Bio-Inspired Tailored HAP-based Powder Composites for Dental Applications

PhD Thesis Defense by Yen-Shan Lin

Committee members
Professor Eugene A. Olevsky (Chair)
Professor Marc A. Meyers (Co-Chair)
Professor Joanna M. McKittrick
Professor Sungho Jin
Professor Satchi Venkataraman
Professor David J. Benson

Outline

- **Introduction: Literature survey**

  - Basic components and structure of human and animal dental materials

  - Background of spark-plasma sintering, material system (HAP), and consolidation of HAP-based materials

- **Research objectives and tasks**
- **Characterization of natural dental materials and structures of Arapaima scale**
- **Fabrication of HAP and CNT-HAP tailored powder composites**
- **Conclusions**

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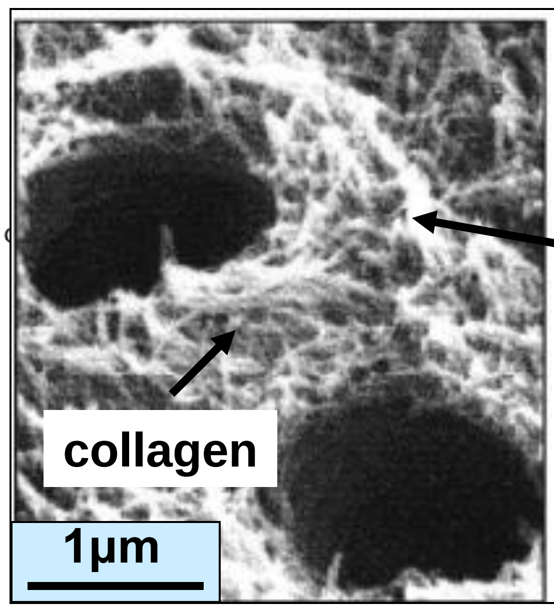
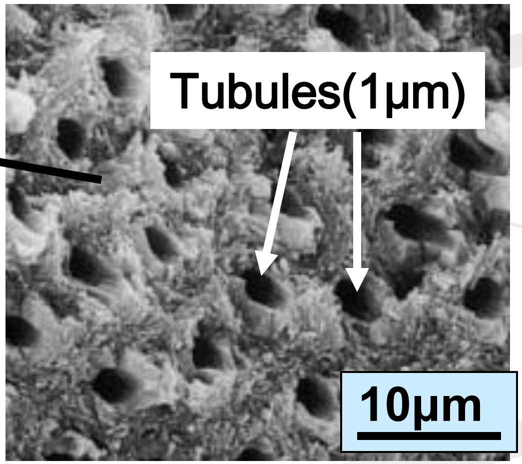
Basic components and structure of human dental materials

- **Teeth are composed of an internal region called dentin ,which is tougher ,and external layer called enamel ,which is harder.**
- **Enamel has high degree of mineralization and no collagen.**
- **Dentin is a hydrated composite material composed of 30vol%type-I collagen fibrils, 25vol% fluid and 45vol% nanocrystalline carbonated apatite mineral.**

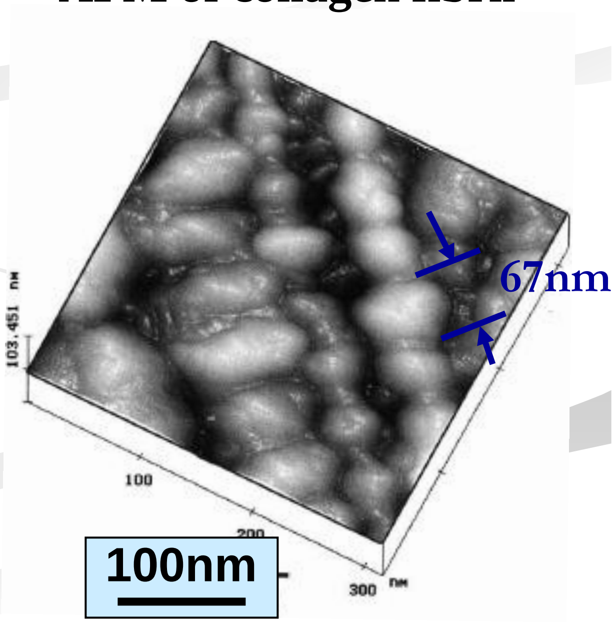
Demineralized dentin SEM





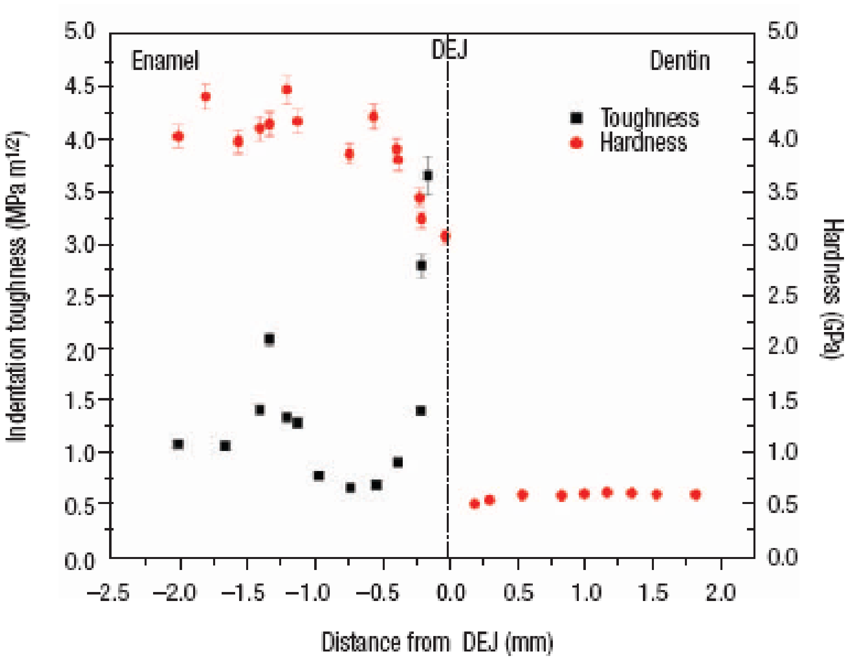
SEM of dentin

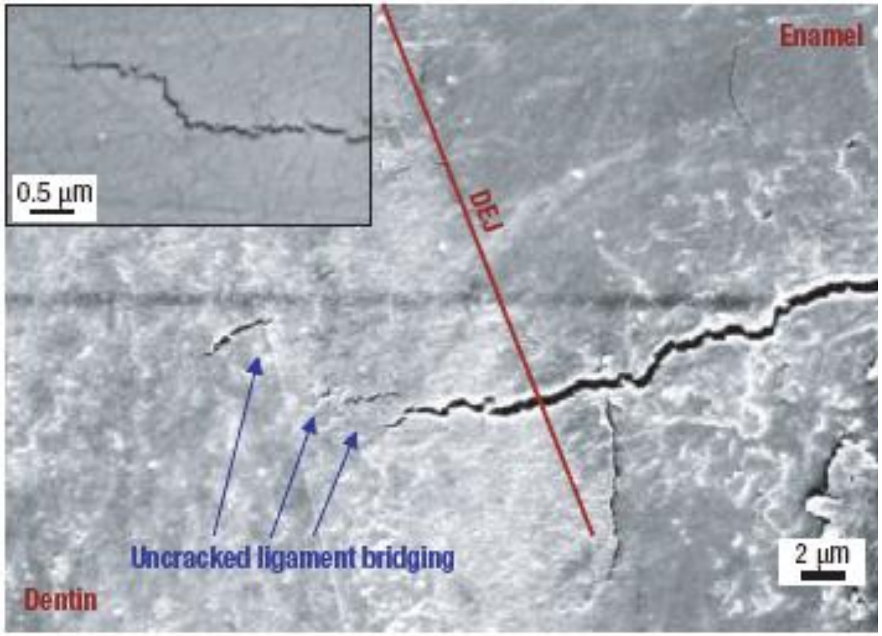
AFM of collagen fibril



Imbeni. V et al. Biomed Mater Res A 2003:66:1-9 & Snead ML et al. Mater Sci Eng C 2006:26:1296-30

Dentin-enamel junction (DEJ)

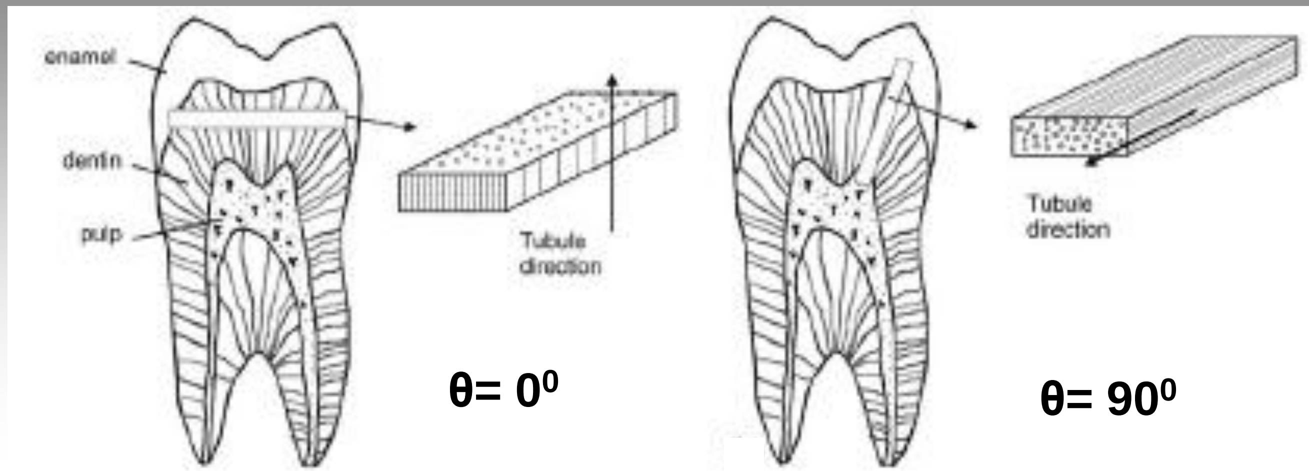


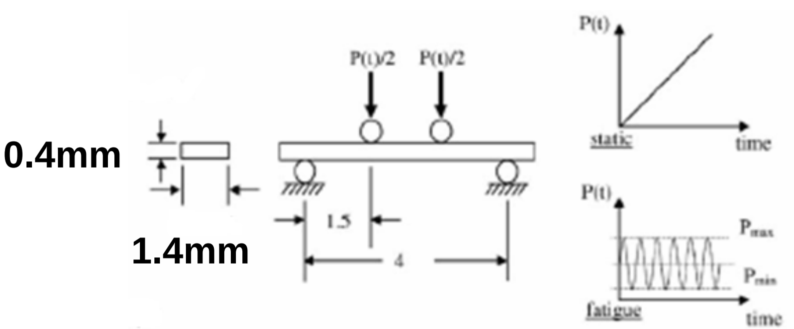


- The hardness decrease form enamel to dentin
- DEJ is a functionally graded structure in natural material
- The crack propagation was arrested when it cross the DEJ

S. J. Marshall et al J. of the European Ceramic Society 23 2003 2897-2904, Imbeni. V et al Nature Material 2005;4:229-232

Effect of tubule orientation



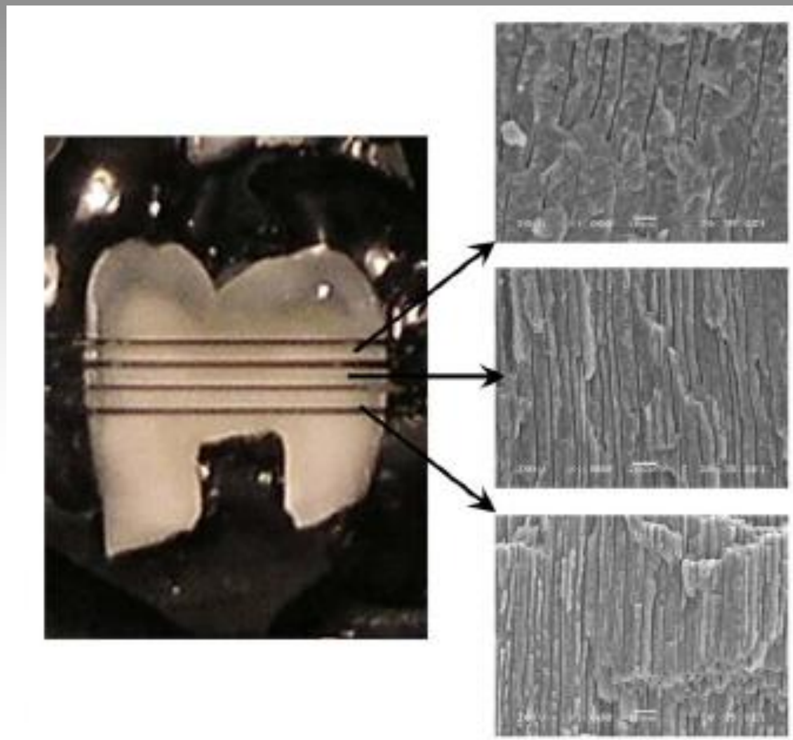


	$\theta = 0^0$	$\theta = 90^0$
Flexural Strength(MPa)	160±22	109±10
Modulus (GPa)	18.7±3.5	15.5±2.8
Fatigue strength 10^7 (MPa)	44	24

- **The loading direction parallel to the tubule has higher flexural strength**
- **The anisotropic collagen fibrils play a significant role in strengthening the structure**

Dwayne D.Arola et al. Biomaterials 27(2006)2131-2140

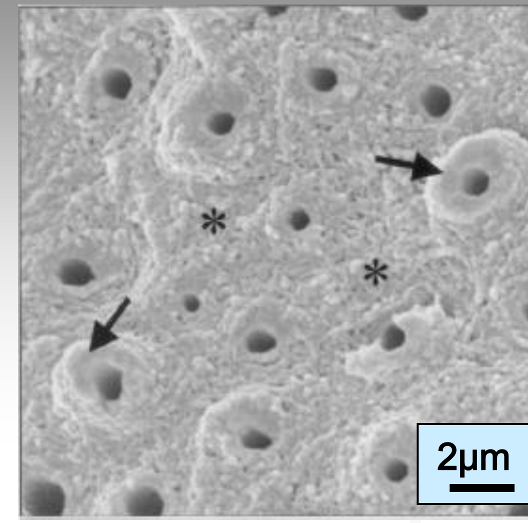
Effect of tubule density



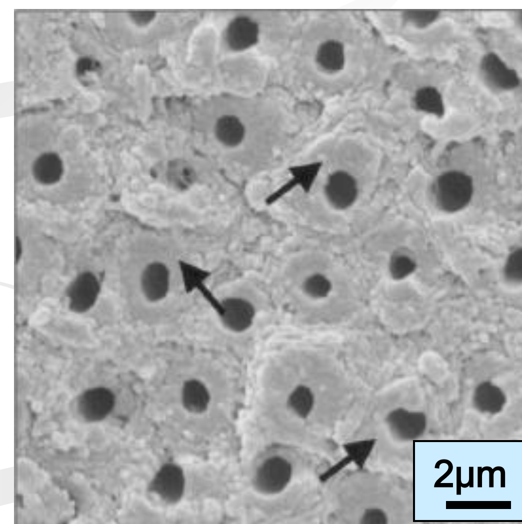
(a)

(b)

(c)



superficial



deep

Tooth structure	Mean UTS (MPa)	Hardness (GPa)
(a) Superficial dentin	60.6±16.3	0.91±0.15
(b) Middle dentin	48.7±16.7	0.85±0.19
(c) Deep dentin	33.9±8.0	0.52±0.24

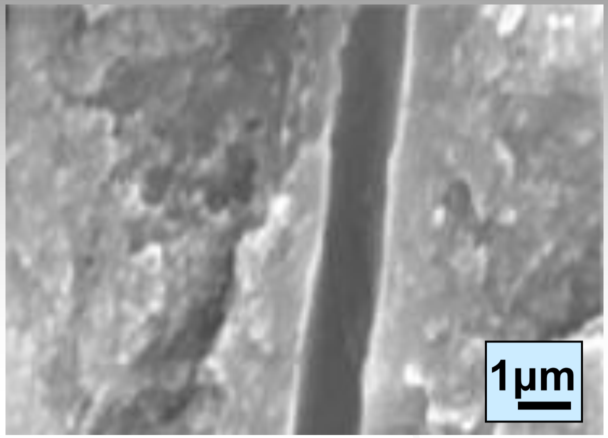
- **The higher UTS and hardness appear in lower tubule density**
- **The hollow tubules do not contribute to strength of dentin**

Narcelo Giannini et al. Dental materials 20(2004)322-329, Linny Angker et al. Journal of Dentistry (2003);31:261-267

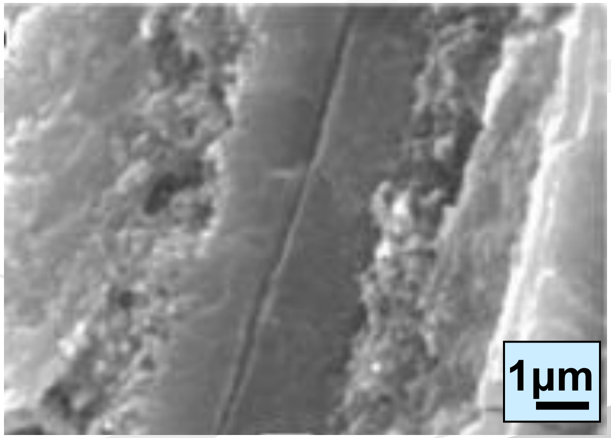
Effect of age

Young dentin (19-30)	Aged dentin (40-70)
Unfilled tubule	Filled tubule
More microcracks and microbranching	Fewer microcracks and microbranching tubules due to fewer unfilled tubule
Straight crack deflection	Less straighter crack path
Crack bridge forms between tubules	Crack bridge is formed by filled tubule itself

Age 20



Age 67



	Tubules/10000μm^2	Filled tubule fraction
Young(19-30)	129±60	0.04±0.03
Aged (40-70)	128±48	0.87±0.19

- Fatigue, crack growth toughness, and flexural strength of dentin deteriorate as the age increases due to the filling of carbonated apatite in aged dentin
- The crack mechanism is also different in aged and young dentin

K. J. Koester et al. Biomaterials 2008;29:1318-1328, D. Arola et al. Biomaterials 2005;26:4051-4061

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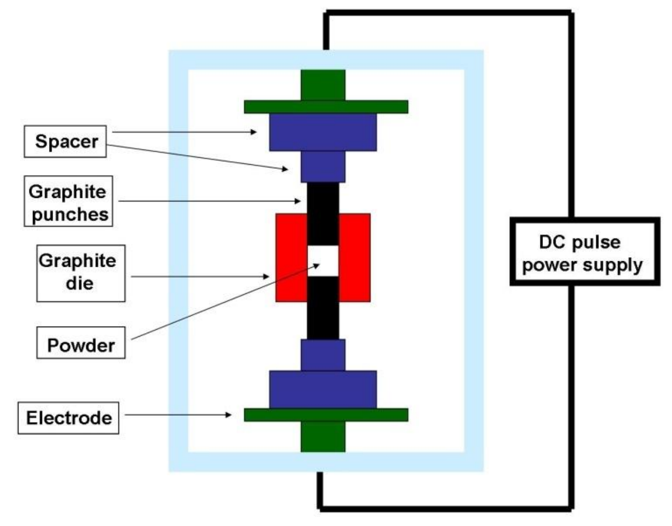


INTRODUCTION

Spark-plasma sintering (SPS) is an emerging powder consolidating technique, which provides potentially revolutionary capabilities to the processing of materials into configurations previously unattainable. SPS consists essentially of the conjoint application of high temperature, high axial pressure and electric current assisted sintering.

Spark-Plasma Sintering System (MPS) Dr. Sinter 515S at SDSU. Max Load 50kN, max current 1500 A

BRIEF HISTORY OF SPARK-PLASMA SINTERING

1906 A.G. Bloxam, GB Patent No. 9020

1922 F. Sauerwald, Apparatus for direct resistance heating to high temperatures under high pressure, Zeitschrift fur Elektrochemie, 28, 181-183

1933 G.F. Taylor, Apparatus for making hard metal compositions, US Patent N1,896,854

1955 F. V. Lenel, Resistance sintering under pressure, Trans. AIME, 203, (1), 158-167

1962 K. Inoue, Electric-Discharge Sintering, US Patent N3,241,956

1966 K. Inoue, Apparatus for Electrically Sintering Discrete Bodies, US Patent N3,250,892

1970s Research on Spark Sintering and Electric-Spark Sintering in USA and USSR, respectively

1980s Research on Plasma Activated Sintering in Japan

1990s SPS Machines are developed by Sodick Co. and Sumitomo Coal Mining Co. Ltd., Japan

2000s Extensive experimentation throughout the world on SPS of various material systems

SPS APPROACHES AND MODIFICATIONS

- Resistance Sintering
- Electric-Discharge Sintering
- Field-Assisted Sintering
- Electric Spark Sintering
- Electroconsolidation
- Discharge Powder Compaction
- Plasma Activated Sintering
- Electric Pulse Sintering
- Pulse Electric Current Sintering

COMMERCIALLY AVAILABLE SPS DEVICES

- Metal Processing Systems, Inc. (MPS) - North American representative of SPS Syntax, Inc., Japan.
- FCT (Fine Ceramics Technologies) Systeme GmbH, Germany.
- Thermal Technology LLC, USA.
- ELTec Co., South Korea.

HAP ($Ca_{10}(PO_4)_6(OH)_2$) background

- Hydroxyapatite has Ca/P ratio of 1.67 which is similar to bone
- HAP can decompose into TCP at about 1200-1450^{o}C
- HAP is a promising material for biomedical applications due to its biocompatibility
- Coating of HAP on implant can improve the osseointegration with bone
- Low mechanical strength of HAP limits its application

J.S. Sun et al. Biomaterials 1999;2:1807-1813

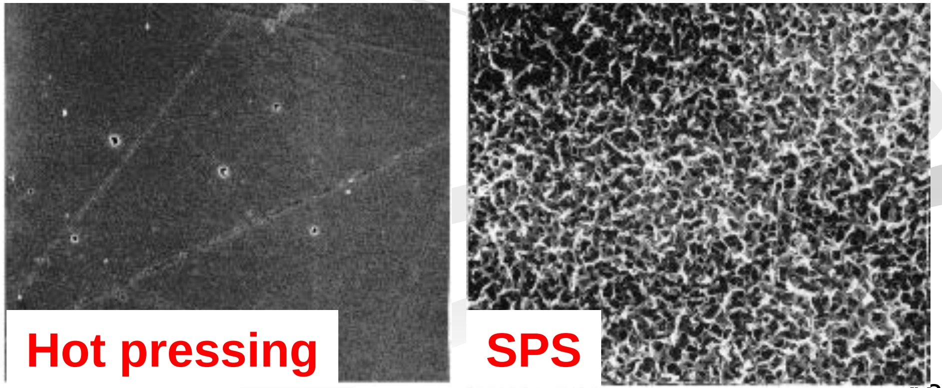
Spark-plasma sintering of HAp

- Several mechanical properties including fracture toughness, Knoop hardness, and Young's modulus show the maximum value at maximum sintering temperature of 950^{o}C

	RD	Knoop hardness	Young's modulus	Fracture toughness
950^{o}C	99.6%	~5.5GPa	~115GPa	1.25MPam$^{1/2}$

- Y.Moriyoshi et al. fabricated transparent HAP at maximum sintering temperature 1200^{o}C by SPS for window application.

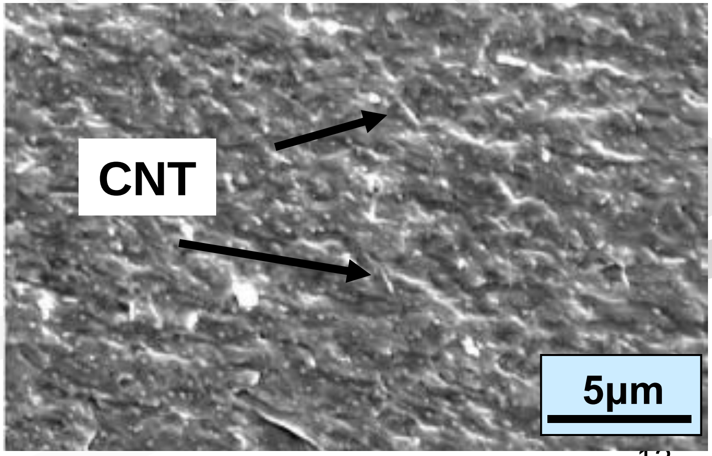
- Hydroxyapatite prepared by SPS is more bioactive than that prepared by conventional hot pressing.



Y.W.Gu et al. Biomaterials 2002;23:37-43, Y.Moriyoshi et al. J.Am.Ceram.Soc. 2005; 88:243-245,A.Nakahira et al.J.Biomed. Mater Res.2002;62:550-557

HAP based composite

- One of the common approaches to reinforce pure HAP is to add a second phase such as Ti_3SiC_2 , Zirconia, and CNT
- The reinforcement of HAP with Ti_3SiC_2 by SPS at 1200^oC shows increasing in elastic modulus, fracture toughness, bending strength but decreasing in Vickers hardness with increasing content of Ti_3SiC_2
- The addition of ZrO_2 to HAP can reduce the pore and grain size
- 2vol% CNT-HAP composite was fabricated and found that the Young's modulus and hardness are higher than HAP at sintering temperature of 1100^oC



W.N.Chen et al. Mater.Sci.Eng.C 2009;29:44-49, Y.F.Zhen et al. J.Am.Ceram.Soc 2006;89:743-745

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Research objectives and tasks

Bio-inspired tailored HAP-based powder composite for dental applications

Study the structure and mechanical properties of natural dental materials

Mechanical properties measurement:
- Micro and nano-indentations
- Tensile and compression tests

Structure characterization:
- SEM investigation
- X-ray diffraction

Conclusions of characterization of natural materials

Fabrication of bio-inspired tailored HAP-based composite

Green specimen processing
- Freeze drying
- Ultrasonication
- Ball milling

Spark plasma sinterintg
- Pressure assisted
- Free pressureless

- CNT reinforced HAP composite
- HAP-based composite with microchannel structure
- Functionally graded CNT-HAP composite

Materials with tailored structures for dental applications

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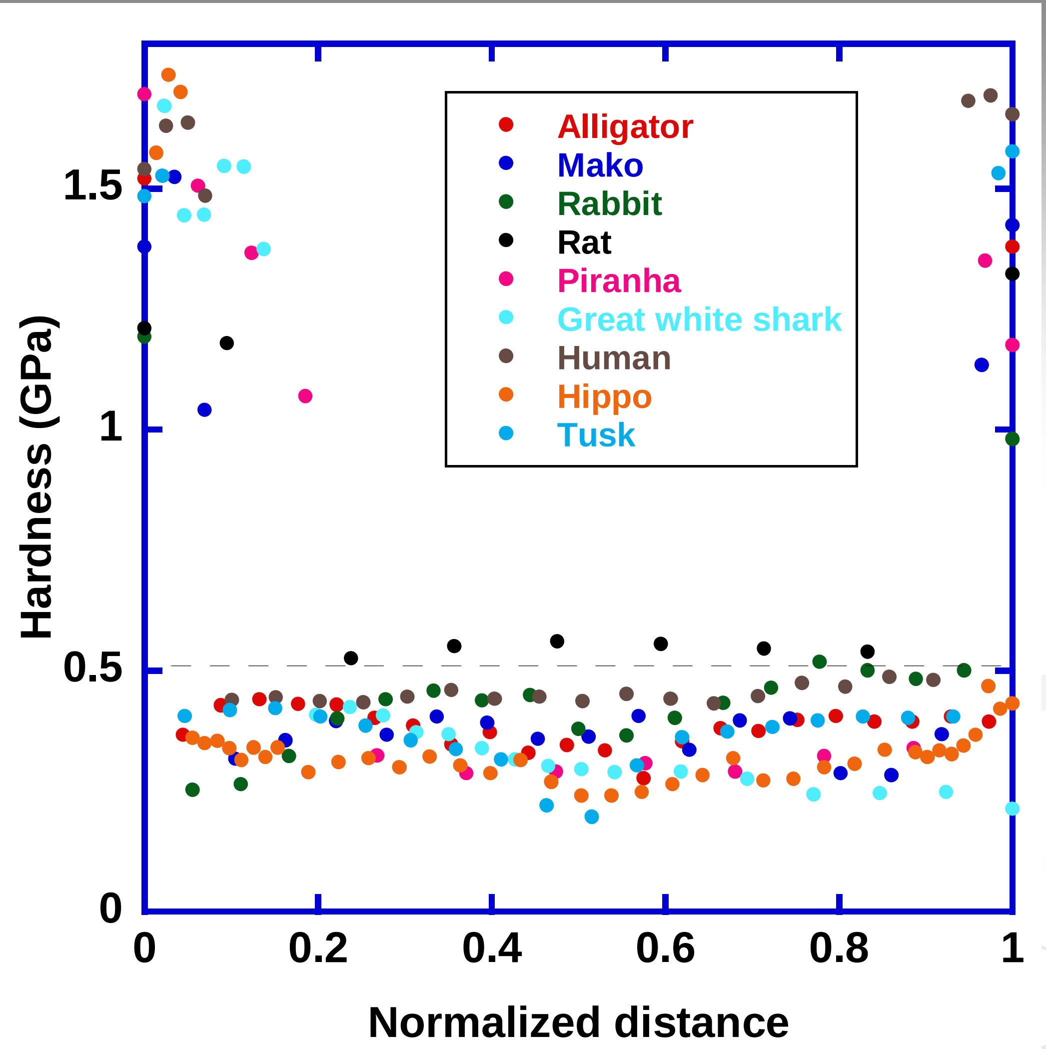
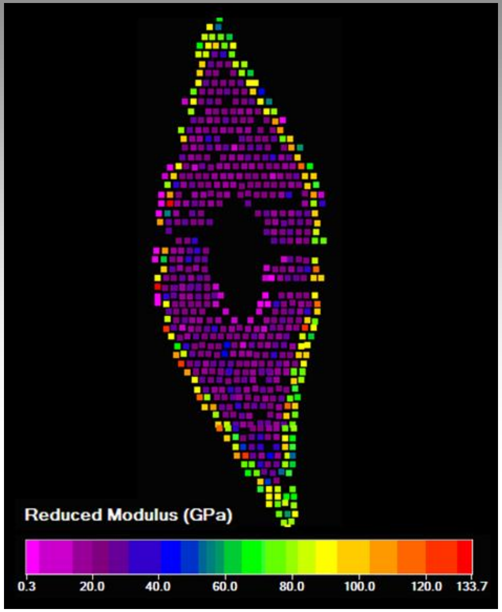
Micro-indentation test on several animal teeth

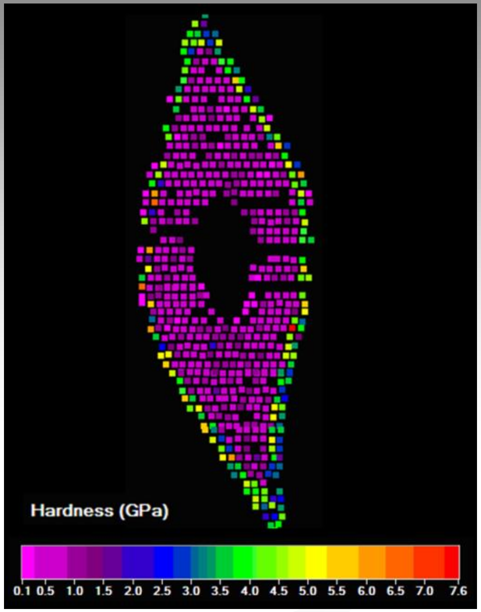


	Human	Great white shark	Mako	Piranha	Rabbit	Rat	Alligator	Tusk	Hippo
Enamel(GPa)	1.70±0.08	1.56 ±0.19	1.30 ±0.20	1.36±0.22	1.26±0.15	1.20±0.08	1.45±0.10	1.52±0.04	1.67±0.09
Dentin(GPa)	0.45±0.02	0.31 ±0.07	0.36±0.04	0.31±0.02	0.42±0.08	0.55±0.01	0.49±0.04	0.36±0.06	0.32±0.05

Nano-indentation test on great white shark and piranha teeth

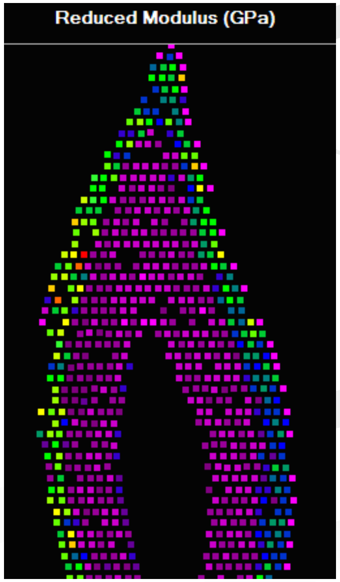
Piranha

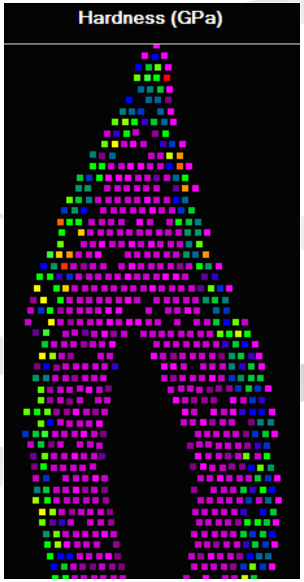




Reduced modulus mapping **Hardness mapping**

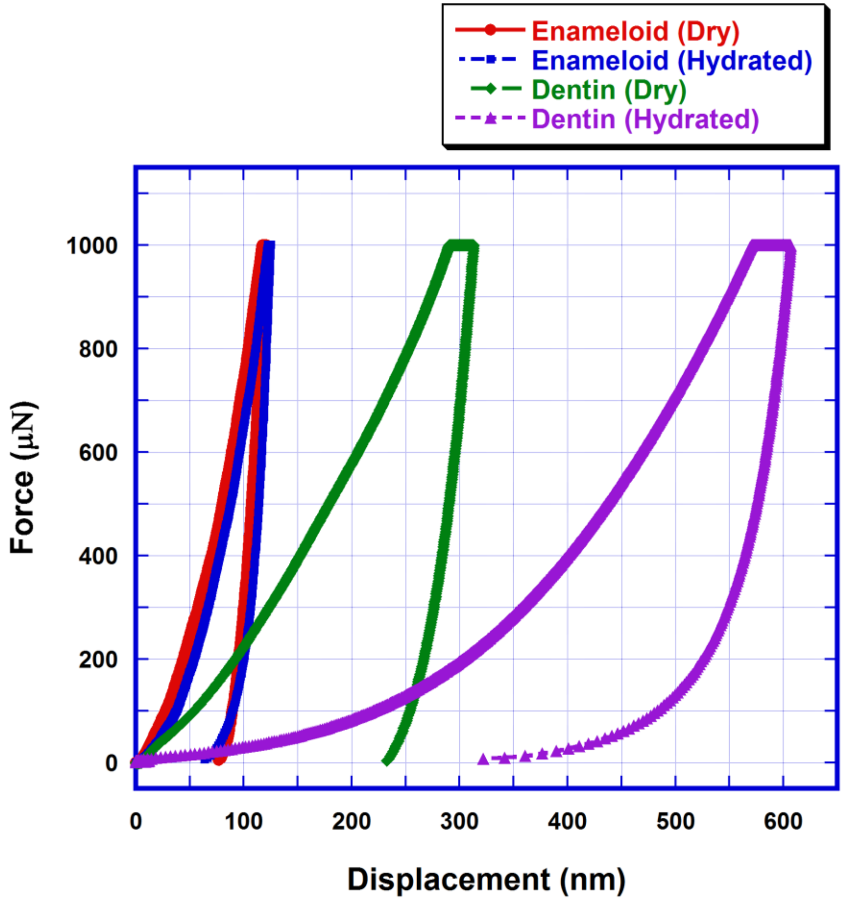
Great white shark



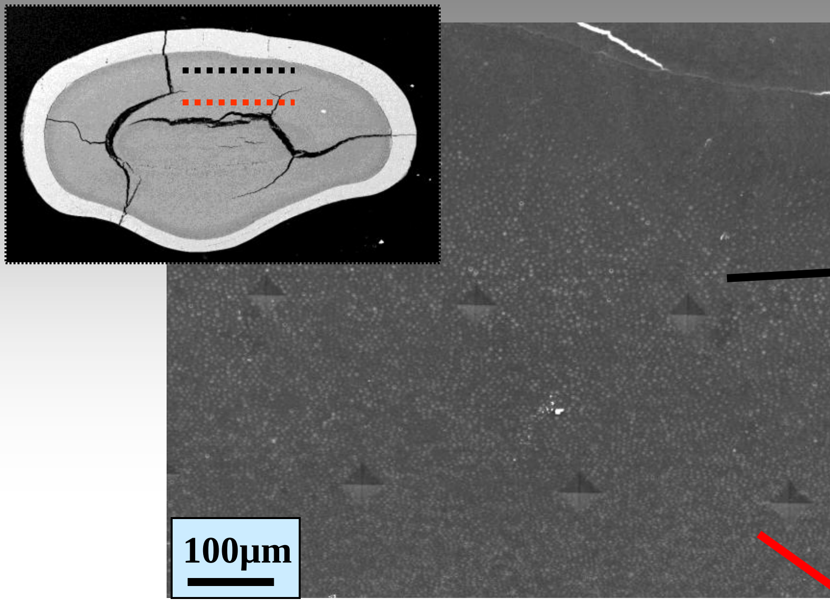


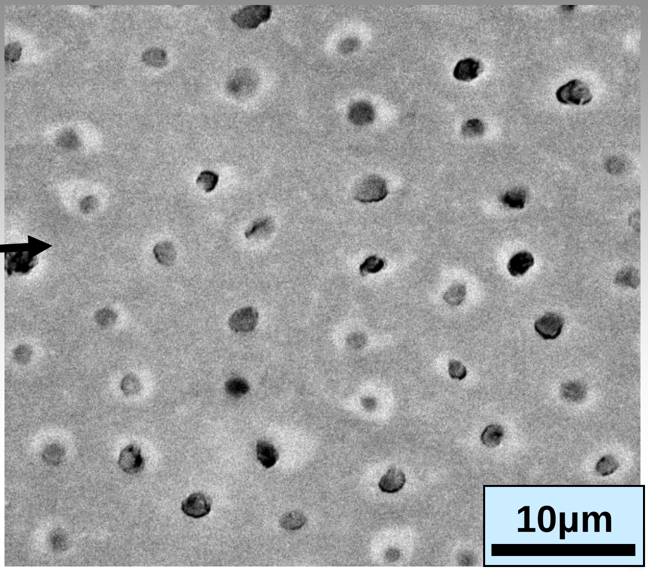
Nano-indentation in dry and hydrated condition

Load and unload curve of shark tooth

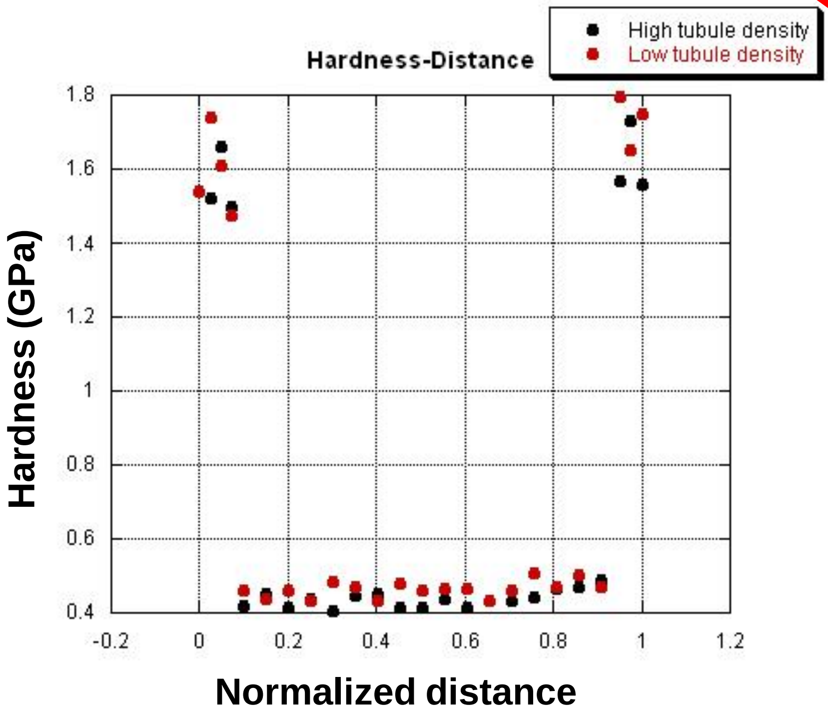


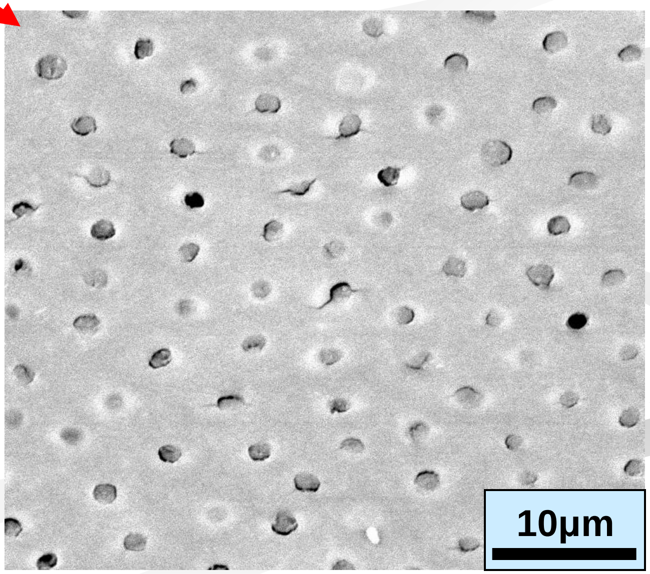
Effect of tubule density on human dentin





outer part (24000/mm^2)

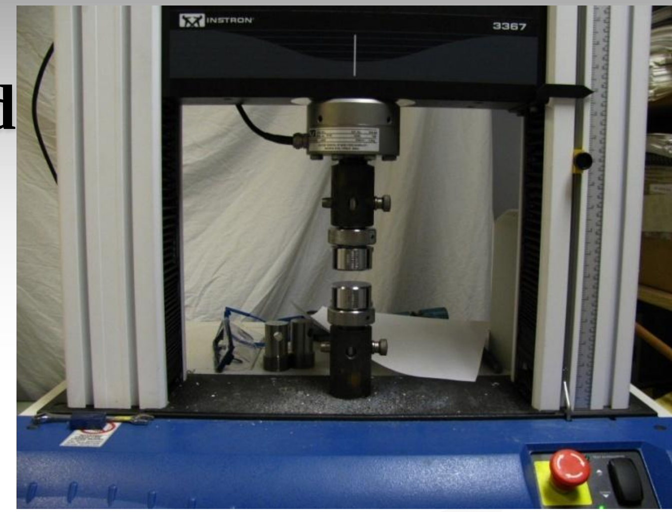


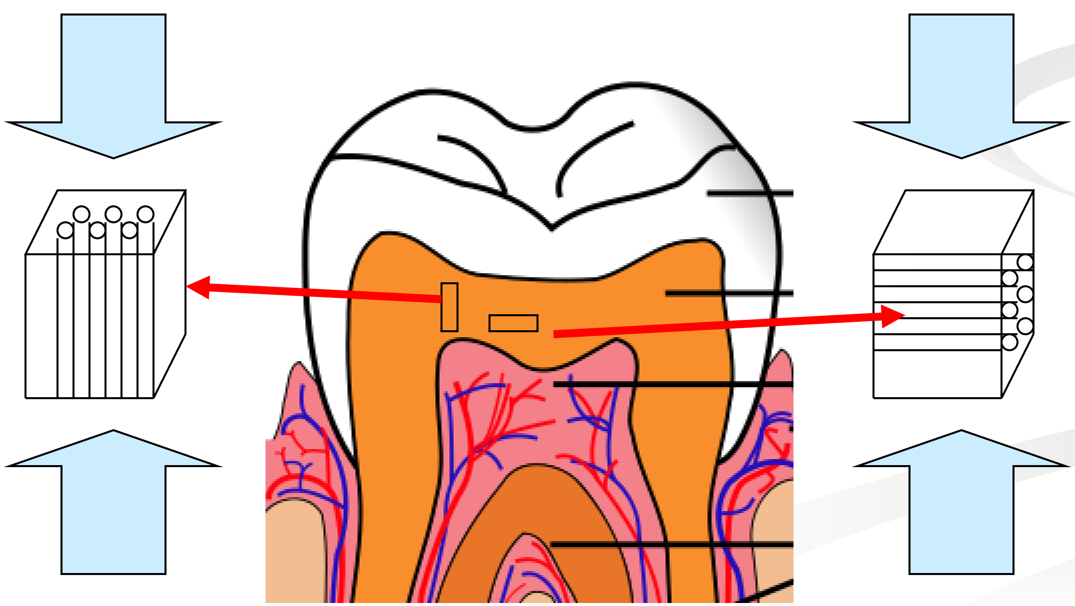


inner part (44000/mm^2)

Compression test on human dentin: Longitudinal vs Transverse

- Specimens are cut from one tooth and divided into two groups: longitudinal and transverse.
- The aspect ratio of the sample is 1.5 and size is about 2mm*2mm*3mm.
- The strain rate: 10^{-3} s^{-1}

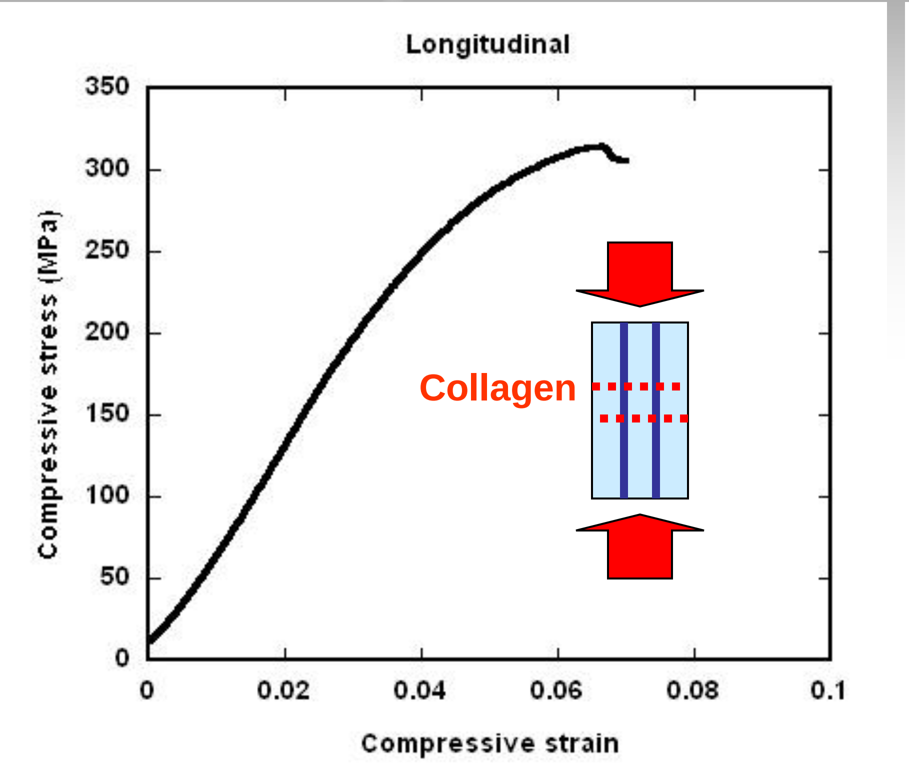


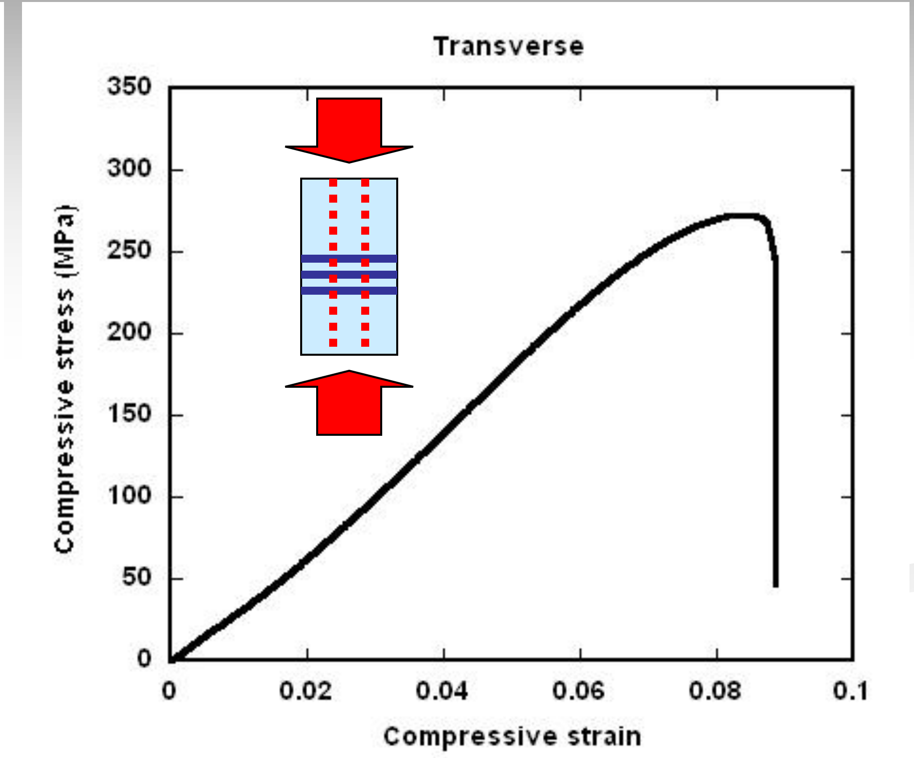


Longitudinal

Transverse

Compression test results on human dentin

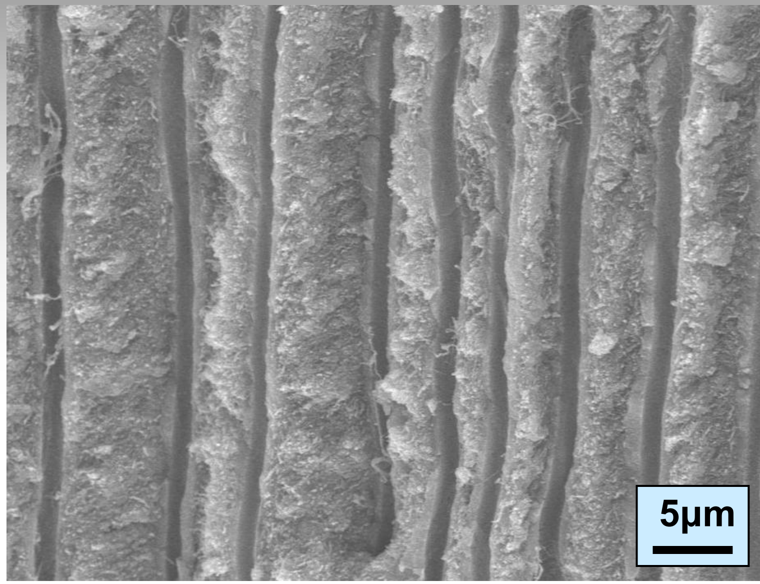


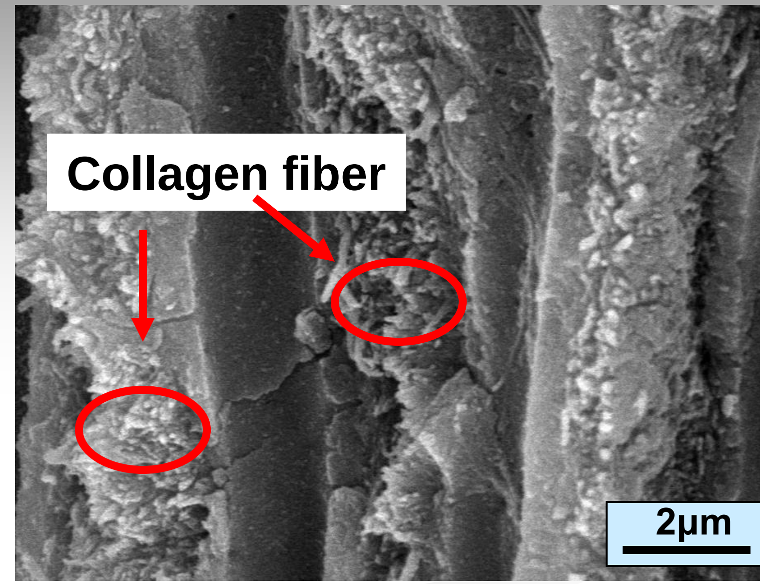


	Compression strength(MPa)	Young's modulus(GPa)
Longitudinal	215±63.9	5.82±0.86
Transverse	207±56.5	3.38±0.30

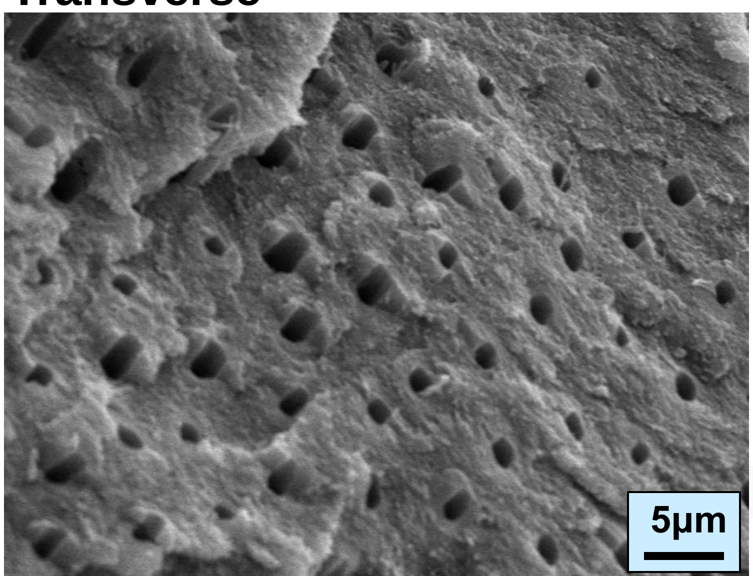
SEM of compression fracture surfaces: human dentin

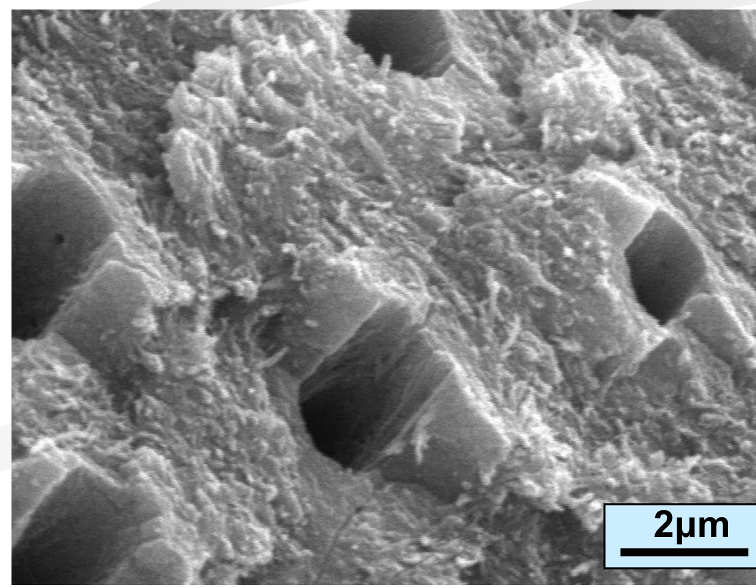
Longitudinal



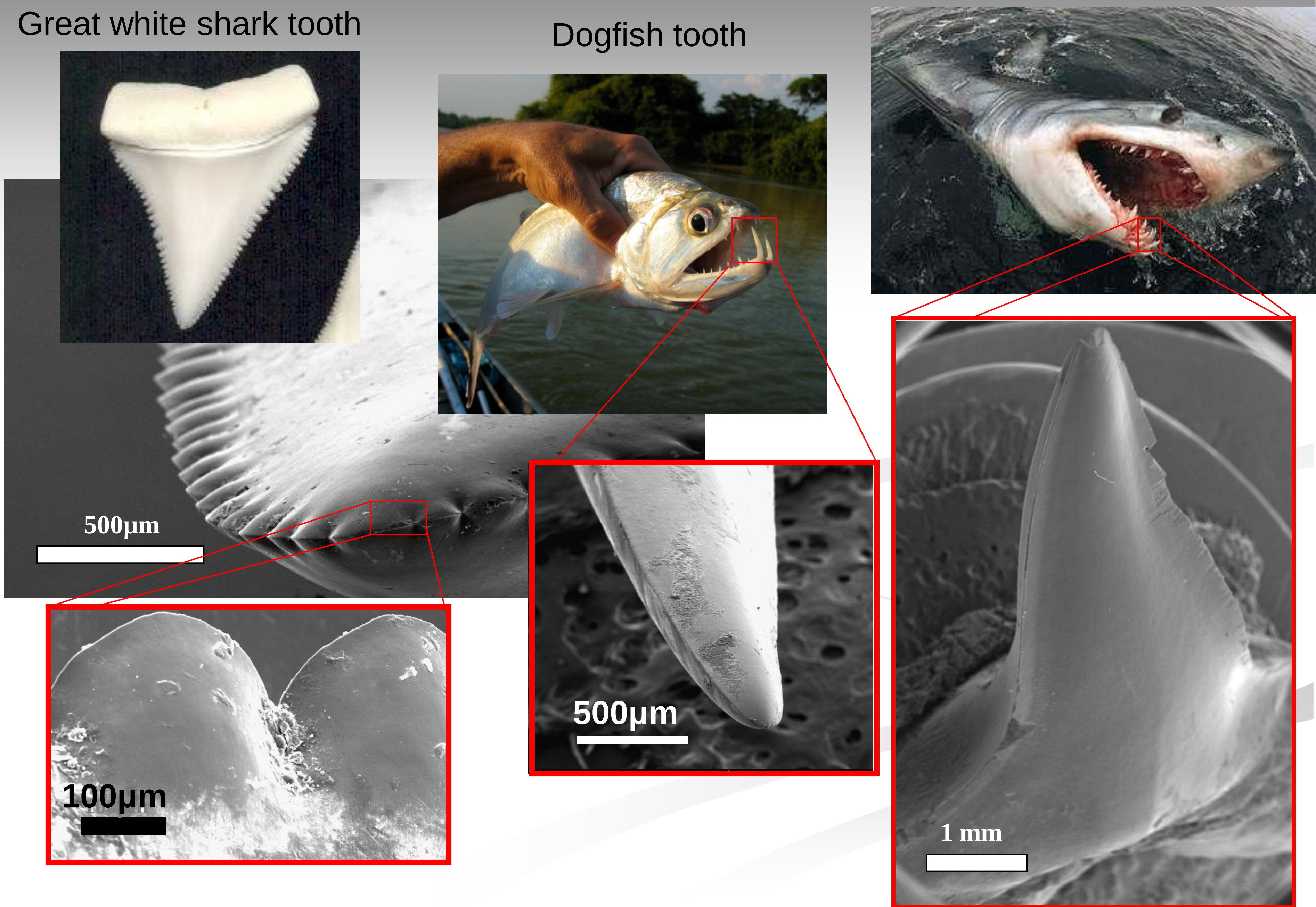


Transverse

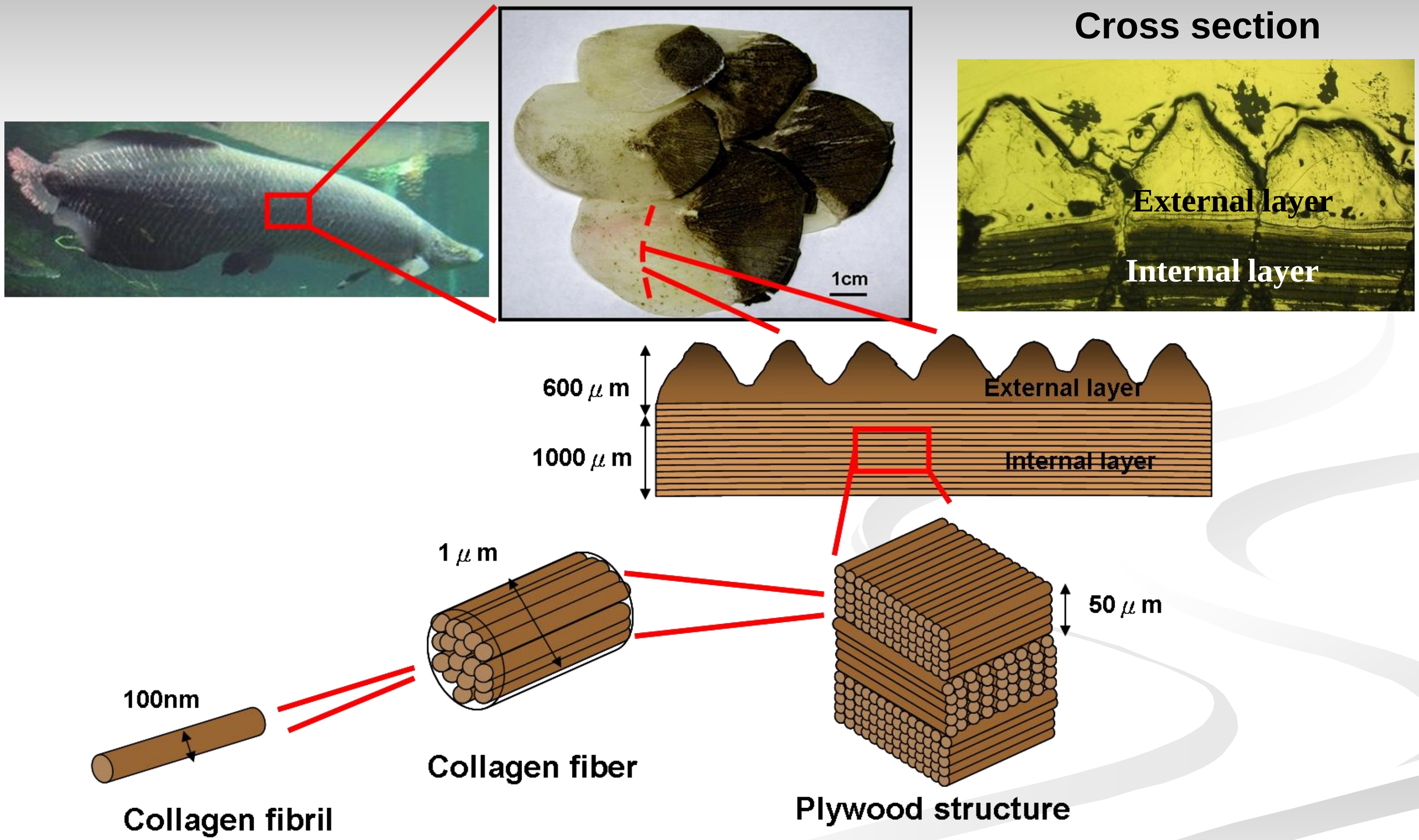




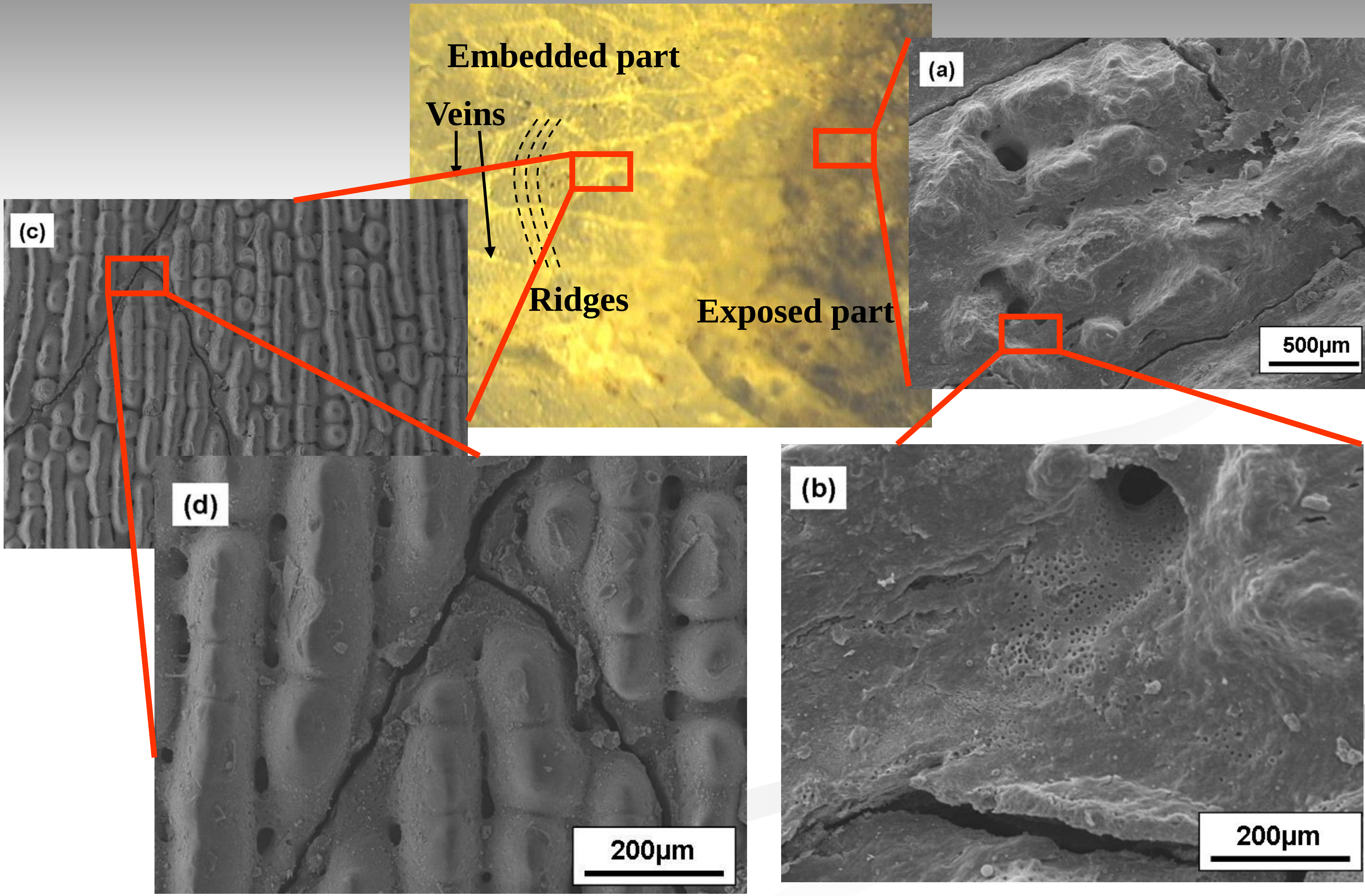
Microstructure analysis of sharp teeth



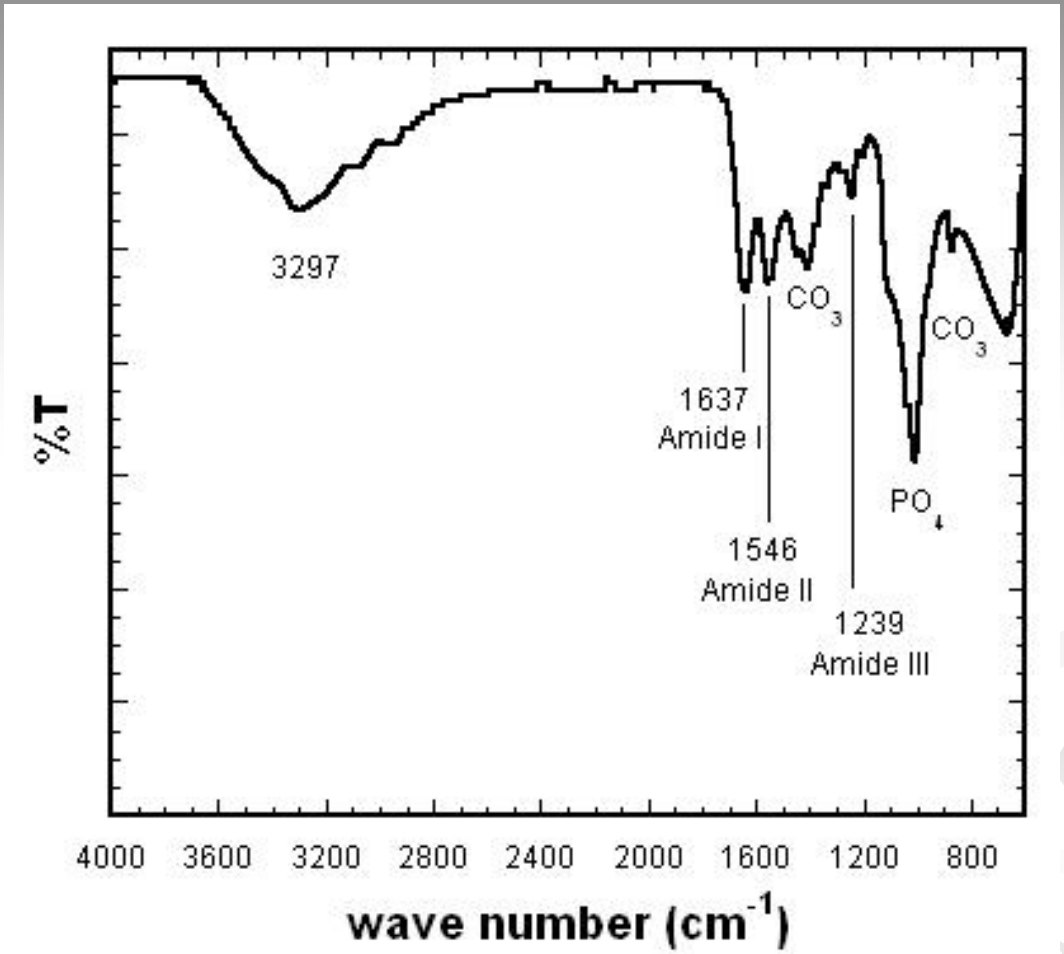
Hierarchical structure of *Arapaima gigas* scale



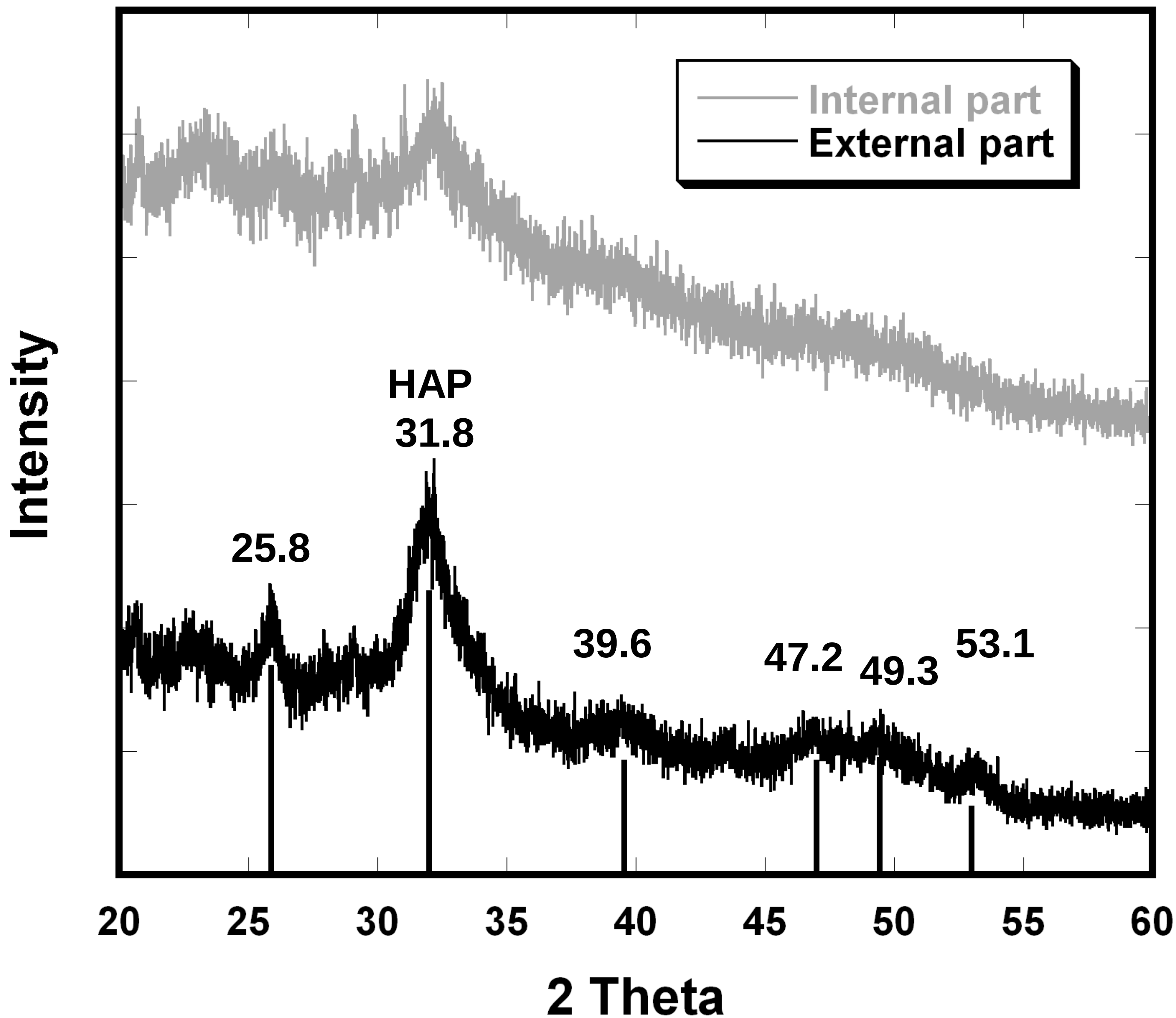
SEM image of the scale surface



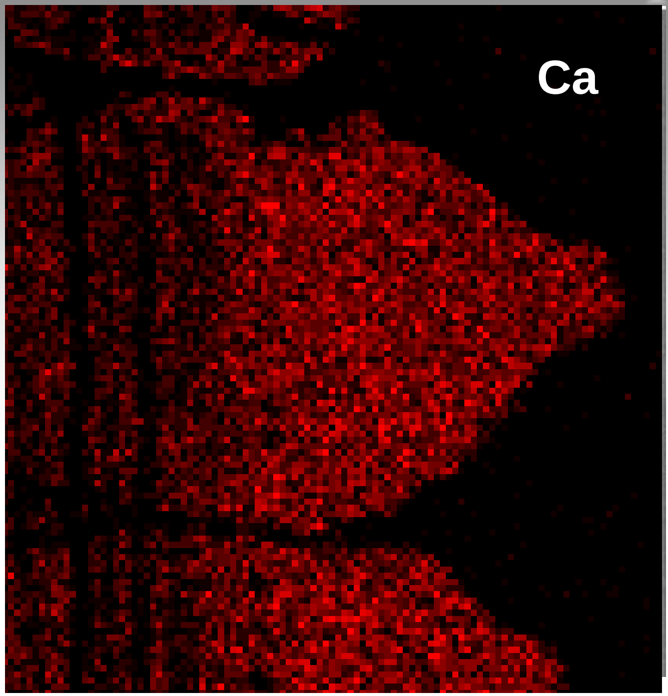
Fourier transform infrared spectroscopy of A.G. scale

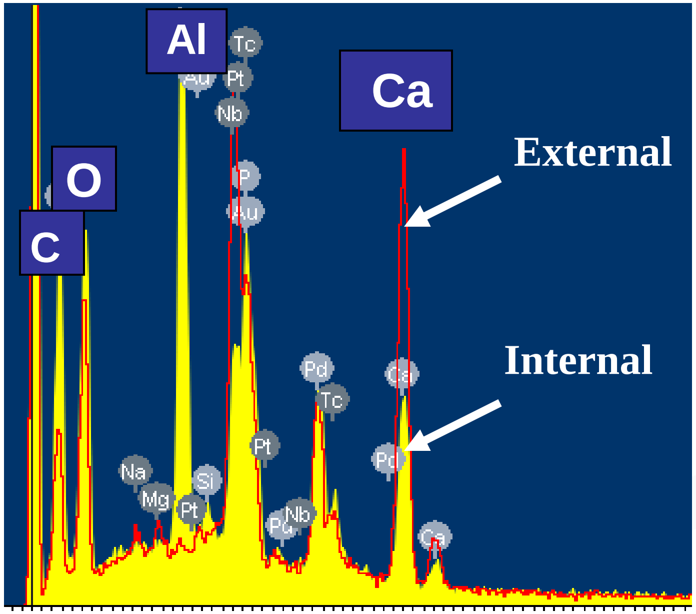


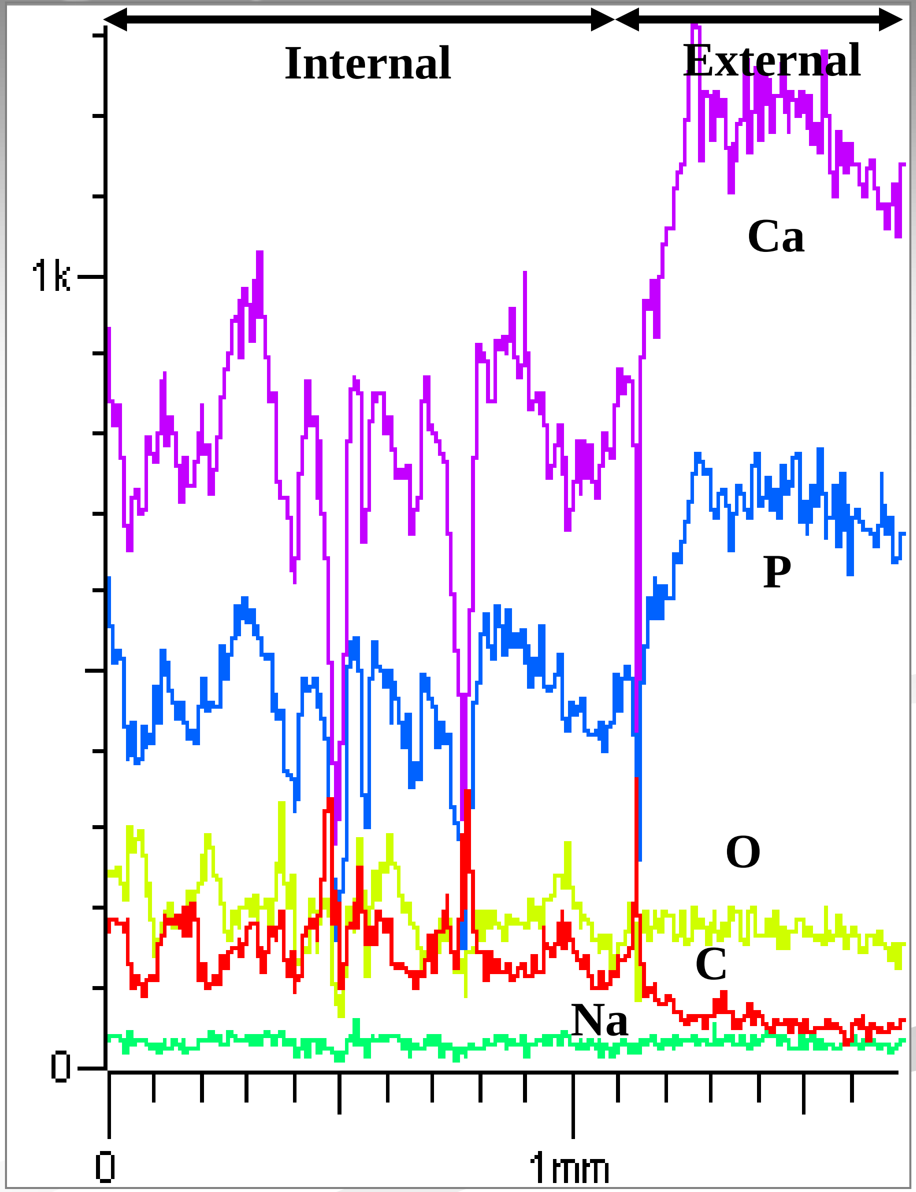
	Present study	Torres et al.	Toshiyuki et al.
Amide I (cm^{-1})	**1637**	**1662**	**1657**
Amide II (cm^{-1})	**1546**	**1560**	**1520**
Amide III (cm^{-1})	**1239**	**1242**	**1447**


Internal part
External part
HAP
31.8
25.8
39.6
47.2
49.3
53.1
Intensity
20
25
30
35
40
45
50
55
60
2 Theta

EDS and element mapping analysis of A.G. scale

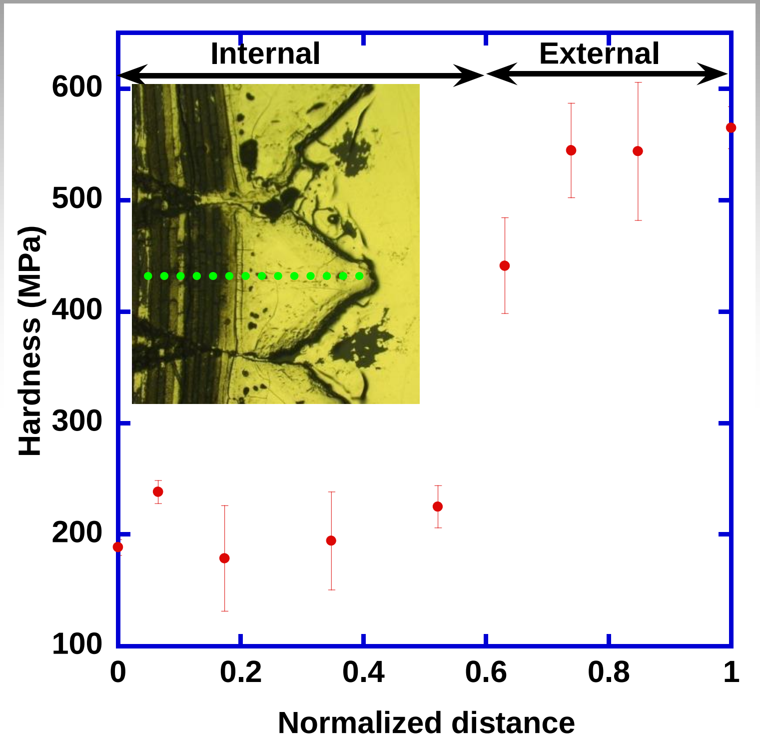


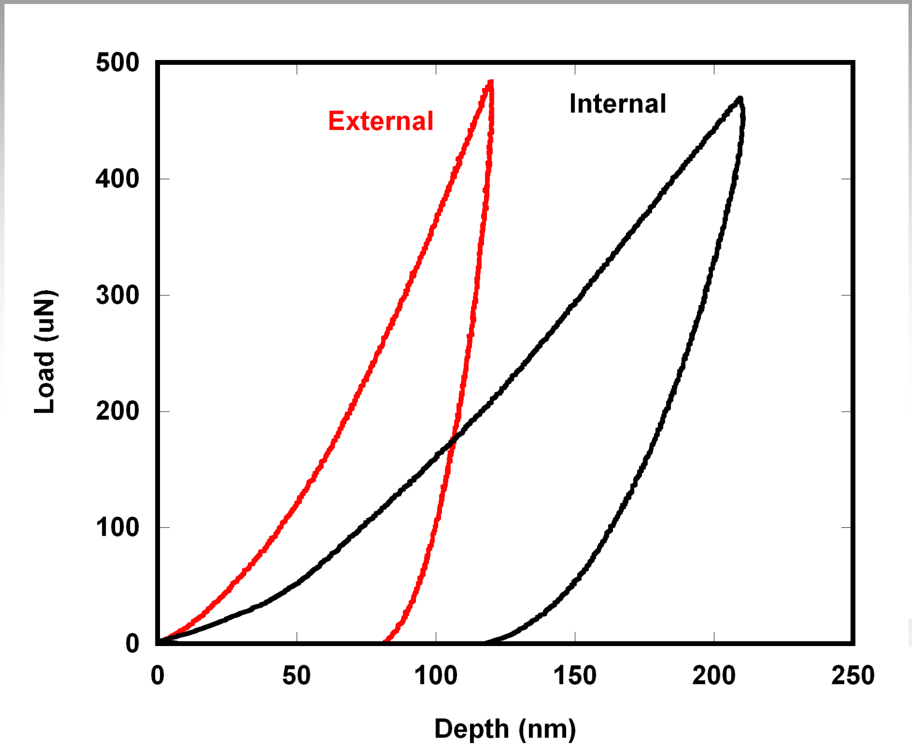




Y.S.Lin, E.A.Olevsky, M.A.Meyers et al.
J.M.B.B.M. 2011; 4: 1145-56

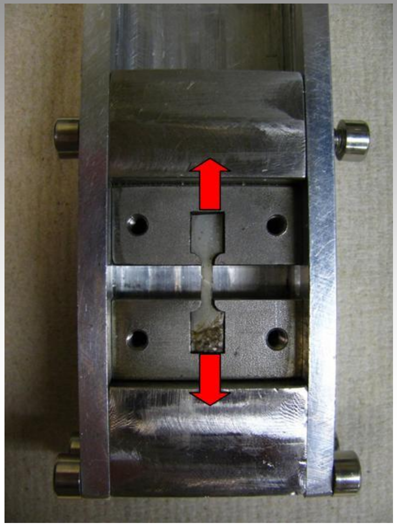
Micro and nano-indentation tests of A.G.scale



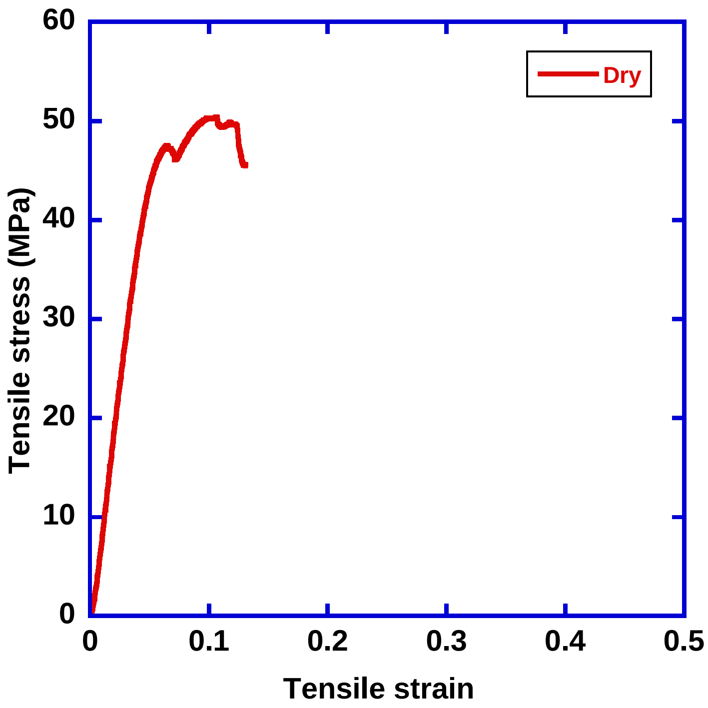


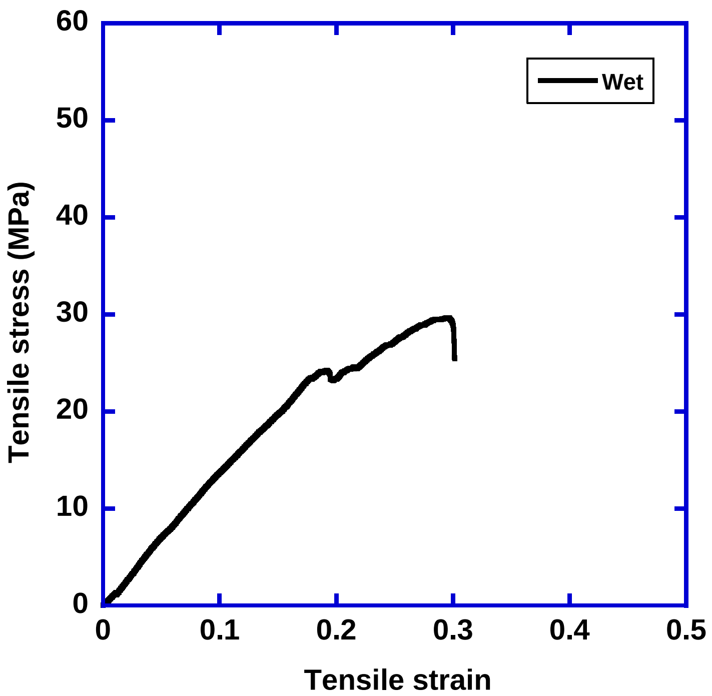
	External	Internal
Nanohardness (GPa)	2.0±0.4	0.6±0.1
Elastic modulus (GPa)	46.8±8.9	16.7±4.0

Tensile tests of A.G. scale: dry vs. wet

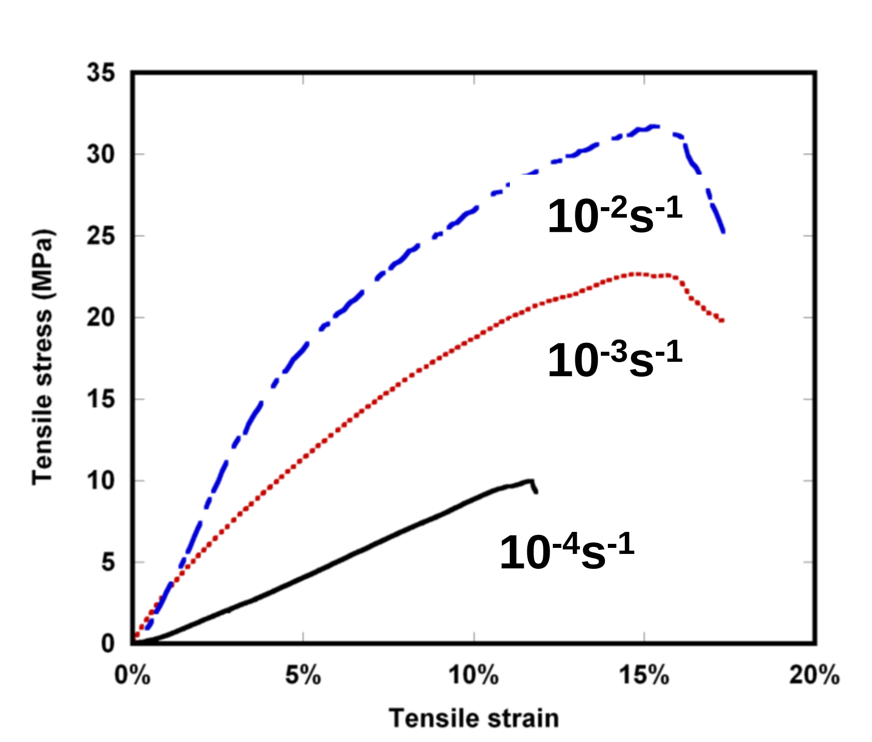


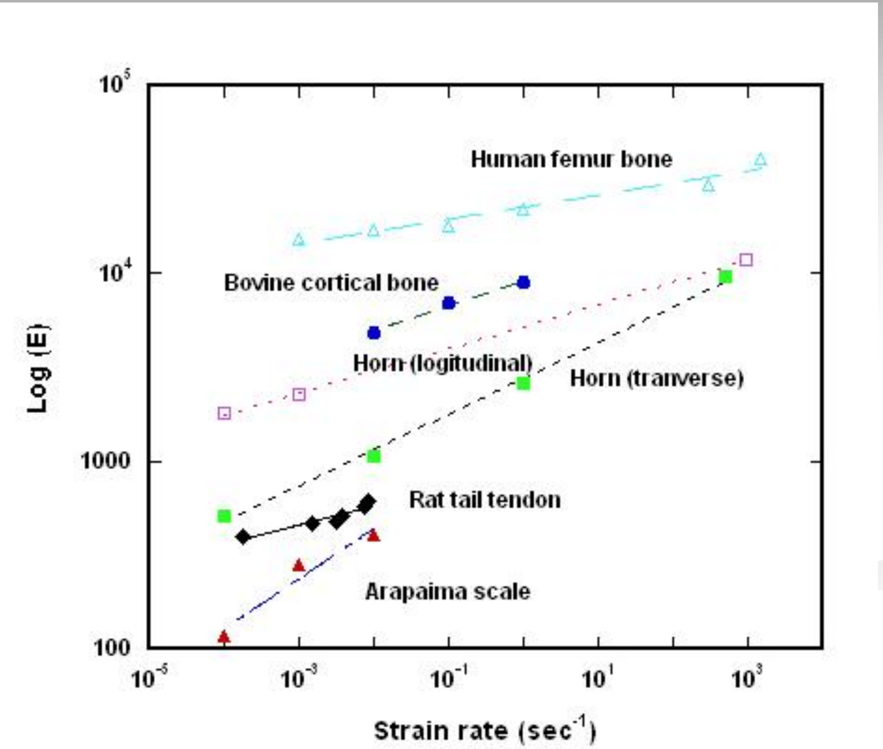
	Dry	Wet
Water content weight %	16%	30%
Tensile strength (MPa)	48.59±2.63	30.38±2.23
Young's modulus (MPa)	1290.37±116.27	118.03±28.23





Tensile test on A.G. scale: strain rate effect



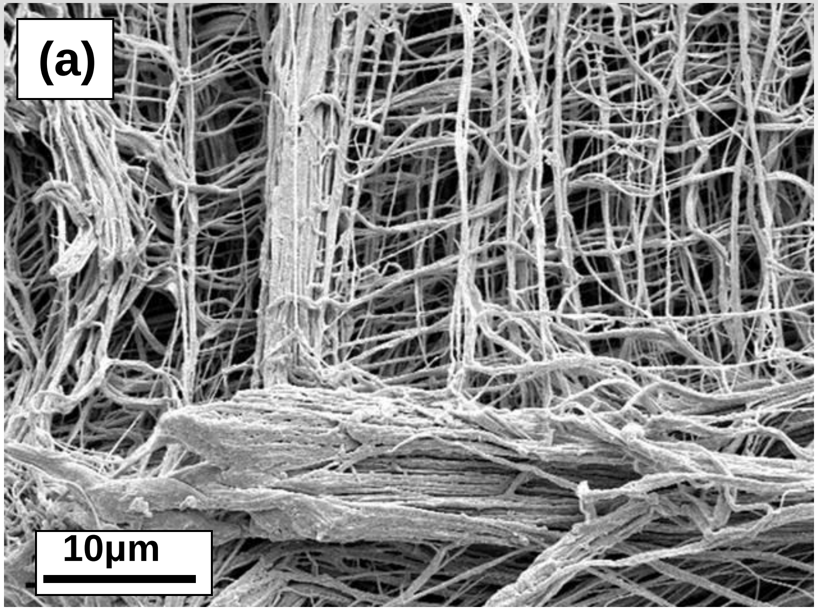


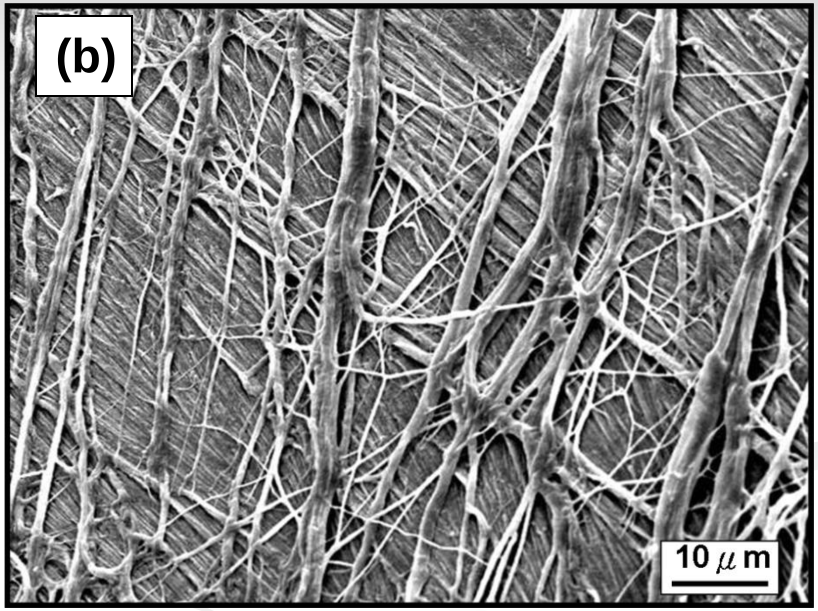
Ramberg-Osgood : $E=C(\acute{\varepsilon})d$

E: elastic modulus, $\acute{\varepsilon}$:strain rate , C, d are experimental parameters

P.Y.Chen, J.McKittrick et al. Acta Biomaterialia 2010; 319-330

SEM of tensile fracture: A.G. scale

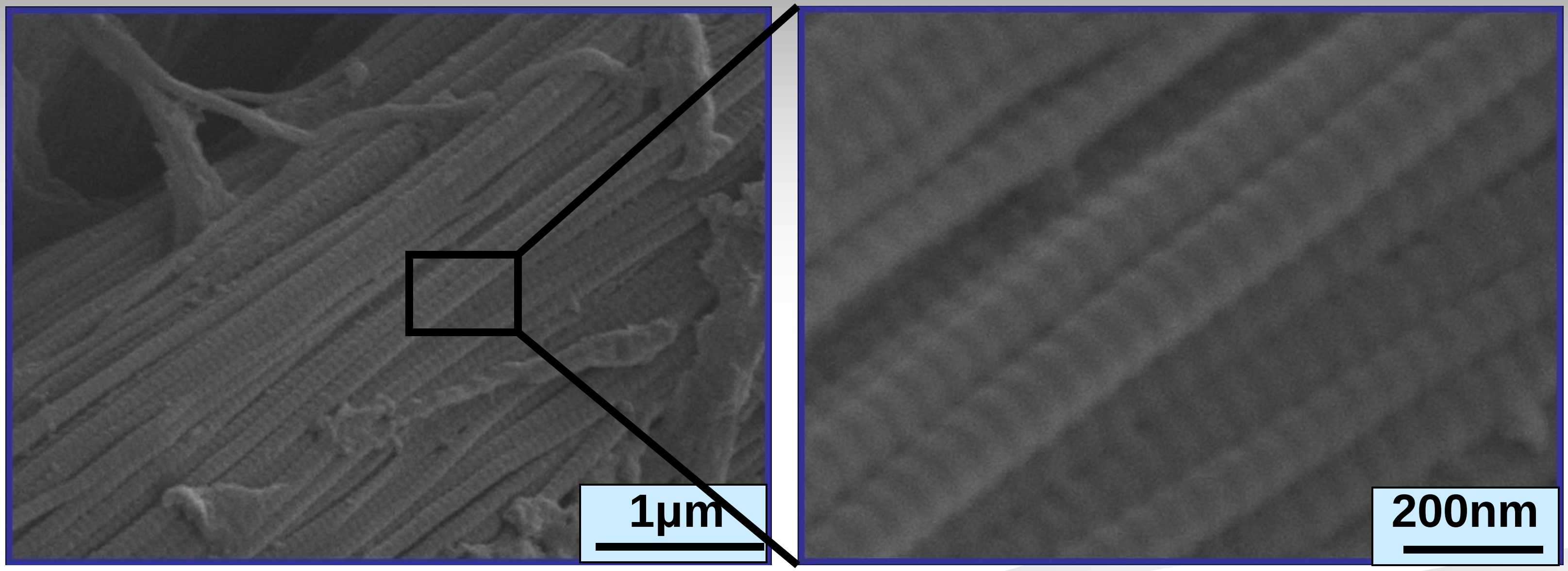




(a) SEM images showing pulling out of collagen bundles

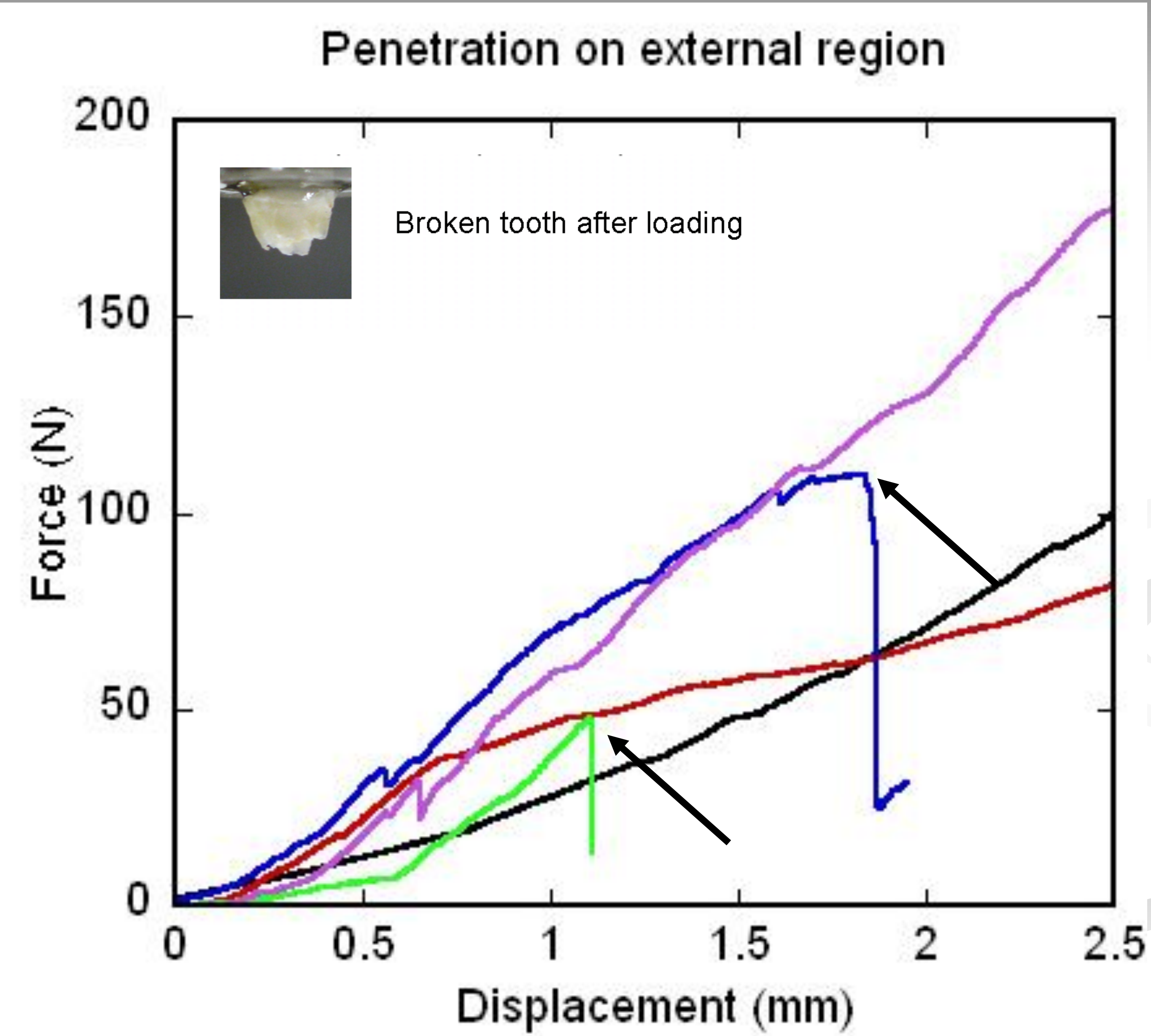
(b) SEM images showing collagen fibers orient in the same direction in each layer

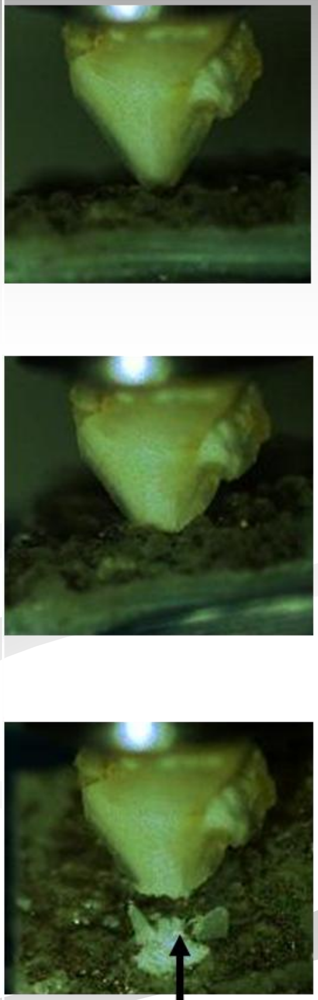
Microstructure of scale after demineralization



SEM images of demineralized scale showing the periodic structure of the collagen

Penetration test: piranha tooth vs A.G.scale





M.A.Meyers, Y.S.Lin, E.A.Olevsky et al. Advanced Biomaterials 2012

Outline

- **Introduction: Literature survey**

  - Basic components and structure of human and animal dental materials

  - Background of spark-plasma sintering, material system (HAP), and consolidation of HAP-based materials
- **Research objectives and tasks**
- **Characterization of natural dental materials and structures of Arapaima scale**
- **Fabrication of HAP and CNT-HAP tailored powder composites**
- **Conclusions**

Fabrication of HAP and CNT-HAP tailored powder composites: Material system

- Hydroxyapatite($Ca_{10}(PO_4)_6(OH)_2$)

  Melting point: 1670℃, density: 3.14 g/cm^3

  The main component in human bone and tooth

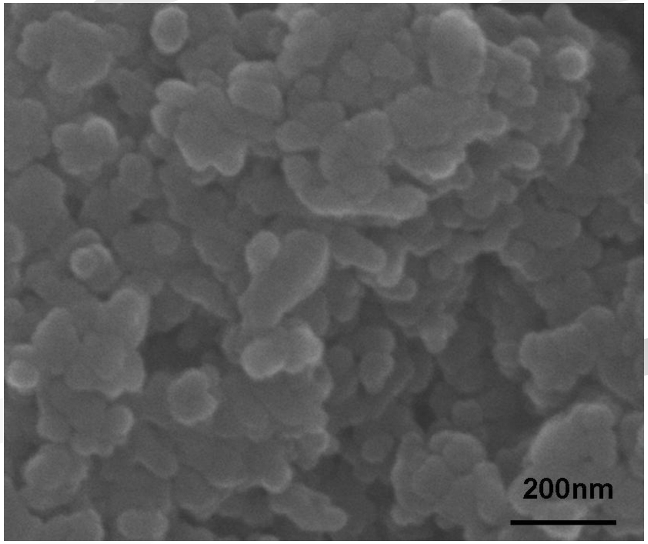
  Used for medical application due to its biocompatibility

- MWCNT

  Density 2.1 g/cm^3

  Inner diameter of 5-10 nm, outer diameter of 20-30 nm

  Specific area 110 m^2/g



SEM of raw HAP powder

Preparation of different volume concentrations of CNT-HAP powders

CNT+DI water
SDS(Sodium Dodecyl sulfate)

HAP powder

HAP+CNT solution

↓

High ultrasonication

↓

Freeze with LN

↓

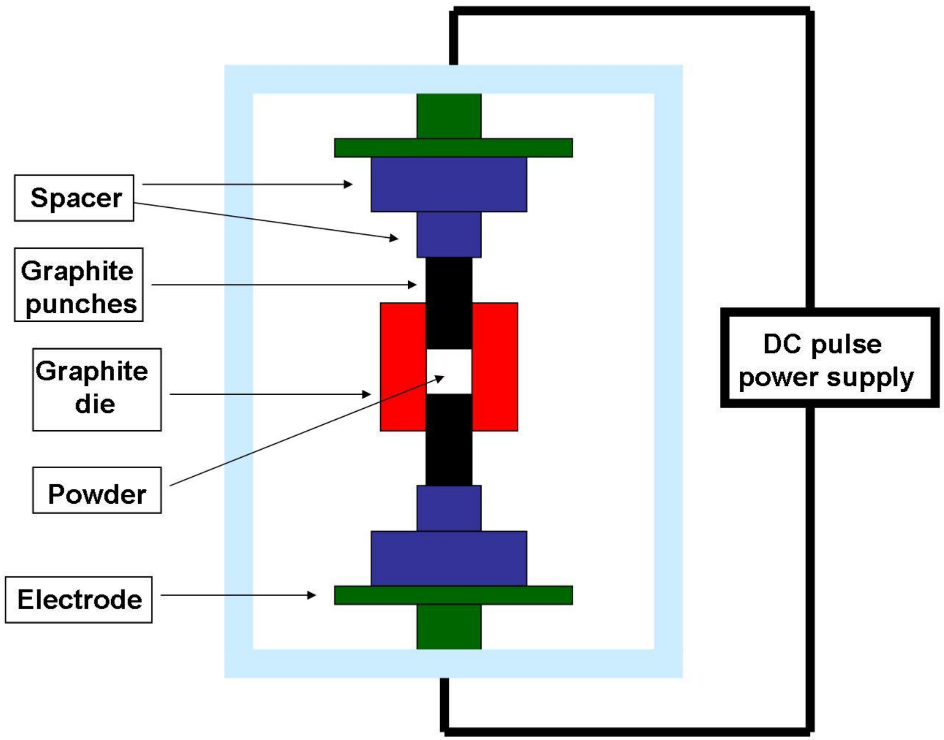
Remove water by freeze drying

Freeze dryer

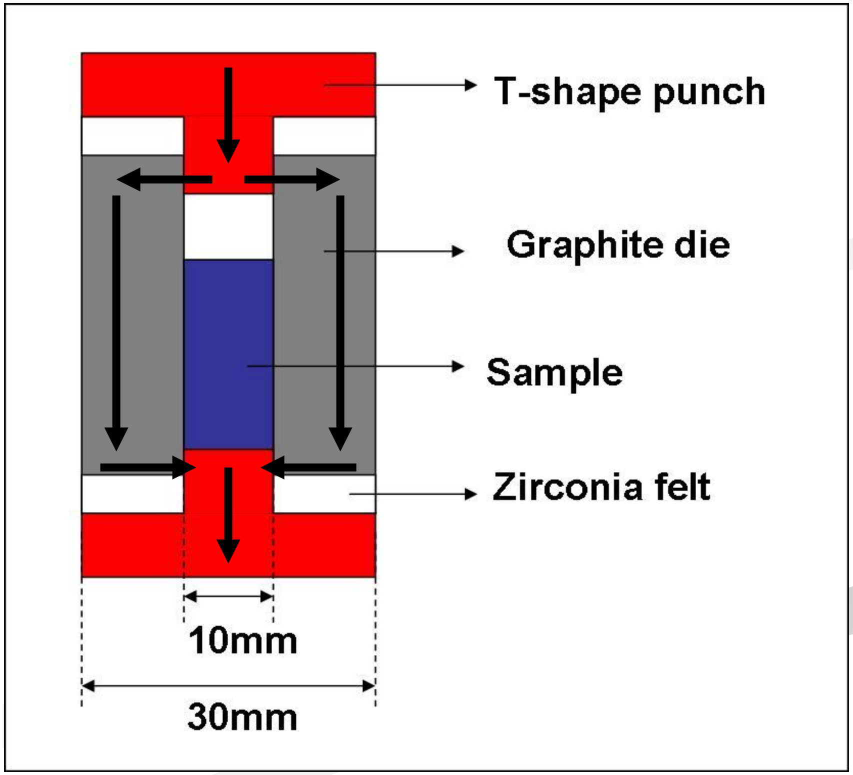
High ultrasonication

Different sintering process: (free pressureless spark plasma sintering)

- Conventional sintering
- Spark plasma sintering
- Free pressureless spark plasma sintering

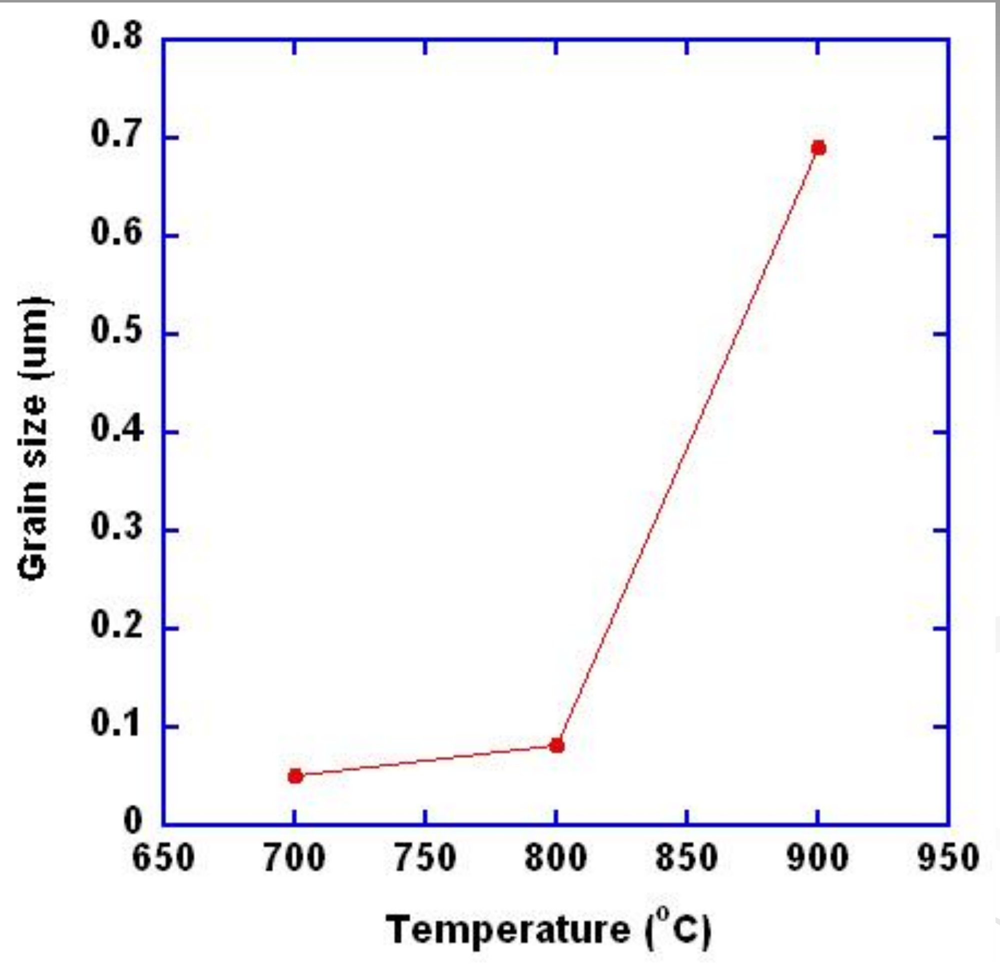


Spark plasma sintering



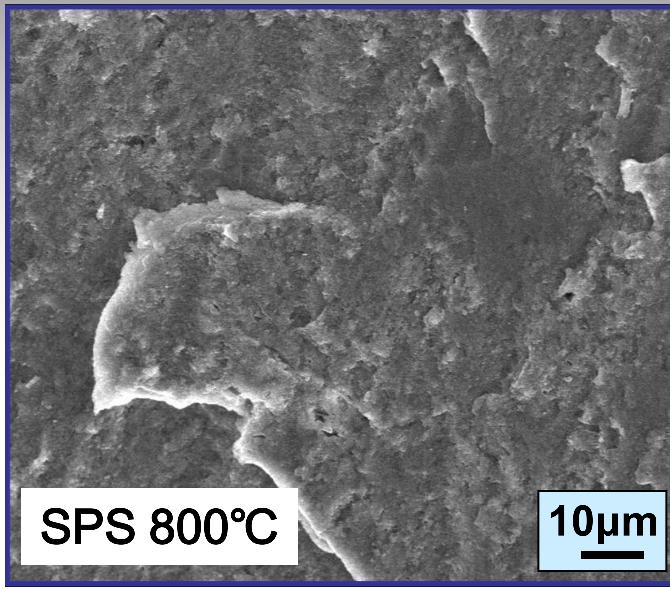
Free pressureless spark plasma sintering

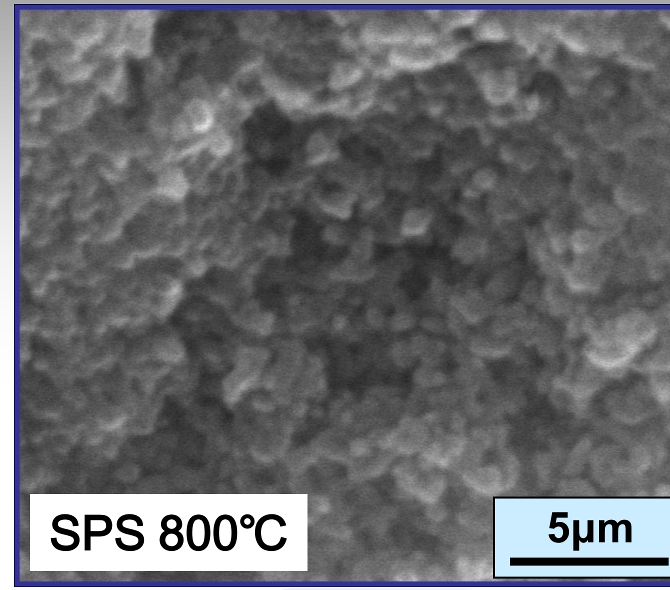
Pure HAP powder processed by SPS: relative density

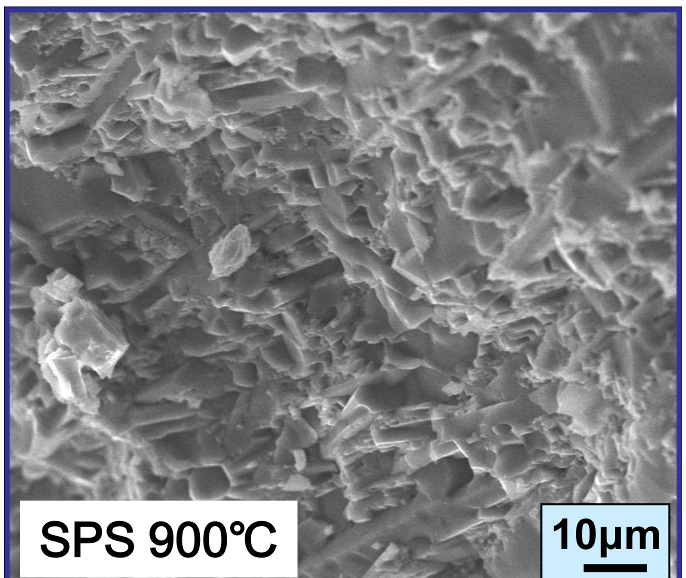


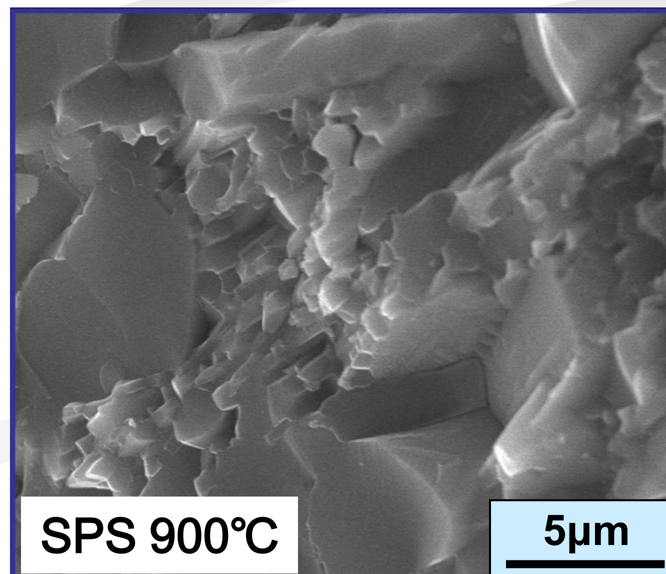
	700 ℃	800℃	900℃
Relative density(%)	97.38	97.67	98.2
Grain size (μm)	0.052	0.082	0.692

Microstructure of the fracture surface of HAP SPS at 800 and 900℃

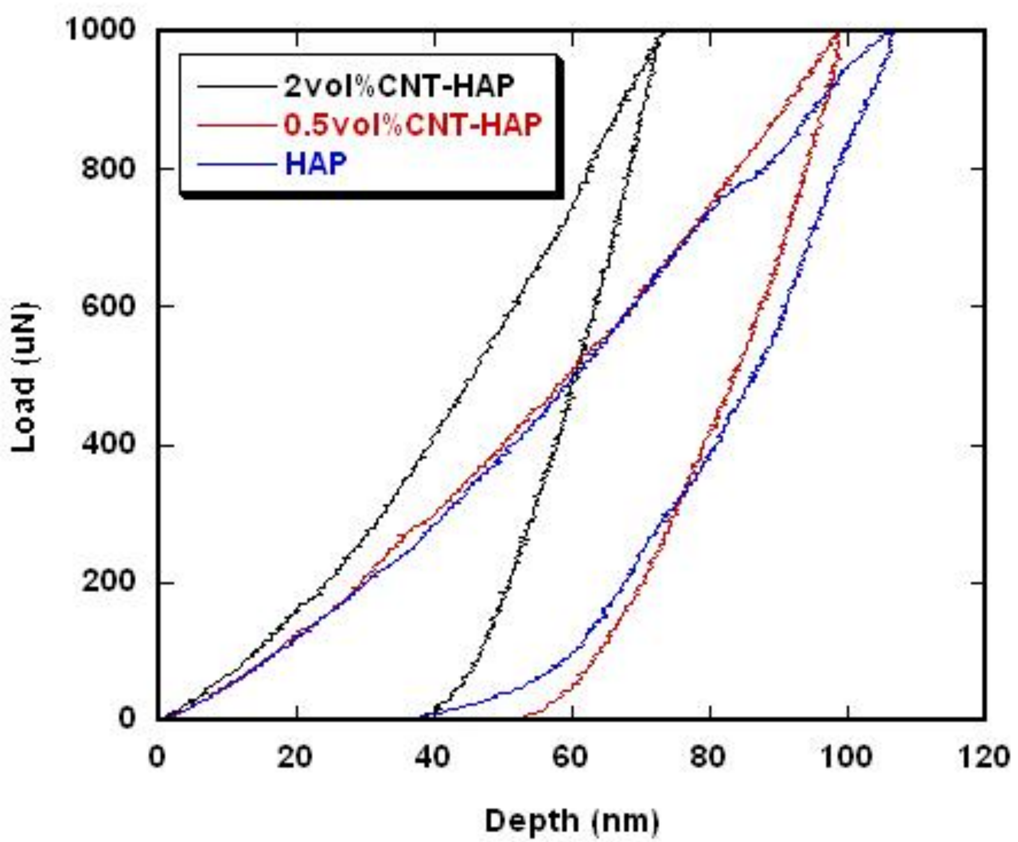


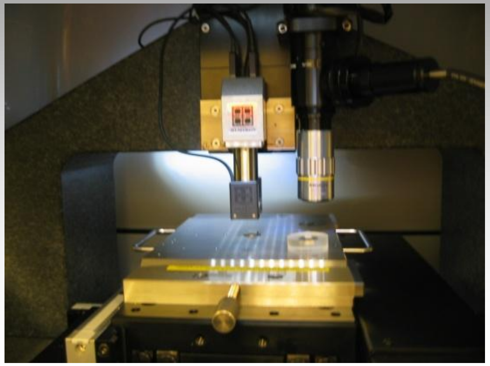






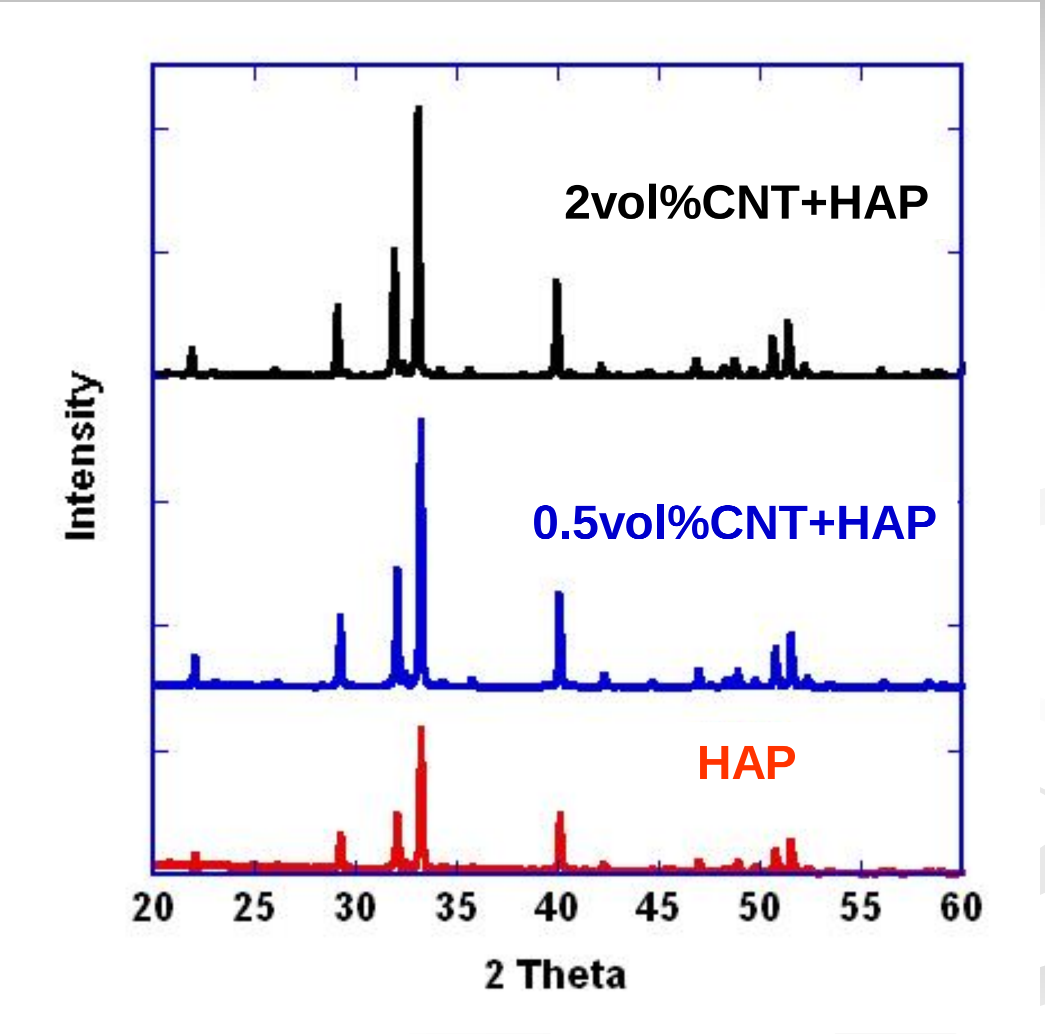
Nanoindentation of HAP and CNT-HAP composites processed by SPS





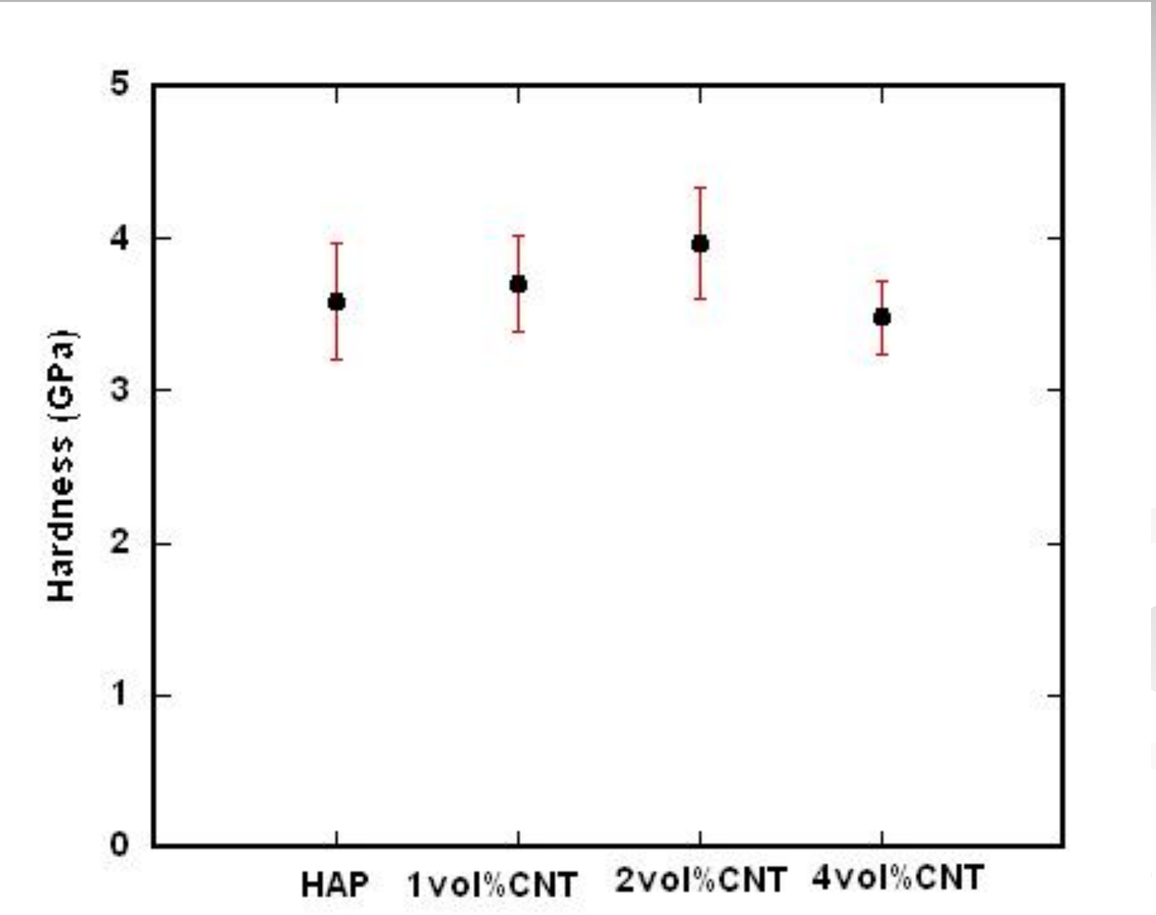
	HAP	0.5vol%CNT-HAP	2vol%CNT-HAP
Elastic modulus (GPa)	67.7	71.4	125.7
Hardness (GPa)	6.6	7.9	9.2

XRD of different vol% of CNT-HAP



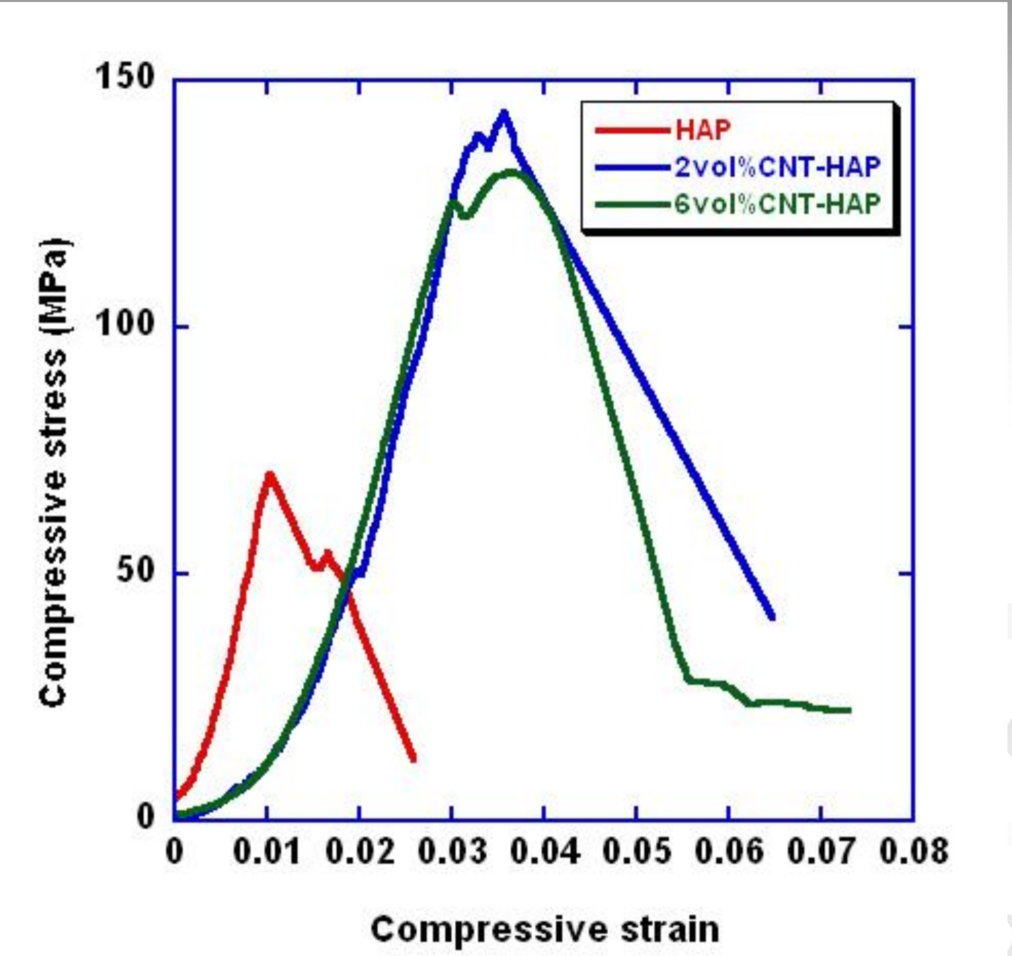
Micro-indentation on CNT-HAP composites

- 1vol%, 2vol%, and 4vol% CNT-HAP composite were fabricated by SPS
- Hardness show a highest value at a critical CNT vol%



	HAP	1vol%CNT-HAP	2vol%CNT-HAP	4vol%CNT-HAP
Hardness(GPa)	3.59±0.38	3.71±0.32	3.97±0.37	3.48±0.24

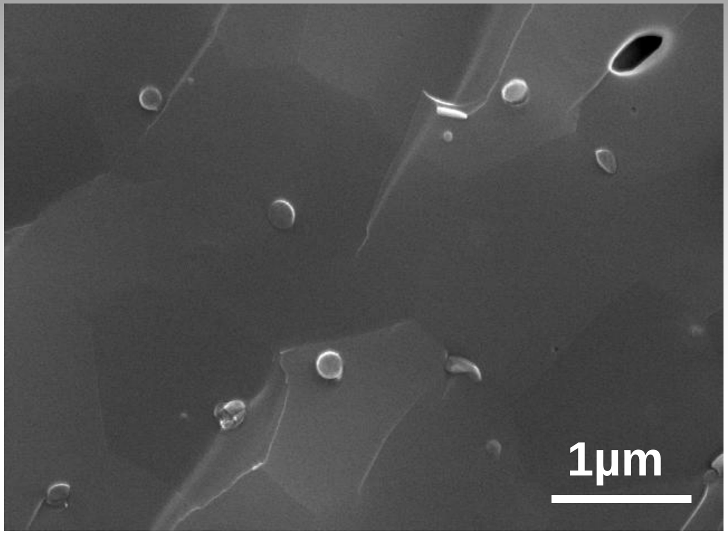
Compression test: HAP vs. CNT-HAP composite by FPSPS at 1200℃



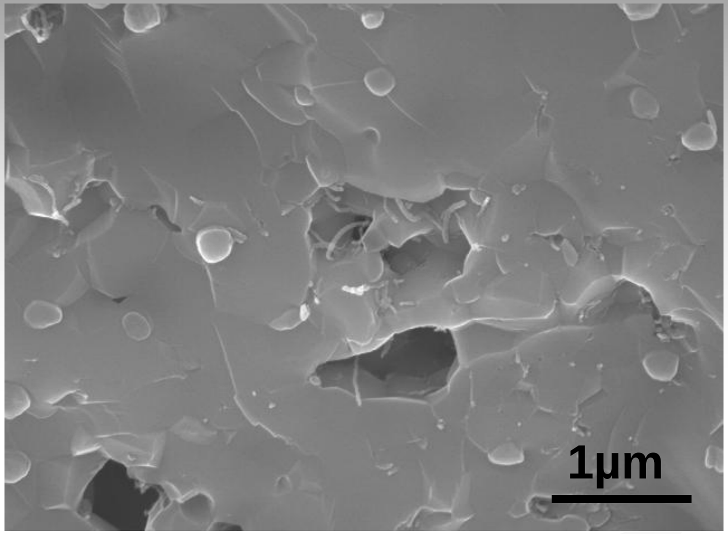
	Young's modulus (GPa)	Compressive strength (MPa)
HAP	8.2	70.6
2vol%CNT-HAP	7.0	143.9
6vol%CNT-HAP	7.0	131.6

SEM of fracture surface: CNT-HAP composites

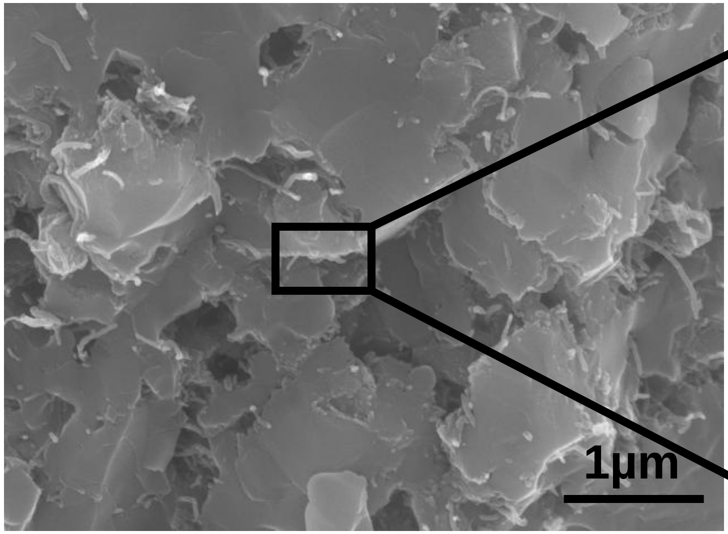
Pure HAP

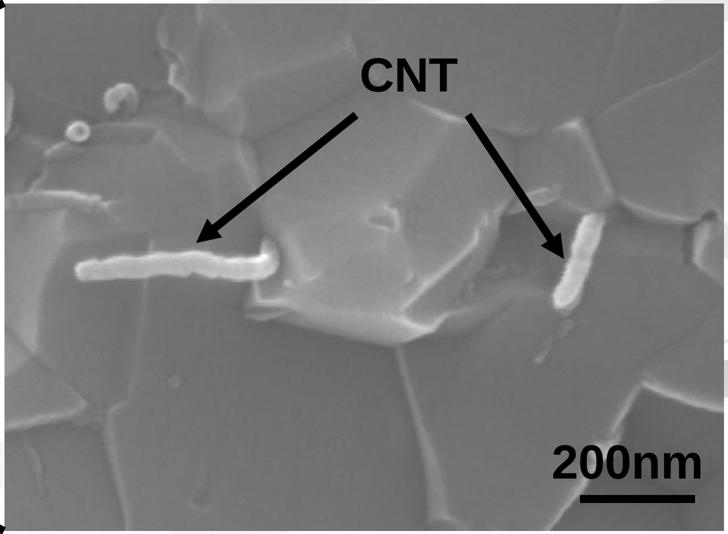


2vol%CNT-HAP

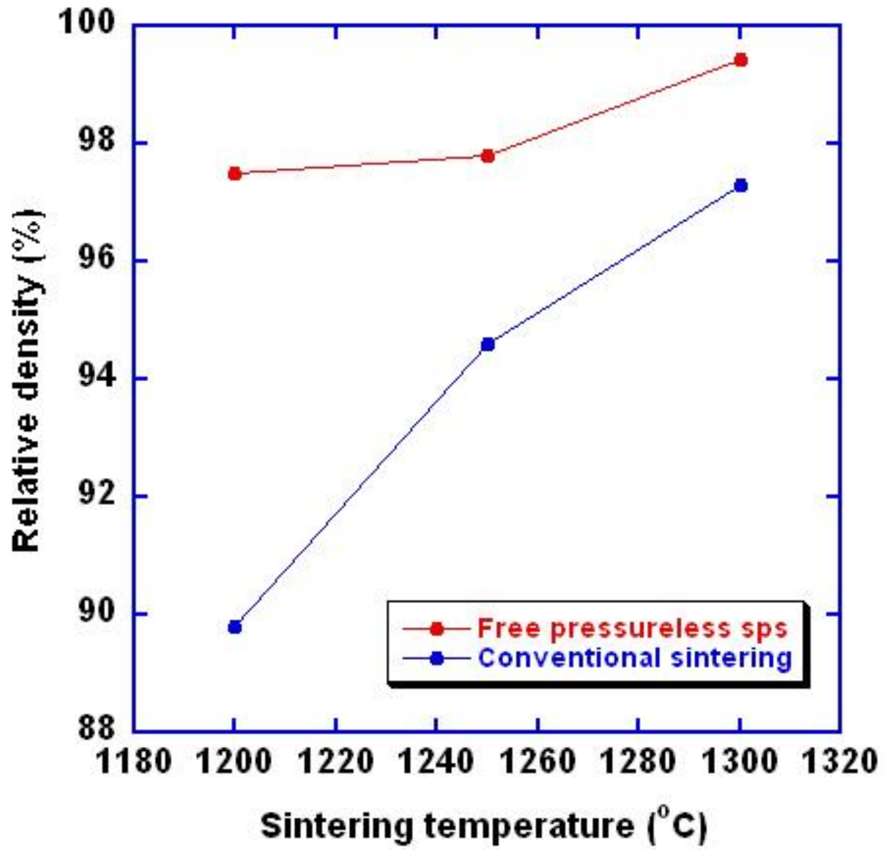


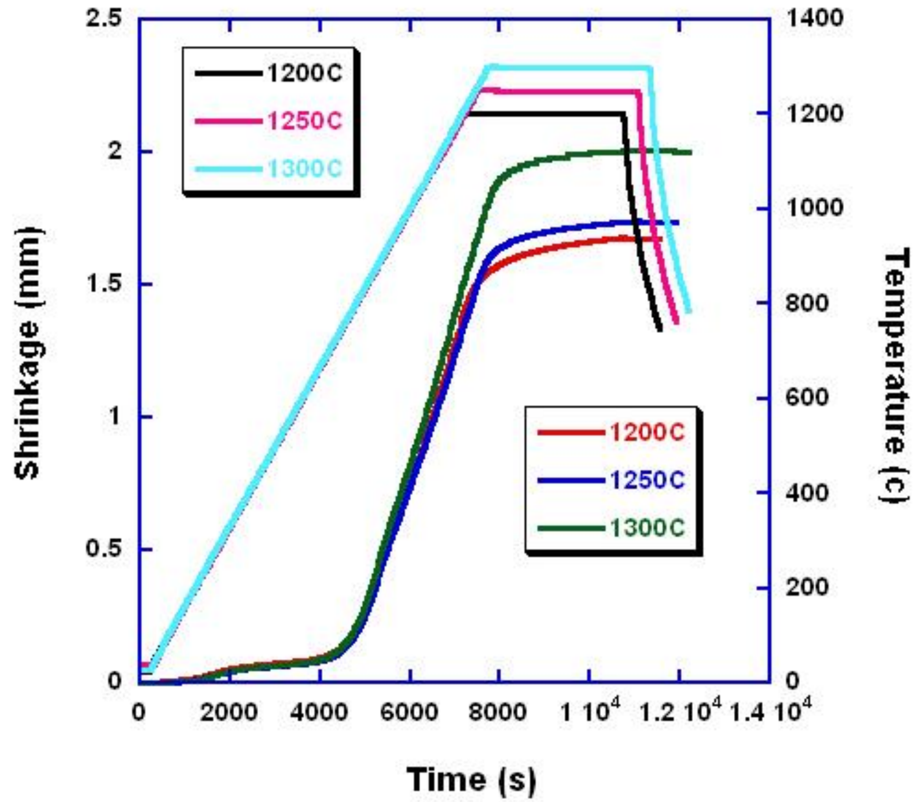
6vol%CNT-HAP





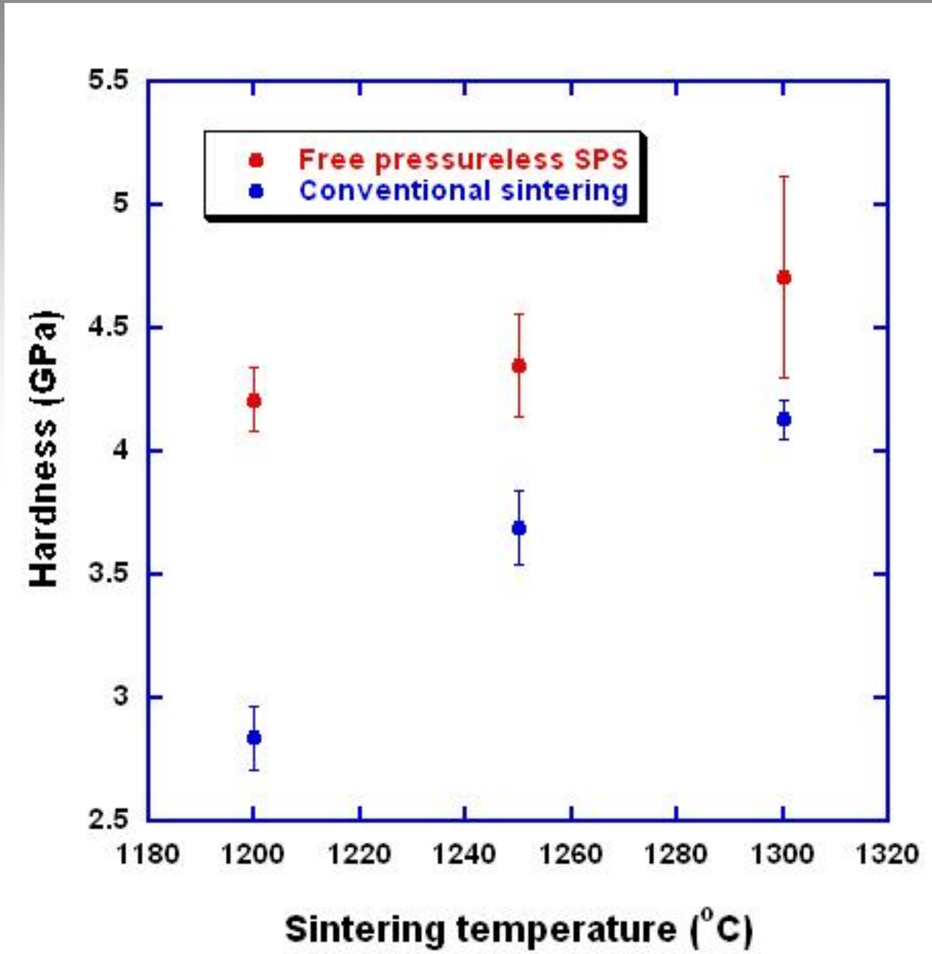
Comparison of HAP sintered by FPSPS and Conventional sintering



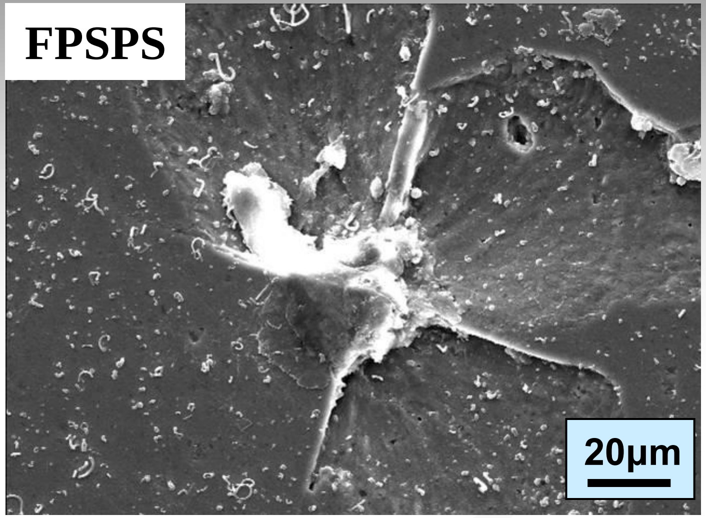


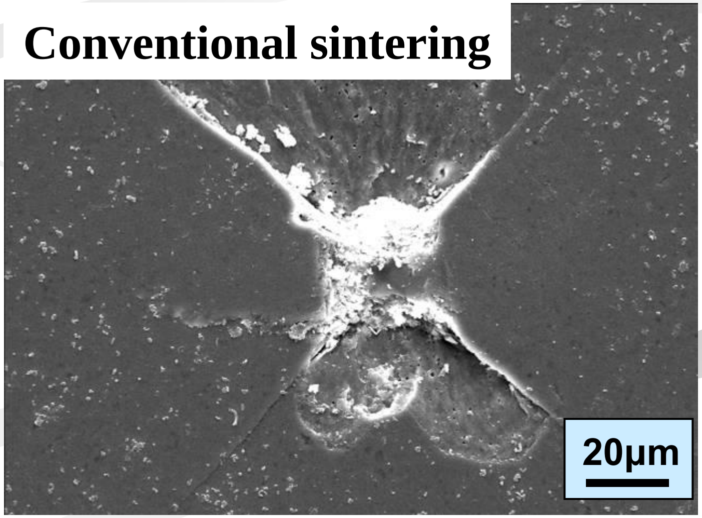
	1200C	1250C	1300C
FPSPS	97.5	97.8	99.45
Conventional sintering	89.8	94.6	97.3

Microindentation test

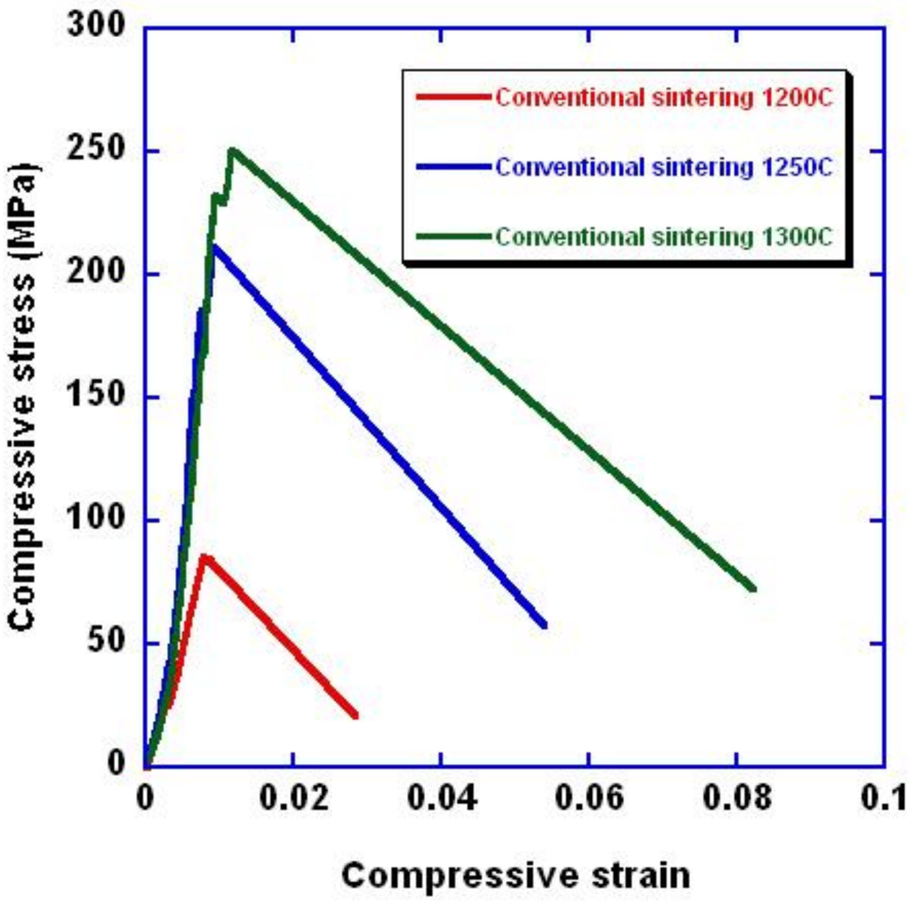


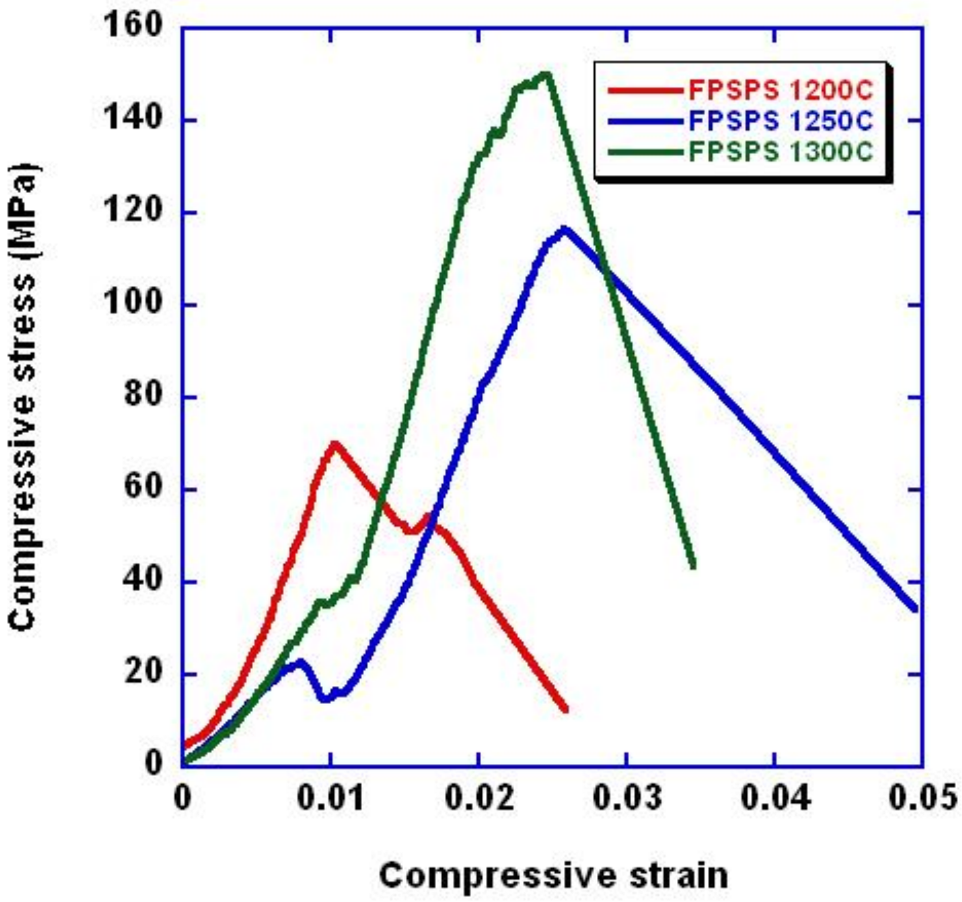
	1200℃	1250℃	1300℃
FPSPS (GPa)	4.21±0.13	4.35±0.21	4.71±0.41
Conventional sintering (GPa)	2.84±0.13	3.69±0.15	4.13±0.08



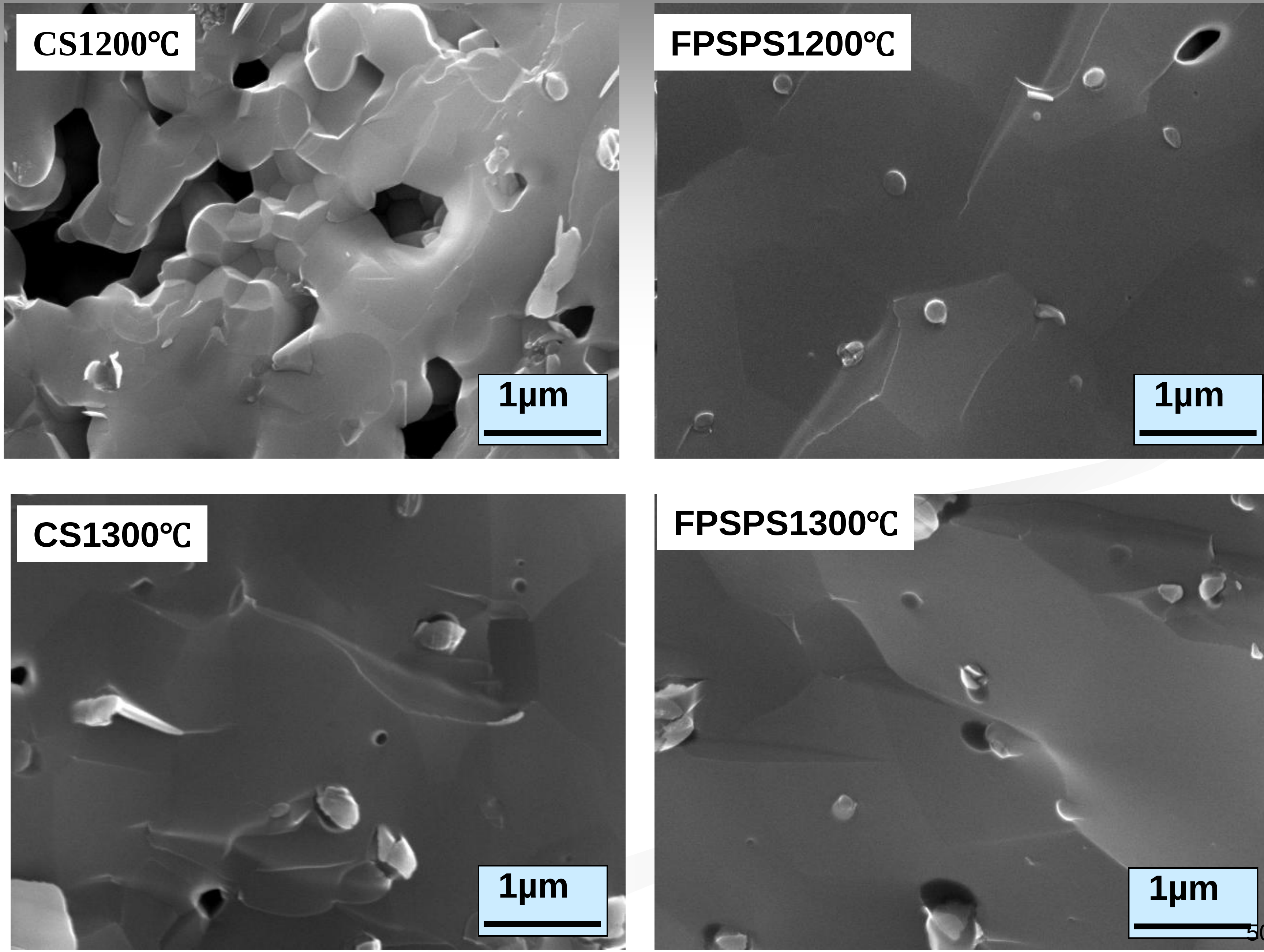


Compression tests of FPSPS and Conventional Sintering

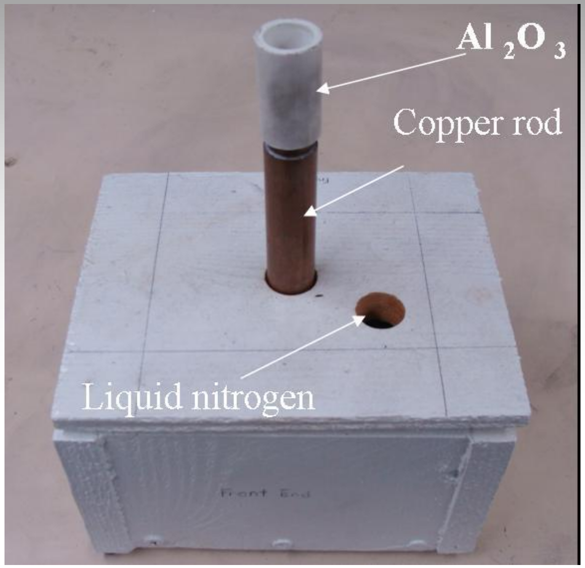




SEM images of fracture surface after compression tests



Fabrication of micro-channel structure HAP



Uniformly mixing of HAP with DI water and additives

↓

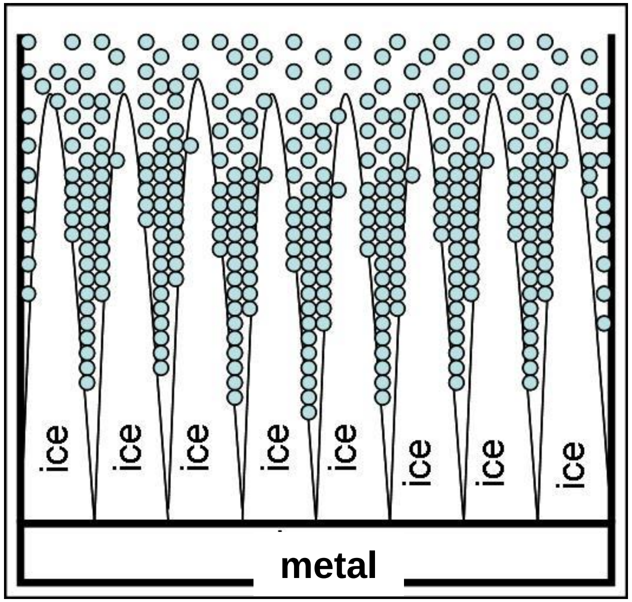
Freeze the slurry into solid state to form channel structure

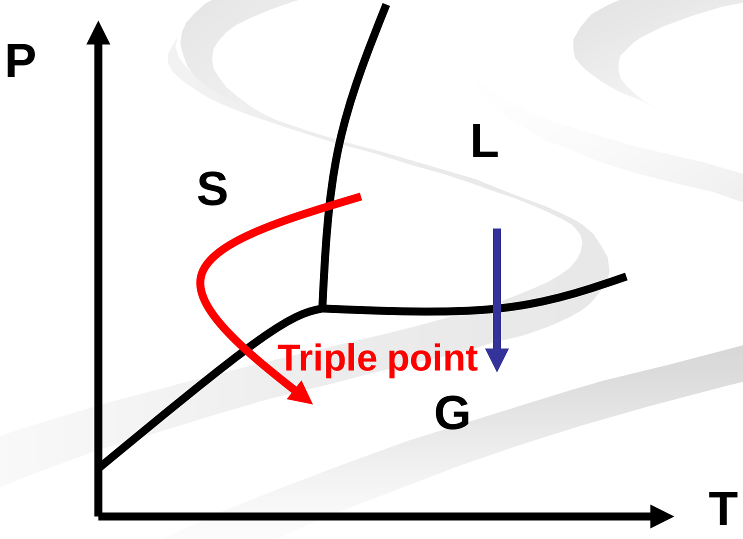
↓

Subject to freeze drying unit to sublimate the ice

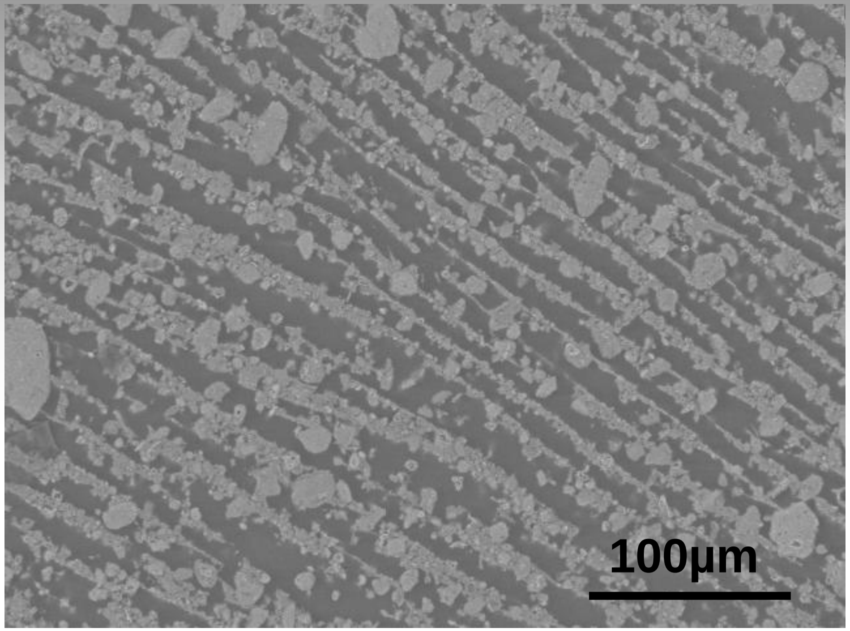
↓

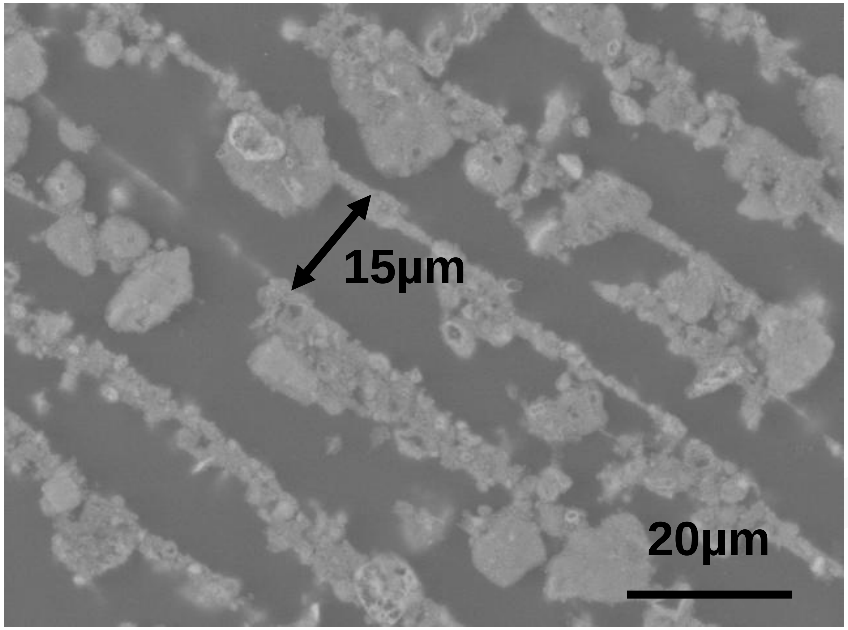
Sintering the green specimen by FPSPS





SEM images of micro-channel structure after freeze drying process





Green specimen
(after freeze drying)

↓

Infiltrate with acrylic solution

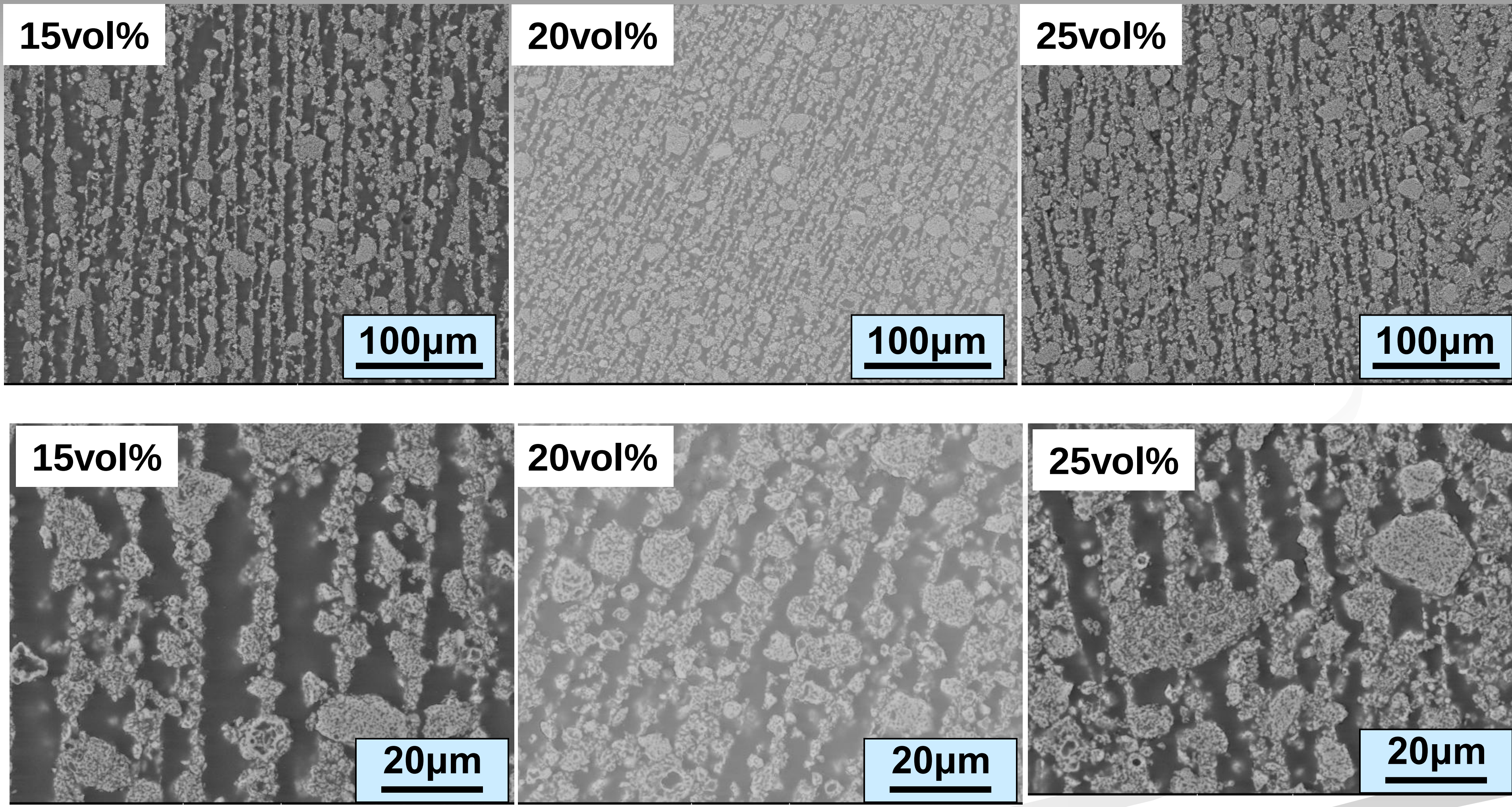
↓

Put in vacuum to remove the air in the channel

↓

Cut the specimen to do the BSE

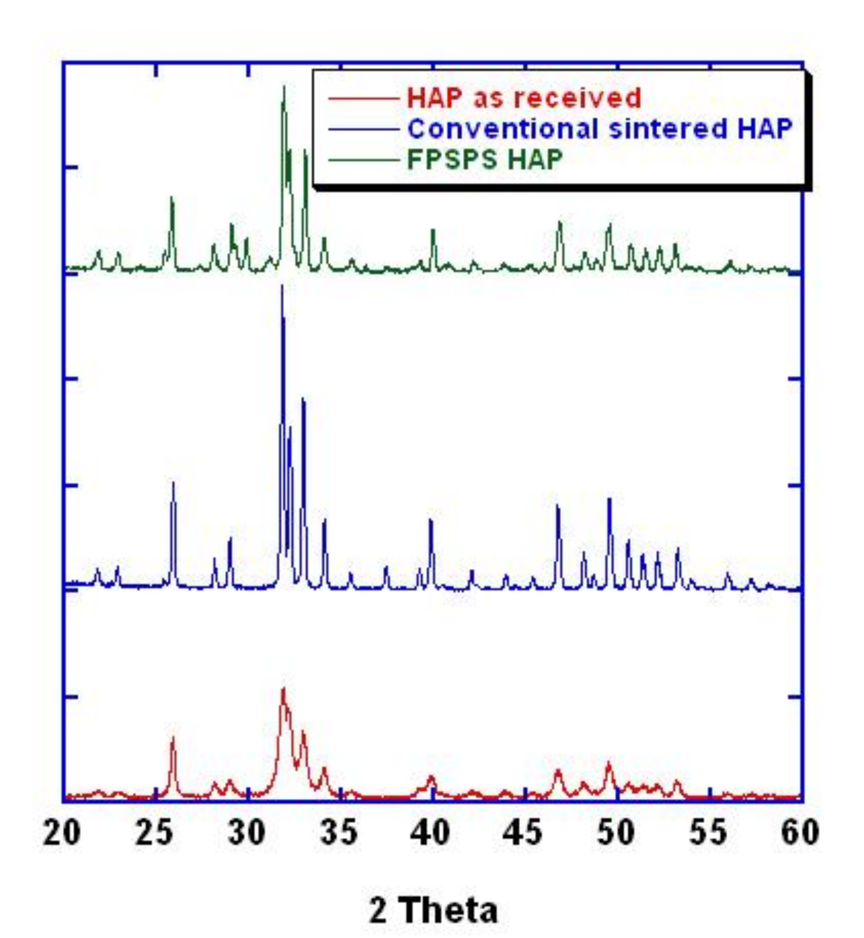
SEM images of micro channel structure after FPSPS



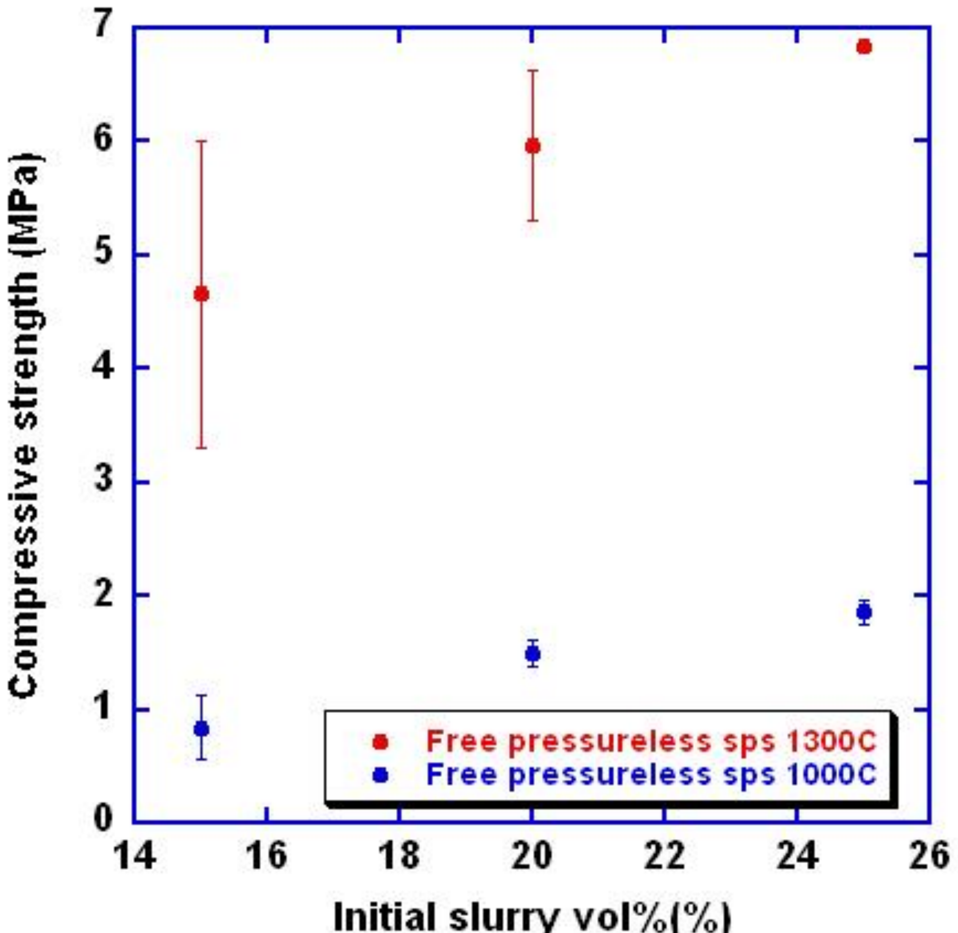
The channel diameter decrease with the increase of the initial slurry concentration

Y.S.Lin, M.A.Meyers, E.A.Olevsky et al Advances in applied ceramics.accepted

X-ray diffraction on different sintering methods

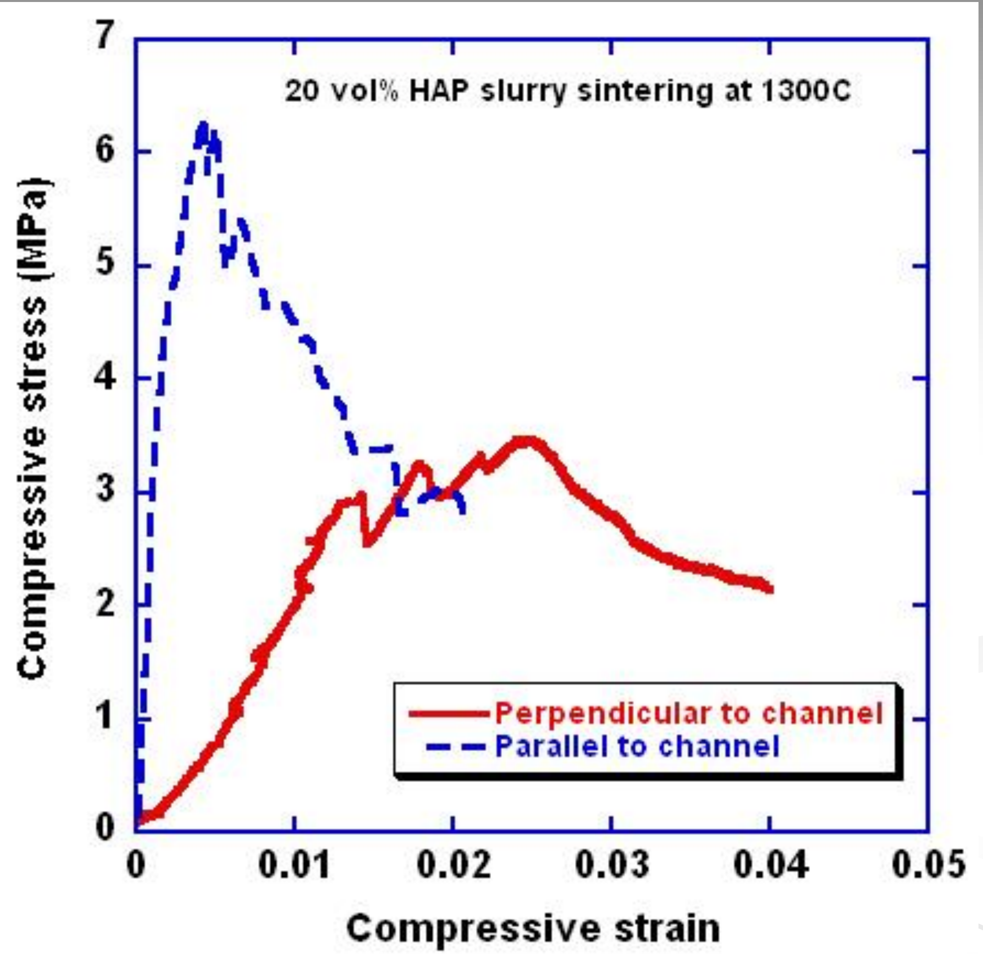


Compressive strength vs. initial slurry vol %



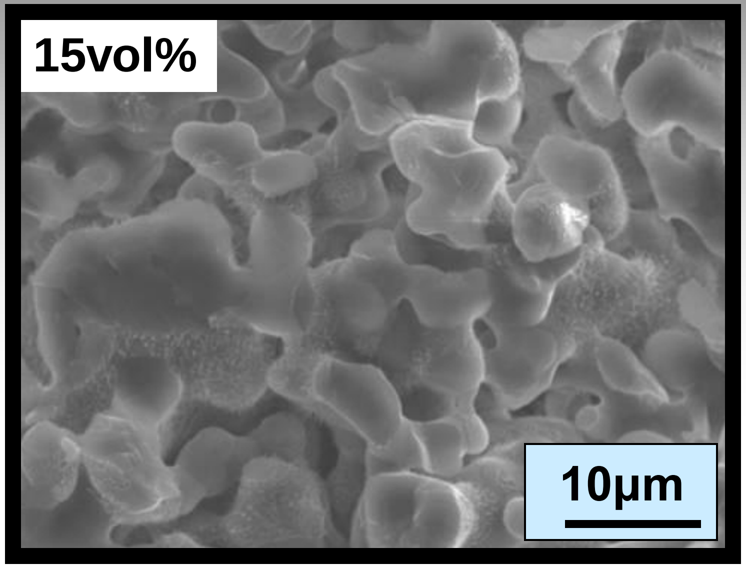
Initial slurry vol %(%)	FPSPS1300℃	FPSPS1000℃
15	4.66±1.35MPa	0.84±0.28MPa
20	5.97±0.67MPa	1.5±0.11MPa
25	6.85±0.06MP	1.86±0.10MP

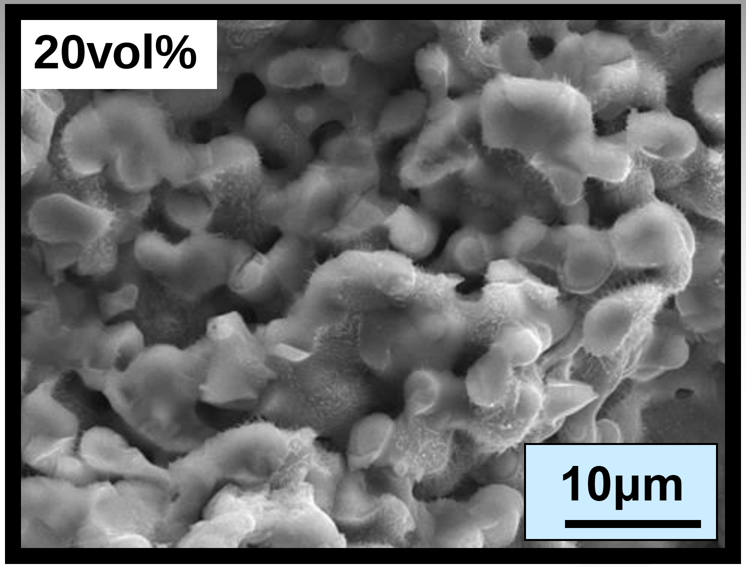
Compression tests in different loading directions

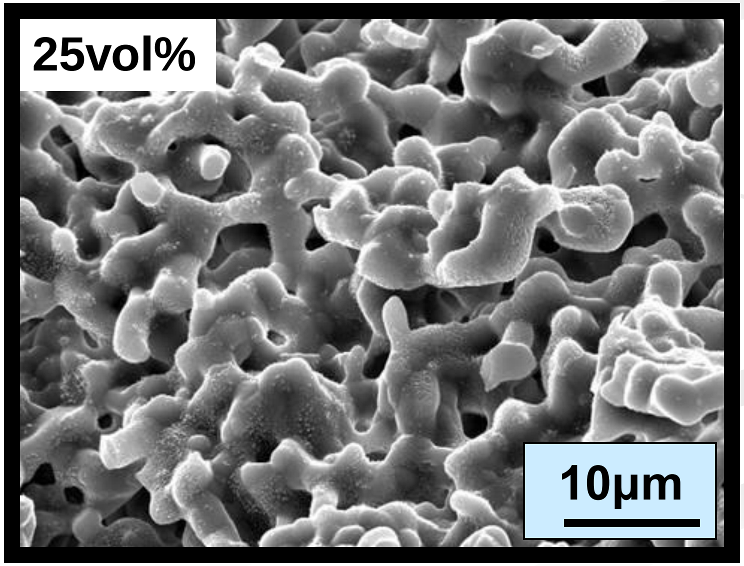


	Parallel to channel	Perpendicular to channel
Compressive strength (MPa)	5.97±0.67	3.04±0.57

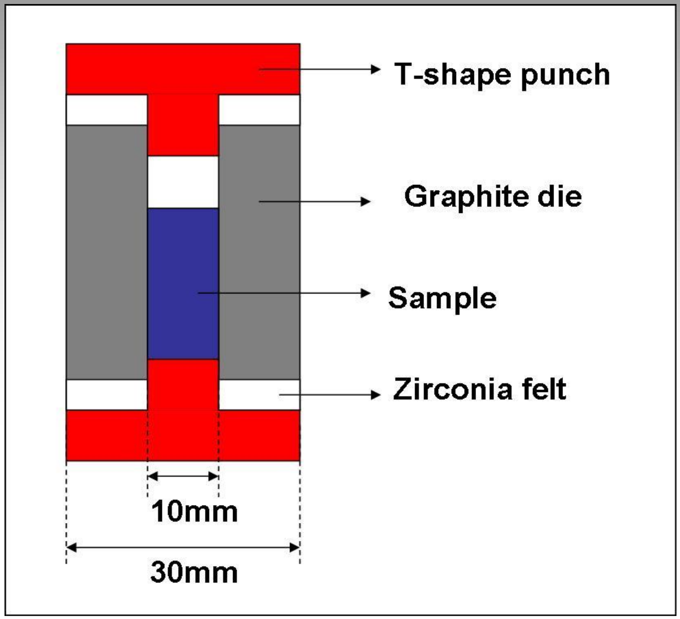
SEM images of fracture surface after compression tests

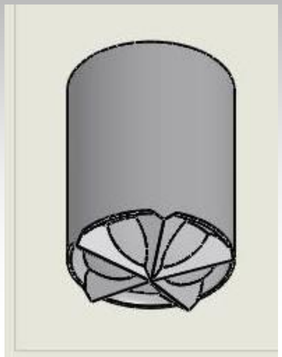






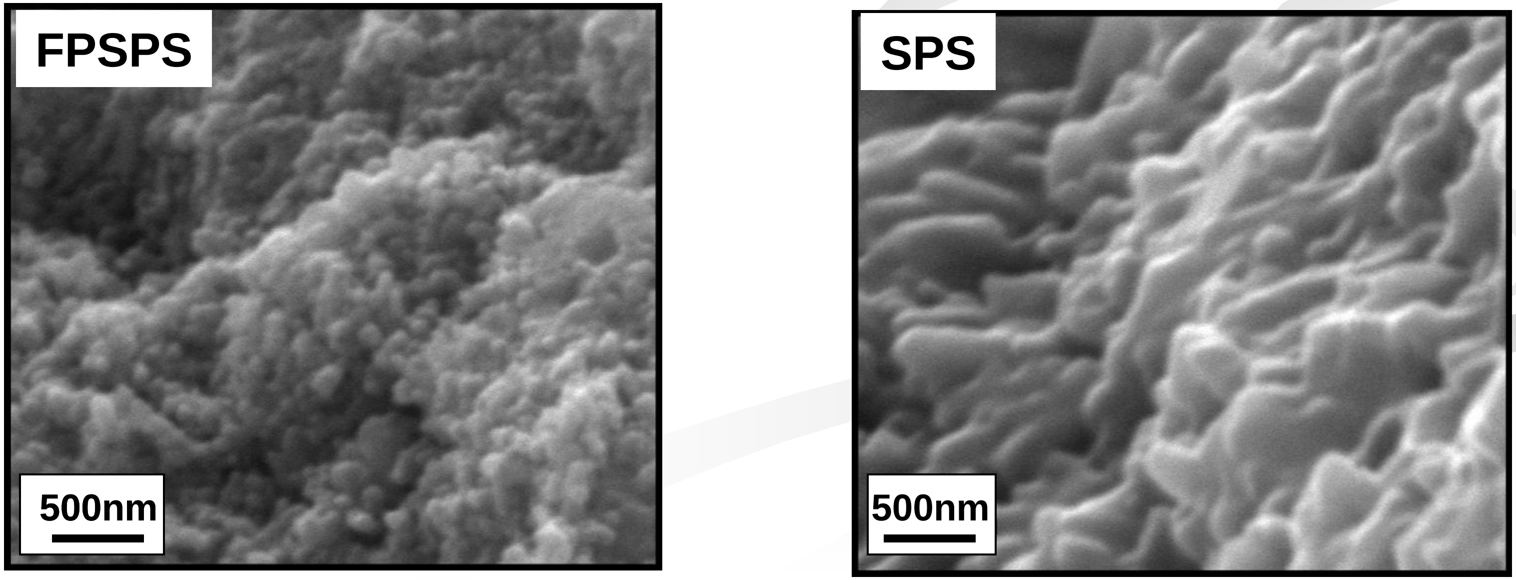
Free pressureless SPS of HAP



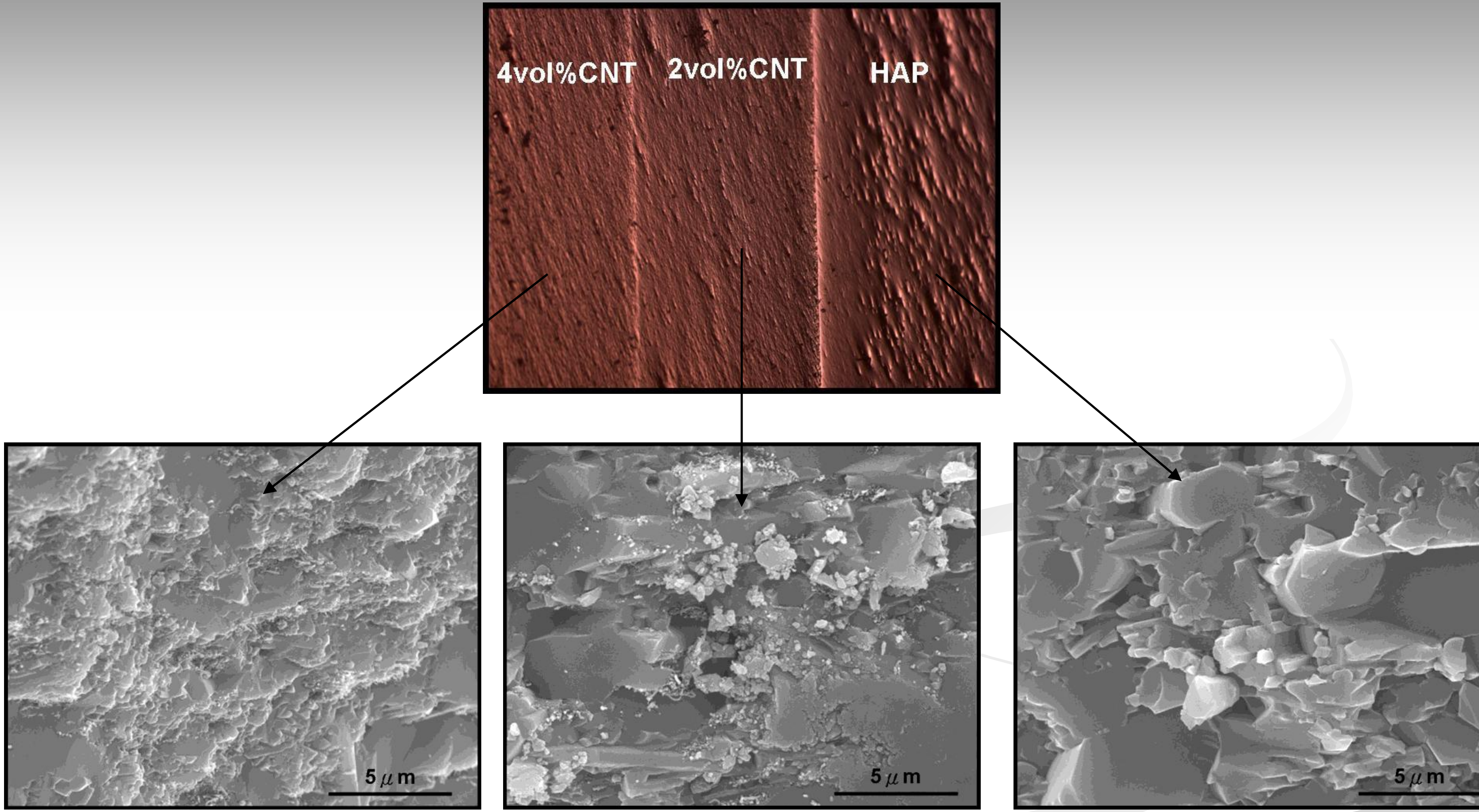


Machined punch

Complex shape HAp-based dental implant prototype produced by FPSPS



Functionally graded CNT-HAP composite



- Functionally graded CNT-HAP composite was consolidated by SPS
- The SEM showing the different concentration of CNT in the three layers

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- Conclusions

Conclusions

- **Hardness values of several species of animals is higher in enamel than in dentin.**
- **The compressive properties are higher in the longitudinal than in the transverse direction due to the different tubule orientation**
- **Arapaima scale has laminate structure composed of collagen and HAP**
- **External layers of Arapaima scales have higher mechanical properties than internal layers**
- **SPS and FPSPS can consolidate the CNT-HAP composite without CNT dissociation, which occurs in conventional sintering.**
- **The addition of CNT increases the microhardness, nanohardness elastic modulus and compression strength of HAP composite.**
- **Microchannel structure in HAP can be fabricated by sequential freeze drying and FPSPS**
- **HAP prepared by FPSPS show higher relative density and higher microhardness than those prepared by conventional sintering**
- **A dental implant prototype was successfully fabricated by FPSPS employing a special geometry punch**

Publications based on the research conducted on the course of the PhD study:

- Y.S.Lin, E.A.Olevsky, and M.A.Meyers. Structure and mechanical properties of Arapaima Gigas scale. J.Mech.Behav.Biomed.Mater. 2011;4:1145-56
- Y.S.Lin, M.A.Meyers, and E.A.Olevsky. Micro-channel hydroxyapatite components by sequential freeze drying and free pressureless spark plasma sintering. Advances in Applied Ceramics. accepted
- M.A.Meyers, Y.S.Lin, E.A.Olevsky, and P.Y.Chen. Battle in the Amazon: Arapaima v.s. piranha. Advanced Biomaterials. accepted
- P.Y.Chen, A.Y.M.Lin, Y.S. Lin, Y.Seki, A.G.Stokes, J.Peyras, E.A. Olevsky, M.A.Meyers, J.McKittrick. Structure and mechanical properties of of selected biological materials. Mat.Sci.Eng. . 2008;208-226
- E.Khaleghi, Y.S.Lin, M.A.Meyers and E.A.Olevsky. Spark plasma sintering of tantalum carbide Scripta. Mater. 2010:63:577-580
- M.A.Meyers, A.Y.M.Lin, Y.S.Lin, E.A.Olevsky, and S.Georgalis. The cutting edge: Sharp biological materials J.O.M. 2008;3:19-24

Presentations

- TMS 2009 Annual Meeting, San Francisco:
  "Teeth: Structure and mechanical properties "
- TMS 2011 Annual Meeting San Diego:
  - "Structure and mechanical properties of Arapaima scale"
  - "Spark plasma sintering of complex shape HAP-CNT composites"

Acknowledgement

Prof. E.A.Olevsky

Prof. M.A.Meyers

Prof. J. McKittrick

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