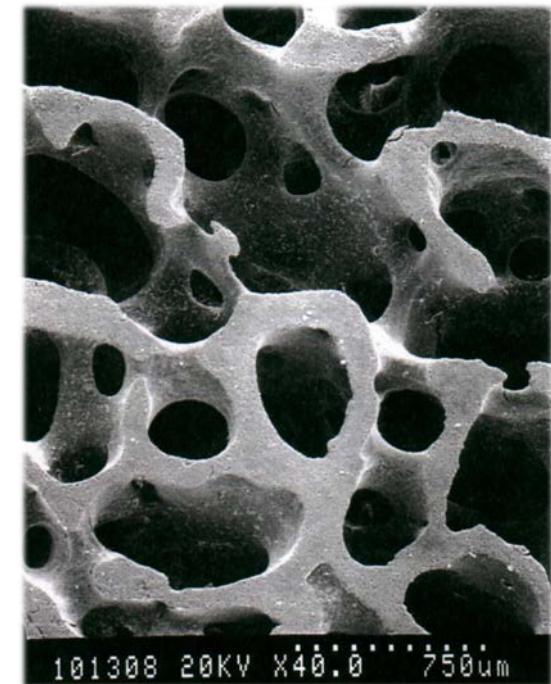


EDTA (5 wt%) added



Surface Active ceramics

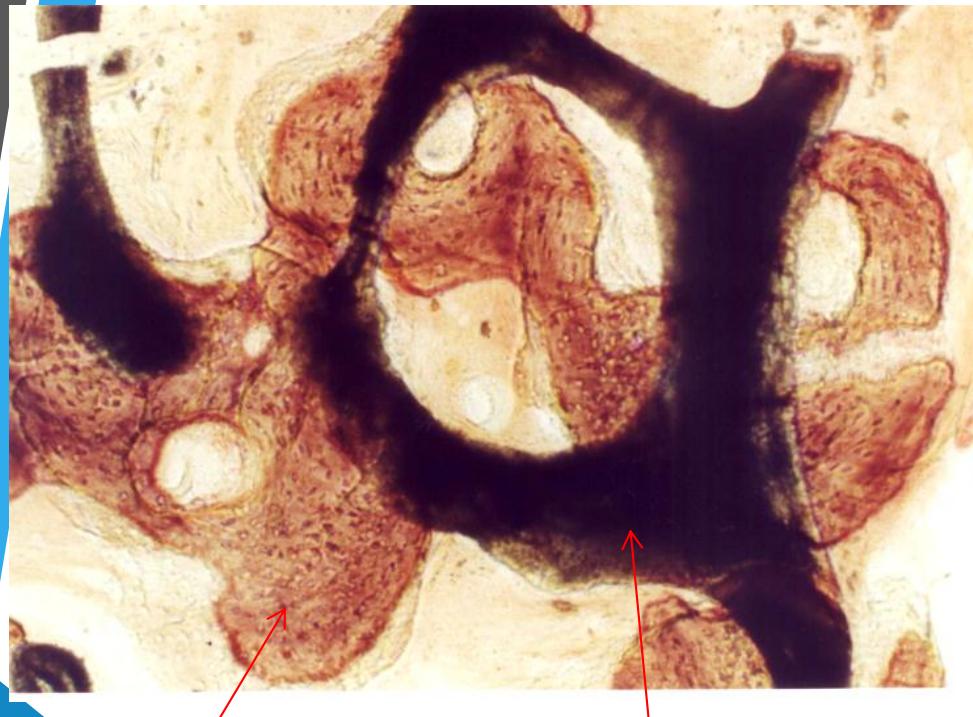
Hydroxyapatite products



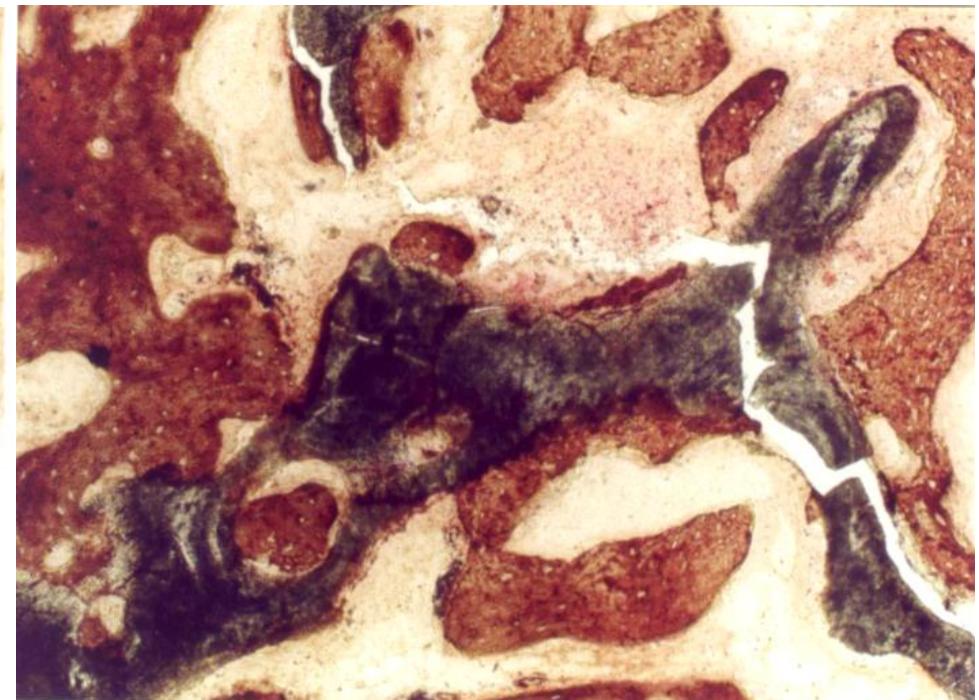
Surface Active ceramics

Bone ingrowth into porous HAP scaffold

Von kossa stain



New bone



HAP

Biodegradable ceramics

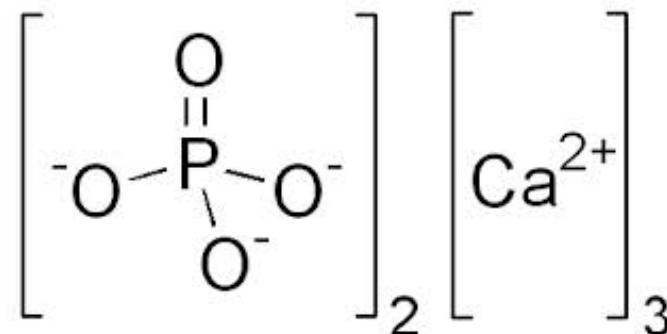
Calcium Phosphate

- Direct and strong chemical bond with tissue
- Fixation of implants in the skeletal system
- Low mechanical strength and fracture toughness

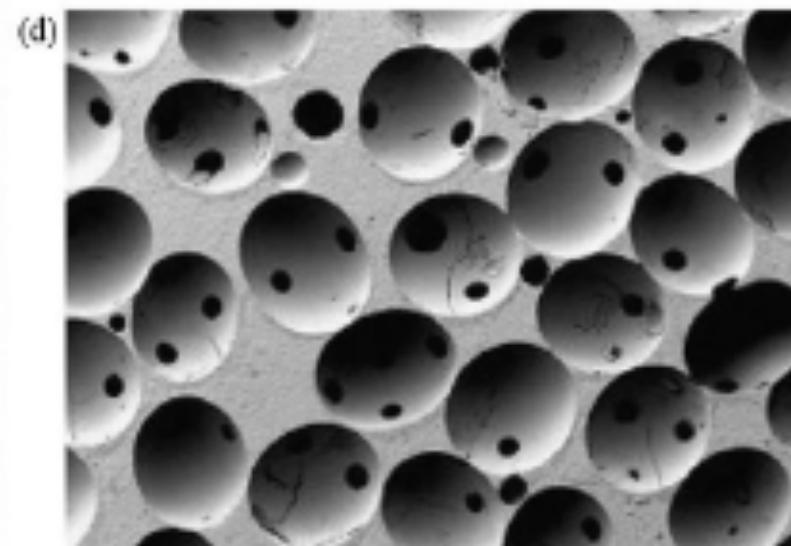
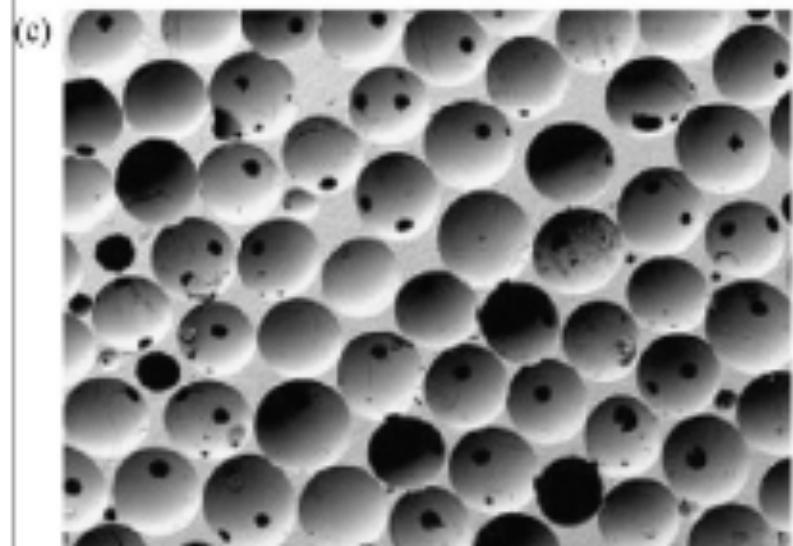
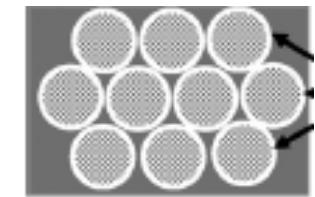
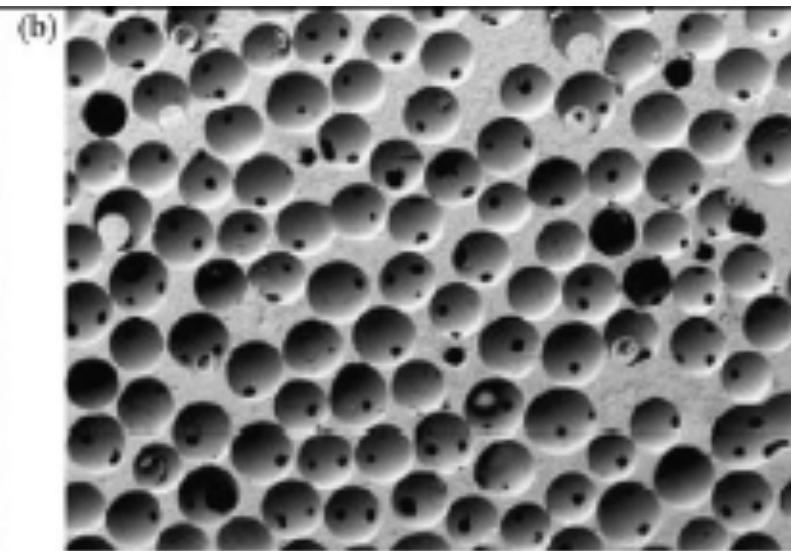
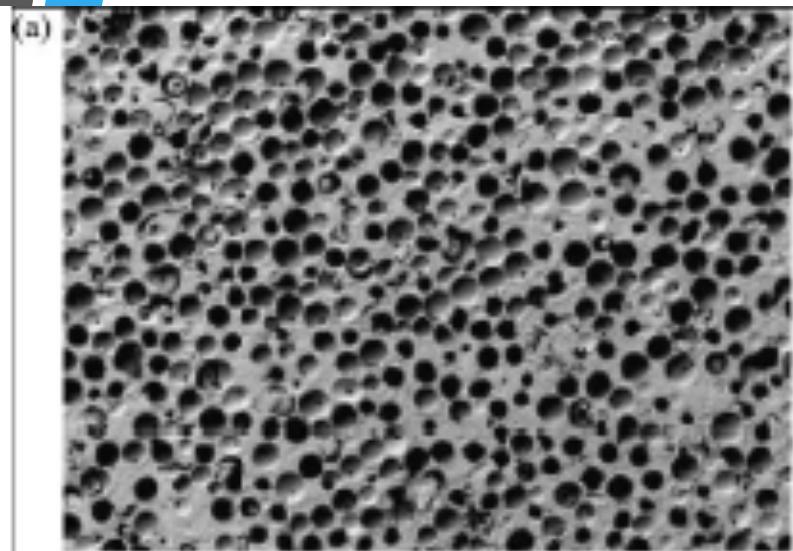
Tricalcium phosphate, β -TCP



Ca/P = 1.5



1360°C



β -TCP porous ceramics with different pore sizes prepared using polymethylmethacrylate balls with the diameters: (a) 100–200; (b) 300–400; (c) 500–600 and (d) 700–800 μm . Horizontal field width is 45 mm.

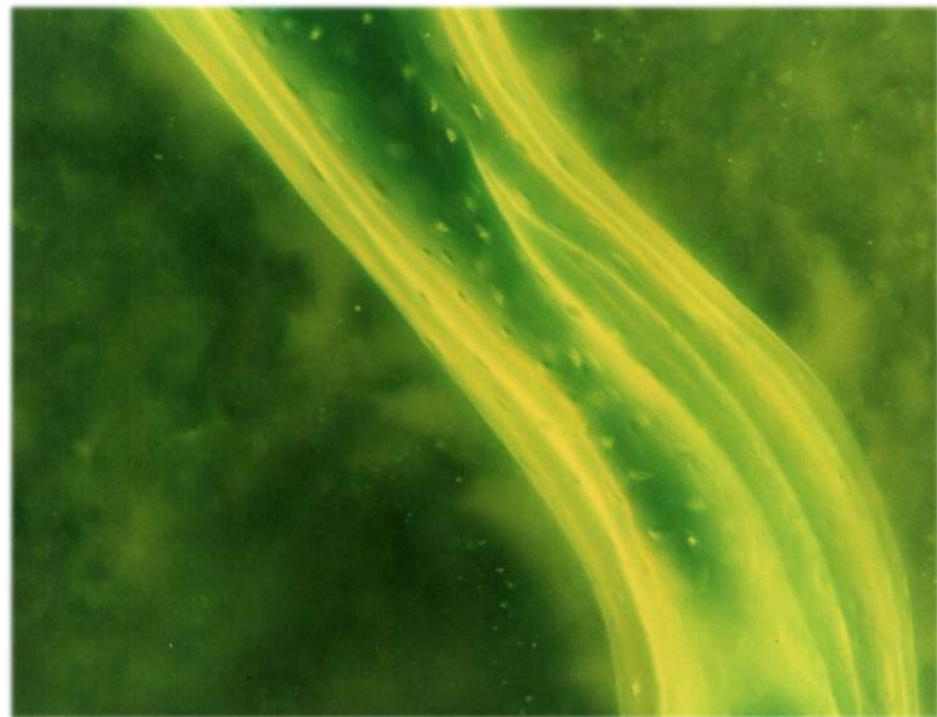
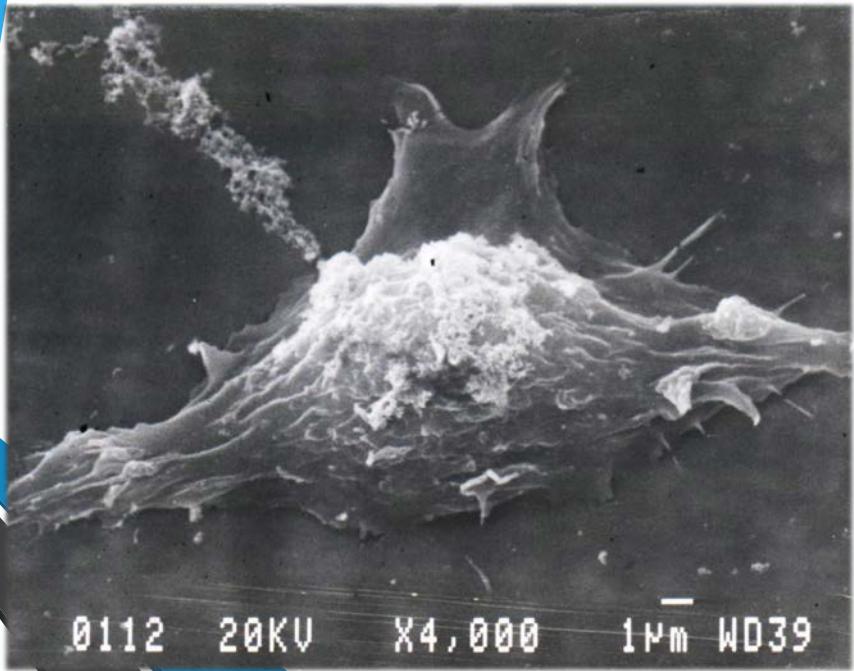
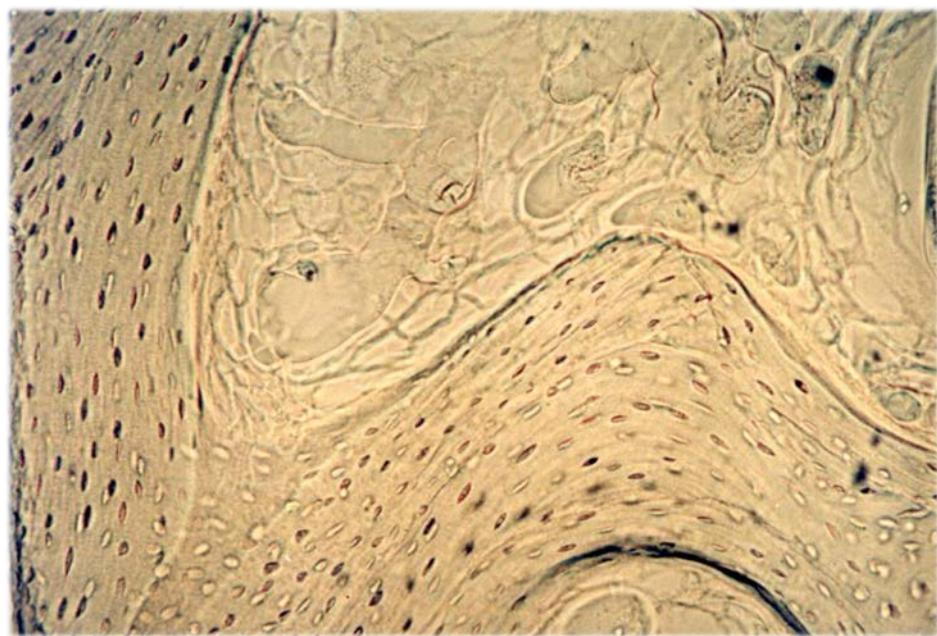
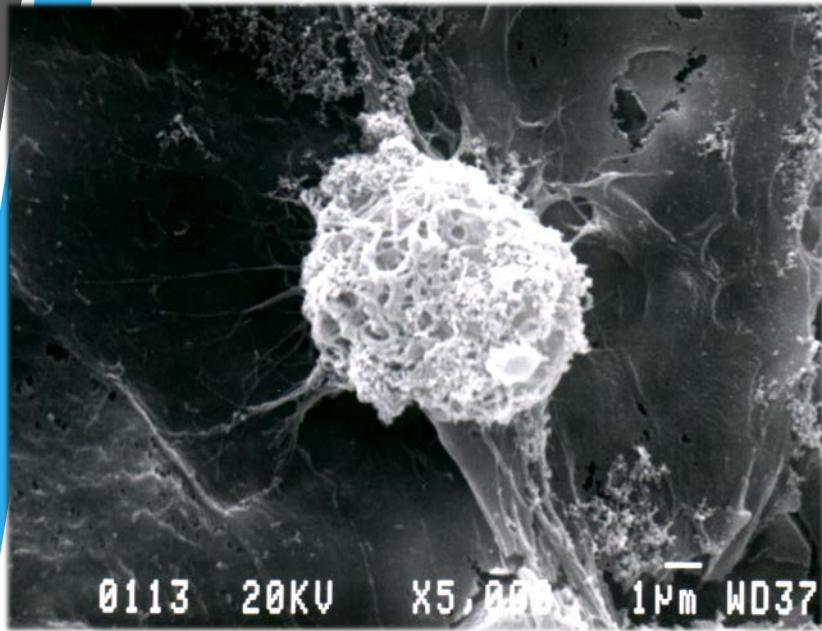
Biodegradable ceramics

Calcium Phosphates with $1.50 < \text{Ca/P} < 1.67$

- Salts with Ca/P ratio's between 1.50-1.67 are the most intensively studied calcium phosphate.
- In this group belong materials described as tricalcium phosphate and hydroxyapatite.
- Slurry and Powder form **HAP** & TCP was found to be **degradable and absorbed**.
- Since a slurry has almost no clinical use, due to **lack of mechanical strength**, efforts to produce stronger samples.

Calcium Phosphate with $\text{Ca}/\text{P} \leq 1$

- Monocalcium phosphate $\text{Ca}(\text{H}_2\text{PO}_4)_2$ ($\text{Ca}/\text{P} = 0.5$) and Calcium monophosphate CaHPO_4 ($\text{Ca}/\text{P} = 1$).
- After several months, all salts were ***resorbed and replaced by bone***, without adverse reactions.
- We may conclude that calcium phosphate salts with $\text{Ca}/\text{P} \leq 1$ can absorb, except the (dense) glassed that show no visible resorption.



Biodegradable ceramics

How do we choose the Biodegradable Ceramic?

Mineral Composition of Bone Structure	<u>Ca/P ratio</u>
• Hydroxyapatite: $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH}, \text{F}, \text{Cl}, \text{CO}_3..)_2$	1.67
• Tricalcium Phosphate: $\text{Ca}_3(\text{PO}_4)_2$	1.50
• Octacalcium Phosphate: $\text{Ca}_8\text{H}_2(\text{PO}_4)_6$	1.33
• Dicalcium Pyrophosphate: $\text{Ca}_2\text{P}_2\text{O}_7 * n\text{H}_2\text{O}$	1.0
• Dicalcium Phosphate (dihydrate): $\text{CaHPO}_4 (2\text{H}_2\text{O})$ (DCPD)	1.0
• Brushite: $\text{CaHPO}_4 * n\text{H}_2\text{O}$	1.0
• Monocalcium Phosphate: $\text{Ca}(\text{H}_2\text{PO}_4)_2$	0.5
• Amorphous Calcium Phosphates	

K.de Groot
Calcium Phosphate with which $\text{Ca}/\text{P} \leq 1$ will be absorbed.

Biodegradable ceramics

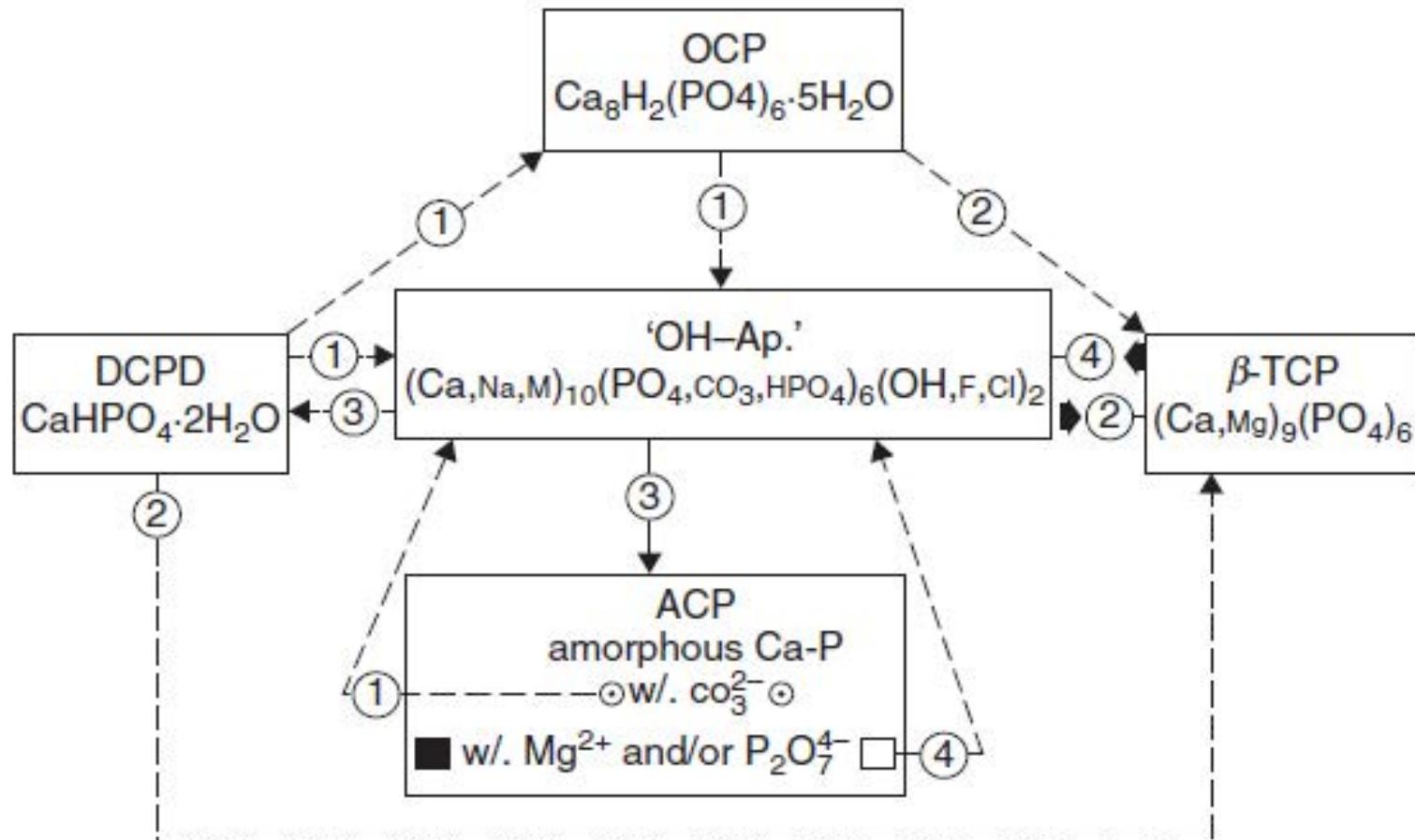
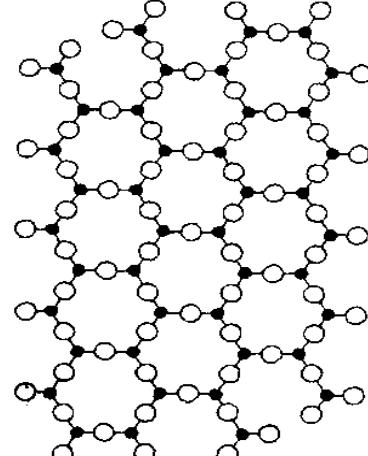


Figure 2.8. Schematic presentation of the transformation of one type of calcium phosphate to another [59,64].

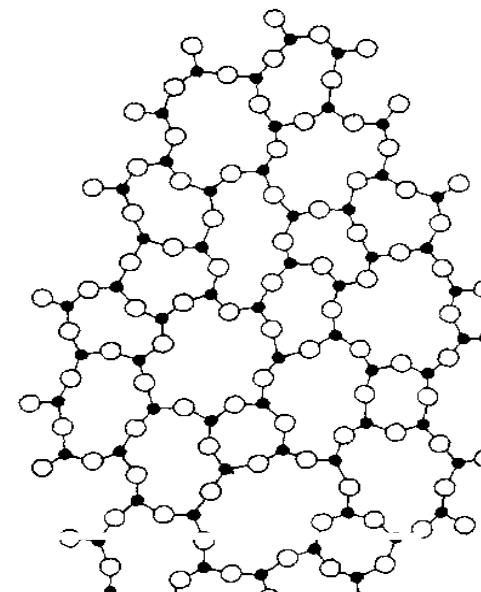
Biodegradable ceramics

Glass

- Any of a number of **noncrystalline, amorphous inorganic substances**, formed, by heating, from metallic or semiconductor oxides or halides
- An **amorphous substance** is one in which **long- range order** *in the atomic arrangement does not exist over distances greater than 10 nm.*
- The most common glasses are based on **silicon dioxide (SiO_2)**



(a) long-range order



(b) non long-range order

Surface Active ceramics

Glass



Preparation

Raw Materials \Rightarrow Mixing \Rightarrow Melting \Rightarrow Quench & Forming

\Rightarrow **Glass** \Rightarrow Annealing \Rightarrow Nucleation \Rightarrow Crystallization

\Rightarrow **Glass-Ceramics**

Oxide Classification from Glass Technology

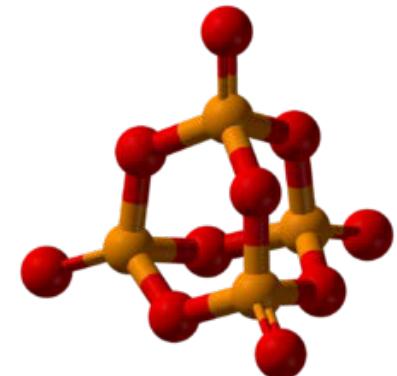
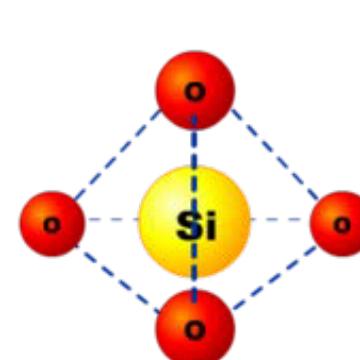
- Glass (Network) Former Oxides: **SiO₂**, V₂O₅, **P₂O₅**, B₂O₃..
- Glass Modifier Oxides (flux): K₂O, **Na₂O**, **CaO**, MgO.....
- Intermediate Oxides: Al₂O₃, ZrO₂, TiO₂.....

Surface Active ceramics

Glass

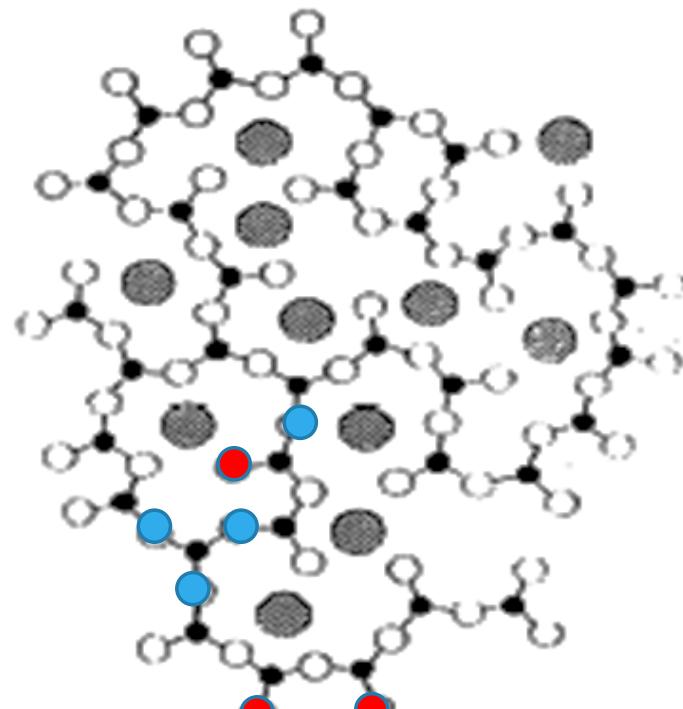
- Network former oxide 網狀形成氧化物

SiO_2 、 P_2O_5



- Network-modifier oxide 網狀修飾氧化物

Na_2O 、 CaO



- Intermediate oxide 中間氧化物

Al_2O_3 、 Zn_2O_3 、 Fe_2O_3

- Bridging oxygen



- Non Bridging oxygen atom



● : Si^{4+} or P^{5+} ● : O^{2-} ● : Na^{+} or Ca^{2+}

Surface Active ceramics

Glass

Quenching 淬火

- is the **rapid cooling** of a workpiece in water, oil or air to obtain certain material properties.
- it prevents undesired low-temperature processes, such as phase transformations, from occurring.



Annealing 退火

- A heat treatment in which a material is exposed to an elevated temperature for **an extended time period** and then **slowly cooled**.

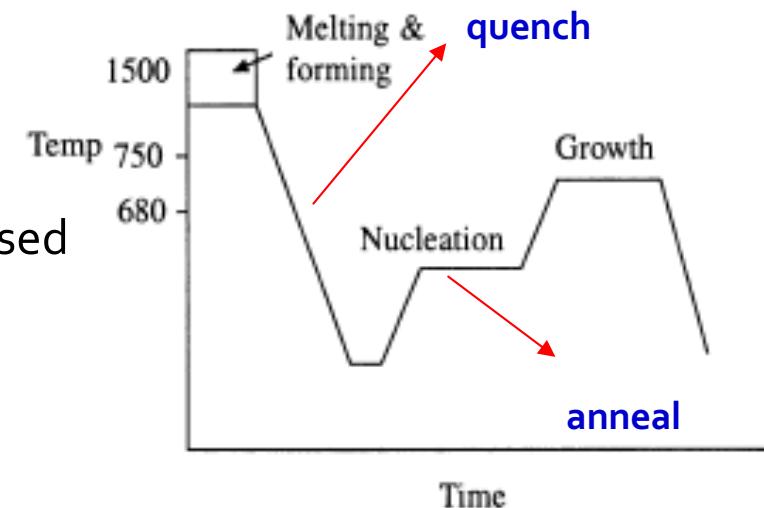


TABLE I.2.4.5

Composition of Bioactive Glasses and Glass-Ceramics (in Weight Percent)

	45S5 Bioglass	45S5F Bioglass	45S5.4F Bioglass	40S5B5 Bioglass	52S4.6 Bioglass	55S4.3 Bioglass	KGC Ceravital	KGS Ceravital	KGy213 Ceravital	A-W GC A: apatite W: Wollastonite	MB GC
SiO ₂	45	45	45	40	52	55	46.2	46	38	34.2	19-52
P ₂ O ₅	6	6	6	6	6	6					
CaO	24.5	12.25	14.7	24.5	21	19.5	20.2	33	31	16.3	4-24
Ca(PO ₄) ₂							25.5	16	13.5	44.9	9-3
CaF ₂		12.25	9.8								
MgO										0.5	
MgF ₂							2.9			4.6	5-15
Na ₂ O	24.5	24.5	24.5	24.5	21	19.5	4.8	5	4		3-5
K ₂ O							0.4				
Al ₂ O ₃											3-5
B ₂ O ₃				5					7		12-33
Ta ₂ O ₅ /TiO ₂										6.5	
Structure	Glass	Glass	Glass	Glass	Glass	Glass-ceramic	Glass-ceramic			Glass-ceramic	Glass-ceramic
Reference	Hench et al. (1982)	Gross et al. (1988)	Gross et al. (1988)		Nakamura et al. (1985)	Höeland and Vogel (1993)					

表 1-2 生醫玻璃與玻璃陶瓷性質、用途比較。

名 樣	Bioglass	Ceravital	切削性玻璃陶瓷	A-W 玻璃陶瓷	新生醫玻璃陶瓷
組 成	$\text{Na}_2\text{O}\cdot\text{CaO}$ · $\text{P}_2\text{O}_5\cdot\text{SiO}_2$	$\text{Na}_2\text{O}\cdot\text{K}_2\text{O}$ · $\text{MgO}\cdot\text{CaO}$ · $\text{P}_2\text{O}_5\cdot\text{SiO}_2$	$\text{Na}_2\text{O}\cdot\text{K}_2\text{O}$ · $\text{MgO}\cdot\text{P}_2\text{O}_5$ · $\text{Al}_2\text{O}_3\cdot\text{SiO}_2\cdot\text{F}$	$\text{MgO}\cdot\text{CaO}$ · $\text{SiO}_2\cdot\text{P}_2\text{O}_5$	$\text{Na}_2\text{O}\cdot\text{CaO}$ · $\text{P}_2\text{O}_5\cdot\text{SiO}_2$
結 晶 相	玻璃	鈣灰石	鈣灰石 金雲母	鈣灰石 矽灰石	$\text{Na}_2\text{Ca}_2\text{Si}_4\text{O}_{14}$ $\beta\text{-Ca}_2\text{P}_2\text{O}_7$
抗折強度 (MPa)	85	150	140-220	220	120-140
壓縮強度 (MPa)	-	500	550	1100	600-750
彈性模數 (MPa)	79	-	77-88	120	-
K_{IC} (MPa·m ^{0.5})	0.5	-	0.5-1	2.0	-
生物適應性	良好	良好	良好	良好	良好
與骨骼鍵結程度	低	中	中	高	高
加 工 性	容易	容易	容易	容易	容易
用 途	耳骨 金屬表面板覆	齒槽填充材料 骨泥	人工齒根 人工齒根	人工齒根 人工骨骼	人工骨骼

ERMI: endosseous ridge maintenance implant

Surface Active ceramics

Bioglass Reaction in *in-vitro* Environment

1. Ions Exchange

Na₂O: 10-15%

CaO: 15-20%



Silanol

$$R_1 = k_1 t^{0.5}$$

diffusion controlled reaction

Increase the hydroxyl concentration of the solution and alkaline interfacial pH leads to glass network attack and additional Silanol formation.

Surface Active ceramics

Bioglass Reaction in *in-vitro* Environment

2. Network structure hydrolysis



$$R_2 = k_2 t^{1.0}$$

interfacial controlled reaction

Network dissolution results are **pH > 9.5.**

Surface Active ceramics

Bioglass Reaction in *in-vitro* Environment

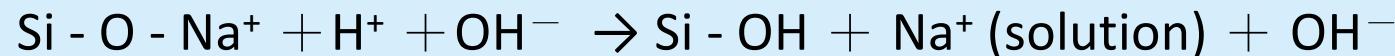
3. Re-polymerization of Si-O-Si Bond

At intermediate alkaline pH (< 9.5), the rate of re-polymerization of Si-O-Si bonds from the surface SiOH groups:



Surface reaction of Si-rich bioglass in biological environment

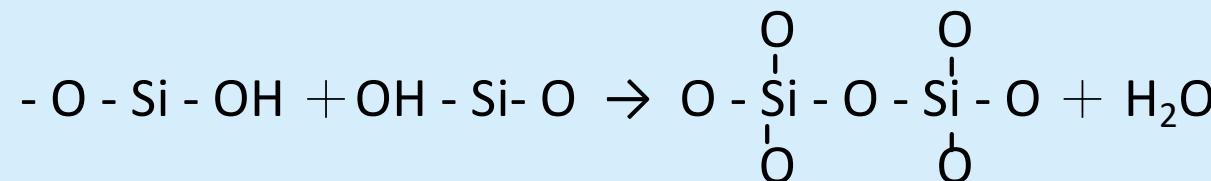
Stage 1 Exchange Na⁺ with H⁺ from solution



Stage 2 Loss of SiO₂ in form of Si(OH)₄ and formation Si-OH at glass-solution interface



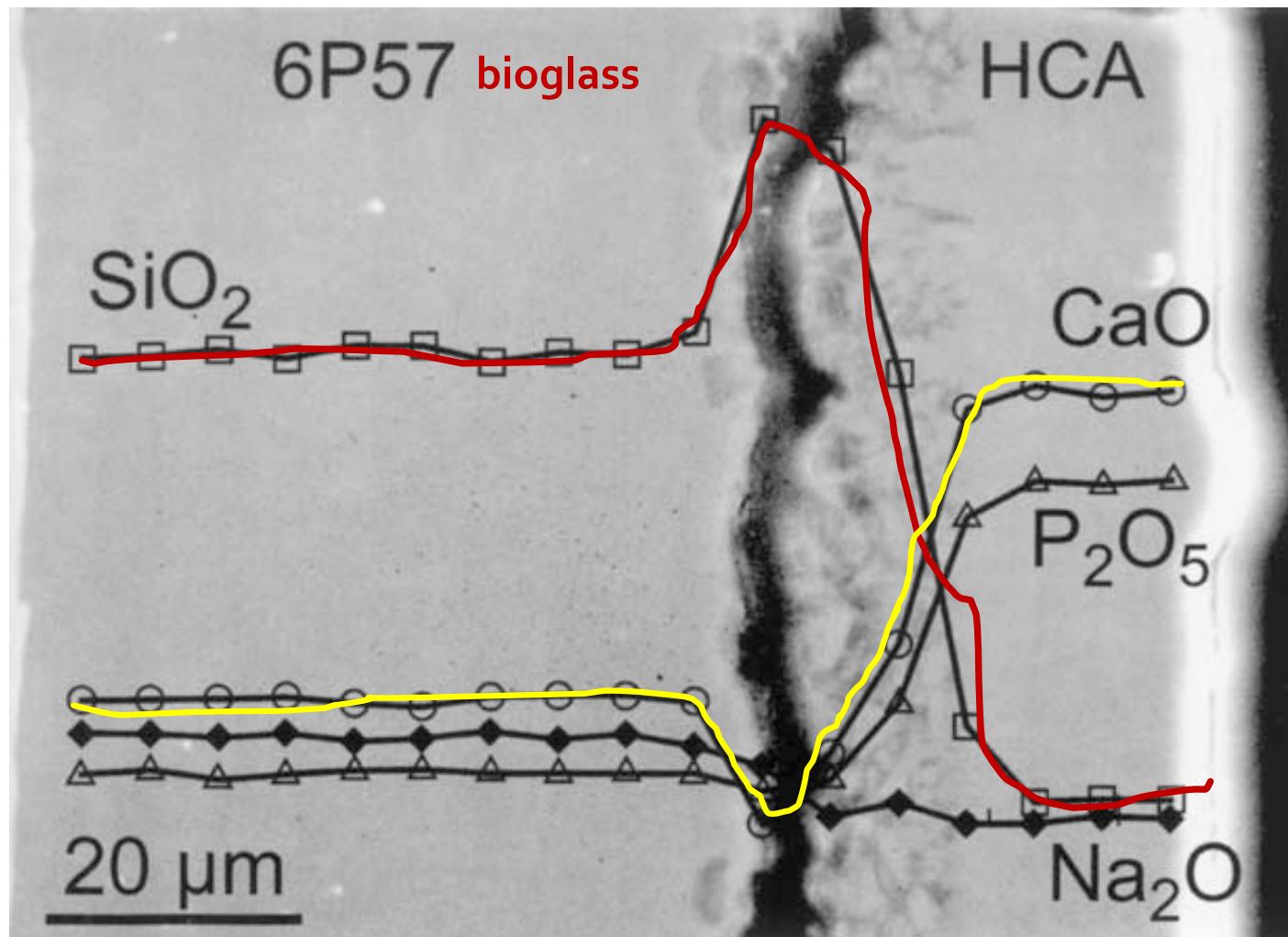
Stage 3 Poly-condensation of SiOH to form SiO₂ layer on glass surface



Stage 4 Migration Ca²⁺ and PO₄³⁻ to form an amorphous CaO-P₂O₅ film on the Surface

Stage 5 Crystallization of Hydroxyl Carbonate Apatite (HCA)

Surface reaction of Si-rich bioglass



Elemental cross section analysis (SEM-EDS) of a 6P57 coating after 2 months in SBF. A 20 μm thick apatite layer is visible on the 6P57 coating surface growing on a Si-rich region.

Surface Active ceramics

Bioactive glass

The Biological Role of **Silicon** in Bioactivity

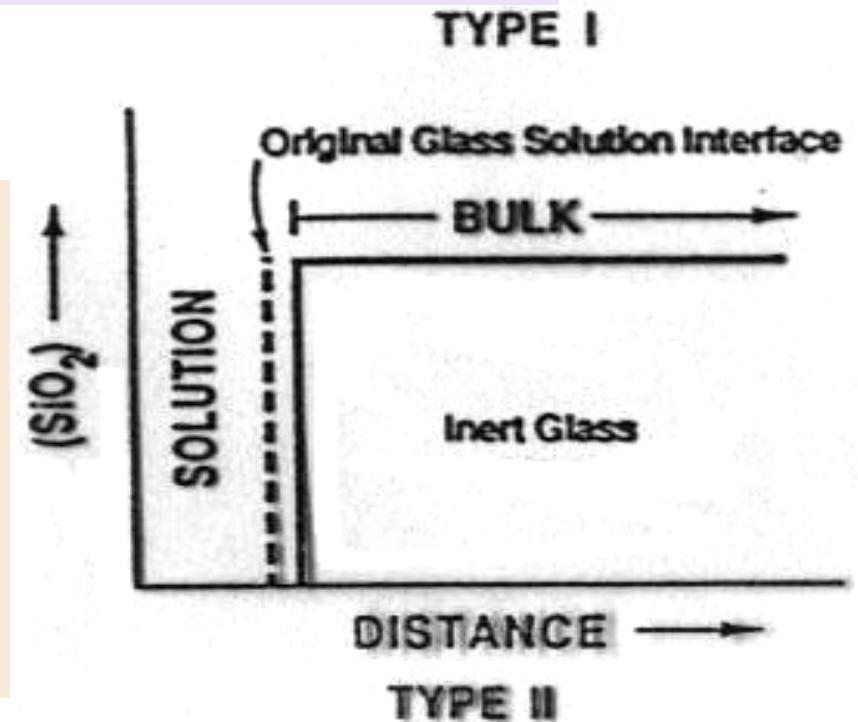


- Mineralization front concentrate a lot of biological silicone.
- Bioglass \Rightarrow SiO₂-rich layer \Rightarrow Ca-P rich layer \Rightarrow HCA layer \Rightarrow bone bonding
- HAP (no silicon) \Rightarrow calcium/silicon concentrate (incubation time) \Rightarrow bone bonding
- SiO₂ (no Ca-P) \Rightarrow fibrous tissue \Rightarrow bone bonding

The Biological Role of Silicon in Bioactivity

1. Type I: high SiO₂ (100%)

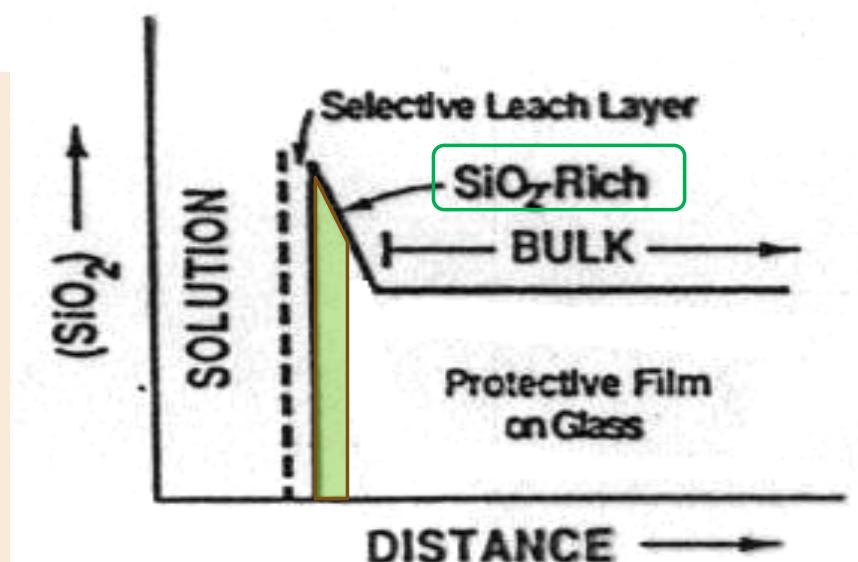
- A type I surface has undergone only a thin, less than 50 Å, surface layer hydration.
- No significant surface compositional change by either loss of alkali or silica network has occurred.
- Fibrous tissue grow around the implant material in the physiological environment.



2. Type II : high SiO₂ (<60%)

Inert

- Traditional soda-lime-silicate glass or more than 60 mole % of SiO₂.
- Surface possesses a silica-rich protective film due to selective alkali ion removal.
- Glass that form type II surfaces also generally behave as nearly inert implant materials.

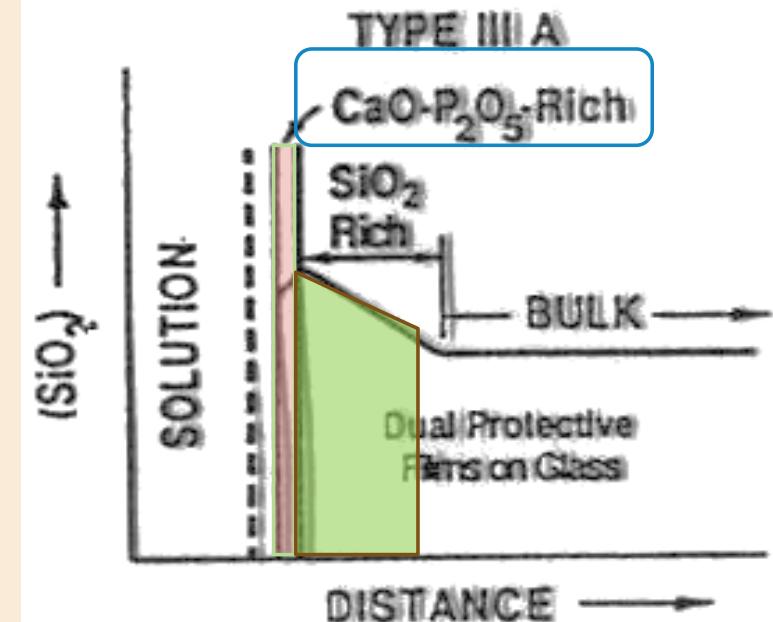


The Biological Role of Silicon in Bioactivity

3. Type IIIA Surface active

P₂O₅ Addition (high CaO & P₂O₅ ratio)

- Addition of P₂O₅ to converts the glass to type IIIA surface behavior, and results in a **high rate of bioactivity**.
- The CaO and P₂O₅ groups crystallize into a mixed **hydroxyl-carbonate apatite (HCA)** phase on the top of the SiO₂-rich layer formed on the glass surface.
- The HCA crystallize nucleate and bond to interfacial metabolites, such as mucopolysaccharides, glycoproteins and collagen.

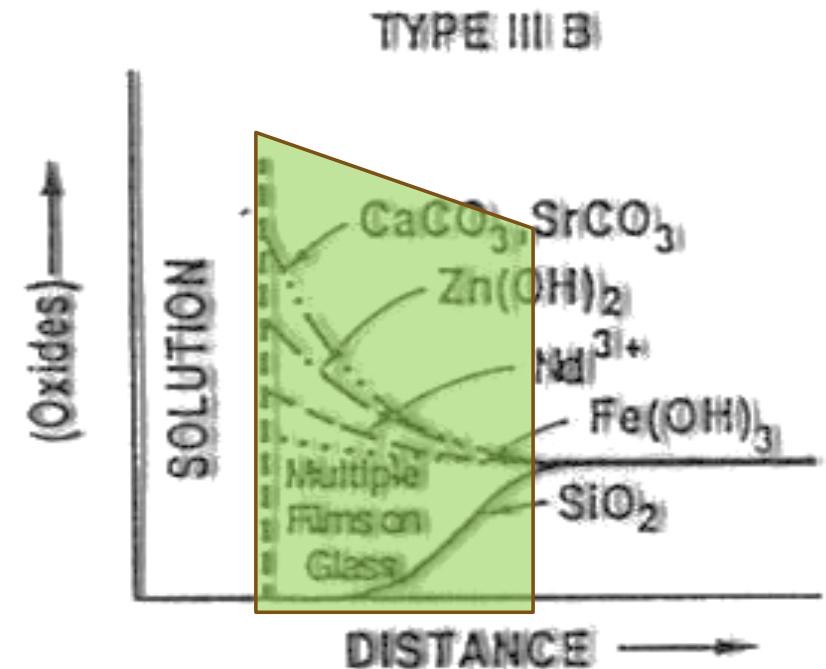


The Biological Role of Silicon in Bioactivity

4. Type IIIB:

- Addition of **Multivalent metal ions** (ZnO or Fe_2O_3)
- Addition of multivalent elements to either bioactive glass or glass-ceramics will eliminate bioactivity.

Network dissolution

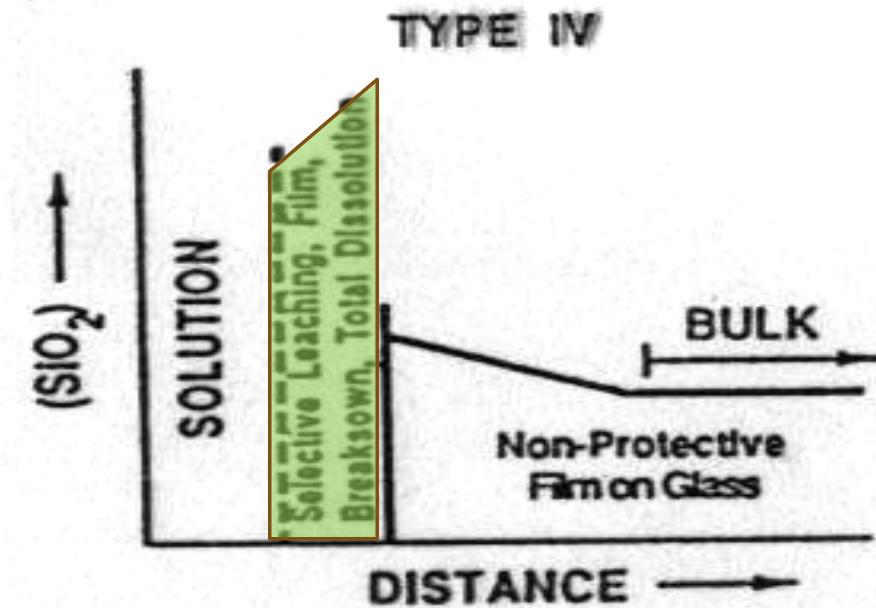


The Biological Role of Silicon in Bioactivity

5. Type IV:

biodegradable

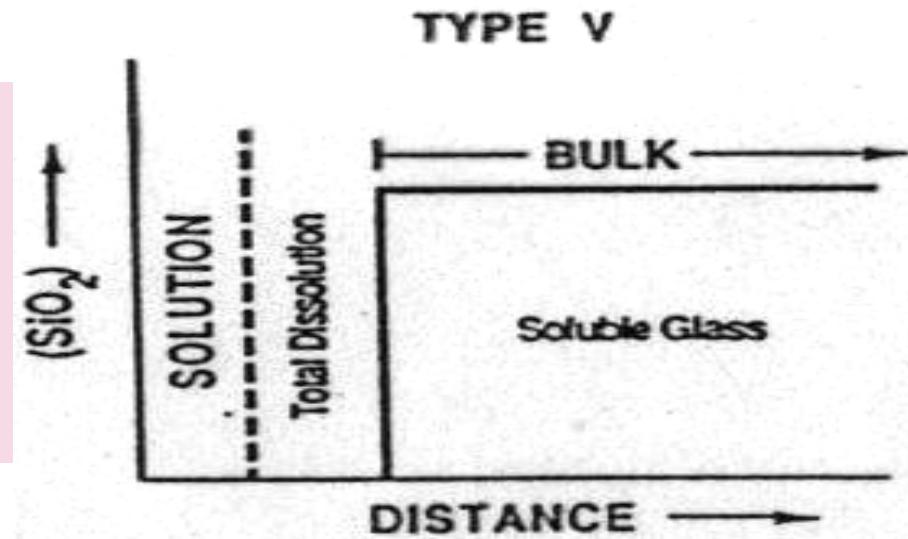
- High Na_2O and CaO ratio.
- Binary or ternary soda-silica or potassium silicate glasses rich in alkali form type IV surface and poor durability.



6. Type V:

biosoluble

- Low network former ratio ($\text{SiO}_2 < 40\%$).
- A glass exhibiting Type V behavior is losing considerable quantities of ions into solution.



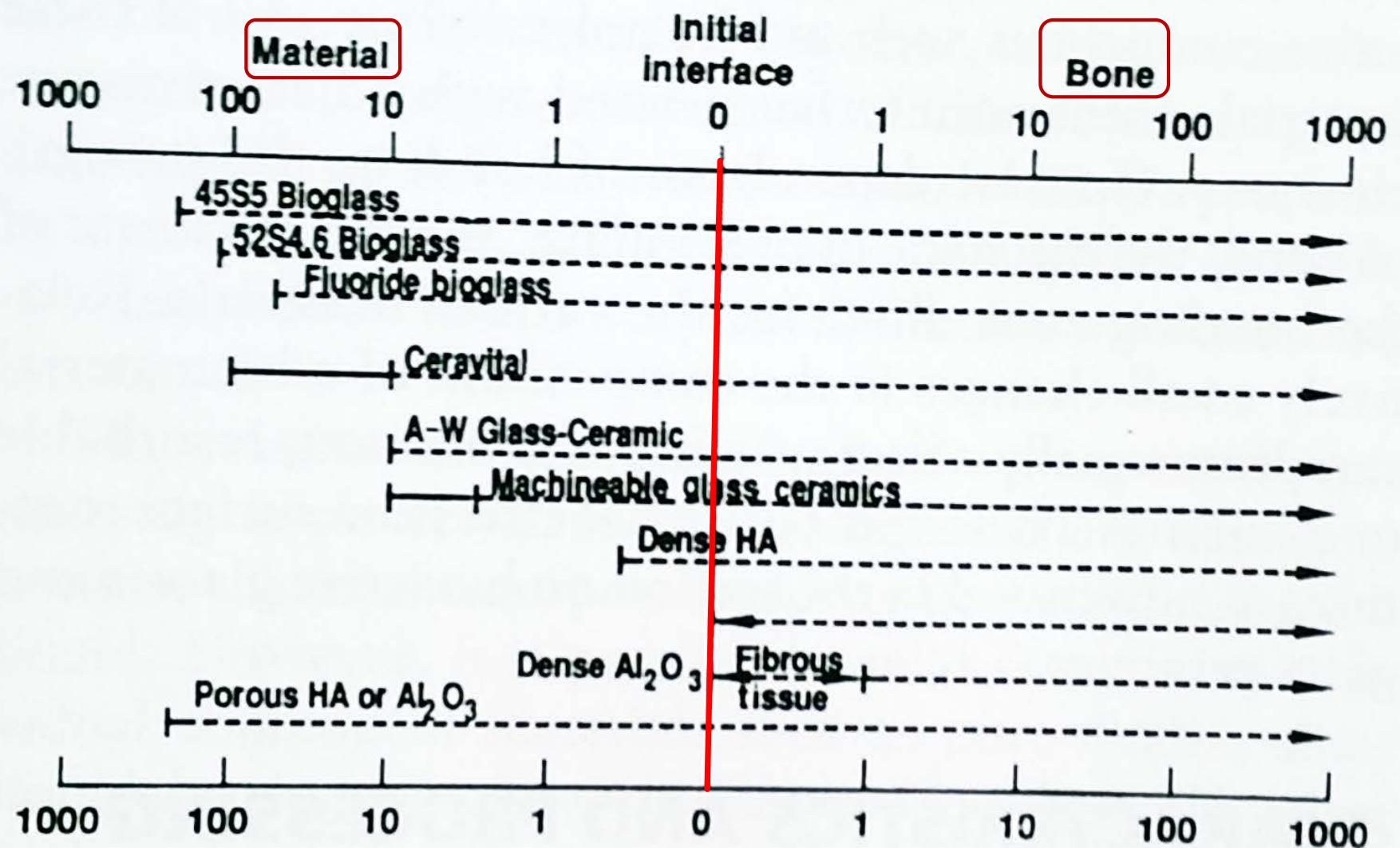


FIGURE I.2.4.2 Comparison of interfacial thickness (μm) of reaction layer of bioactive implants of fibrous tissue of inactive bioceramics in bone.

The Biological Role of Silicon in Bioactivity

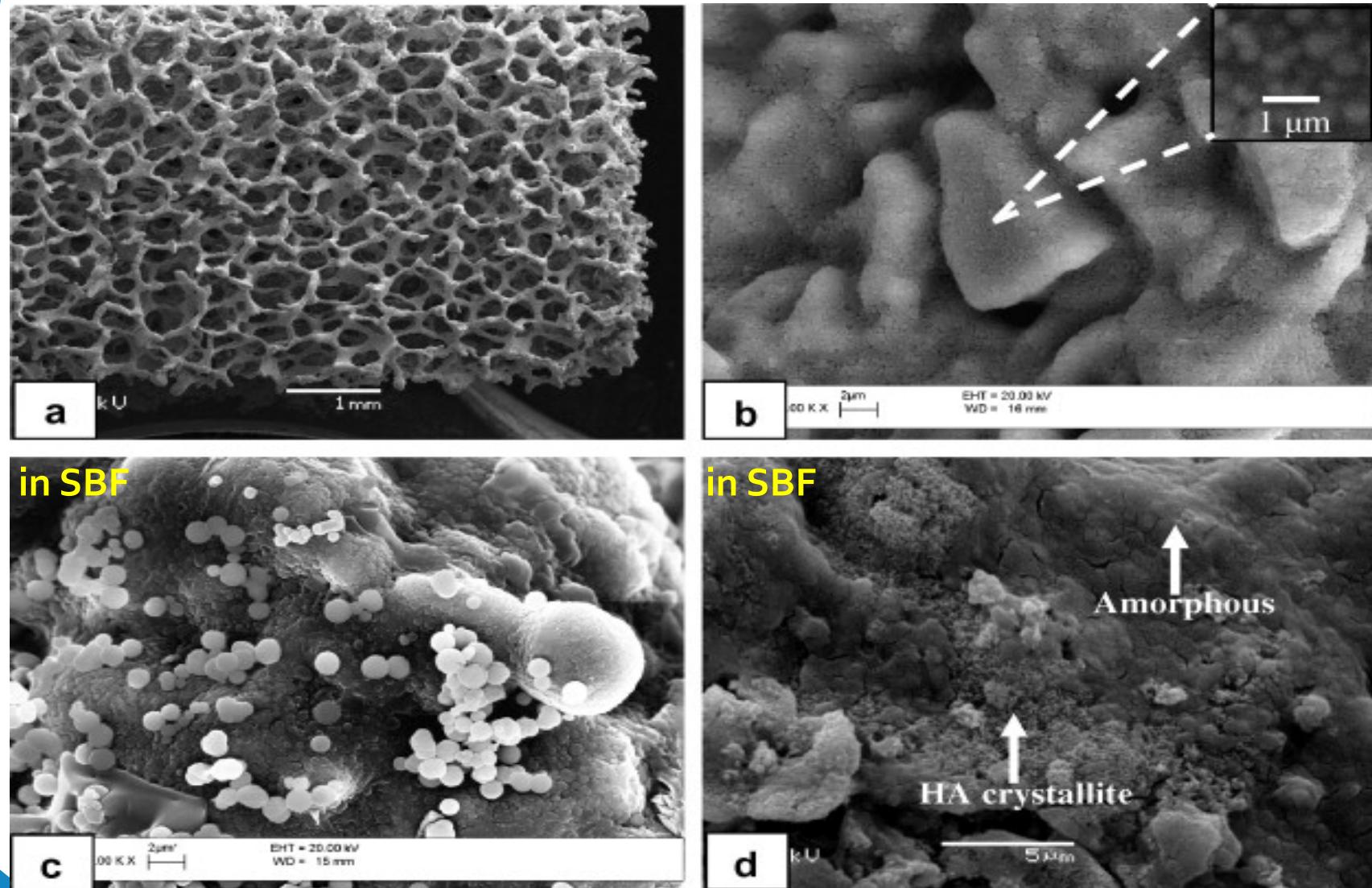


Fig. 3. (a) Macroporous structure of Bioglass®-derived scaffold sintered at 1000 °C for 1 h. Surface microstructure of struts of foams sintered at 1000 °C for 1 h followed by immersion in SBF for (b) 0, (c) 1 and (d) 2 weeks.

The Biological Role of Silicon in Bioactivity

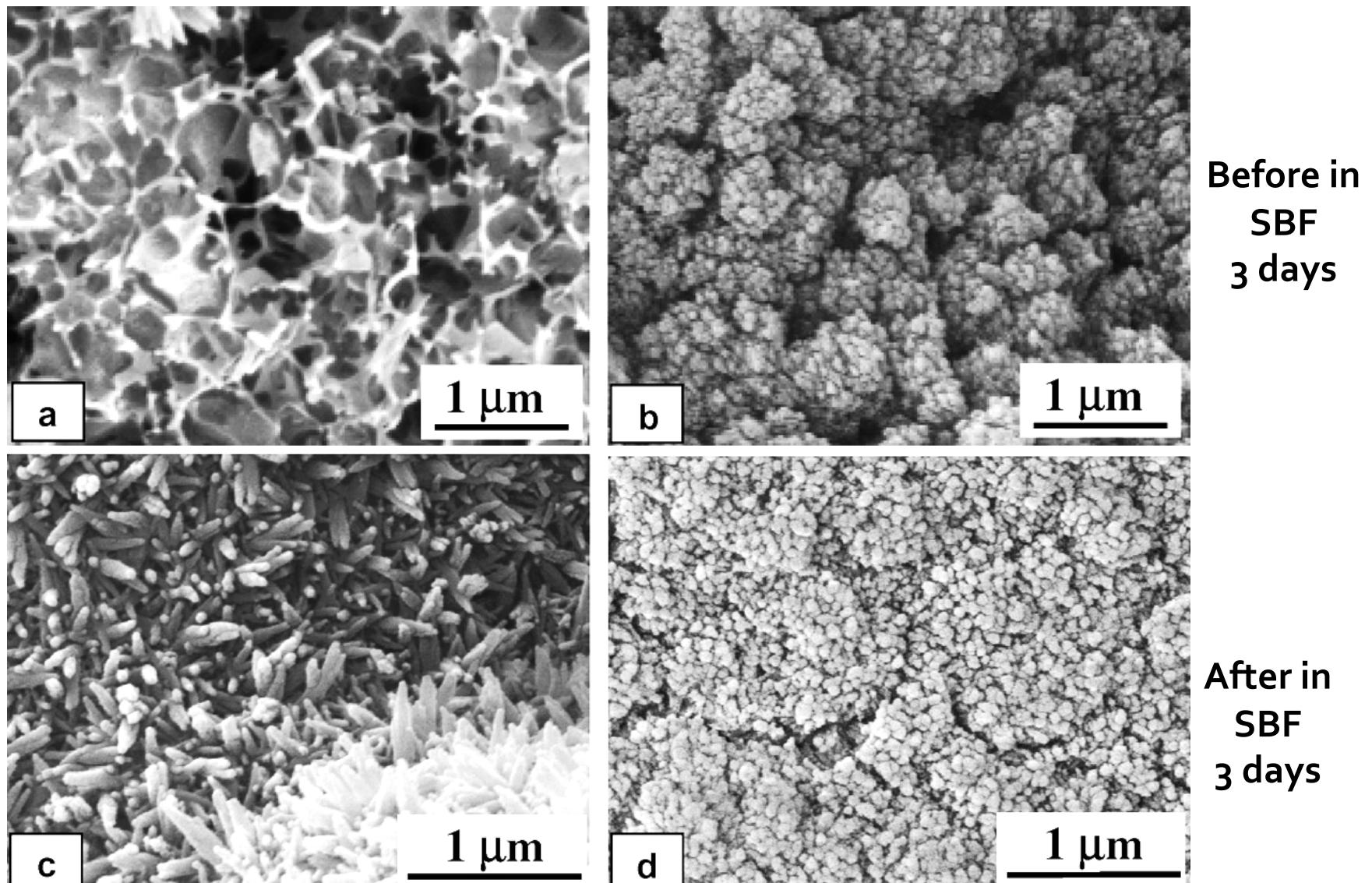


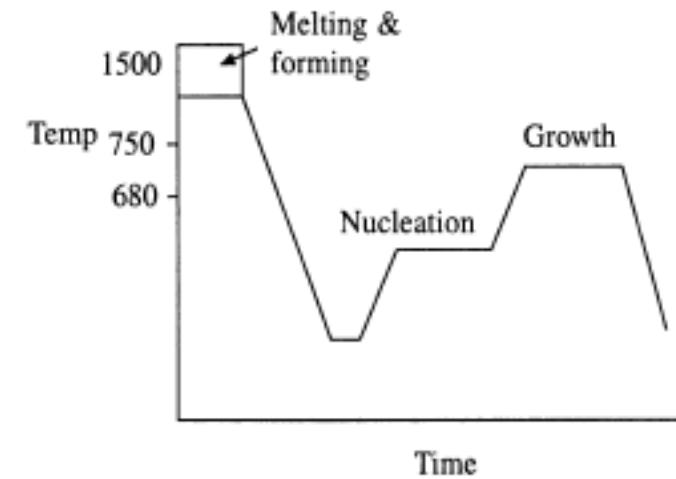
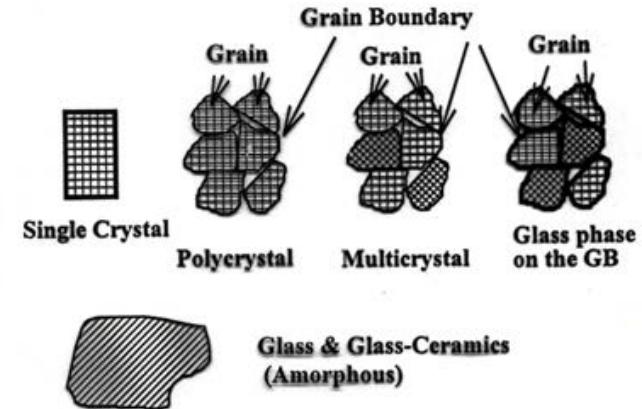
Fig. 4. SEM images of the microstructures of foams sintered at 1000 °C for 1 h followed by functionalization: (a) before immersion in SBF and (b) soaked in SBF for 3 days; or followed by water-treatment: (c) before immersion in SBF and (d) soaked in SBF for 3 days

Surface Active ceramics

Glass-Ceramics

- Glass-ceramics are **crystalline materials** obtained by the controlled crystallization of **an amorphous parent glass**.
- Controlled crystallization requires:
 - Specific compositions
 - Usually a two-stage heat treatment
 - Controlled nucleation
- Controlled crystallization will initiate growth of crystal of small uniform size

Materials' Microstructures:



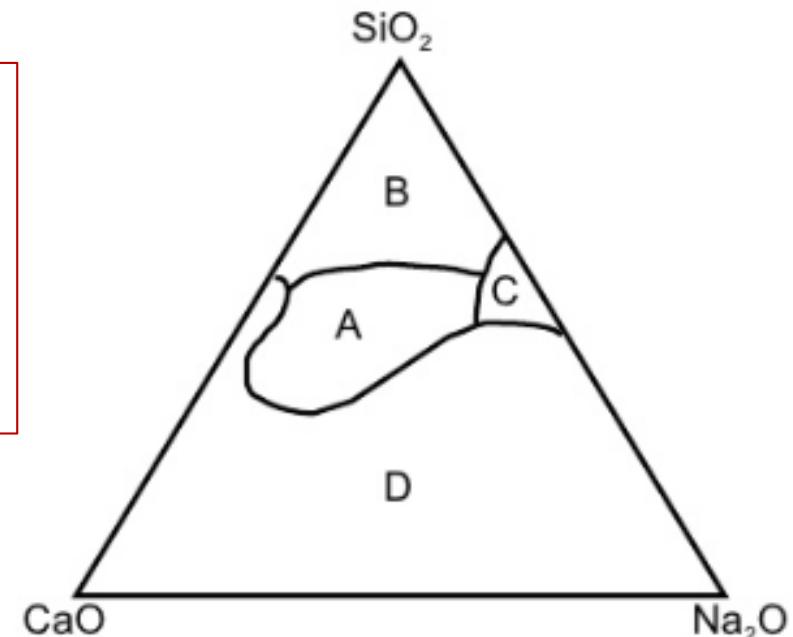
Temperature-time cycle for a glass ceramic

$\text{SiO}_2\text{--CaO--Na}_2\text{O--P}_2\text{O}_5$

Glass-Ceramics

- The bonding is related to simultaneous formation of a calcium phosphate and an SiO_2 -rich film layer on the surface,
- As exhibited by 46S5.2 type Bioglass®
- If an SiO_2 -rich layer forms first and a calcium phosphate film develops later (46–55 mol% SiO_2 samples) or no phosphate film is formed (60 mol% SiO_2), then **no direct bonding with bone is observed**.

- A: bonding in 30 days with bone.
- B: nonbonding—too low reactivity.
- C: nonbonding—too high reactivity region
- D: bonding but does not form glass.



Surface Active ceramics

Glass-Ceramics

Desirable properties

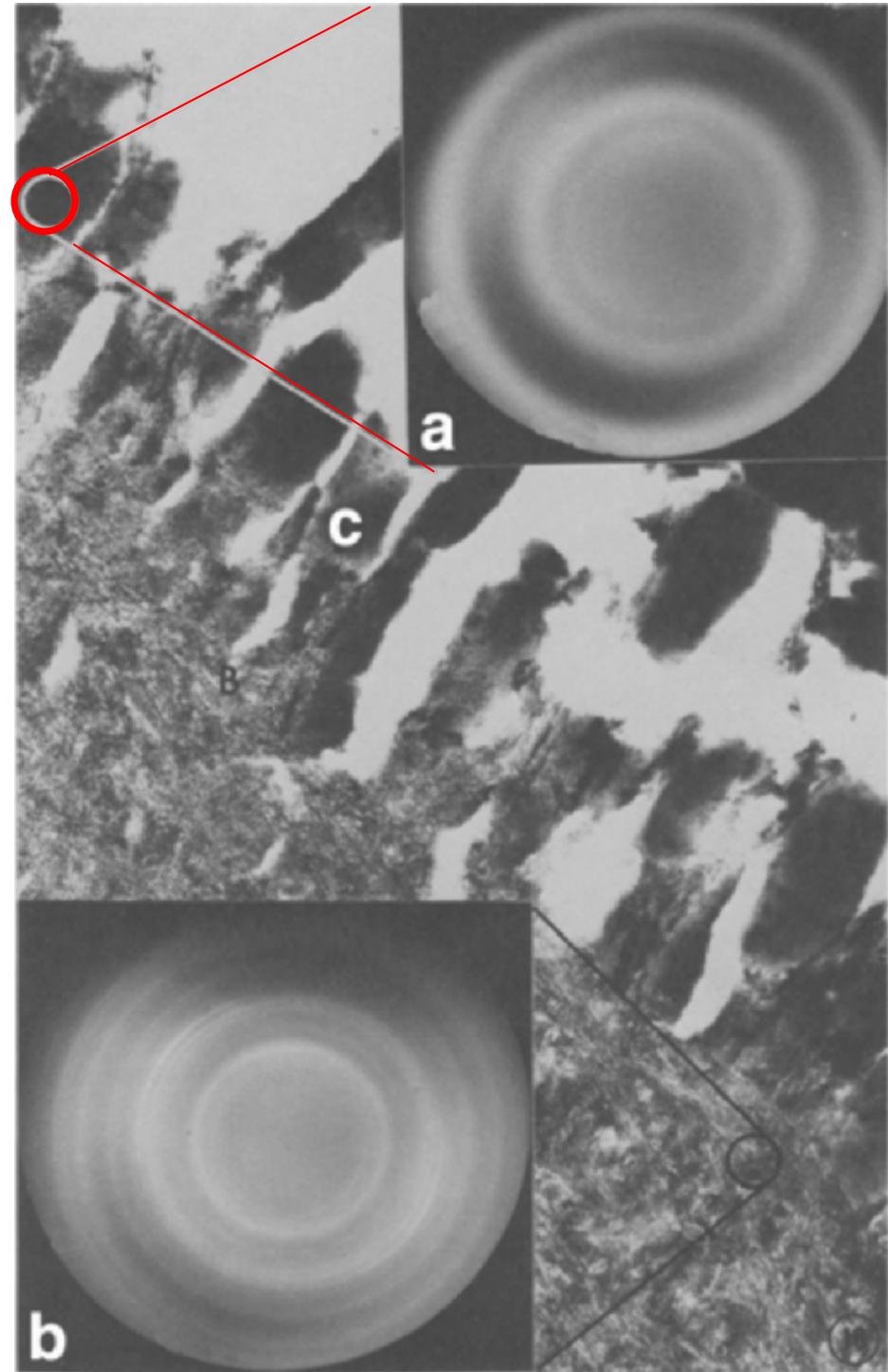
- Coefficient of expansion is very low, typically 10^{-7} to 10^{-5} per degree C.
- Due to the **controlled grain size** and **improved resistance to surface damage**, the tensile strength of these materials can be increased by at least a factor of two, from about 100 to 200 MPa.
- **Resistance to scratching and abrasion** are close to that of sapphire.
- Main drawback of the glass-ceramic is its **brittleness**, as is the case with other glasses and ceramics.

Glass-Ceramics

Properties of Glass-Ceramics

Transmission electron micrograph (TEM) of well-mineralized bone

- (a) diffraction pattern from the ceramic area
- (b) Bone area
- (c) which was fractured during sectioning.



Types of Bioceramic tissue attachment and their classification

1. Dense, nonporous, near inner ceramics attach by bone growth into surface irregularities by cementing the device into a defect (termed "morphological fixation")
 - Al_2O_3 (single crystal and polycrystalline)
2. For porous inert implants, bone ingrowth occurs that mechanically attaches the bone to the materials (termed "biological fixation")
 - Al_2O_3 (polycrystalline)
 - Hydroxyapatite-coated porous metals
3. Dense, nonporous surface-reactive ceramics, glasses and glass-ceramics attached directly by chemical bonding with the bone (termed "bioactive fixation")
 - Bioactive glasses
 - Bioactive glass-ceramics
 - Hydroxyapatite
4. Dense, nonporous (or porous) resorbable ceramics are designed to be slowly replaced by bone.
 - Calcium sulfate (plaster of paris)
 - Tricalcium phosphate
 - Calcium –phosphate salts

Reference:

- J. S. Temenoff & A.G. Mikos (2008) “ Biomaterials - The Intersection of Biology and Materials Science. Pearson Prentice Hall.
- 王盈錦、林峰輝、胡孝光、黃玲惠、黃義侑、蔡瑞瑩、闢山璋 (2007) 第9章生醫陶瓷材料. “生物醫學材料” , 合記圖書出版社.
- Joon Park & R.S. Lakes (2007) Chap 6 ,Ceramic implant materials. “Biomaterials -An Introduction” 3rd edition . Springer.

Hip joint replacement

<https://www.youtube.com/watch?v=OgJVZoU6nBU>