

中国力学学会第四十次青年学术沙龙

# 天然生物陶瓷材料的微结构及其强韧化机制研究

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# 报告内容

1. 贝壳珍珠母的微结构与力学性能
2. 牙齿的微结构与类金属性



# 1. 贝壳珍珠母的微结构与力学性能

- 珍珠母微结构及性能介绍
- 珍珠母中的矿物桥
- 矿物桥对珍珠母力学行为的影响
- 小结



# Introduction



# Introduction



对数螺线



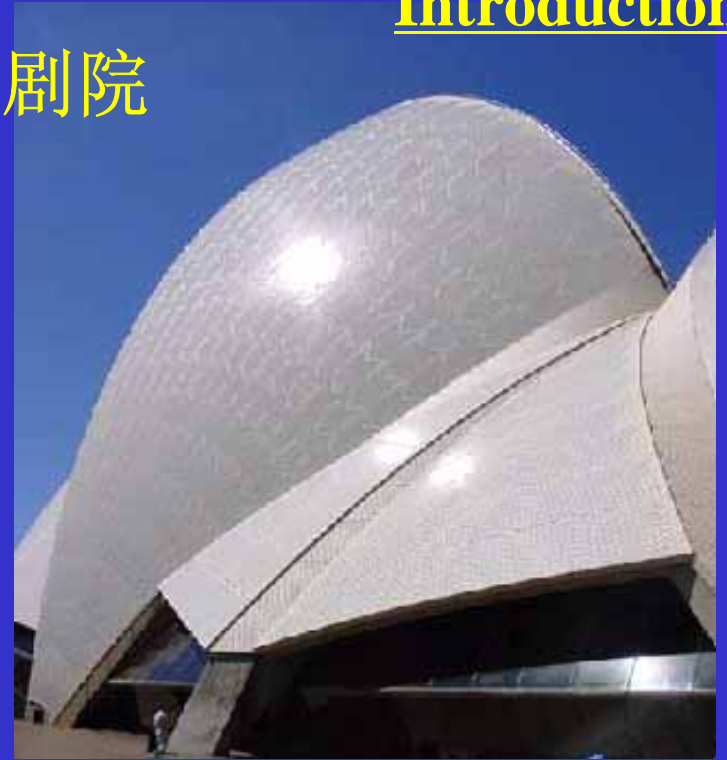
放射线



对数螺线+放射线

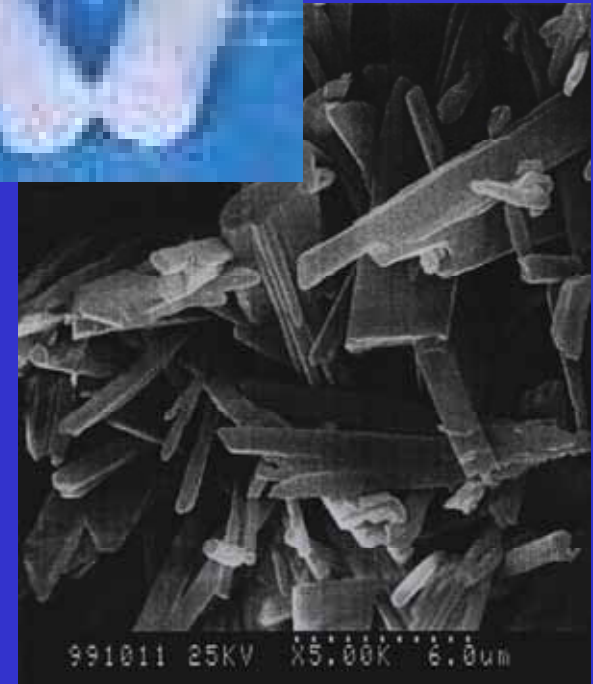
# Introduction

## 悉尼歌剧院





# Introduction



**SEM images of cross section of nacre and chalk**



# Introduction



Argonauta argo



Calliostoma annulatum



Cypraea cervus



Lischkea imperialis



Littorina scabra  
angulifera 1



Littorina scabra  
angulifera 2



Lyropecten nodosa



Nautilus pompilus



Patinopecten caurinus



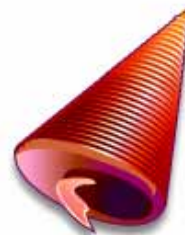
Philippia radiata



Stellaria solaris



Strombus gigas

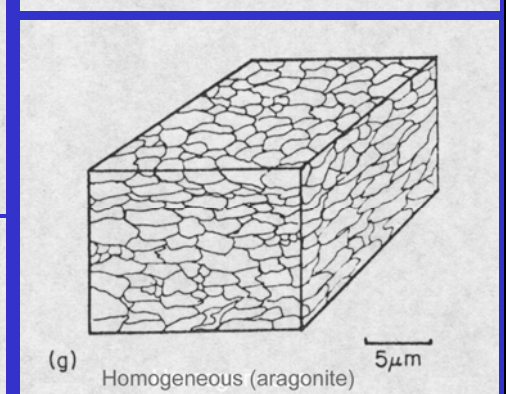
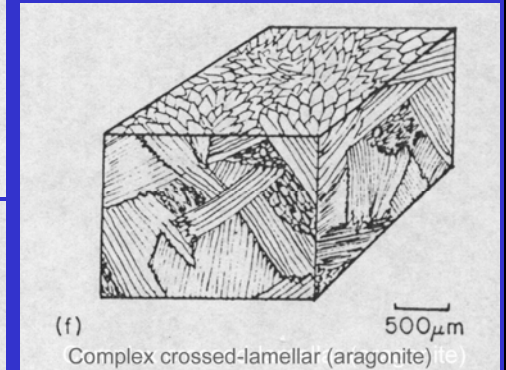
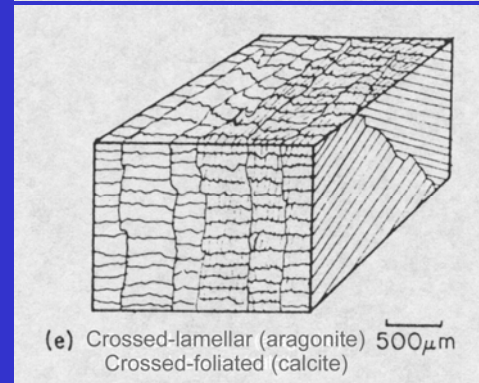
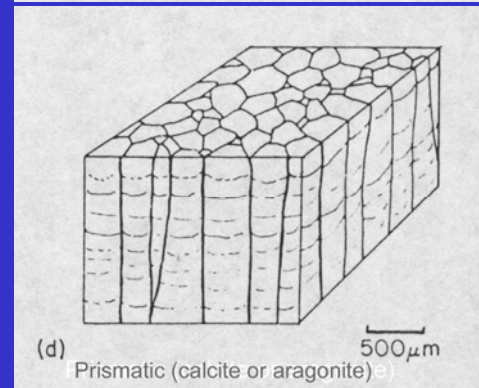
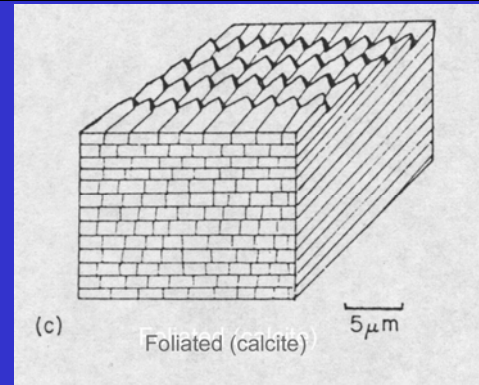
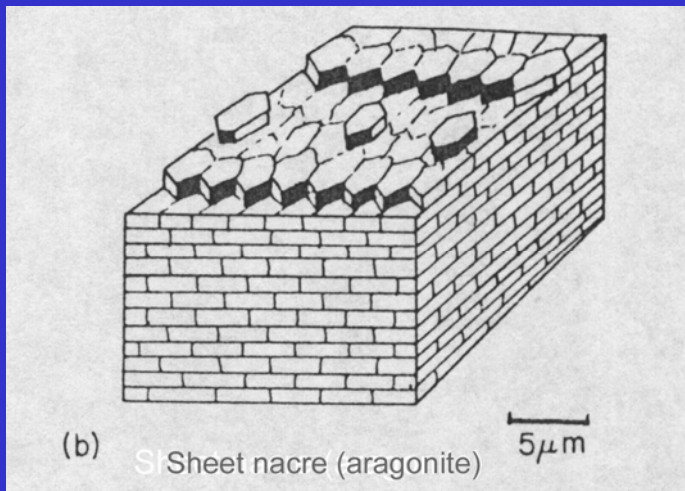
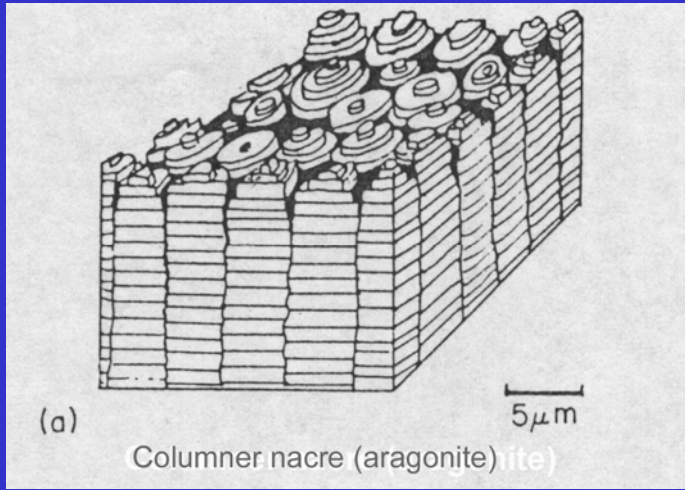


Telescopium telescopium

## Sea Shells



# Introduction



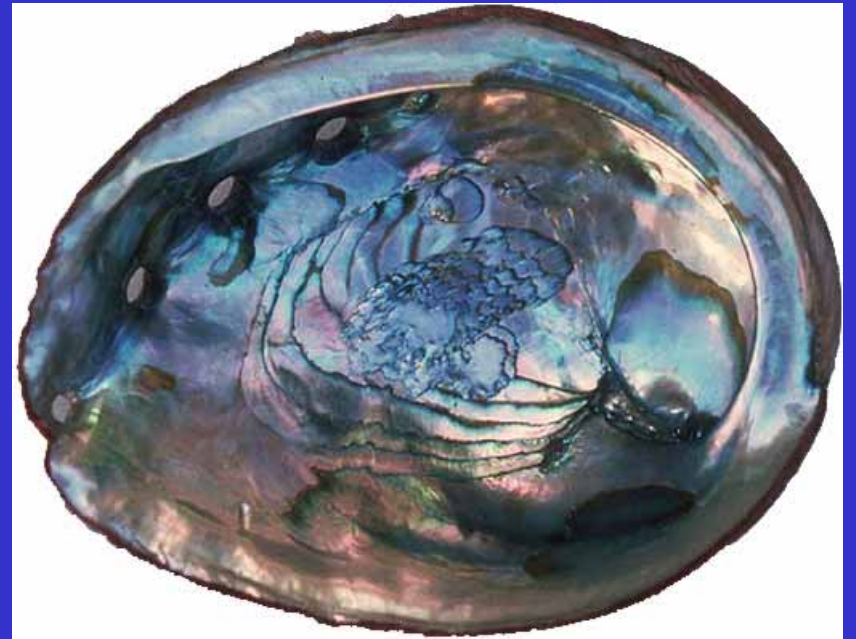
贝壳中微结构形式



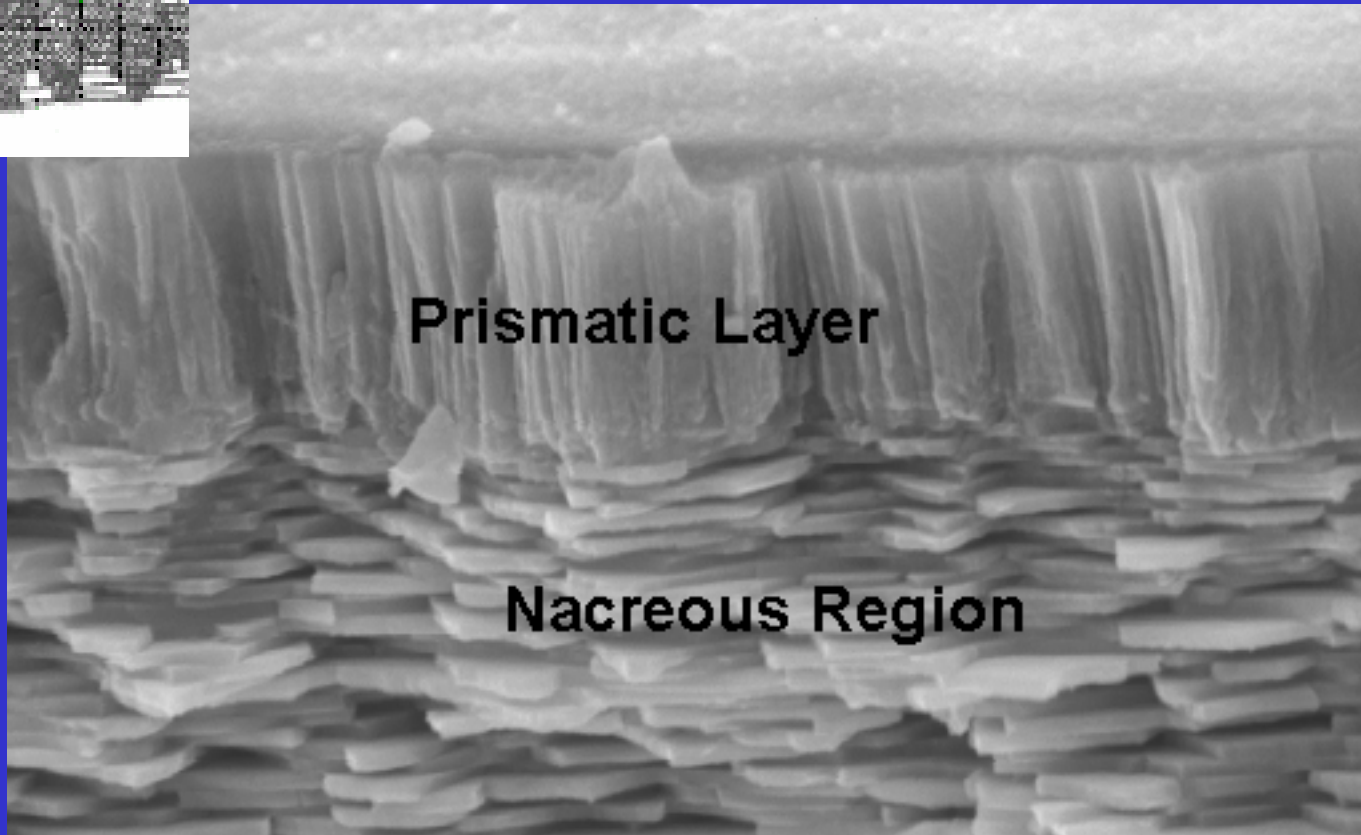
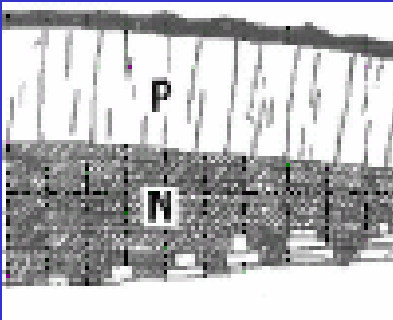
# 贝壳中珍珠母微结构研究



鲍鱼(*Haliotis*)壳外部形貌



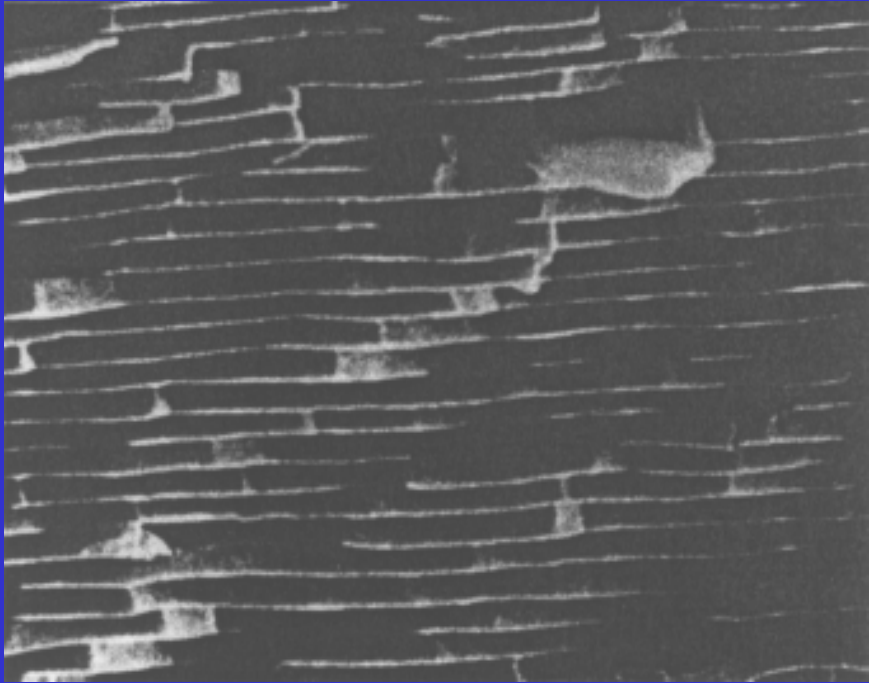
鲍鱼(*Haliotis*)壳内部形貌



鲍鱼(*Haliotis*)壳横截面形貌



## Introduction

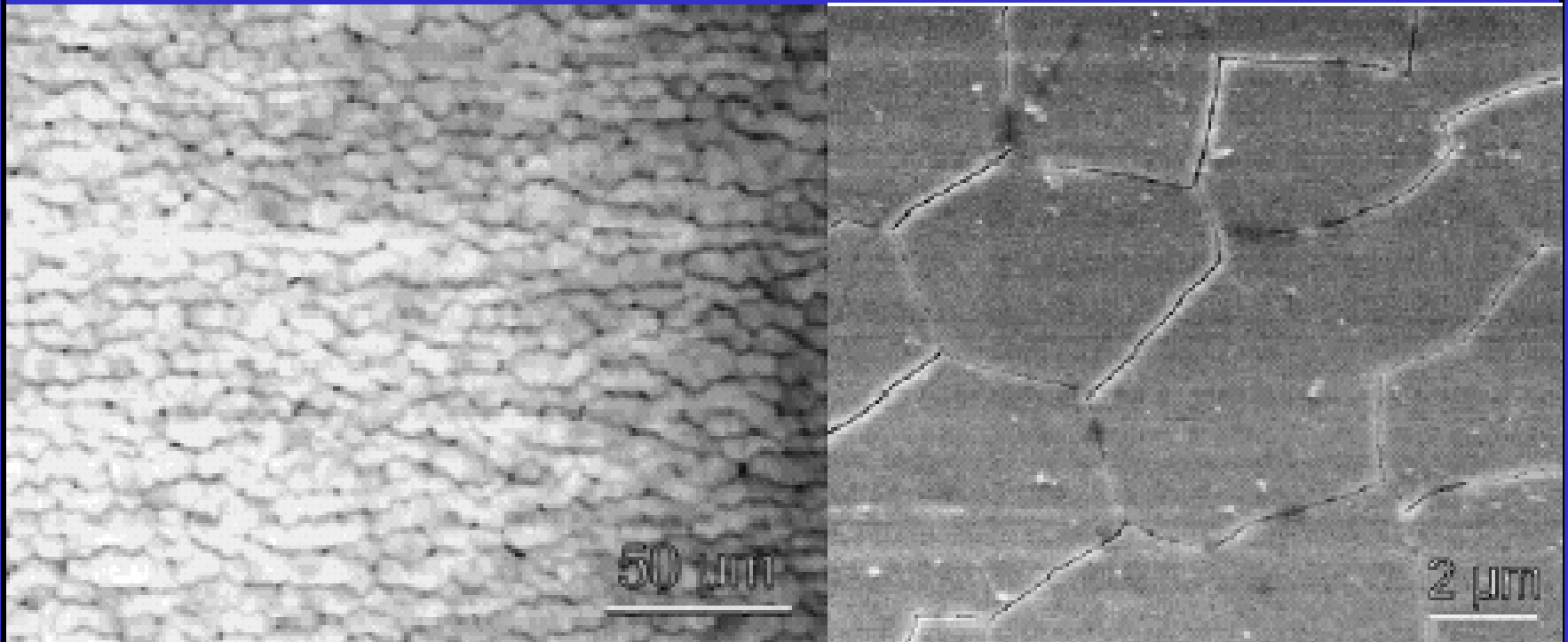


珍珠母材料微结构形貌



珍珠母材料断口微结构形貌

## Introduction



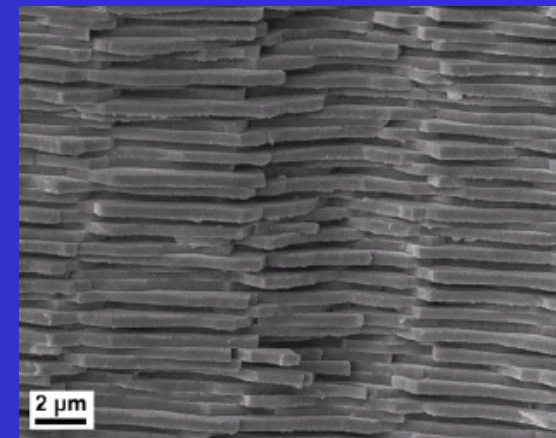
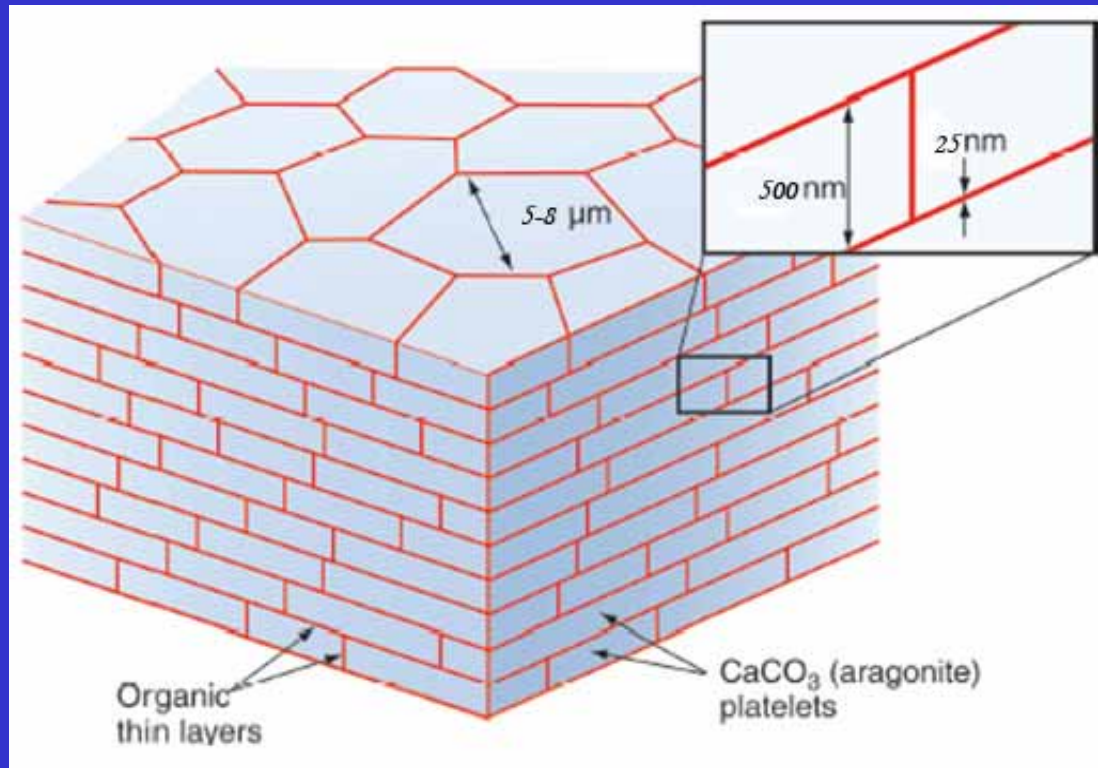
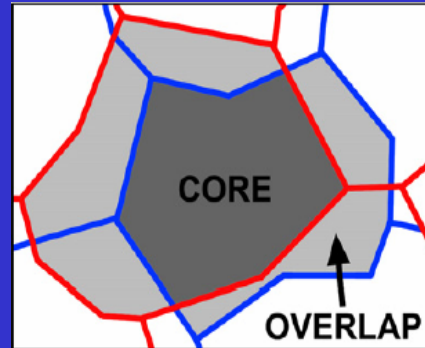
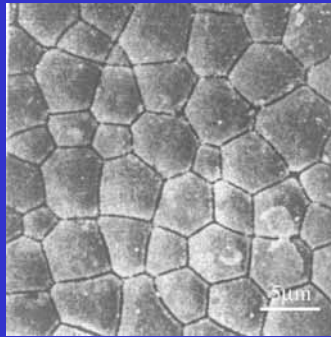
珍珠母材料层面微结构形貌



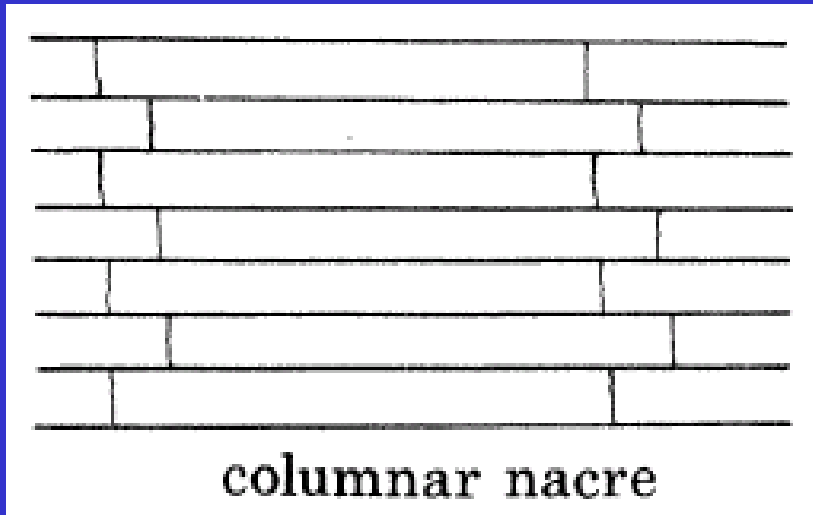
# Introduction

## 珍珠母微结构示意图

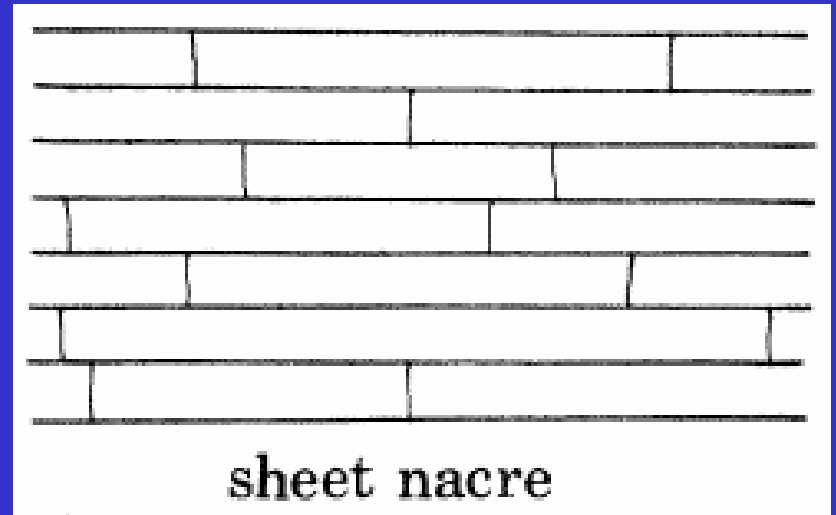
无机相: 95 vol.%  
有机质: 5 vol.%



- 珍珠母分为柱状和片状两种



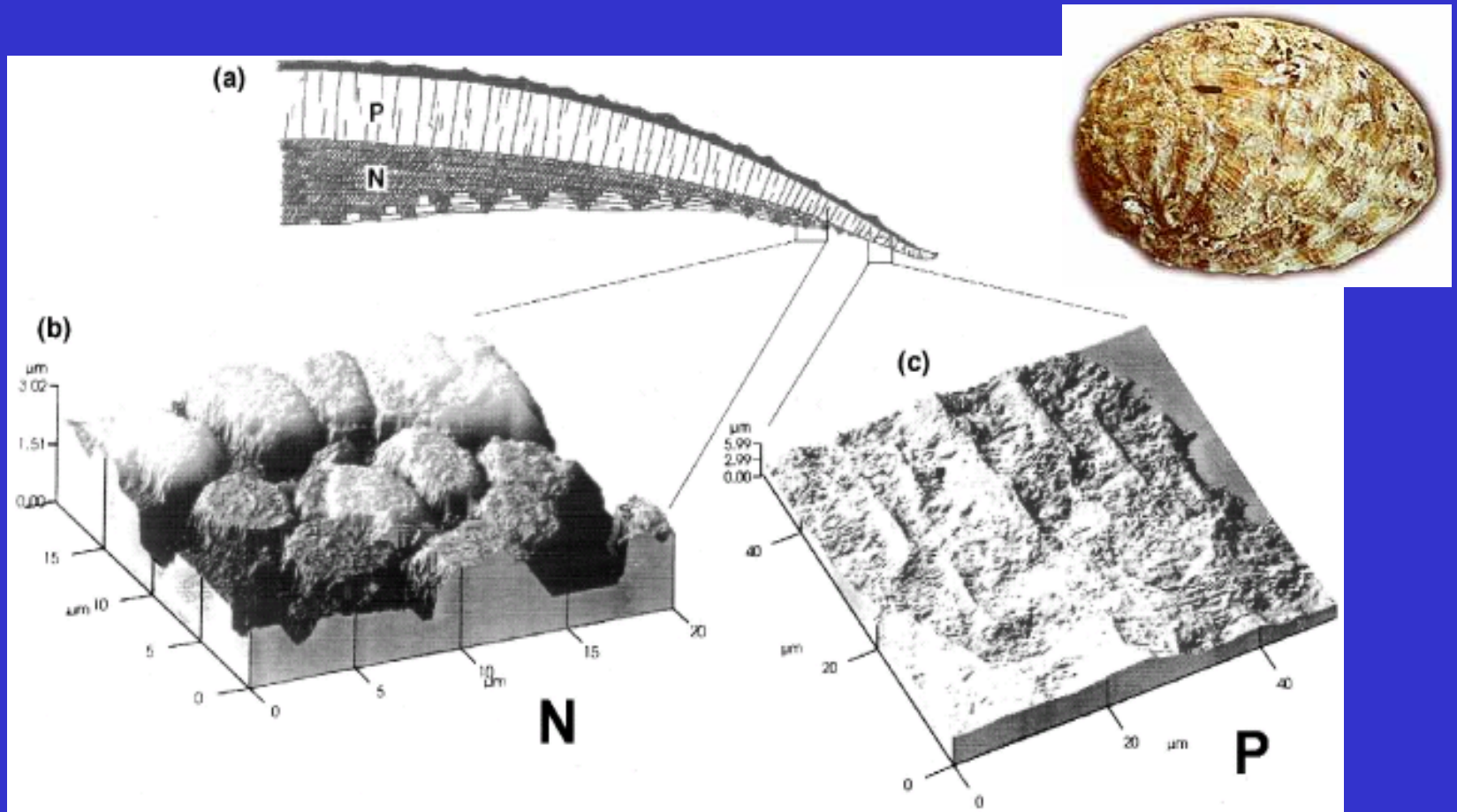
柱状



片状

- 珍珠母是有机基质(蛋白质和多糖)为基体、文石晶片为增强相的两相相间的层状复合材料，传统上称为：**Brick-Mortar** 结构。

# Introduction



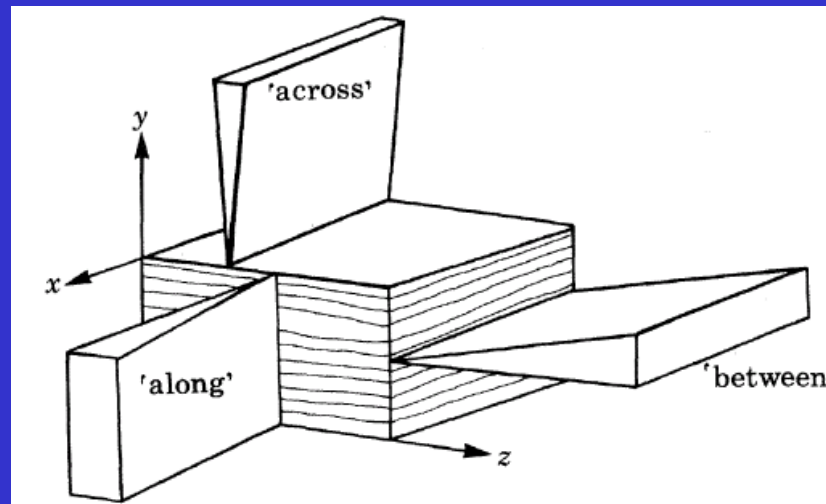
鲍鱼(*Haliotis*)壳横截面生长示意图

- 传统上认为：珍珠母的生长是在有机基质指导下的、钙离子的外延沉积过程。



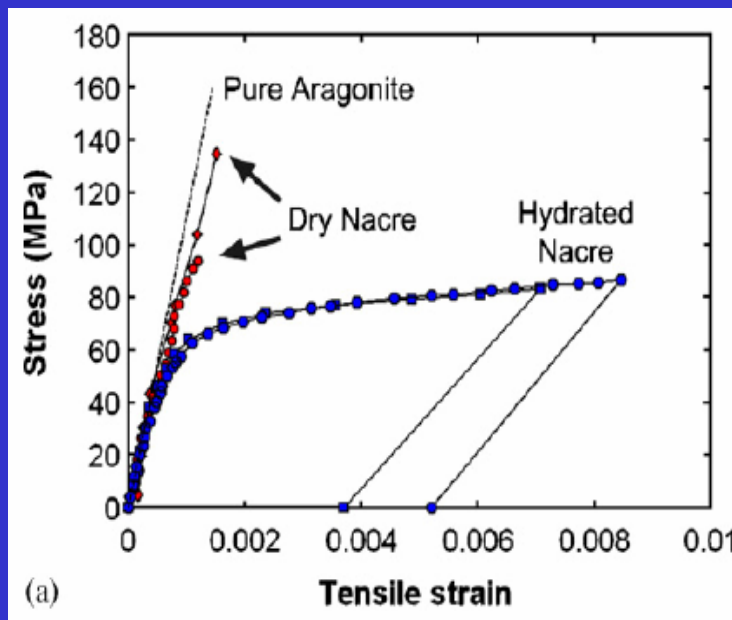
# 珍珠母力学性能研究

- **Currey (1977)** 系统地实验测定、研究了珍珠母的强度、韧性等力学性能，并提出：矿物层片在材料中精确的几何分布方式是珍珠母优异力学性能的关键；



## Introduction

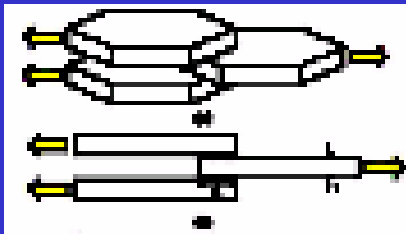
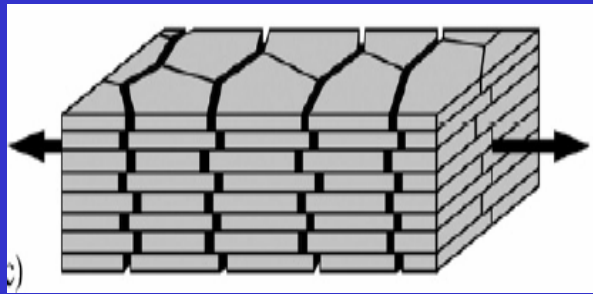
- **Jackson等 (1988)** 进一步研究了干、湿态珍珠母的力学性能，指出：1) 干与湿珍珠母的水分含量相差0.2%，但强韧性存在较大差异；2) 控制珍珠母力学性能的关键因素是其微结构；



“ With such a high proportion of ceramic the material should be brittle, yet nacre has a work of fracture about 3000 times greater than that of pure ceramic.”

## Introduction

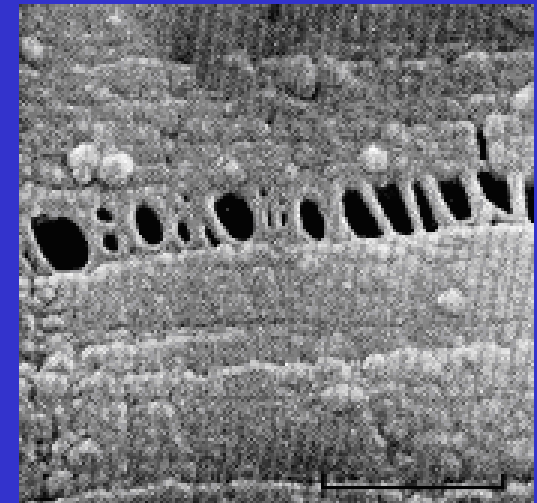
- Sarikaya 等 (1995) 提出了珍珠母结构优异力学性能的三点耗能增韧机制；



1) 晶片拔出



2) 裂纹偏转



3) 有机基质桥联

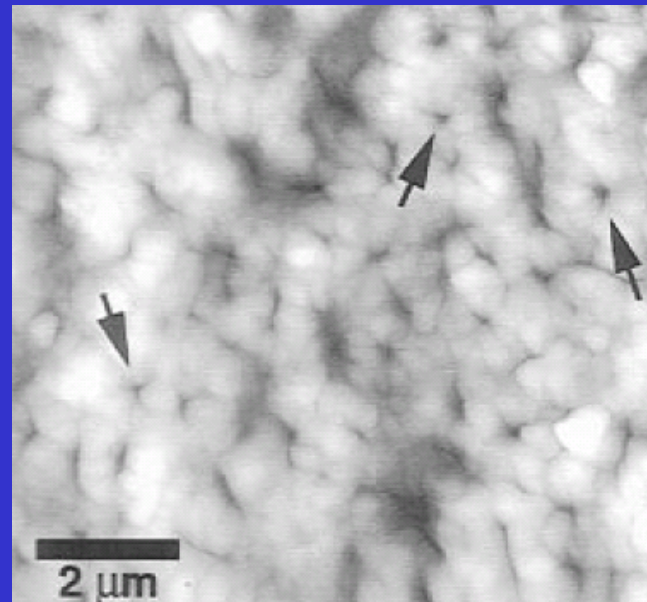
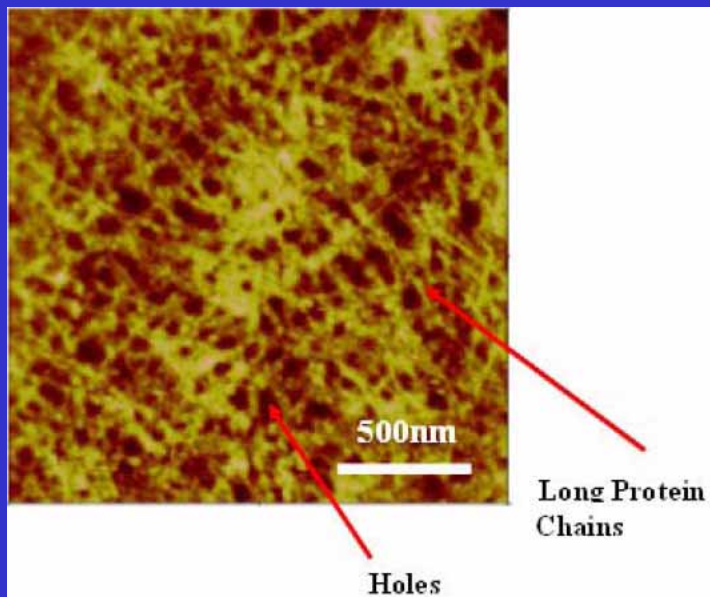
## Introduction

- **Almqvist *et al.* (1999)** indicated that ceramics laminated with organic material are more fracture resistant than non-laminated ceramics, but the synthetic ceramics made of the “brick and mortar” arrangement do not have a toughness comparable to nacre.



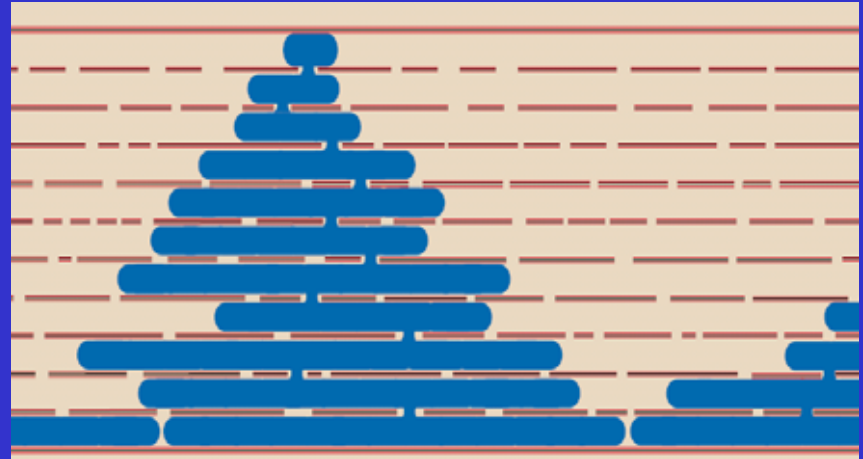
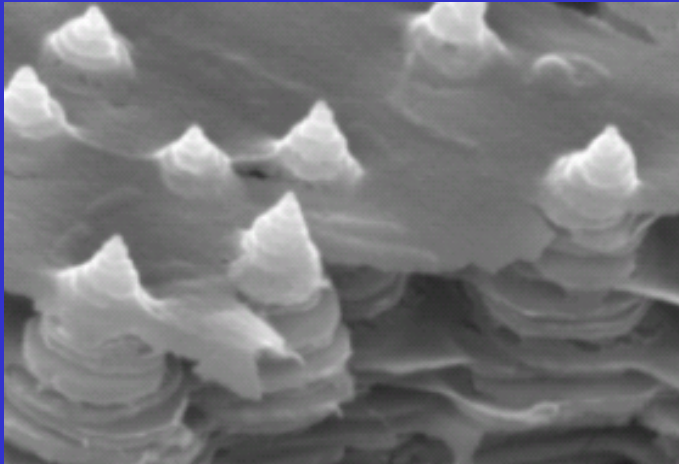
## Introduction

- **Schaffer**等(1997)在珍珠母的有机基质层中发现空洞，提出：有机基质中可能存在矿物桥，珍珠母的生长不是钙离子的外延沉积生长，而是通过矿物桥的连续生长；





- **Addadi等(1997)**提出珍珠母的矿物桥生长模型，由此解释了珍珠母的相关材料性能；



珍珠母生长模型

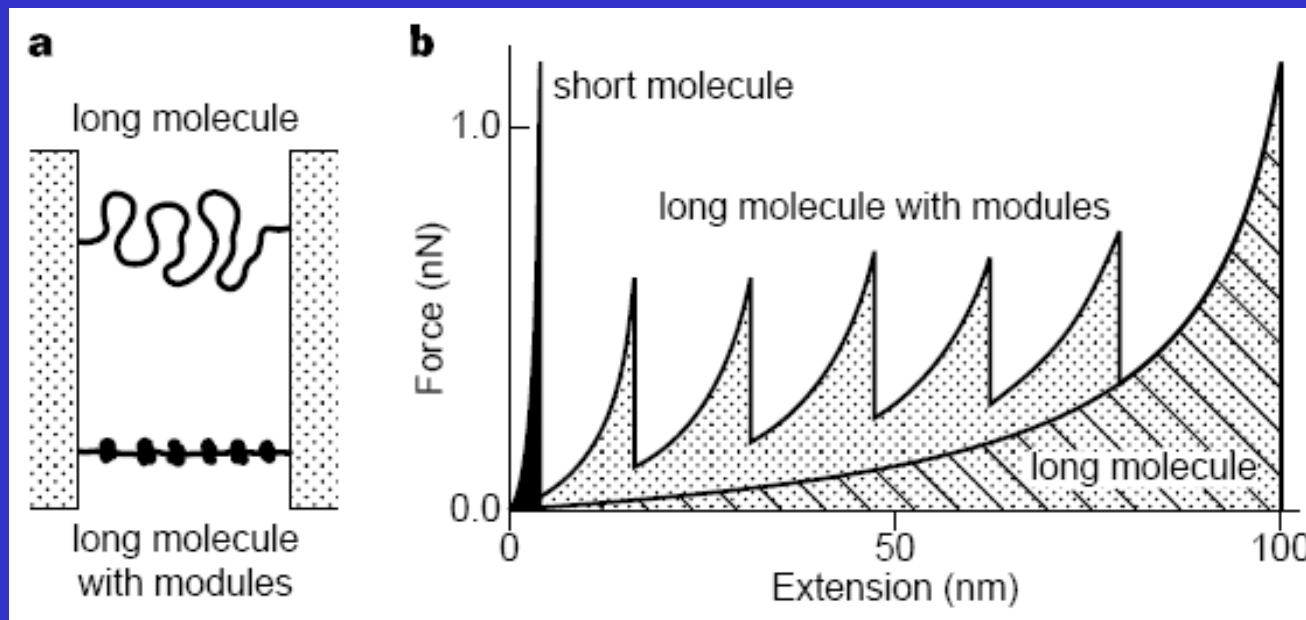
矿物桥的存在性未能得到证实！



- **Schaffer等(1997)**通过采用盐酸溶液溶解掉硬层文石晶片的方法，对有机基质作观察后发现：湿态有机基质很软呈橡胶态，而干的有机基质则很脆易碎；
- **de Gennes等 (2000, 2001)**给出珍珠母中裂纹尖端应力场的量级分析，指出：有机基质层对整个材料断裂韧性存在巨大影响；

## Introduction

- **Smith等(1999)**通过原子力显微镜微悬臂探针直接拉伸单个有机基质分子，获得分子链的“多结模型”。指出：珍珠母的高韧性源于其有机基质界面中的有机高分子；





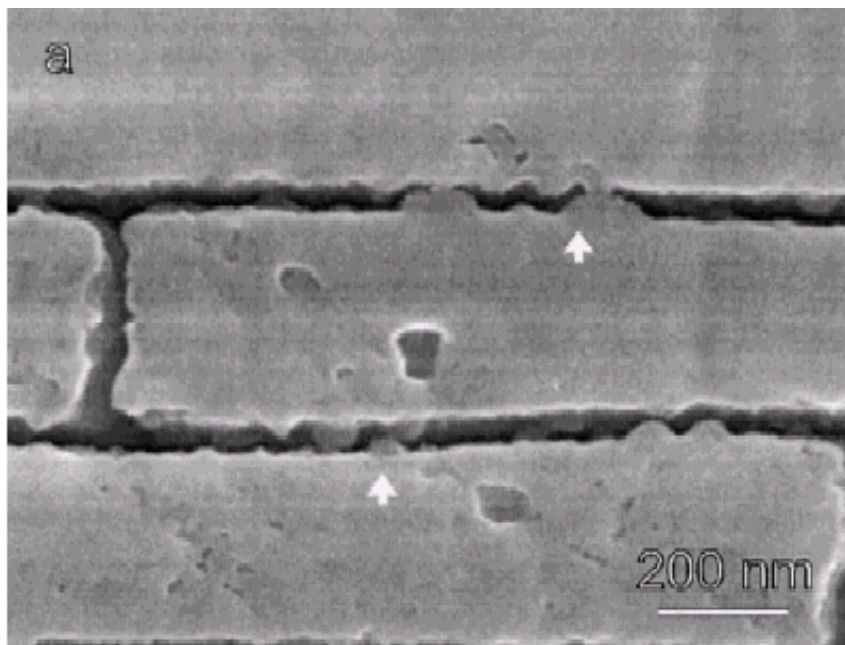
中国科学院力学研究所

INSTITUTE OF MECHANICS CHINESE ACADEMY OF SCIENCES



## 研究背景简介

- Wang, Suo, Evans 等 (2001), 发现文石晶片表面存在纳米尺度的粗糙微小颗粒, 并相继提出珍珠母的纳米粗糙颗粒强韧化机制;



粗糙颗粒







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## 研究背景简介

上述所有微结构机制能仍不能完整地解释已观察到的珍珠母力学行为。如：在珍珠母的大变形，等等。



**The studies of mollusc nacre are at the very forefront of this quest---the pearl in the crown.**

**L.Addadi and S.Weiner**

***Nature, 1997, Vol. 398: 912.***



- 珍珠母结构已成为目前仿生材料研究的热点，是高性能人工合成材料（特别是工程陶瓷材料）仿生设计和制备的目标之一；

**Biomimic layered structures, which have been proved to be able to control the cracks in ceramics and increase the damage tolerance of ceramics, will be the most promising new approaches in the strengthening and toughening design of synthetic ceramics in the future.**

**W.J. Clegg**

***Science, 1999, Vol.286:1097.***



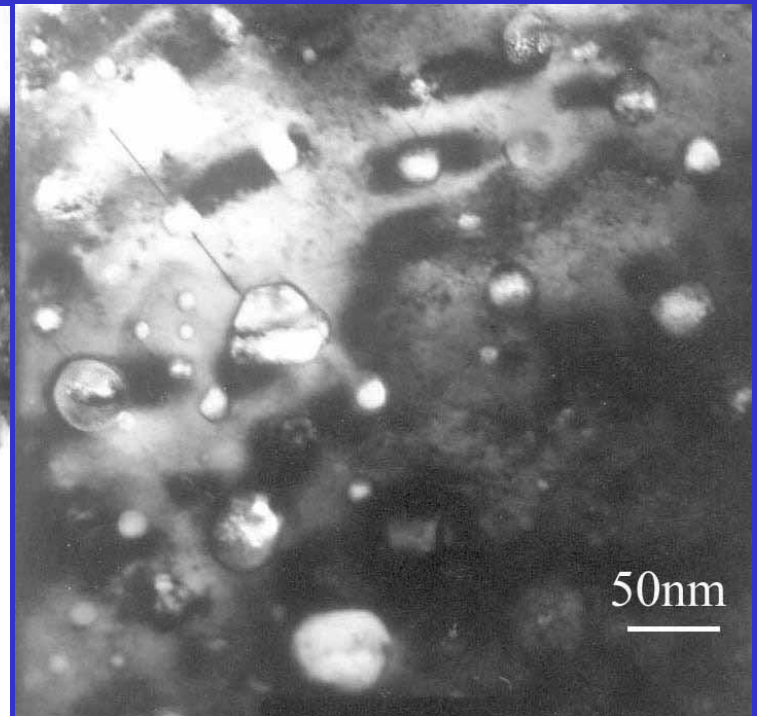
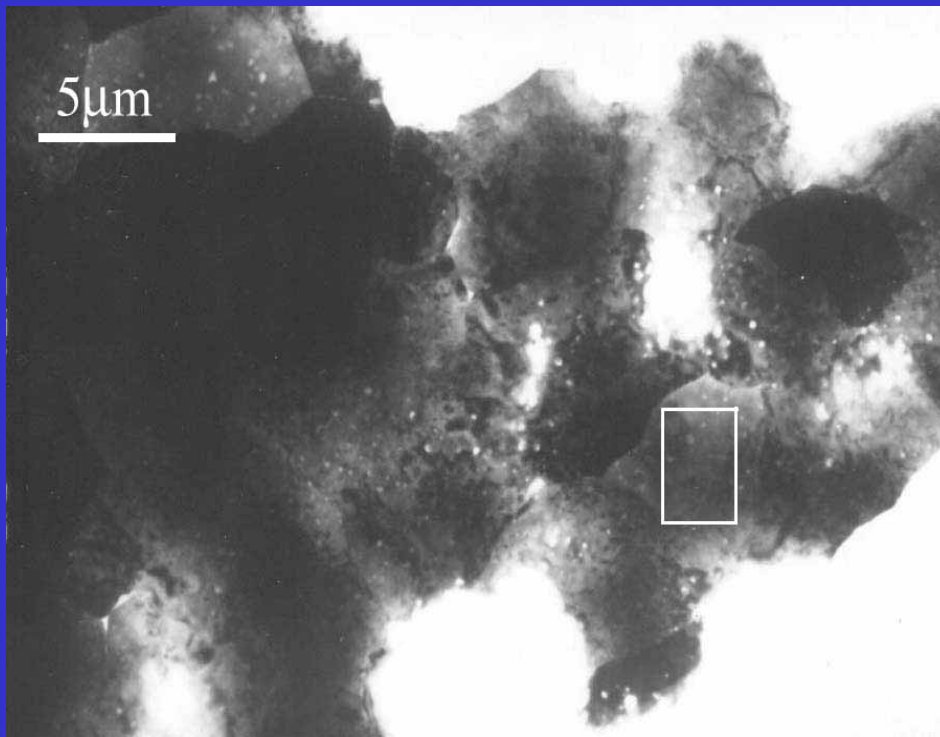
- **The mineral bridges in organic matrix layers of nacre are really of existence?**
- **How effects does the nanostructure produce on the mechanical behaviors of nacre?**

# Nanostructure in the organic matrix layers of nacre



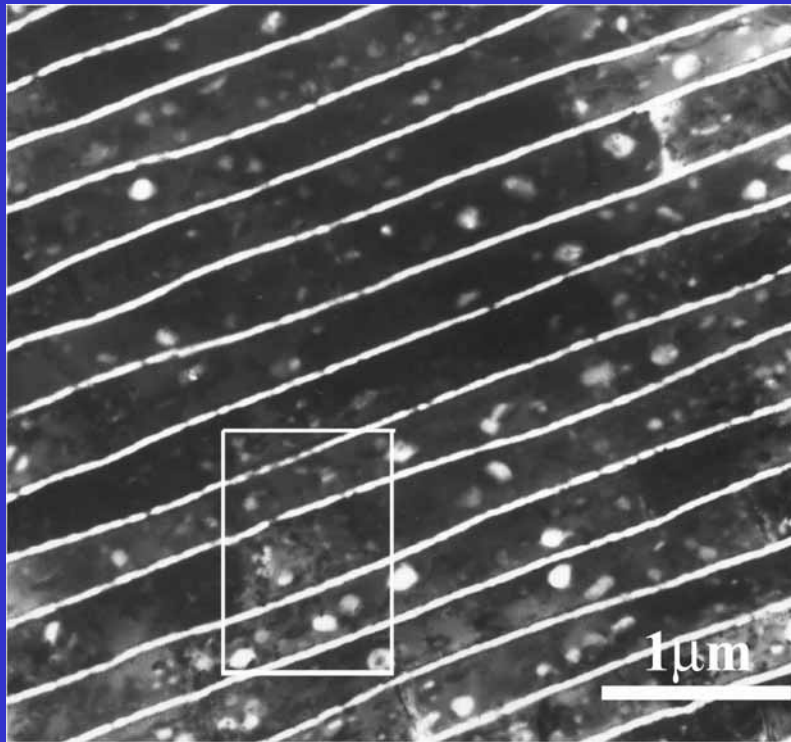


## 珍珠母有机基质层中的微结构

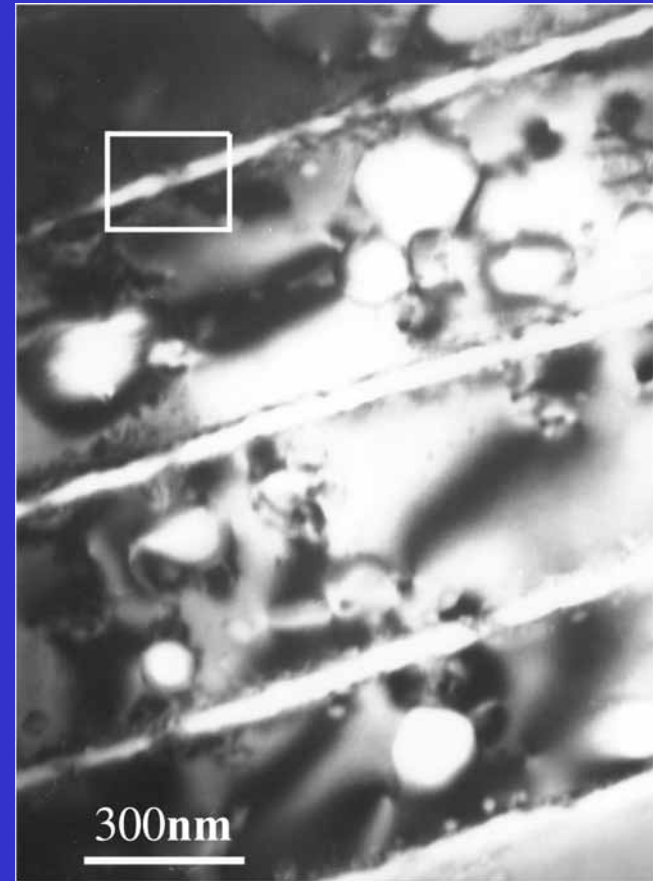


有机基质中的矿物桥

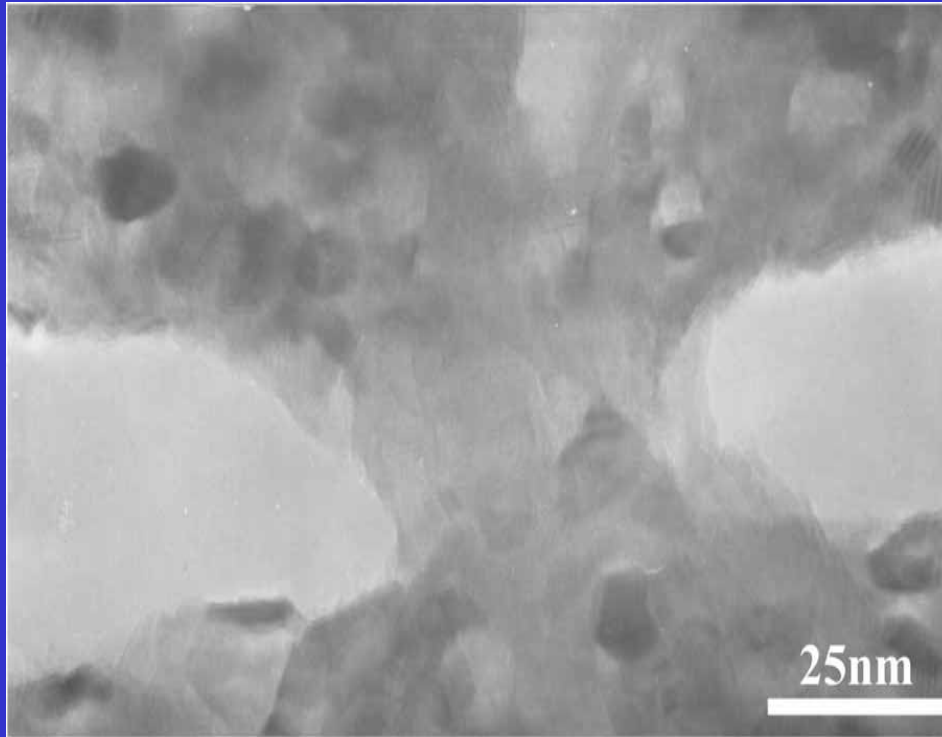
## 珍珠母有机基质层中的微结构



TEM image of the cross section



珍珠母有机基质层中的微结构



**Diameter:**

$$D=46 \pm 8 \text{ nm}$$

**Height:**

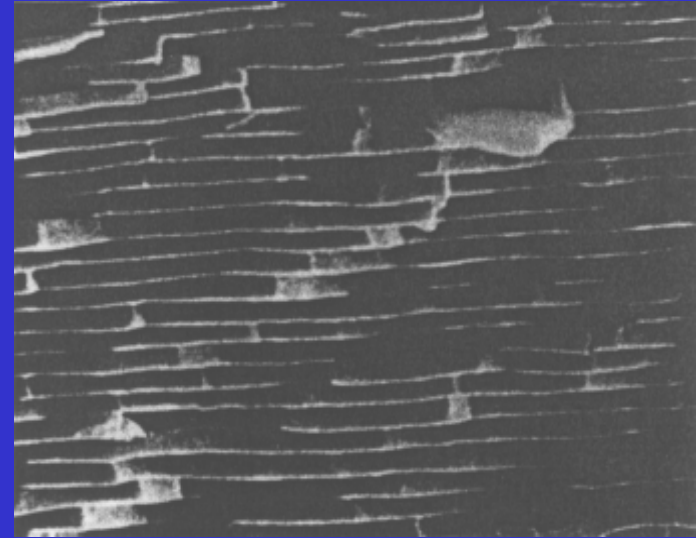
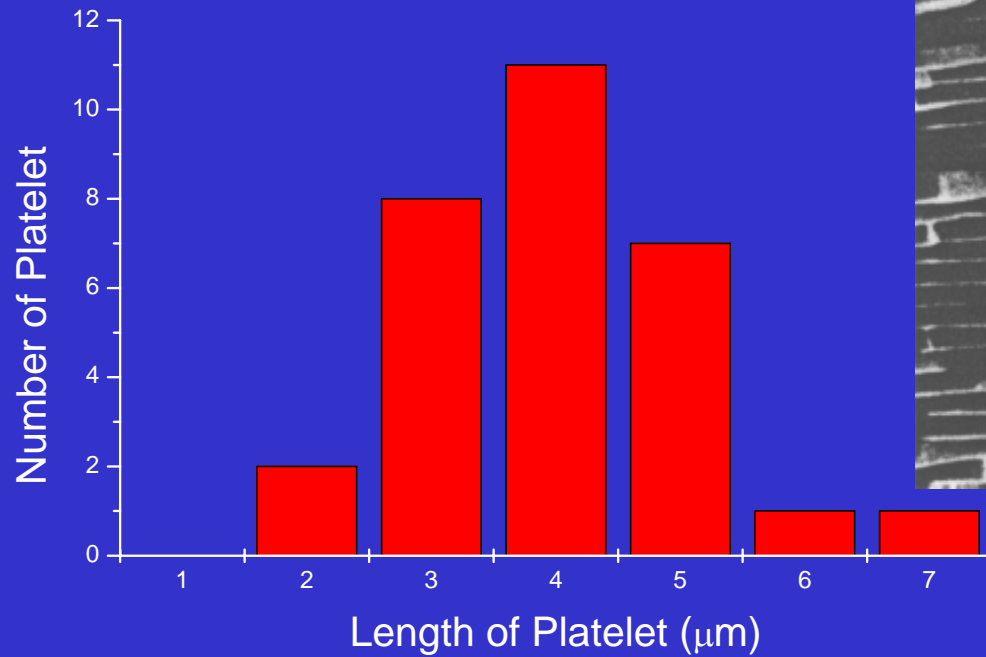
$$t=29 \pm 4 \text{ nm}$$

**TEM image showing a nanostructural column in an organic matrix layer**



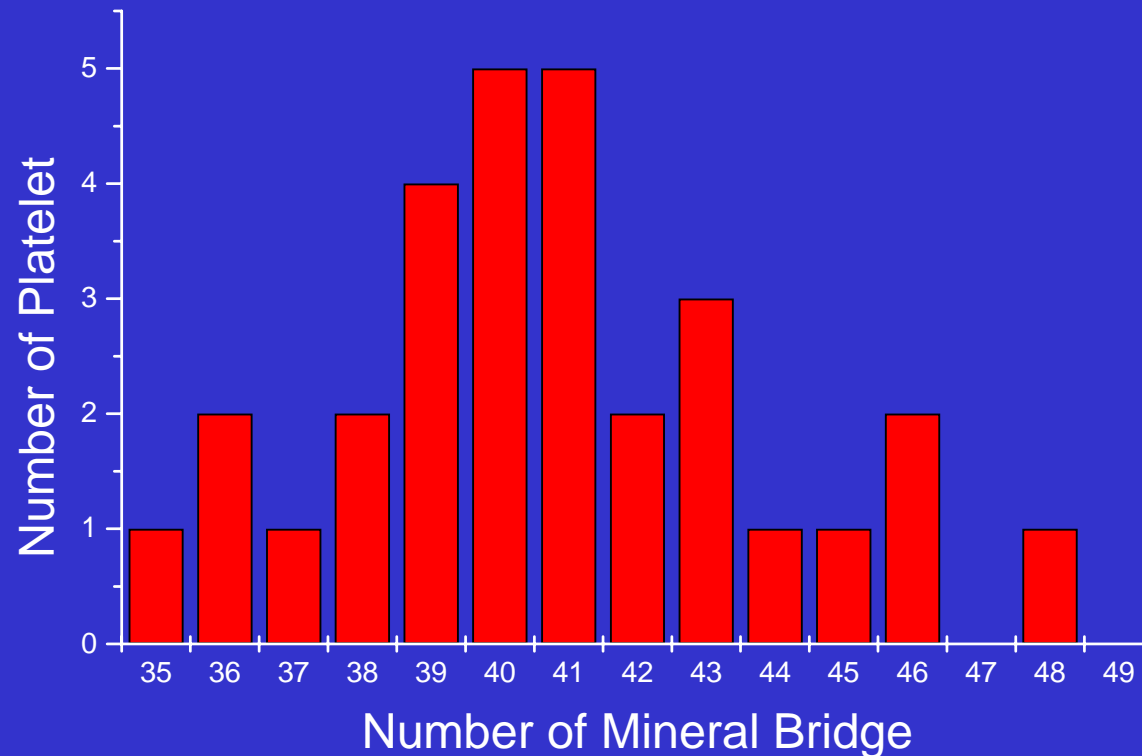
- **There exists the nanostructural columns (or mineral bridges) in the organic matrix layers of nacre;**
- **The columns approximately appear to be circular, and stochastically come up in the organic matrix layers.**

## Distribution of the nanostructure



The average width of the platelets on the cross section of nacre :  $l_0 = 4 \pm 0.8 \mu\text{m}$

## Distribution of the nanostructure

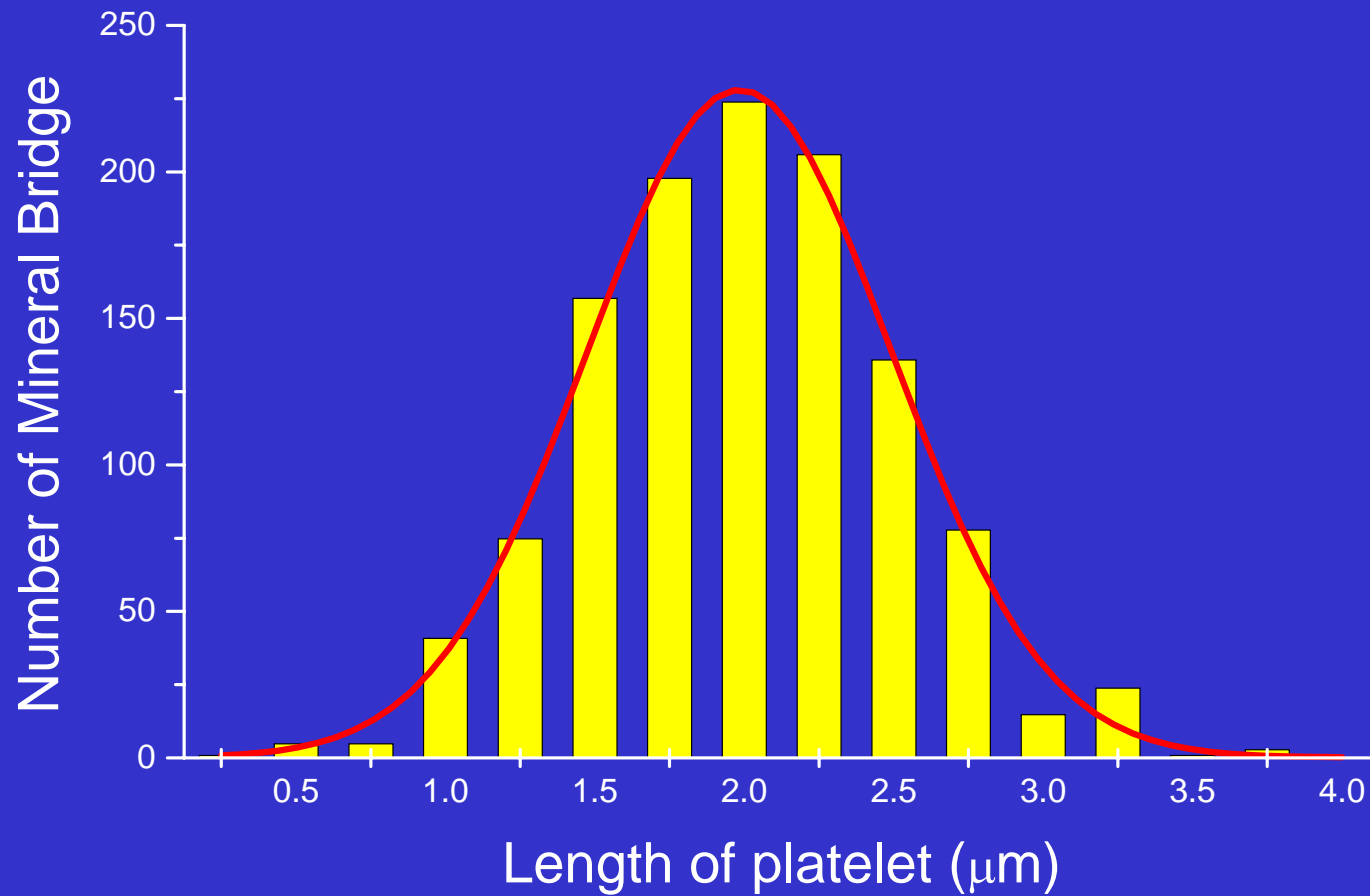


- The average number of the nanostructural columns on a platelet on cross section is  $N_x = 40 \pm 5$ ;





## Distribution of the nanostructure



## Distribution of the nanostructure

- **The distribution of the nanostructure in the layer on a platelet on the cross section :**

$$f(x) = \frac{N_x}{\sqrt{2\pi}\sigma} \exp \left[ -\frac{(x - \mu)^2}{2\sigma^2} \right]$$

- **The average value and standard deviation:**

$$\mu = 2, \sigma = 0.67; 0 \leq x \leq 4.$$



## Distribution of the nanostructure

- **There is a central region of the nanostructures in each platelet on the cross section:**

$$(\mu - \sigma, \mu + \sigma) = (1.33, 2.67)$$

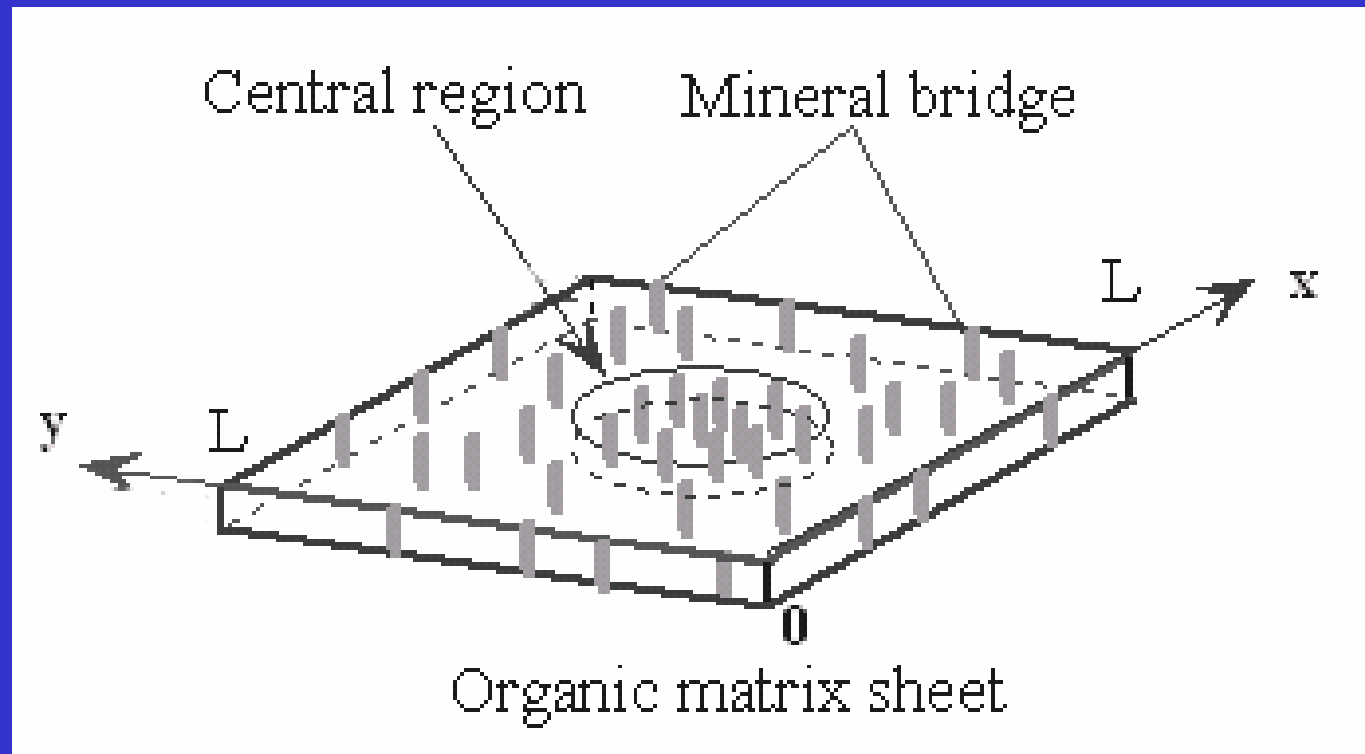
- **The number of the nanostructures in the central region:**

$$\int_{\mu - \sigma}^{\mu + \sigma} f(x) dx \approx 0.68 N$$

Song, F., *et al.*, 2002, *J. Mater. Res.*, Vol.17 (7): 1567.



## Distribution of the nanostructure



有机基质层微结构示意图

## Distribution of the nanostructure

- **The Linear density of the nanostructure in the layer on a platelet on the cross section :**

$$\rho(x) = 2\rho_0 \exp \left[ -V_p \frac{l_0}{l_D} \left( x - \frac{l_0}{2} \right)^2 \right]$$

- $\rho_0 \approx N_x / l_0 = 10 \mu\text{m}^{-1}$   
 $V_p = 0.95$

Song, F., *et al.*, 2003, *Biomaterials*, Vol.24 : 3622.



## Distribution of the nanostructure

- The average bridge-to-bridge spacing between the neighboring bridges for each platelet :

$$\langle s \rangle_{\text{whole}} = \int_0^{l_0} x \rho(x) dx \approx 80 \text{ nm}$$

- The average bridge-to-bridge spacing between the neighboring bridges in the central region :

$$\langle s \rangle_{\text{center}} = \int_{\mu-\sigma}^{\mu+\sigma} x \rho(x) dx \approx 50 \text{ nm}$$

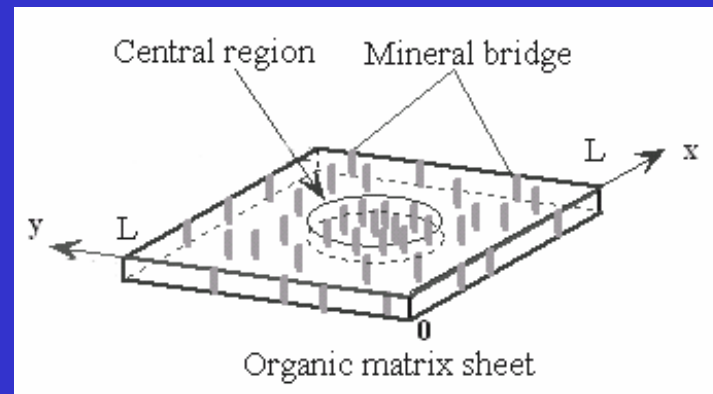


- 每一晶片上矿物桥的分布：

$$n(x, y) = \rho(x)\rho(y)$$

$$= 4n_0 \exp \left\{ -V_P \frac{l_0}{l_D} \left[ \left( x - \frac{l_0}{2} \right)^2 + \left( y - \frac{l_0}{2} \right)^2 \right] \right\}$$

- $n_0 = \rho_0^2$



- 每一晶片上桥的平均密度： $n_o = 100\mu\text{m}^{-2}$
- 每一晶片上存在一个桥的中央区
- 中央区中桥的数目为：

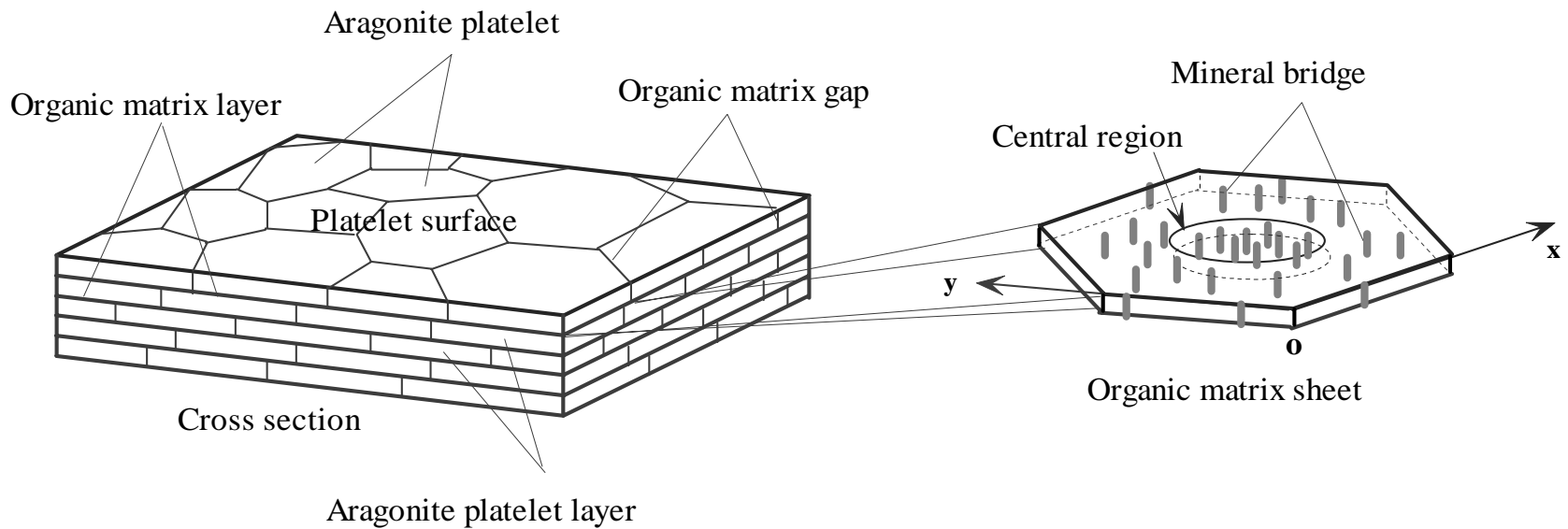
$$\int_{\mu-\sigma}^{\mu+\sigma} \int_{\mu-\sigma}^{\mu+\sigma} n(x, y) dx dy \approx 0.46N.$$

- 中央区面积为晶片面积的1/9

Song, F., *et al.*, 2003, *Biomaterials*, Vol.24 : 3622.

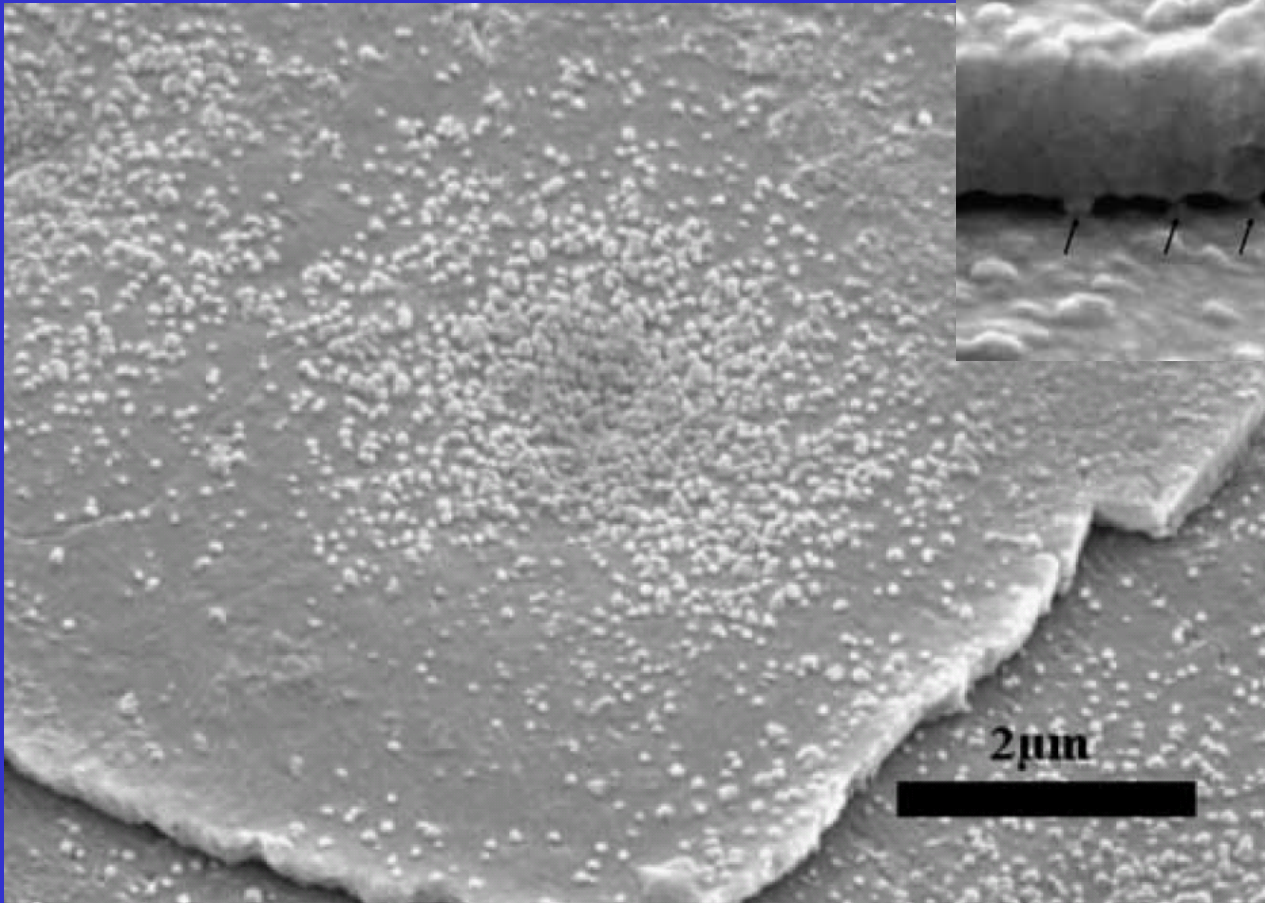


## 珍珠母有机基质层中的微结构



珍珠母微结构示意图

## 珍珠母有机基质层中的微结构



层面上有机基质中的矿物桥分布 (SEM)

## 小 结

- 珍珠母的有机基质层中存在矿物桥这种无机纳米结构；
- 矿物桥在有机基质层中是随机分布的，并满足一定的分布律；



# The effects of nanostructure on the mechanical behaviors of nacre



- **The volume fraction of the nanostructures in a region,  $(l_1, l_2)$ :**

$$V_f|_{l_1}^{l_2} = \frac{\pi D^2}{4l_0(l_2 - l_1)} \int_{l_1}^{l_2} \left( \int_0^{l_0} n(x, y) dy \right) dx,$$

- **The volume fraction of the organic matrix in  $(l_1, l_2)$  :**

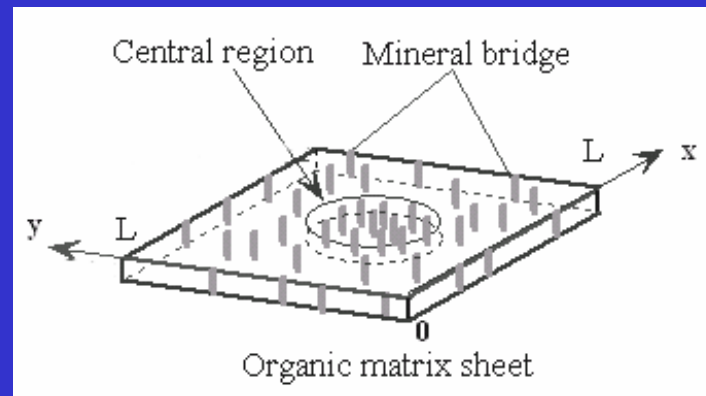
$$V_m|_{l_1}^{l_2} = 1 - V_f|_{l_1}^{l_2}$$

## Mechanical properties

- Average Young's modulus of the organic layer within  $(l_1, l_2)$ :

$$E_c|_{l_1}^{l_2} = E_m \left( 1 + 24 V_f |_{l_1}^{l_2} \right)$$

- $E_o = E_c|_0^{l_0} = 5E_m$



- **Riley's Model:**

$$E_{nacre} = V_p E_p \left[ 1 - \frac{\ln(u + 1)}{u} \right] + (1 - V_p) E_o$$

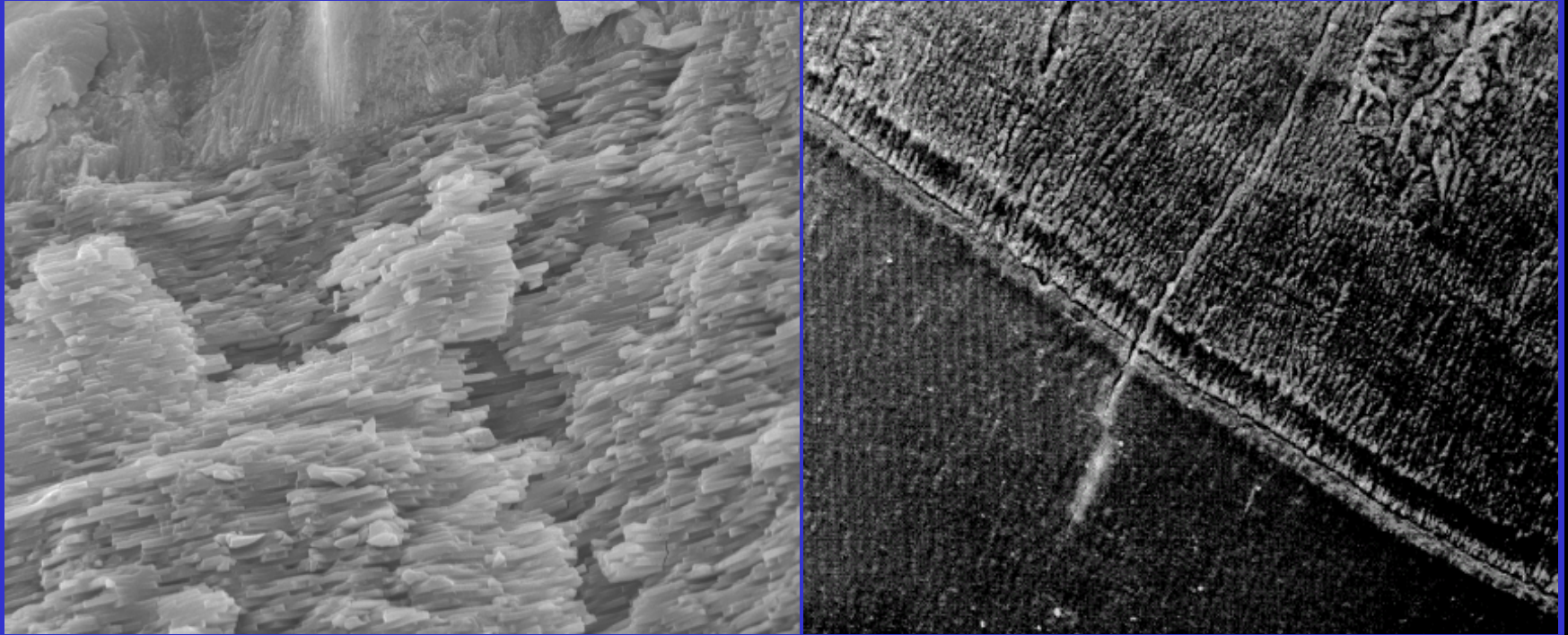
- $$u = s \sqrt{\frac{M V_p}{E_p (1 - V_p)}}$$

- $E_{nacre} = 68.9 \text{ GPa}$

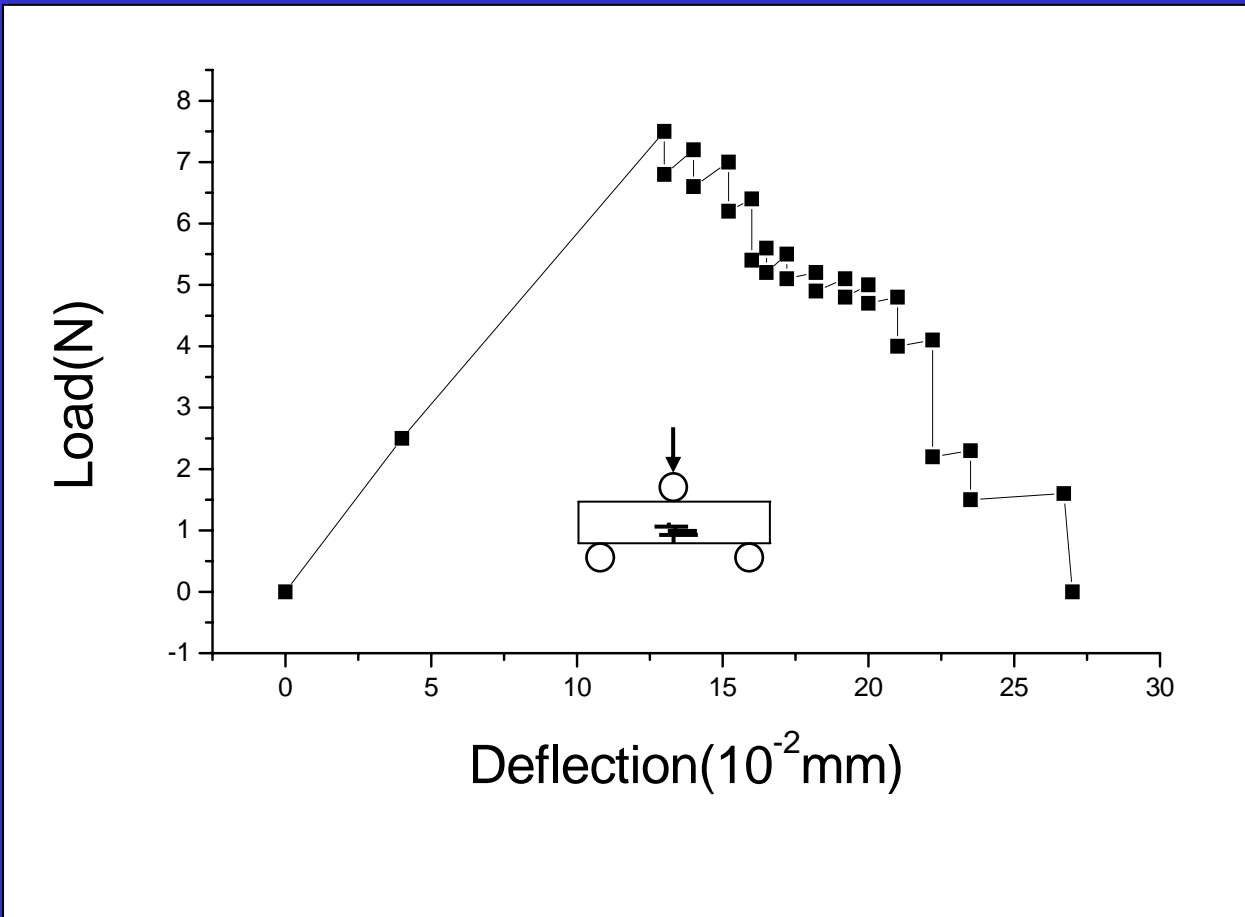
- **Jackson et al :**  $E_{nacre} = 70 \text{ GPa}$

Song, F., et al., 2003, *Biomaterials*, Vol.24 : 3622.

# 贝壳材料中的裂纹传播



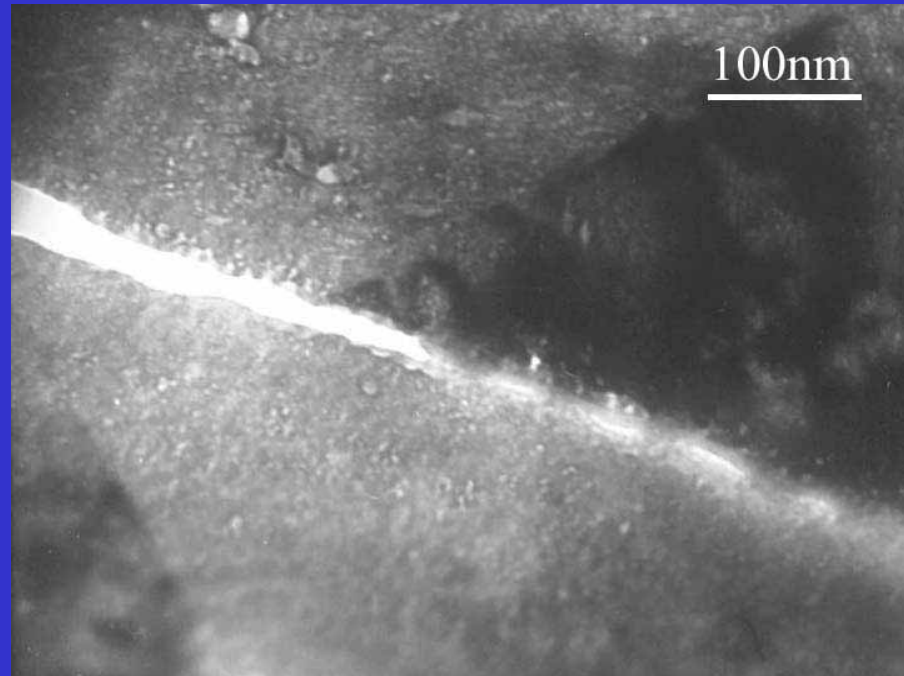
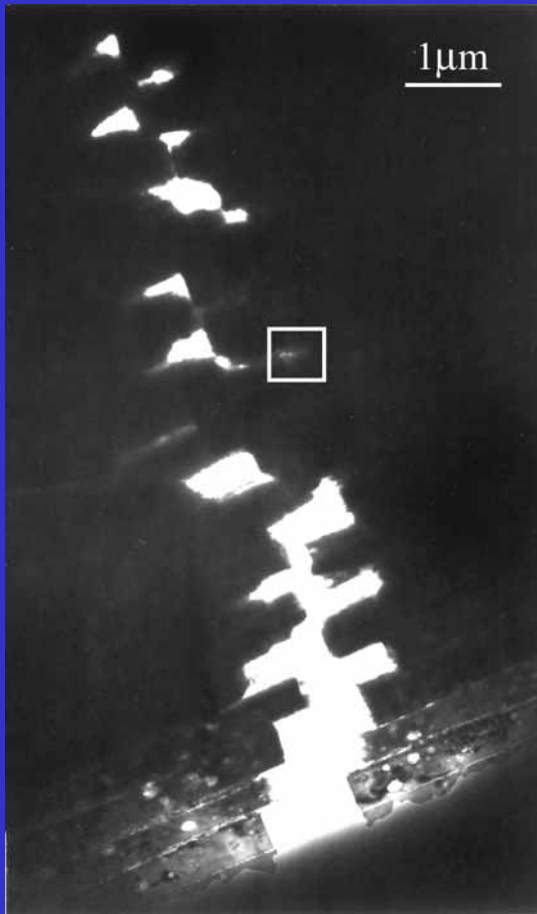
## Fracture experiment



The curve of three-point bending test

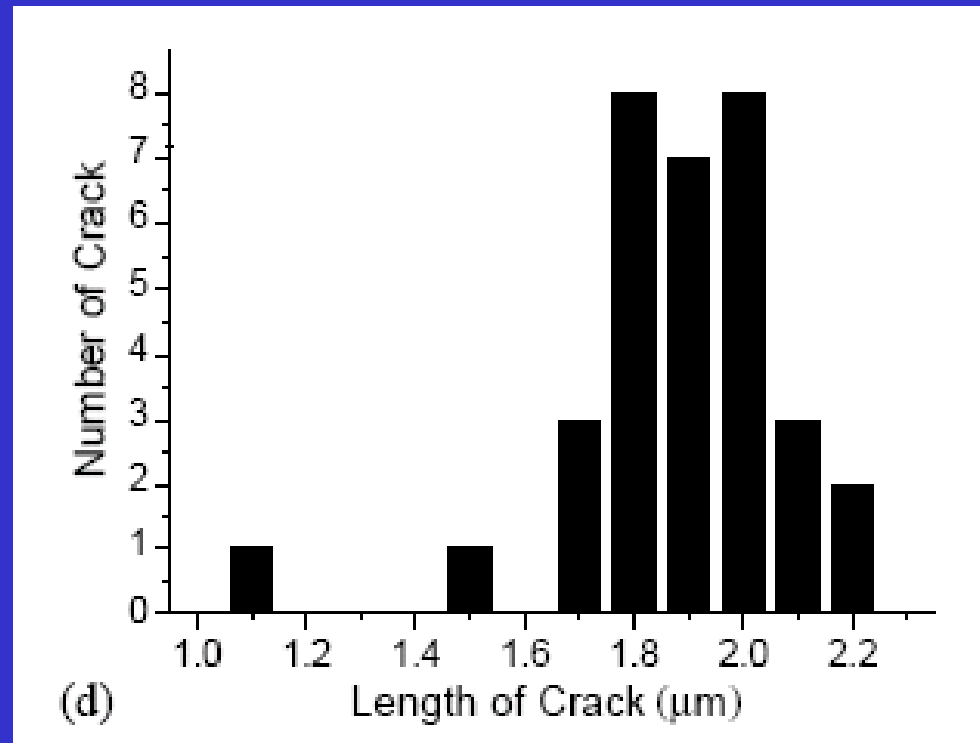


## Fracture experiment



(1) TEM image showing the extension of the crack on the cross section of nacre; (2) TEM image showing the nanostructures arrest the extension of the crack.

## Fracture experiment



- The average length of cracks in the each of the organic layers:

$1.88 \pm 0.20 \mu\text{m}$

## Fracture experiment

- All cracks only extend in the interlamellar organic matrix layers of nacre
- The crack path on a cross section is tortuous and stepwise
- The nanostructures arrest the extension of the cracks in the central regions
- Crack deflection and aragonite platelet pull-out continually occur in the course of the fracture



- The average crack resistance for  $(x_1, x_2)$  of the organic matrix layers:

$$R_c \approx (1 + 1.5V_b \Big|_{x_1}^{x_2}) R_o$$

- $R_o$  : the average crack resistance of the organic matrix

- **For the organic matrix layers on one platelet:**

$$V_b \Big|_0^4 = 0.17, R_c = 1.26 R_o$$

- **For the central region of the platelet**

$$V_b \Big|_{1.33}^{2.67} = 0.35, R_c = 2.04 R_o$$

- **The average fracture toughness for  $(x_1, x_2)$  of the organic matrix layers:**

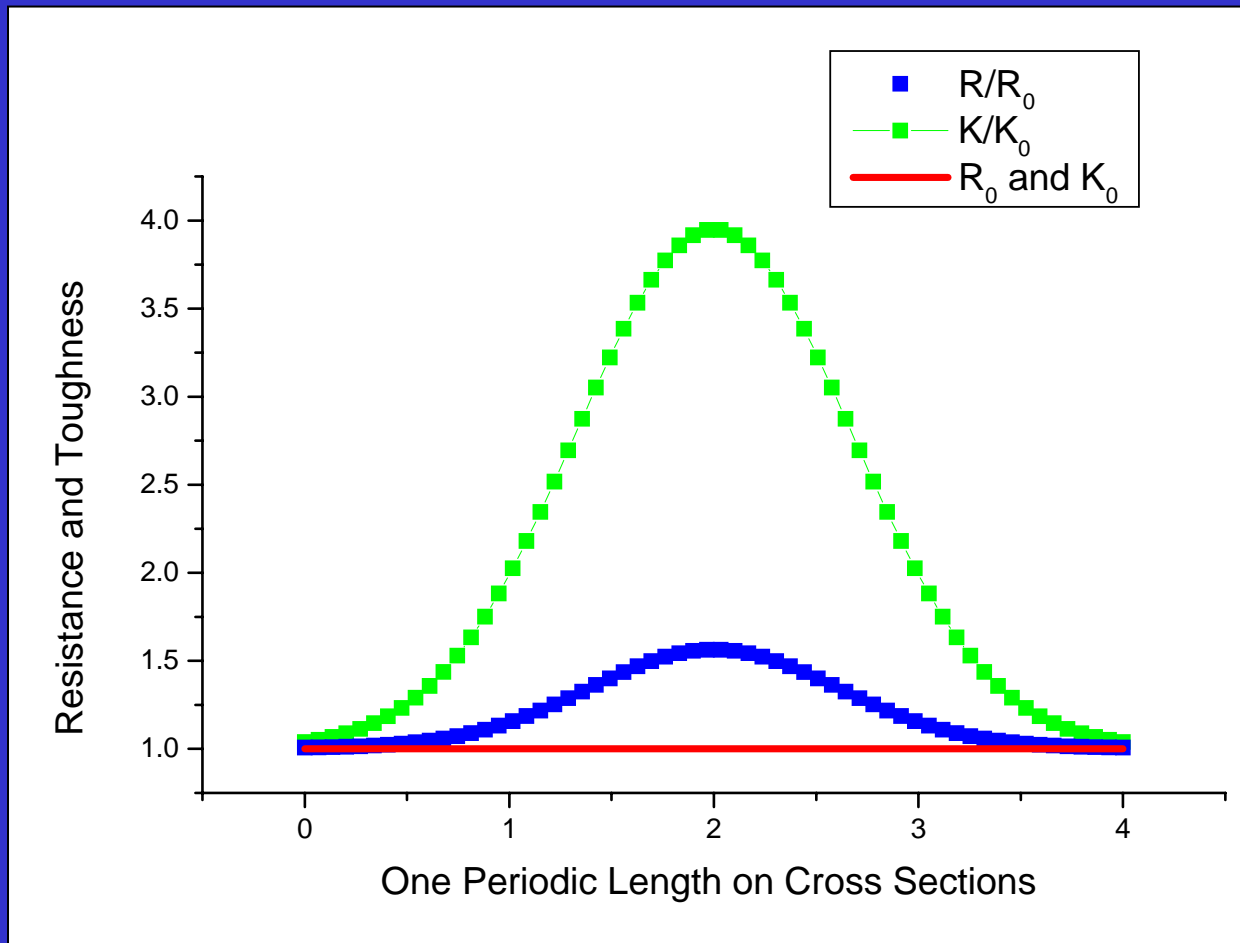
$$K_{Ic}^c = K_{Ic}^o \sqrt{(1 + 24V_b \left| \frac{x_2}{x_1} \right|)(1 + 1.5V_b \left| \frac{x_2}{x_1} \right|)}$$

- **The average fracture toughness for the organic matrix layers without the nanostructures:**

$$K_{Ic}^o = \sqrt{E_o R_o}$$



## Crack resistance



Song, F., et al., 2003, *Biomaterials*, Vol.24 : 3622.





- 界面的强度:

$$\sigma_c \left| \frac{l_2}{l_1} \right. = \sigma_m \left( 1 + 24 V_f \left| \frac{l_2}{l_1} \right. \right)$$

- $\sigma_m$  为不考虑矿物桥时的界面强度

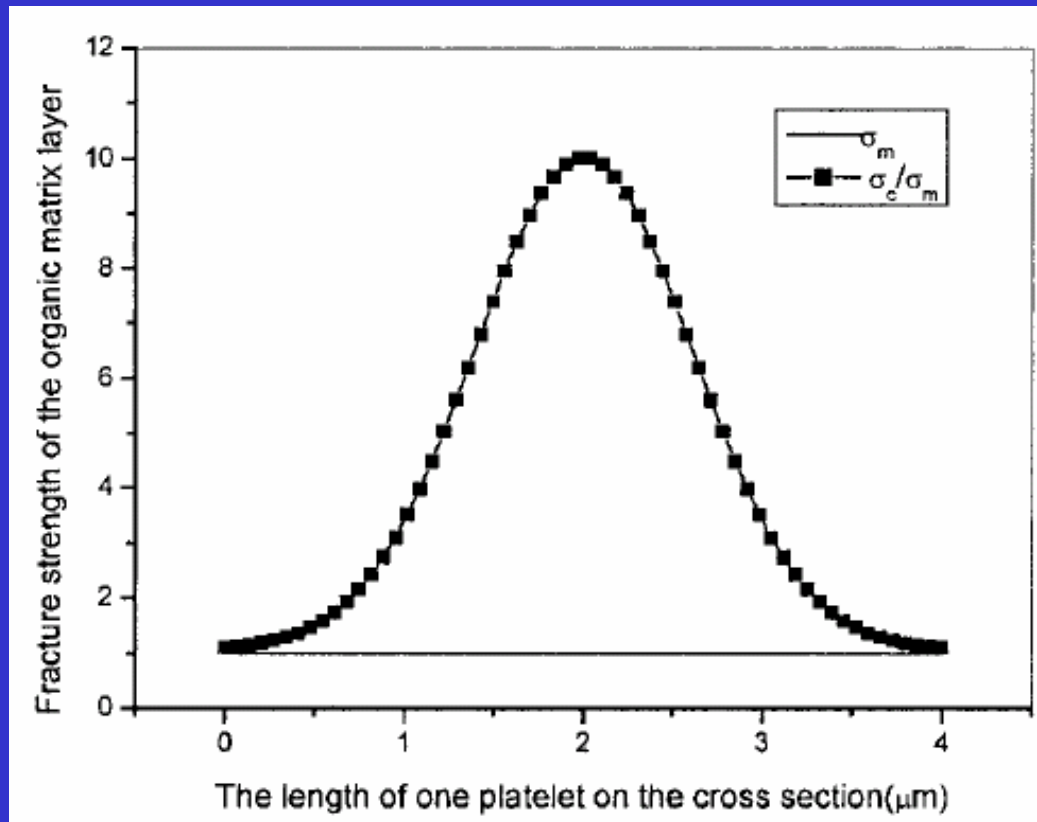
- 对于每一晶片上的有机基质界面

$$V_b \Big|_0^4 = 0.17, \sigma_c \approx 5\sigma_m$$

- 对于每一晶片上有机基质界面的中央区

$$V_b \Big|_{1.33}^{2.67} = 0.35, \sigma_c \approx 9\sigma_m$$

## 界面强度



Song, F. and Bai, Y.L., 2003, *J. Mater. Res.*, Vol.18 : 1741.



- 平均裂纹长度:

$$\frac{a_c}{a_o} = \frac{1 + 1.5V_b|_0^4}{1 + 24V_b|_0^4} \approx \frac{1}{4}$$

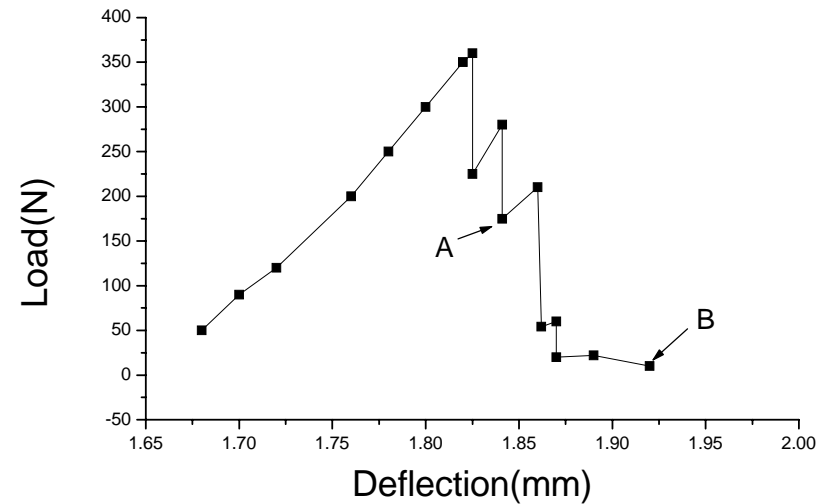
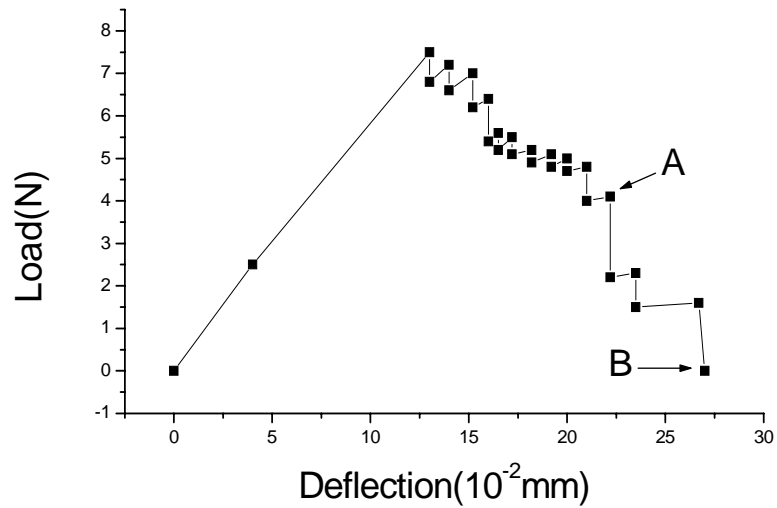
Song, F. and Bai, Y.L., 2005, *J. Am. Ceram. Soc.* Vol. 88, 1094.

## Mechanical properties

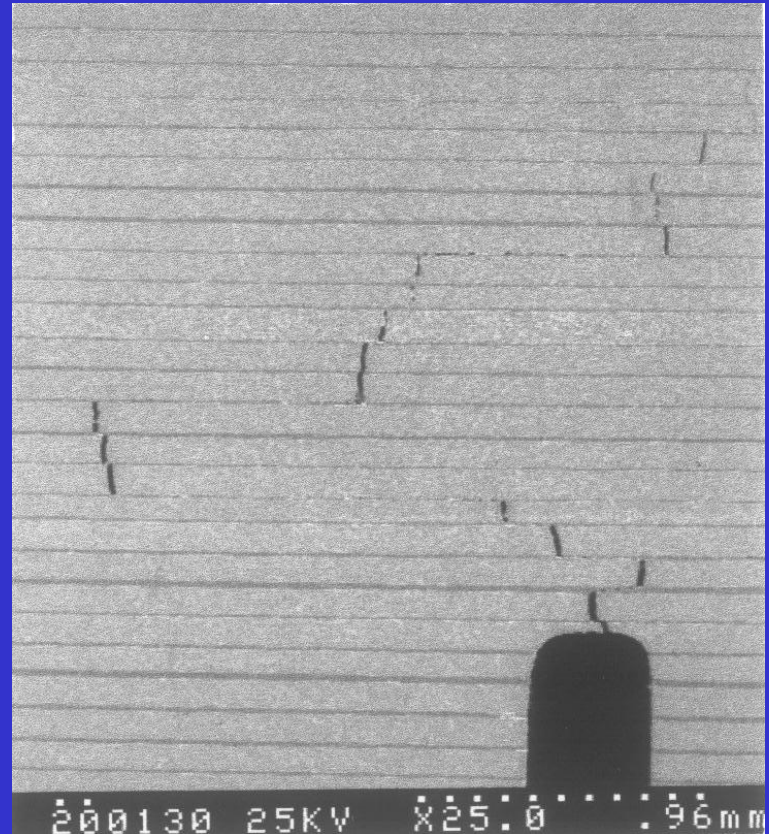
- **The nanostructures can not only effectively increase the crack resistance of the organic matrix interfaces, but also automatically form periodic crack resistance to prevent cracks from extending in nacre;**
- **The nanostructures can effectively increase the fracture strength of the organic matrix interfaces.**



# 层状材料力学性能研究

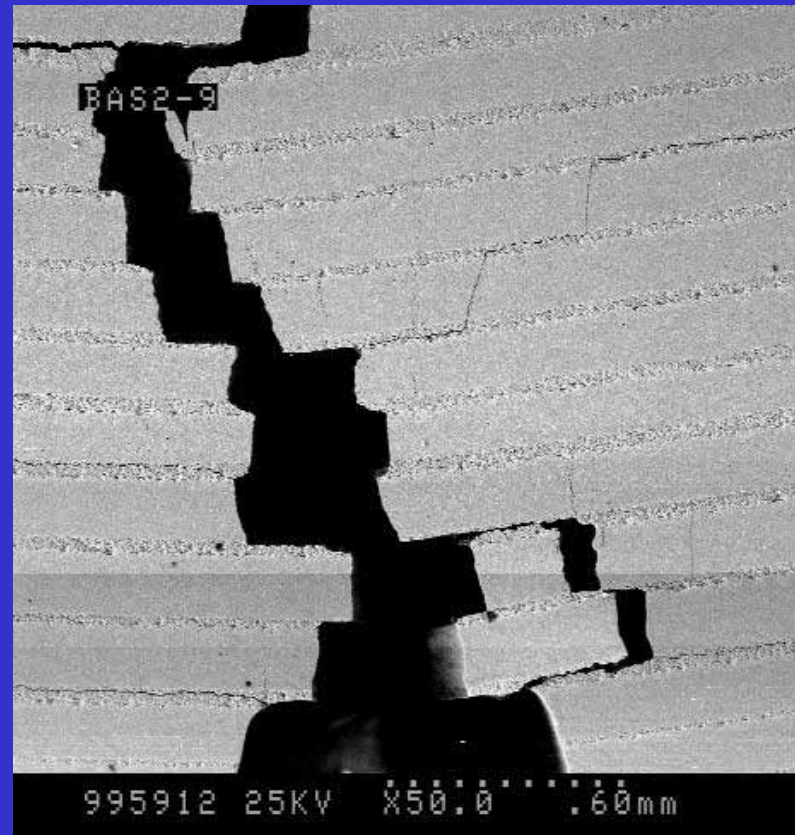
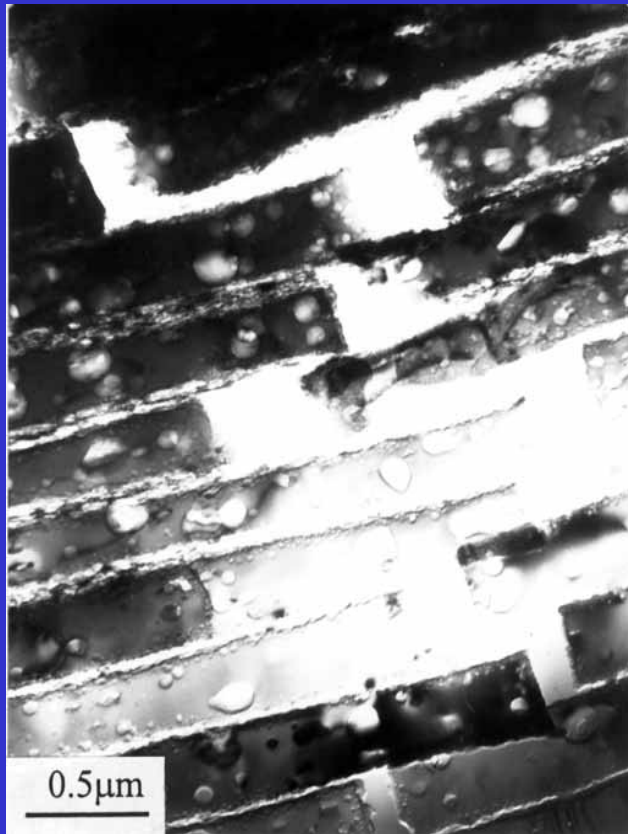


# 层状材料力学性能研究

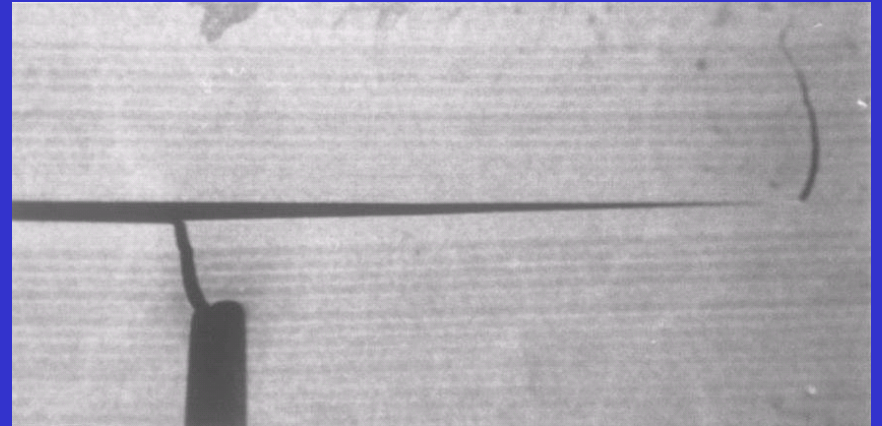
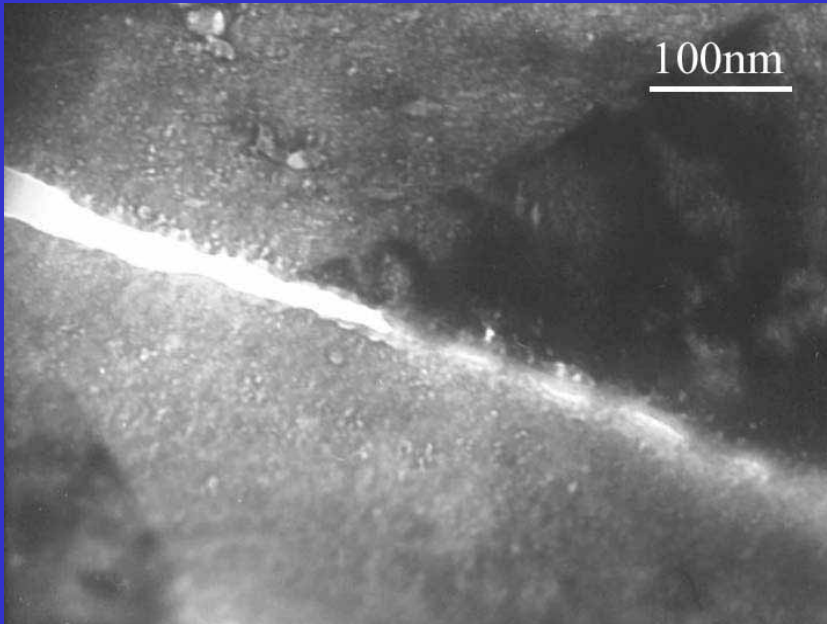




## 层状材料力学性能研究



# 生物层状材料力学性能研究

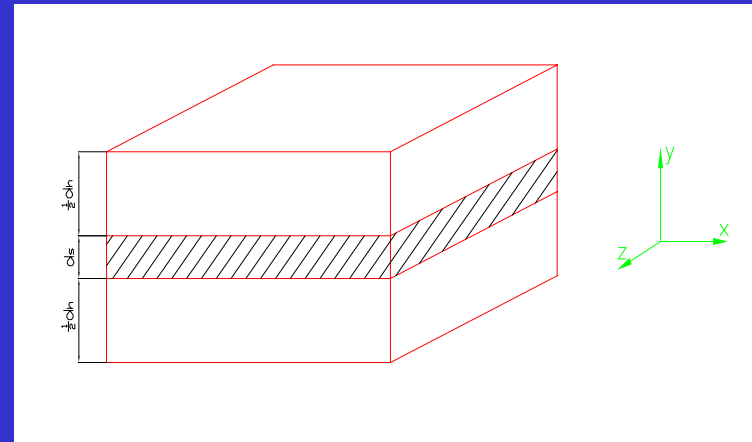


- 共性：裂纹沿软层传播，并发生偏转；
- 异性：珍珠母中矿物桥阻碍裂纹沿软层传播，有文石晶片拔出现象。

# 珍珠母中裂纹特征方程

- 应变能密度函数:

$$f = \varepsilon_{ij} \sigma_{ij} / 2$$



$$= \frac{1}{2} [c_{11} \varepsilon_{xx}^2 + (c_{12} + c_{21}) \varepsilon_{xx} \varepsilon_{yy} + c_{22} \varepsilon_{yy}^2 + 2c_{33} \varepsilon_{xy}^2]$$

## 珍珠母中裂纹特征方程

其中

$$c_{11} = \frac{E}{1-\nu^2} + \frac{\nu^2}{1-\nu} \frac{1}{M}, c_{12} = c_{21} = \frac{\nu}{M}$$

$$c_{22} = \frac{1-\nu}{M}, c_{33} = \frac{1}{1+\nu} \frac{1}{\frac{V_h}{E_h} + \frac{V_s}{E_s}}$$

$$M = (1-\nu) \left( \frac{V_h}{E_h} + \frac{V_s}{E_s} - \frac{\nu^2}{E} \right) - \frac{1}{E} \nu^2 (1+\nu)$$

## Fourier 变换

$$u_{\alpha}(\mathbf{q}) = \frac{1}{(2\pi)^2} \iint_{(-\infty, +\infty)} u_{\alpha}(\mathbf{r}) \cdot e^{-i\mathbf{q} \cdot \mathbf{r}} dx dy$$

$$u_{\alpha}(\mathbf{r}) = \iint_{(-\infty, +\infty)} u_{\alpha}(\mathbf{q}) \cdot e^{i\mathbf{q} \cdot \mathbf{r}} dq_x dq_y$$

其中  $\alpha = x, y, \mathbf{q} = (q_x, q_y), \mathbf{r} = (x, y)$

### 应变能密度函数

$$-f_q = Au_x(r)^2 + Bu_y(r)^2 + Cu_x(r)u_y(r)$$

其中

$$A = \frac{1}{2}c_{11}q_x^2 + \frac{1}{4}c_{33}q_y^2, B = \frac{1}{2}c_{22}q_y^2 + \frac{1}{4}c_{33}q_x^2$$

$$C = \frac{1}{2}q_xq_y(c_{12} + c_{21} + c_{33})$$



## 珍珠母中裂纹特征方程

应变能:  $F = \int f d\mathbf{r} = \frac{1}{(2\pi)^2} \sum_{\mathbf{q}} f_{\mathbf{q}}$

材料状态满足:  $\delta F = 0$

$$\begin{pmatrix} c_{11}q_x^2 + \frac{1}{2}c_{33}q_y^2 & \frac{1}{2}q_xq_y(c_{12} + c_{21} + c_{33}) \\ \frac{1}{2}q_xq_y(c_{12} + c_{21} + c_{33}) & c_{22}q_y^2 + \frac{1}{2}c_{33}q_x^2 \end{pmatrix} \begin{pmatrix} u_x(r) \\ u_y(r) \end{pmatrix} = 0$$

## 珍珠母中裂纹特征方程

应变能1: 
$$-f_q = u_x^2(r) \left[ \frac{1}{2} c_{11} q_x^2 + \frac{1}{4} c_{33} q_y^2 (1 - \varphi) \right]$$

$$\varphi = \frac{q_x^2 (c_{12} + c_{21} + c_{33})^2}{c_{33} (2c_{22} q_y^2 + c_{33} q_x^2)}$$

应变能2: 
$$-f_q = u_y^2(r) \left[ \frac{1}{2} c_{22} q_y^2 + \frac{1}{4} c_{33} q_x^2 (1 - \psi) \right]$$

$$\psi = \frac{q_y^2 (c_{12} + c_{21} + c_{33})^2}{c_{33} (2c_{11} q_x^2 + c_{33} q_y^2)}$$

## 珍珠母中裂纹特征方程

由方程

$$\det \begin{pmatrix} c_{11}q_x^2 + \frac{1}{2}c_{33}q_y^2 & \frac{1}{2}q_xq_y(c_{12} + c_{21} + c_{33}) \\ \frac{1}{2}q_xq_y(c_{12} + c_{21} + c_{33}) & c_{22}q_y^2 + \frac{1}{2}c_{33}q_x^2 \end{pmatrix} = 0$$

得到:

$$Eq_x^4 + Fq_x^2q_y^2 + Gq_y^4 = 0$$

## 珍珠母中裂纹特征方程

其中

$$E = \frac{1}{2}c_{11}c_{33}$$

$$F = \frac{1}{4}[c_{33}^2 + 4c_{11}c_{22} - (c_{12} + c_{21} + c_{33})^2]$$

$$G = \frac{1}{2}c_{22}c_{33}$$

解方程:

$$q_x^2 = \frac{-F \pm \sqrt{\Delta}}{2E} q_y^2$$

## 珍珠母中裂纹特征方程

代入相关材料常数，得到：

$$q_x^2 \approx \xi^2 q_y^2$$

$$q_x^2 \approx \xi^{-1} q_y^2$$

$$u_x \sim \xi u_y$$

$$u_y \sim \xi^{1/2} u_x$$

在珍珠母中

$$\varepsilon = \frac{E_s}{E_h} \ll 1, (E_h \sim 100\text{GPa}, E_s \sim 1-5\text{MPa})$$

$$\xi = \frac{\varepsilon}{V_s} \ll 1, (V_s \sim 5\%)$$

## 珍珠母中裂纹特征方程

代入应变能密度函数， Fourier 逆变换， 得到：

$$f = \frac{1}{2} c_{11} u_{x,x}^2 + c_{33} u_{x,y}^2, (u_y \sim \xi^{1/2} u_x)$$

$$f = \frac{1}{2} c_{22} u_{y,y}^2 + c_{33} u_{y,x}^2, (u_x \sim \xi u_y)$$

## 珍珠母中裂纹特征方程

应变能极小化，得：

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial \hat{y}^2}\right)u_x = 0, (u_y \sim \xi^{1/2}u_x)$$

$$\hat{y} = \sqrt{\frac{c_{11}}{2c_{33}}}y$$

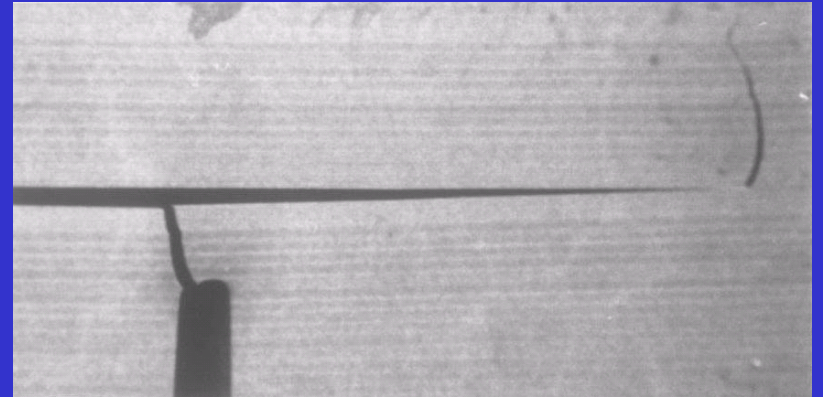
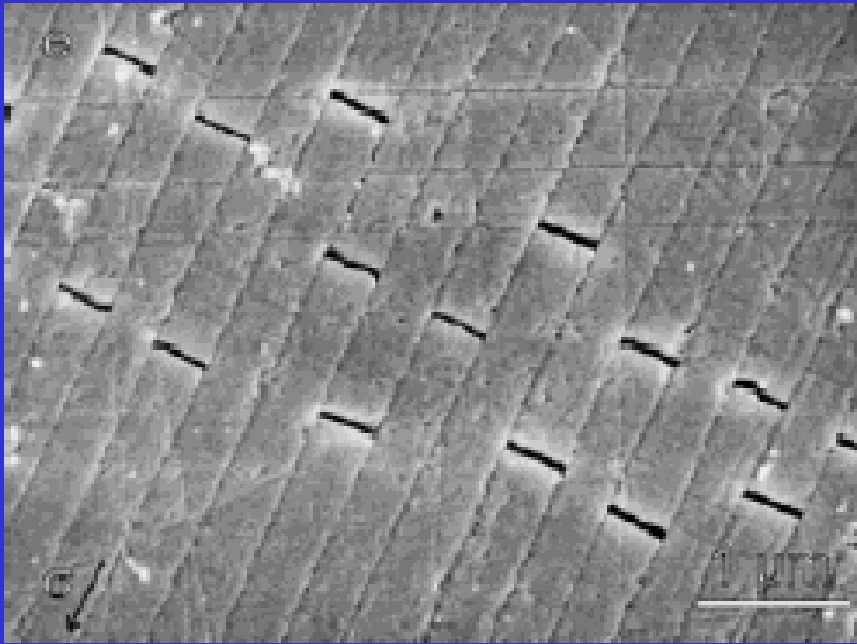
和

$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial \hat{y}^2}\right)u_y = 0, (u_x \sim \xi u_y)$$

$$\hat{y} = \sqrt{\frac{2c_{33}}{c_{22}}}y$$



## 珍珠母中裂纹特征方程



裂纹扩展： a. 珍珠母（拉伸） b. 层状陶瓷（三点弯）

## 珍珠母中裂纹特征方程

- 拉伸状态下的裂纹特征

基本方程

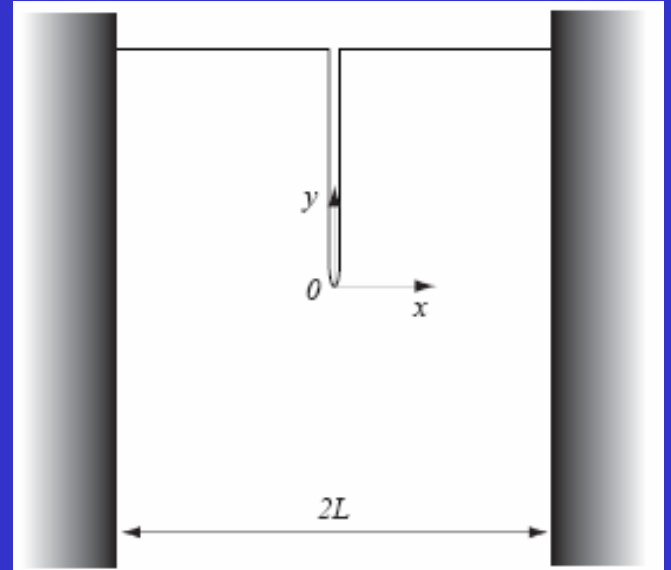
$$\left(\frac{\partial^2}{\partial x^2} + \frac{\partial^2}{\partial \hat{y}^2}\right)u_x = 0$$

边界条件

$$u_x = \pm u_{x_0}, (x = \pm L_x)$$

$$u_x = 0, (x = 0, \hat{y} < 0)$$

$$\frac{\partial u_x}{\partial x} = 0, (x = 0, \hat{y} > 0)$$



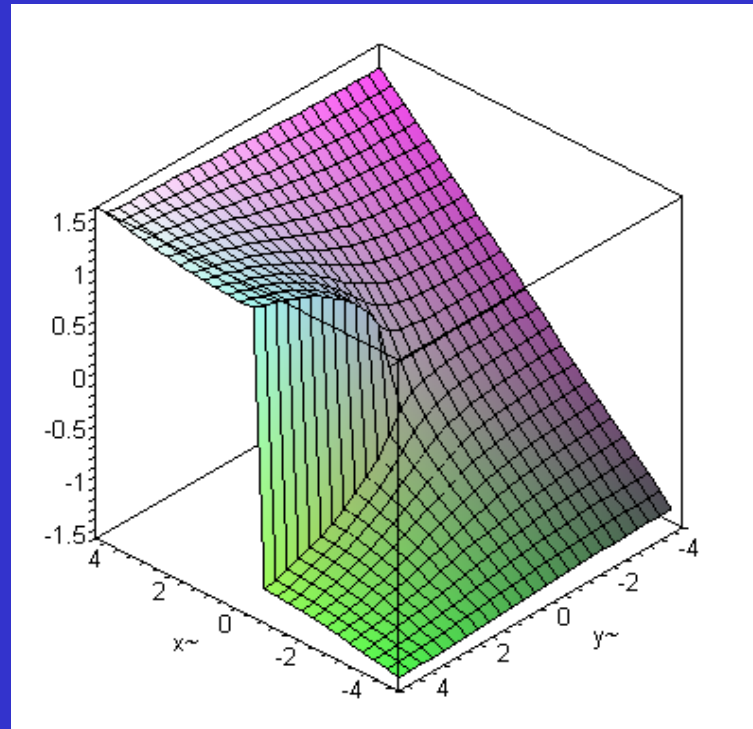
## 珍珠母中裂纹特征方程

方程的解为

$$u_x = \frac{2u_{x_0}}{\pi} \operatorname{Im}[\log(e^{\frac{i\pi z}{2L_x}} + (e^{\frac{i\pi z}{L_x}} - 1)^{\frac{1}{2}})]$$

其中

$$z = x + i y$$



## 珍珠母中裂纹特征方程

### 裂纹形貌

$$u_x^\pm = u_x(x = \pm 0, \hat{y} > 0) = \pm \frac{2u_{x_0}}{\pi} \arctan(e^{\pi \hat{y} / 2L_x} - 1)^{1/2}$$

### 裂纹尖端区域

$$u_x = \pm \frac{2u_{x_0}}{\pi} \sqrt{\frac{y}{\zeta}}$$

其中

$$\zeta = \frac{2}{\pi} \sqrt{\frac{c_{33}}{2c_{11}}} L_x$$

## 珍珠母中裂纹特征方程

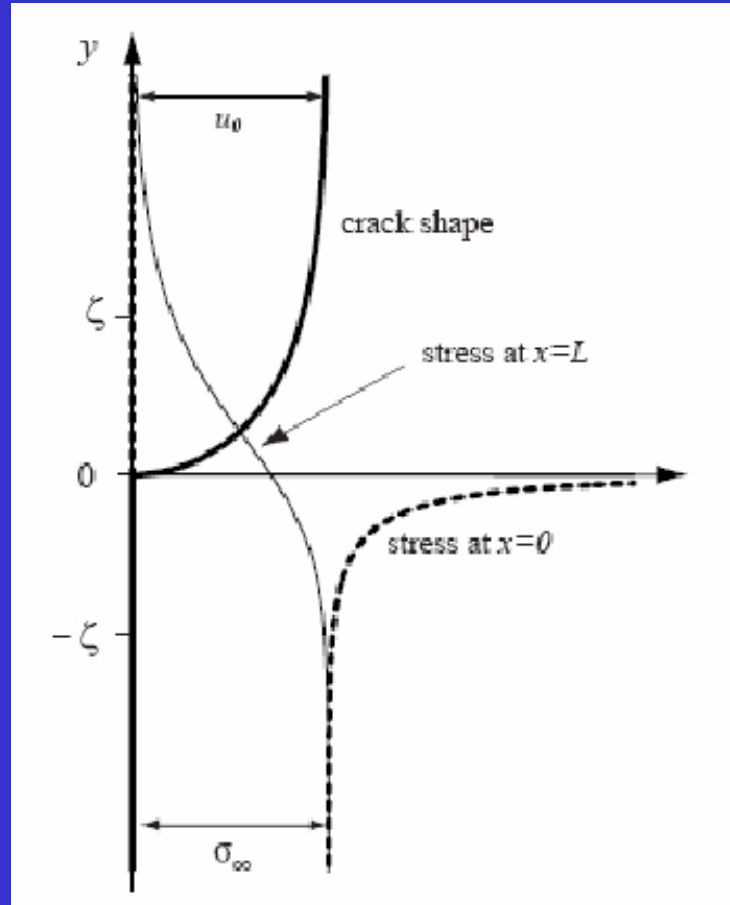
### 裂纹尖端区域

$$\varepsilon_{xx} = \frac{u_{x_0}}{L_x} \sqrt{\frac{-\zeta}{2y}}$$

$$\sigma_{xx} = \sigma_{\infty} \sqrt{\frac{-\zeta}{2y}}$$

其中

$$\sigma_{\infty} = 2c_{11} \frac{u_{x_0}}{L_x}$$



## 珍珠母中裂纹特征方程

- 文石材料

应变能:  $f_0 = \frac{1-\nu^2}{2} \frac{\sigma_\infty^2}{E_h}$

极限应力:  $\sigma_F^{(0)} = \sqrt{\frac{2E_h\gamma_h}{(1-\nu^2)L_x}}$

- 珍珠母

应变能:  $f_0 = \frac{1-\nu^2}{2} \frac{\sigma_\infty^2}{E} = \frac{E}{2(1-\nu^2)} \left(\frac{u_{x_0}}{L_x}\right)^2$

极限应力:  $\sigma_F \approx \sqrt{\frac{dL_x}{a_h\zeta}} \sigma_F^{(0)} \approx 13\sigma_F^{(0)}$



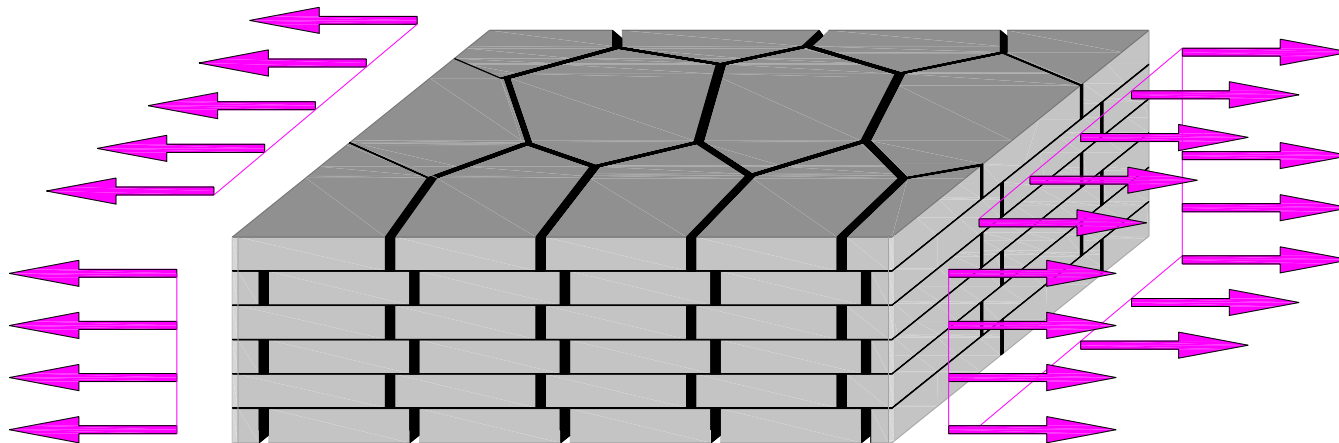
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## 珍珠母的拉伸试验

- 材料: *Hyriopsis schlegeli* , 中国、江西;





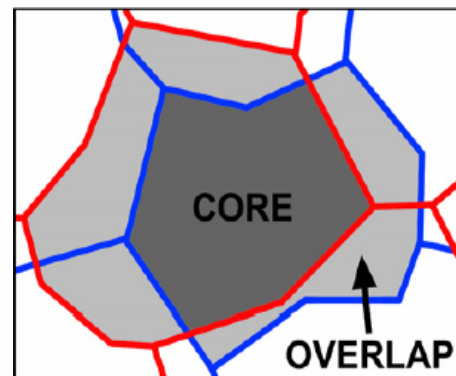
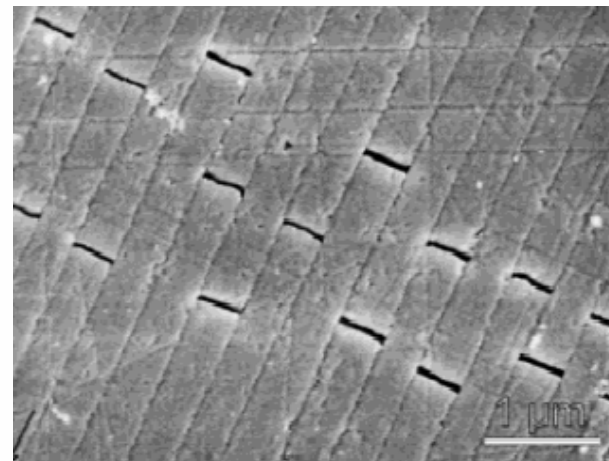
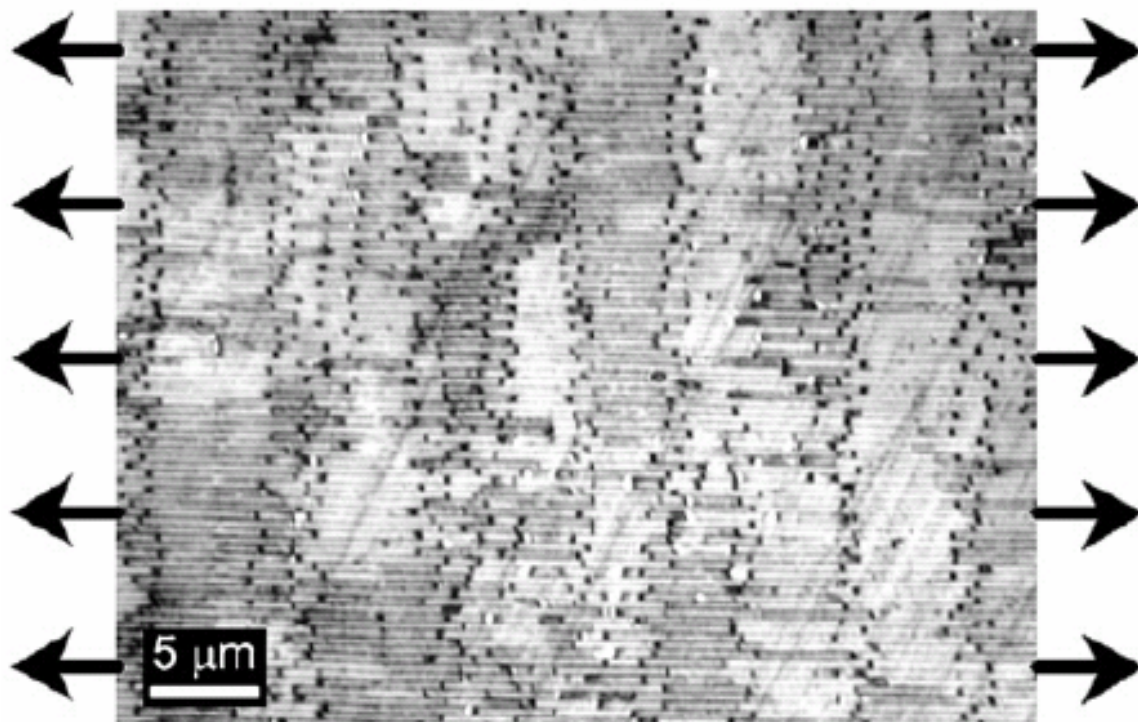
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## 珍珠母的拉伸

## 珍珠母的拉伸





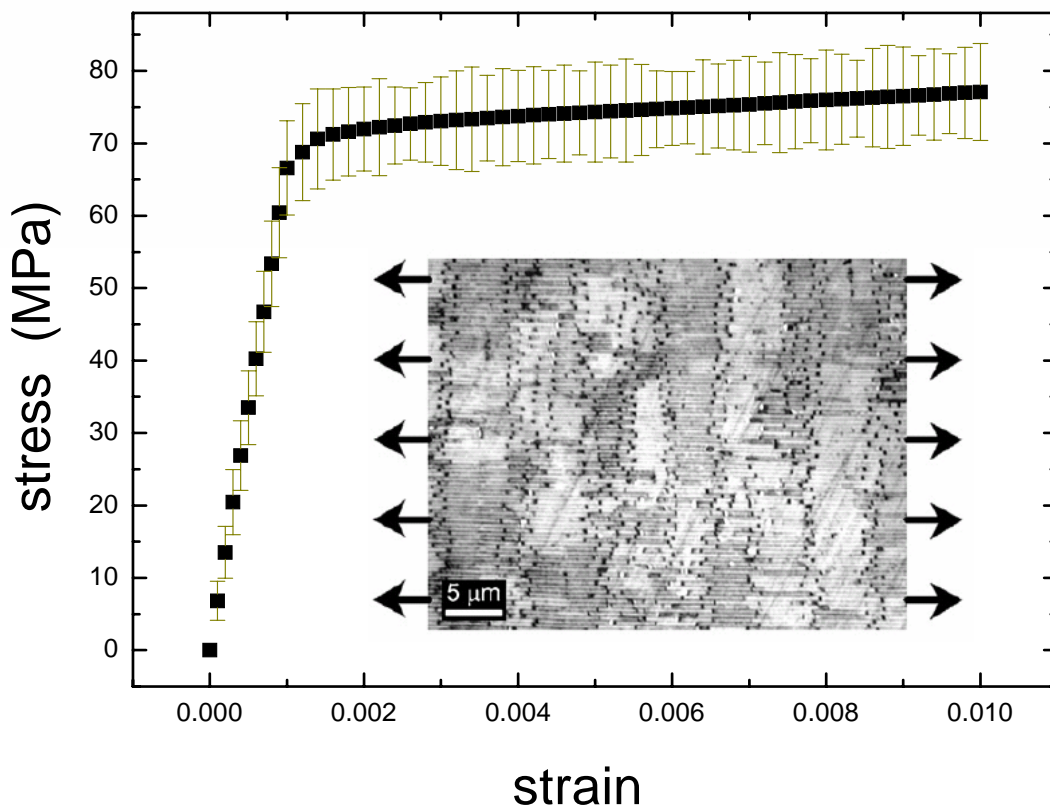


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珍珠母的拉伸

珍珠母的拉伸



拉伸应力应变曲线





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## 珍珠母的拉伸

- 当应变小于  $1.2 \times 10^{-3}$  时，珍珠母拉伸呈线弹性；
- 珍珠母弹性极限应力约为 70 MPa；
- 当应变大于  $1.2 \times 10^{-3}$  时，珍珠母拉伸呈非弹性，略有硬化，最大应变超过 0.01；
- 珍珠母中的变形和破坏均发生在 overlap 区。



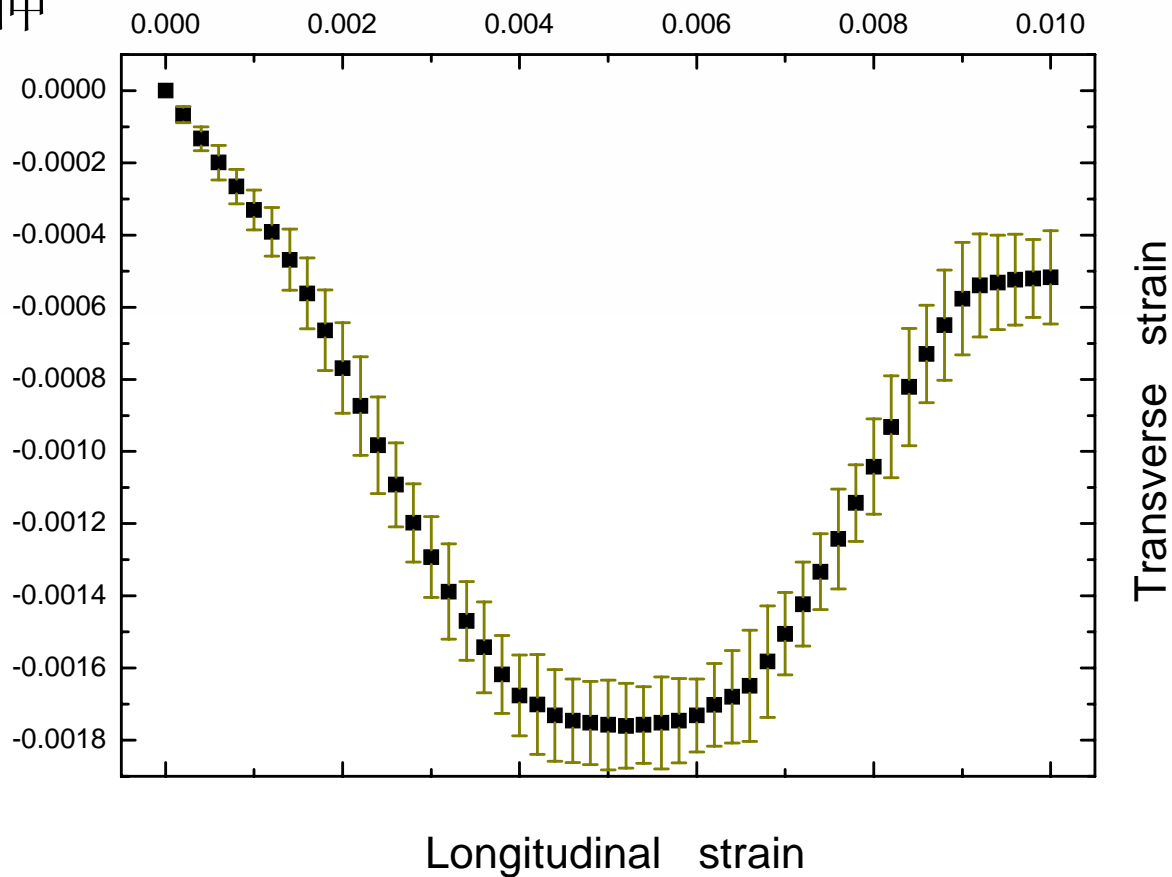


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珍珠母的拉伸

珍珠母的拉伸





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- Poisson's ratio theoretically ranges from -1.0 to 0.5 based on thermodynamic considerations of strain energy in the theory of elasticity

*From S. P. Timoshenko, and J. N. Goodier, *Theory of Elasticity*, 3rd ed. McGraw-Hill, New York, 1970.*

- In practice, all ordinary materials exhibit a positive Poisson's ratio from 0 to 0.5

*From Y. C. Fung, *Foundations of Solid Mechanics*, Prentice-Hill, Englewood Cliffs, NJ, 1968.*





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## 研究背景简介

软木:  $\sim 0$

普通聚合物泡沫:  $\sim 0.1 - \sim 0.4$

普通钢:  $\sim 0.27$

铝:  $\sim 0.33$

铅:  $\sim 0.45$

橡胶、生物软组织:  $\sim 0.5$





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## 研究背景简介

“ The materials with a negative Poisson’s ratio are theoretically permissible but have not, with few exceptions, been observed in real materials. ”

R. Lakes, *Science*, **235**, 1038 (1987)







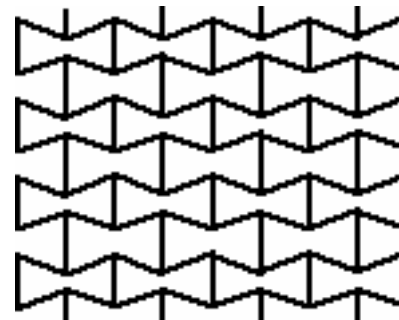
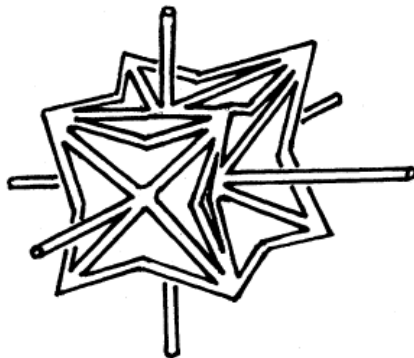
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## 研究背景简介

- Love (1944) presented a single example of cubic “single crystal” pyrite with a negative Poisson’s ratio of - 0.14 and suggested that the effect may result from a twinned crystal;
- Haeri et al (1992) and Baughman et al (1998) indicated that negative Poisson’s ratios may be a feature of cubic metals;
- Lakes (1987,1993) obtained a type of foam materials with a negative Poisson’s ratio by designing cellular structures.





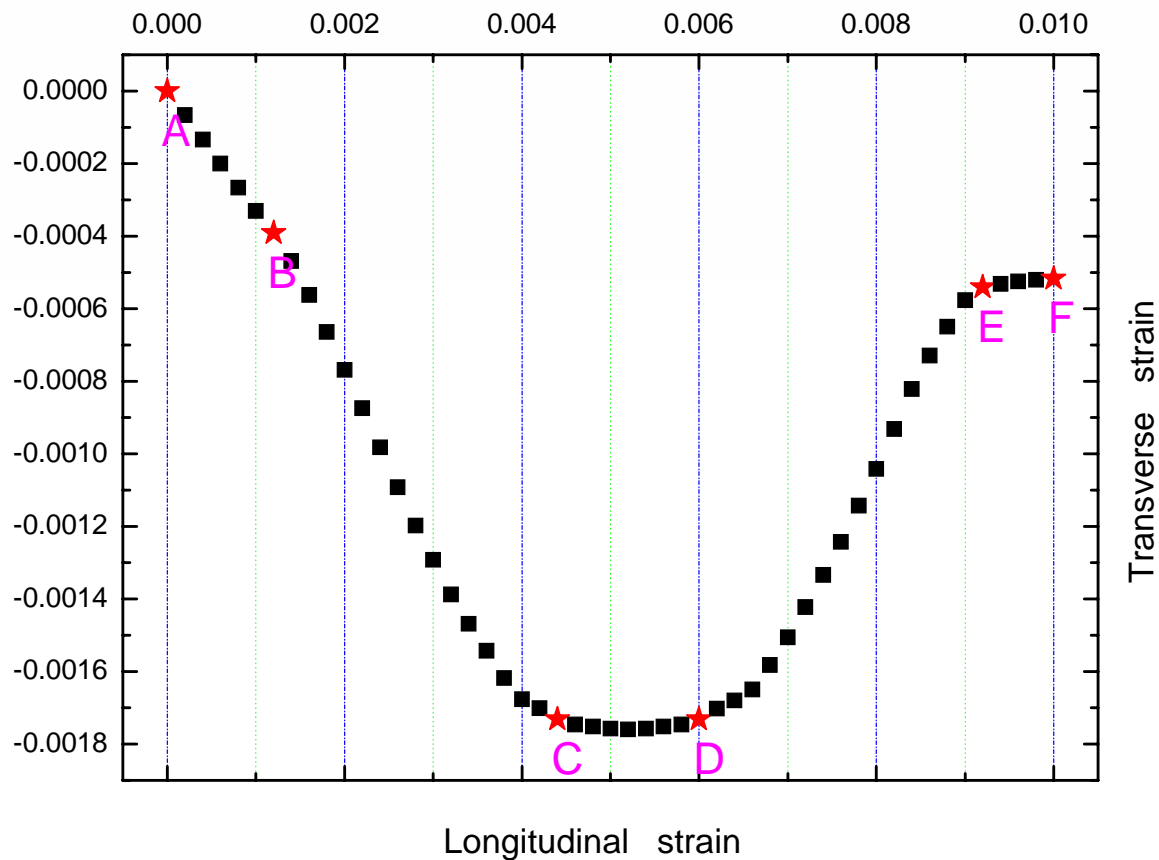
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## 珍珠母的拉伸

## 珍珠母的拉伸

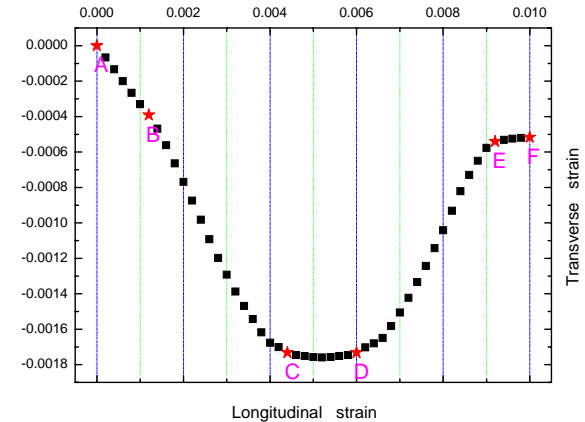






## 珍珠母的拉伸

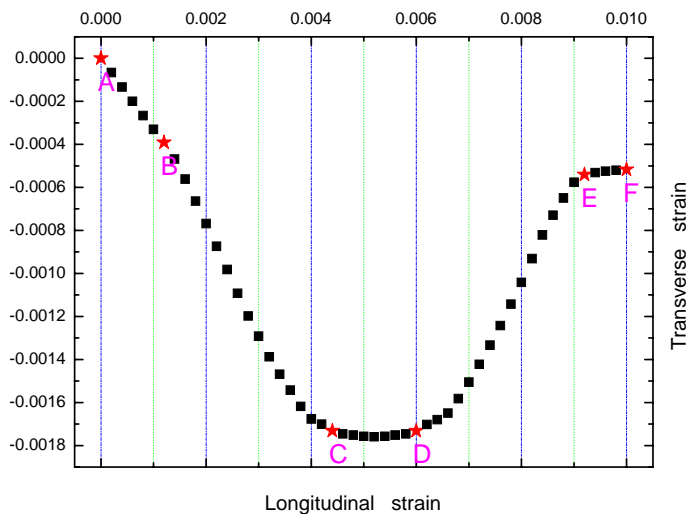
- AB区：纵向应变  $0 \sim 1.2 \times 10^{-3}$ ，  
横向应变  $-0.4 \times 10^{-3}$ ，  
泊松比 0.32；
- BC区：纵向应变  $1.2 \times 10^{-3} \sim 4.4 \times 10^{-3}$ ，  
横向应变  $-1.71 \times 10^{-3}$ ，相对横向应变  $-1.31 \times 10^{-3}$ ，  
泊松比 0.42；
- CD区：纵向应变  $4.4 \times 10^{-3} \sim 6.1 \times 10^{-3}$ ，  
横向应变  $-1.71 \times 10^{-3}$ ，相对横向应变 0，  
泊松比 0；





## 珍珠母的拉伸

- DE区：纵向应变  $6.1 \times 10^{-3} \sim 9.2 \times 10^{-3}$ ，  
横向应变  $-0.54 \times 10^{-3}$ ，相对横向应变  $1.17 \times 10^{-3}$ ，  
泊松比 - 0.38；
- EF区：纵向应变  $9.2 \times 10^{-3} \sim 0.01$ ，  
横向应变  $-0.54 \times 10^{-3}$ ，相对横向应变 0，  
泊松比 0；





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## 负Poisson比效应和产生机制

- 负 Poisson 比效应对珍珠母力学行为的影响

应变能密度:  $U = \sigma^2 / 2E$

体积应变能密度:  $U_e = (1 - 2\nu)\sigma^2 / 6E$

形变应变能密度:  $U_d = (1 + \nu)\sigma^2 / 3E$





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## 负 Poisson 比效应

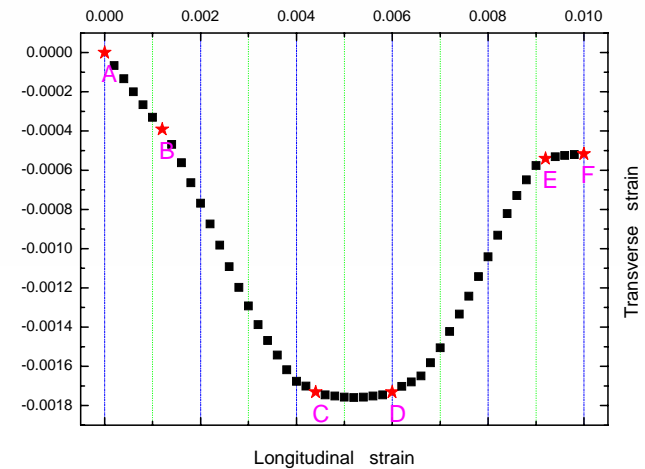
1.  $\nu = 0.42$

体积应变能密度与总应变能密度之比:

$$U_{e1}/U \approx 5.4\%$$

形变应变能密度与总应变能密度之比:

$$U_{d1}/U \approx 94.6\%$$





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## 负 Poisson 比效应

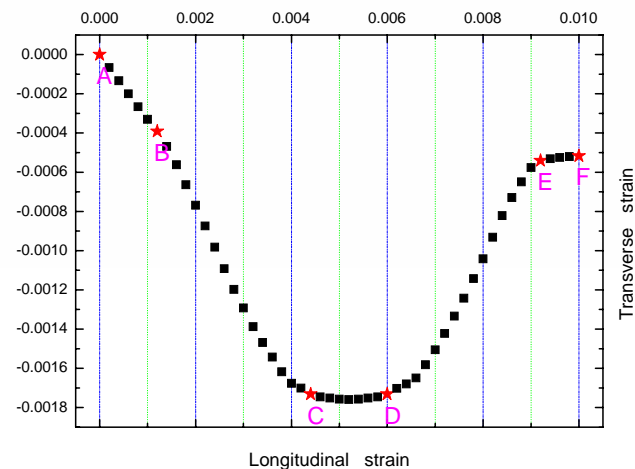
2.  $\nu = 0$

体积应变能密度与总应变能密度之比:

$$U_{e2}/U = 50\%$$

形变应变能密度与总应变能密度之比:

$$U_{d2}/U = 50\%$$





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## 负 Poisson 比效应

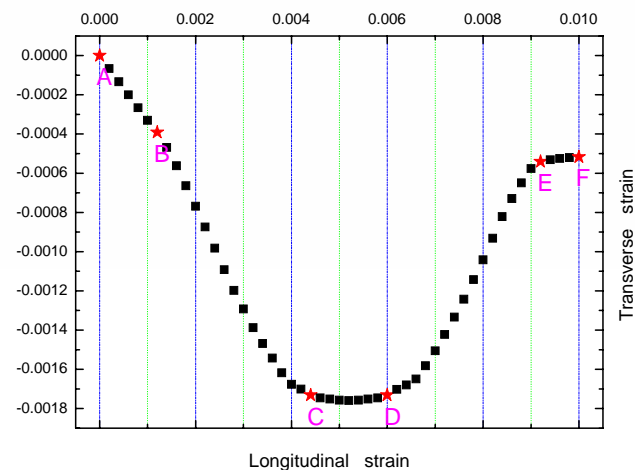
3.  $\nu = -0.38$

体积应变能密度与总应变能密度之比:

$$U_{e3}/U \approx 58.6\%$$

形变应变能密度与总应变能密度之比:

$$U_{d3}/U \approx 41.4\%$$







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## 负 Poisson 比效应

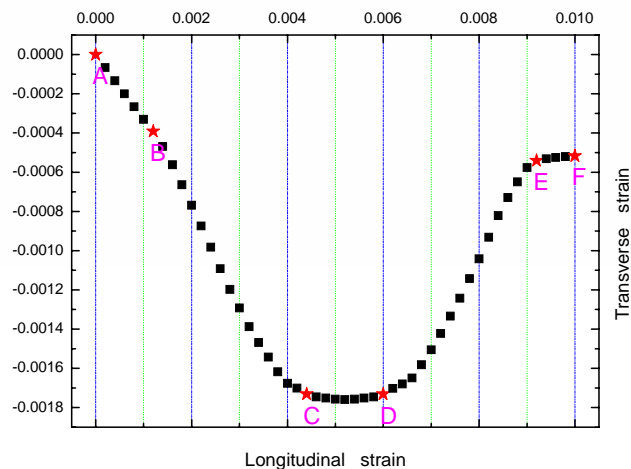
### 4. 正、负泊松比效应对比:

体积应变能密度

$$U_{e3}/U_{e1} = 11$$

形变应变能密度

$$U_{d3}/U_{d1} \approx 0.44$$

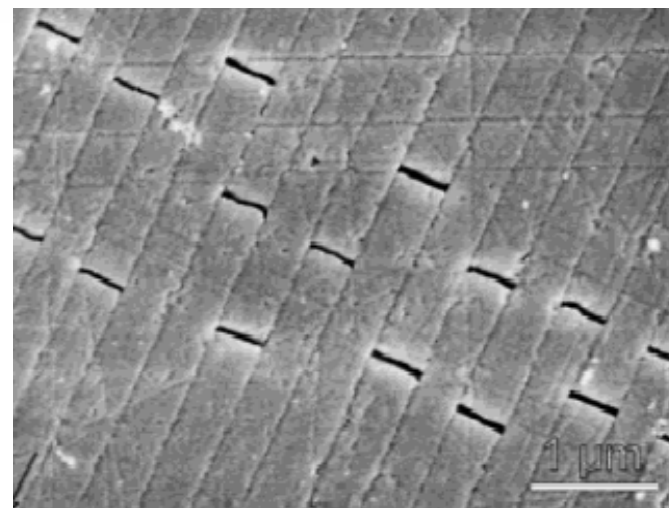
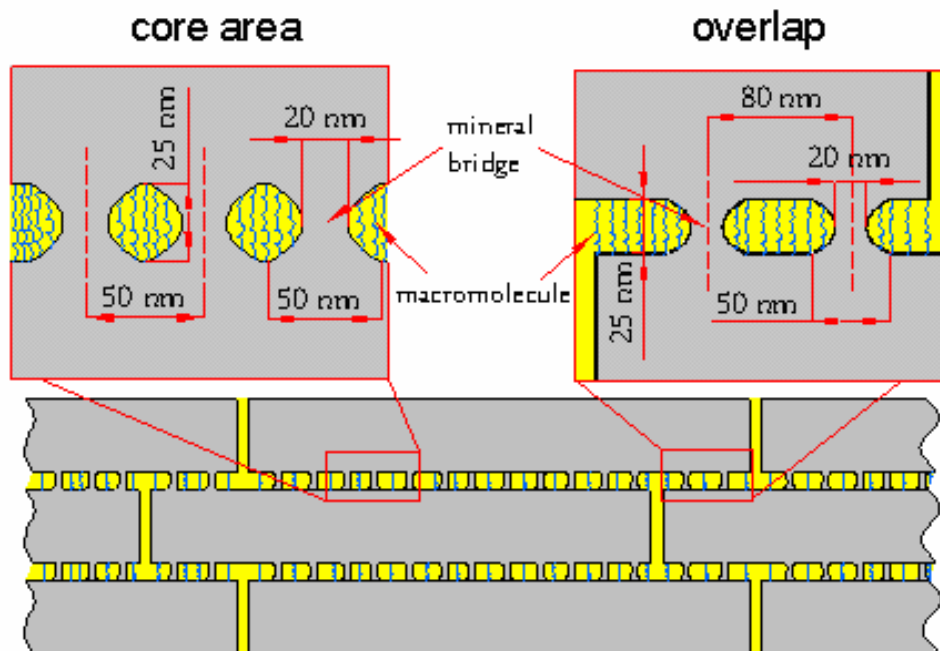




## 微结构机制分析

- 微结构机制分析

$$\Delta l = \varepsilon_L \times l_p = 80nm$$

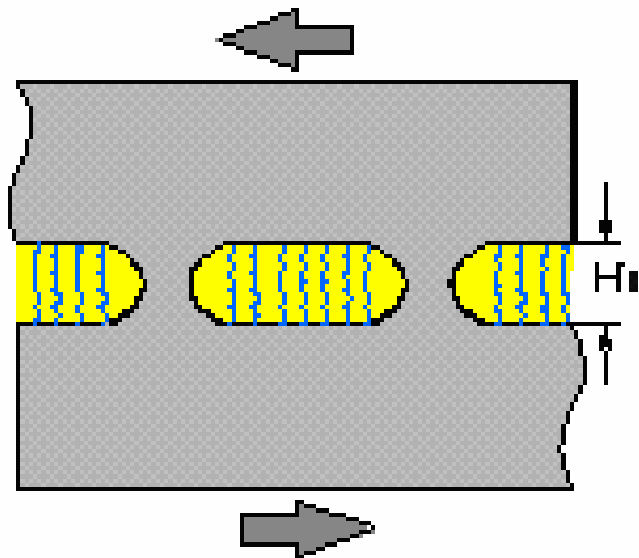


珍珠母有机基质层间微结构

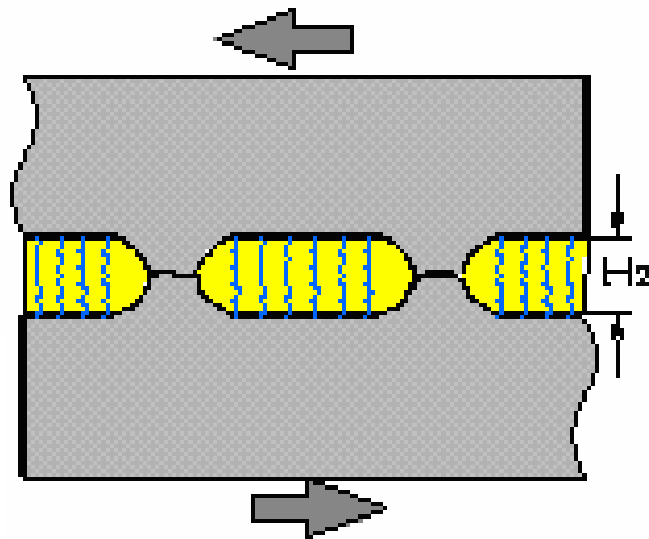




## 微结构机制分析



A、弹性阶段；



B、矿物桥发生剪断，晶片开始滑移，  
由于剪断矿物桥的滑移错开而出现坍塌  
现象；

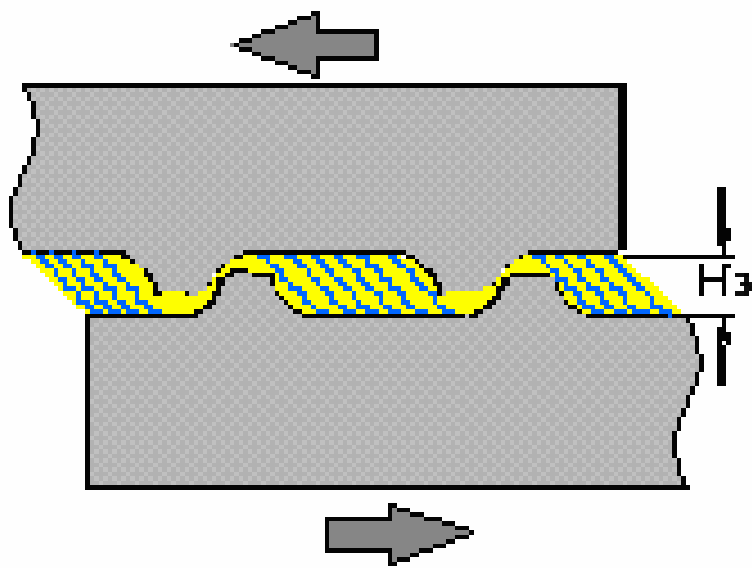


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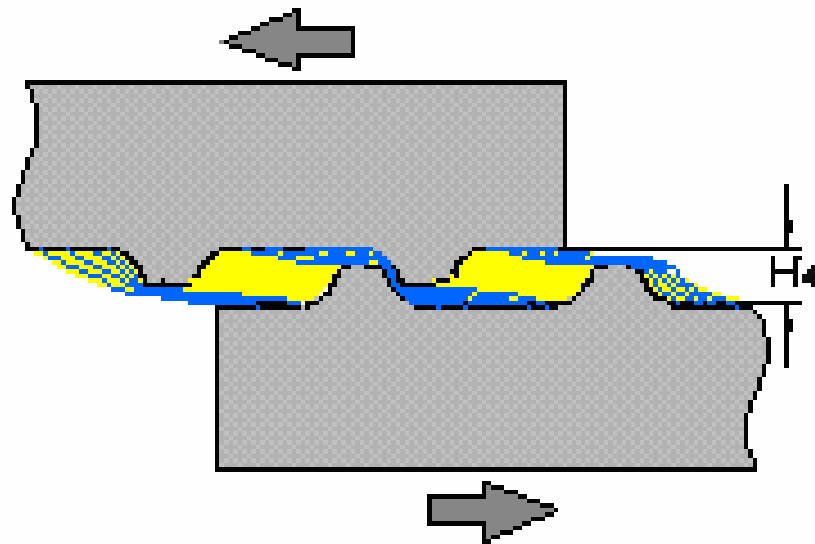
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## 微结构机制分析



C、剪断矿物桥坍塌进行到最大，此后在软层中滑移，厚度保持不变；



D、随着晶片滑移的进行，剪断的相邻矿物桥相遇，相对滑移被阻止，进入矿物桥攀爬阶段；

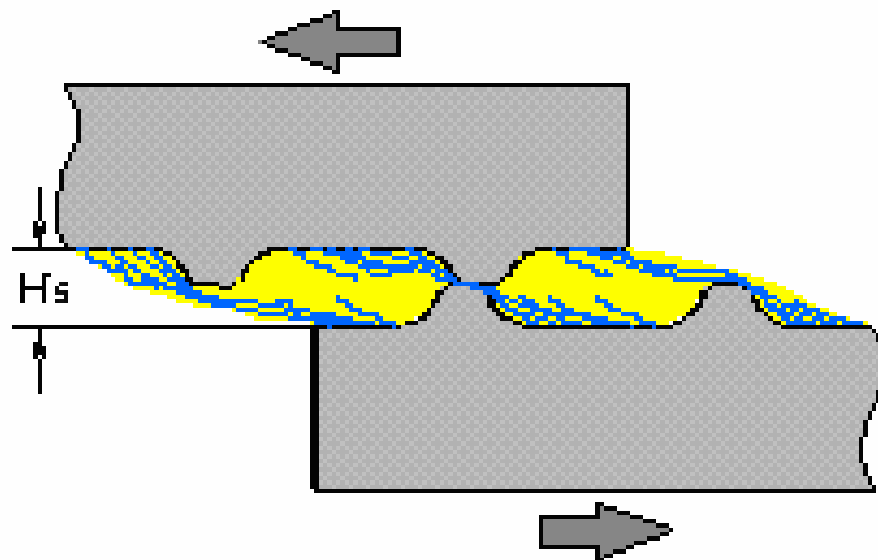


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## 微结构机制分析



E、矿物桥攀爬至最高点，材料濒临破坏；  
当有机基质纤维被矿物桥切断，材料破坏。



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## 结 论

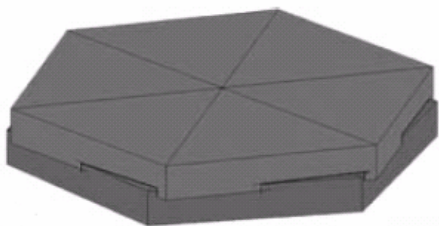
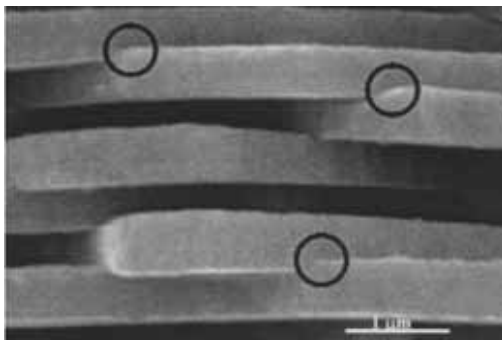
- 珍珠母拉伸变形中存在负泊松比效应；
- 负泊松比效应是由珍珠母的矿物桥所导致；
- 负泊松比效应对珍珠母力学性能产生的较大影响。



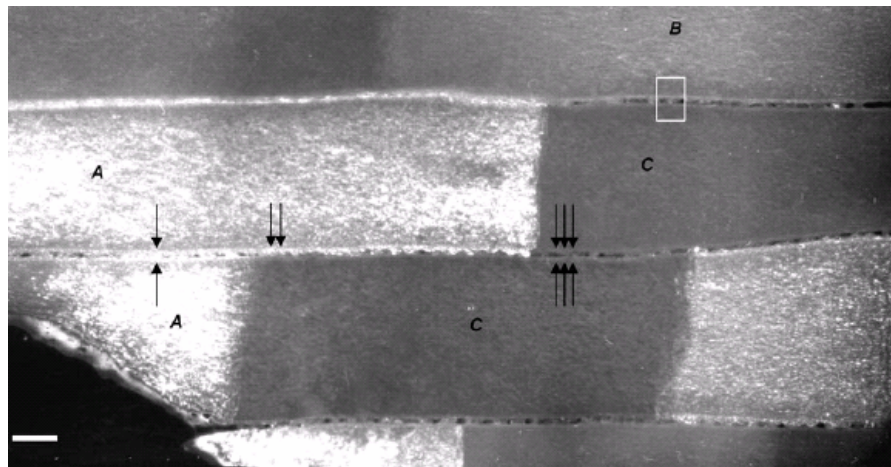


## Discussions

- Katti 等 (2005) 提出珍珠母文石晶片之间的互锁;
- Barthelat 等 (2006,2007) 发现硬层表面轮廓并不是保持平直的, 而是存在微米尺度的波动;



晶片互锁

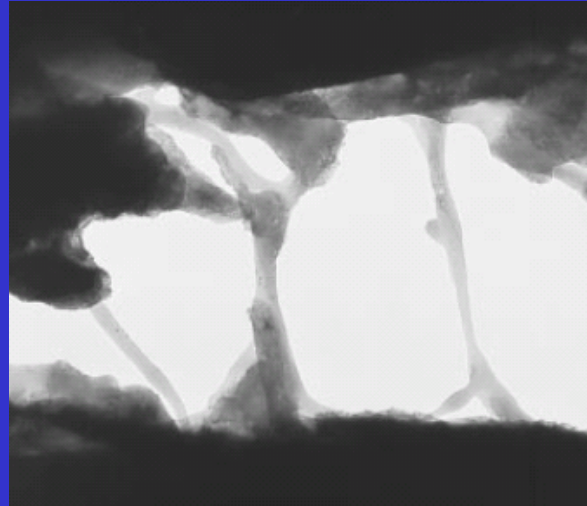
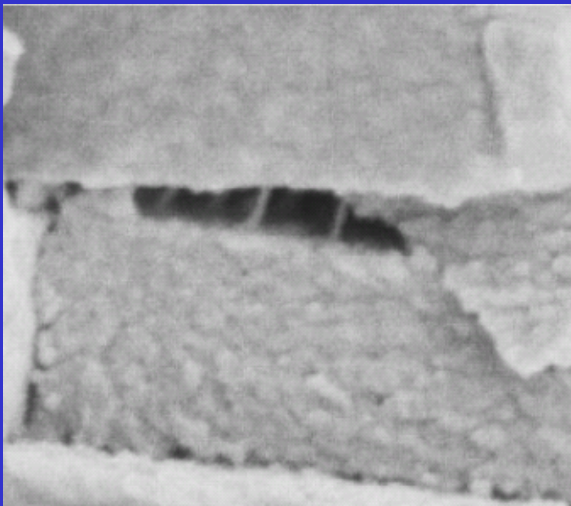
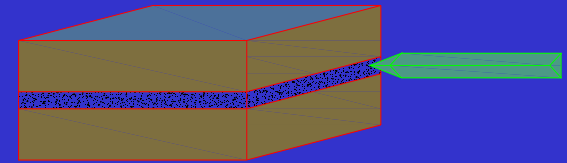
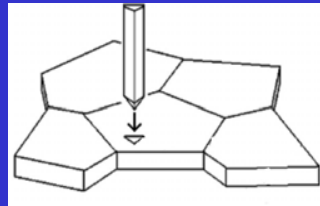


微米波动



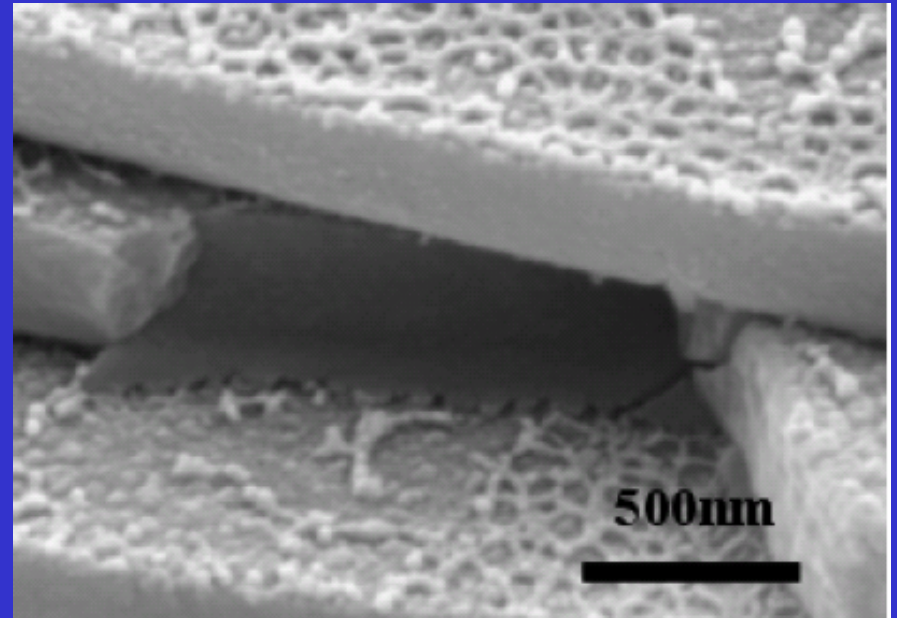
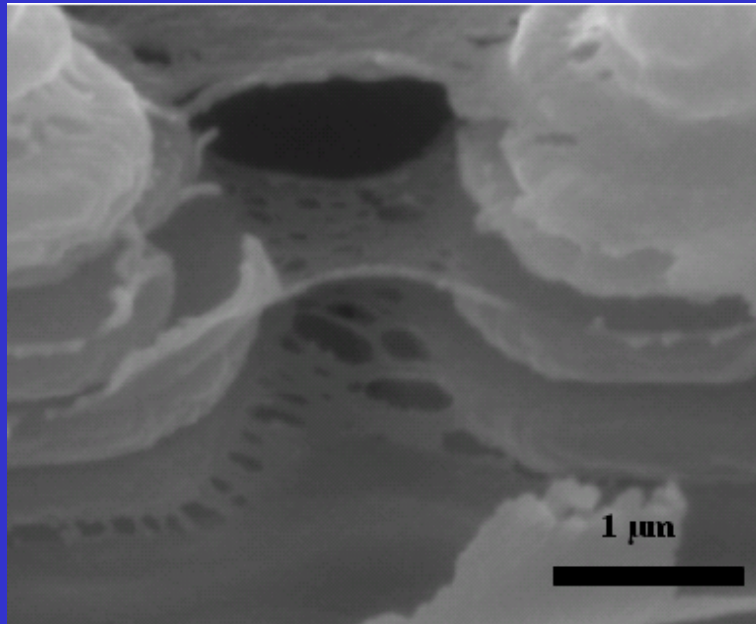
- **Organic matrix**

- 1) 弹性模量的测定;
- 2) 是“生物胶”吗?



Smith 等认为: 高分子生物胶

## Discussions



**Meyers(2007) 等认为：几乎无粘性**



- 对珍珠母微结构及其材料性能的研究远未成熟，特别是珍珠母结构的强韧化等力学机制更是目前研究的热点；
- 仿珍珠母结构人工合成高性能工程材料的设计和制备问题，等等。





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## 2. 牙齿的微结构与类金属性

- 研究背景简介
- 材料及方法
- 结果和讨论
- 结论





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## 研究背景简介

- 牙最重要的功能是持久、能承受几十年的反复咀嚼。
- 主要由牙齿的高度矿化微结构特征及其排列方式所决定。
- 认识牙齿力学性质，不仅在临床实践上，而且在力学、材料科学基础研究和仿生应用上都具有十分重要的意义。





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## 研究背景简介

- 纳米压入技术应用用于牙齿纳米至微米尺度力学行为的研中，获得了若干微力学性质及其分布的新认识。
- Cuy 等 (Arch.Oral.Bio.,2002,47:281-291) 认为人臼齿釉质的力学性质呈非均匀分布。
- Marshall 等 (J.Biomed.Mater.Res.,2001,54:87-95; J. Euro. Cera.Soc.,2003,23:2897-2904) 发现牙本质的力学性质分布均匀、牙本质和釉质之间过渡平稳。





## 材料及方法

### 1. 实验材料:

- 实验所用的牙齿为成人的臼齿和犬齿。
- 样品牙齿浸润20%丙三醇的纱布中密封，4°C下保存。
- 为牙齿提供必需的湿度和温度，防止牙齿开裂和腐败。





## 2. 实验方法:

### • 制样

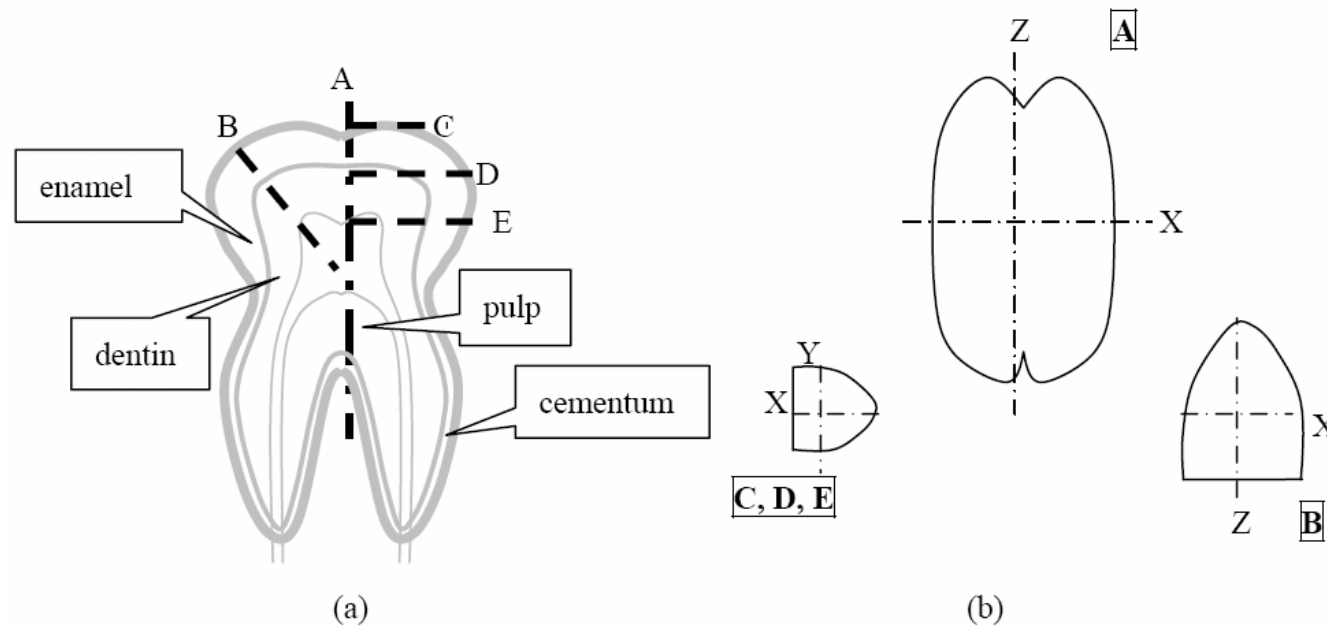


Fig. 1 The anatomic sketch of the third molar showing the positions of the cross sectional area tested and the directions of nanoindentation. (a) the positions of the sections A, B, C, D and E in the tooth; (b) the tested directions of each of the sections.



## 材料及方法

### • 测试方法

1. MTS Nano Indenter XP系统，载荷和位移分辨力分别为50nN和0.01nm。
2. 采用Oliver-Pharr数据处理方法，测试压入深度为1 $\mu$ m。

• 折合弹性模量：
$$E_r = \frac{\sqrt{\pi}}{2\beta} \frac{S}{\sqrt{A}}$$

• 硬度：
$$H = \frac{P_m}{A}$$

• 弹性模量：
$$\frac{1}{E_r} = \frac{1-\nu^2}{E} + \frac{1-\nu_i^2}{E_i}$$

- A为接触面积，S是接触刚度， $\beta = 1.034$  为三棱锥Berkovich压针形状常数， $P_m$ 是最大压力，金刚石压针  $E_i=1141\text{GPa}$ ， $\nu_i=0.07$ ，材料的泊松比取为 $\nu=0.25$ 。



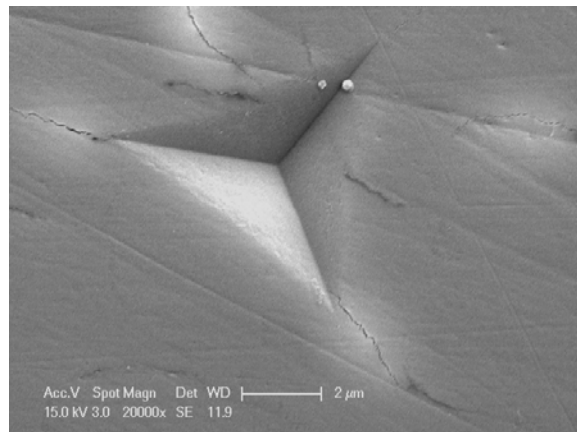
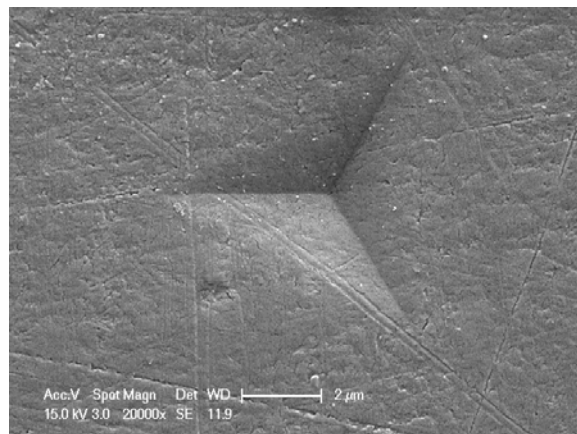




## 结果和讨论

### 1. 牙齿力学性能的空间取向

- 牙本质上，不同位置的纳米压入载荷-深度曲线是光滑的。
- 牙釉质上，当选择的测试横截面不同时，得到的载荷-深度曲线形状不同，而且不同测试位置的结果不重复。
- 在部分压入测试的牙釉质载荷-深度曲线上突然出现了pop-in，说明压针周围的牙釉质出现了微裂纹。





## 结果和讨论

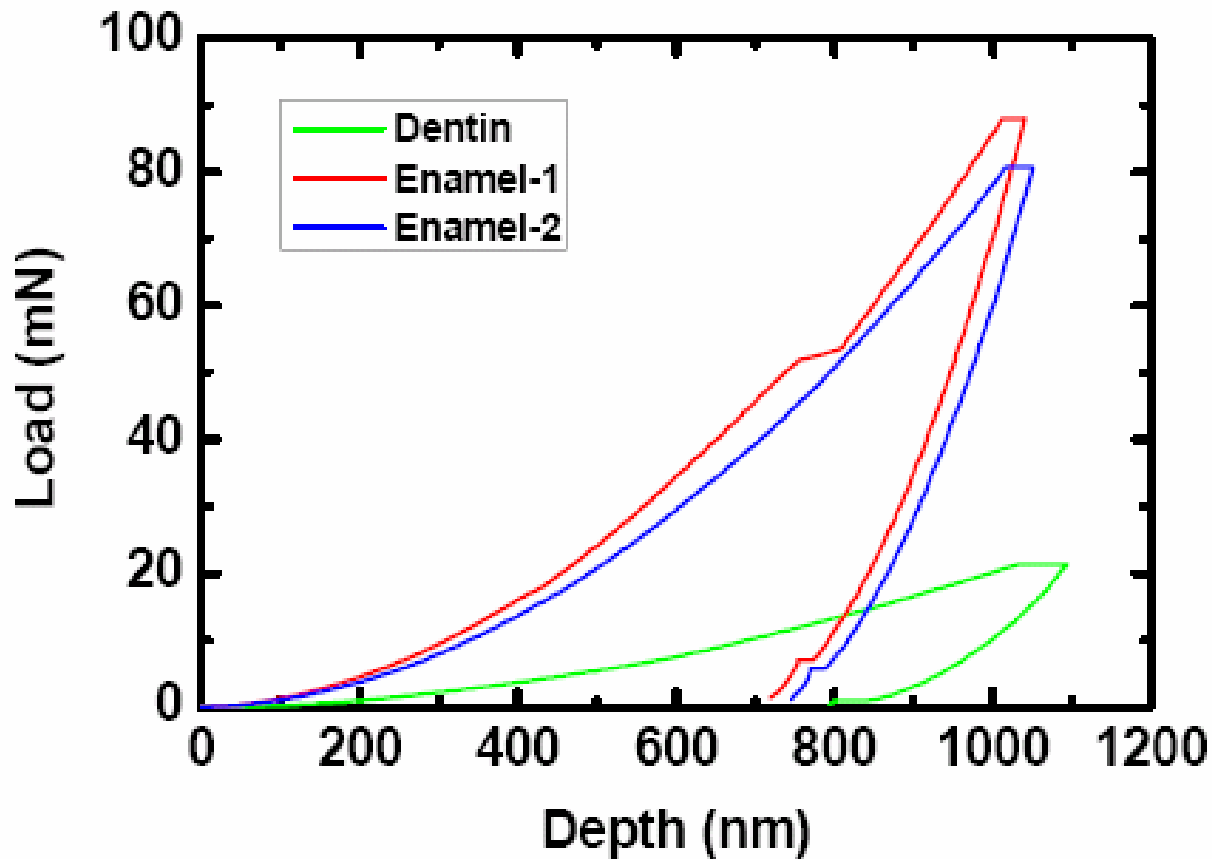


Fig. 2 Curves of load  $P$  against indentation depth  $h$  showing the loading and unloading loops. Green curve: dentin; red curve: enamel, showing a pop-out on section A, i.e. a sudden increase of indentation depth under a fixed load; blue curve: normal enamel.





## 结果和讨论

Table 1: The data of elastic modulus, hardness and  $W_e/W_t$  of the sections A, B, C, D and E.

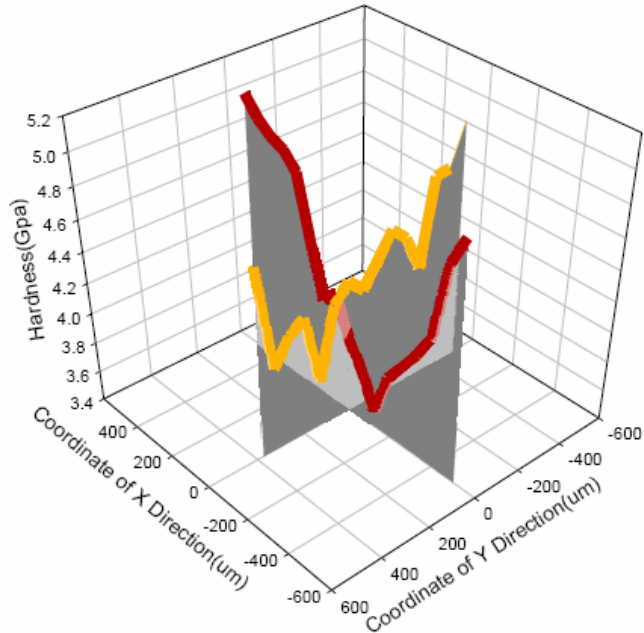
Direction of section		enamel					dentin			
		Vertical section	Horizontal sections			Inclined section	Vertical section	Inclined section	Horizontal sections	
section		A	D	E	C	B	A	B	D	E
Modulus (GPa)	Z/Y	81.02	83.39	91.93	97.59	82.57	24.11	24.36	23.55	23.34
	X	80.56	83.06	95.83	98.88	66.67	22.77	22.26	24.18	24.49
Hardness (GPa)	Z/Y	4.11	4.02	4.27	4.98	3.93	0.85	0.87	0.85	0.88
	X	4.13	4.04	4.53	4.87	3.83	0.81	0.81	0.85	0.89
$W_e/W_t$ (%)	Z/Y	31.37	30.64	33.31	31.37	30.84	25.53	26.15	26.01	26.53
	X	32.03	30.45	34.97	31.54	33.65	25.20	25.032	25.50	26.58

- 牙釉质的力学性能趋向为非各向同性，牙本质接近于各向同性。



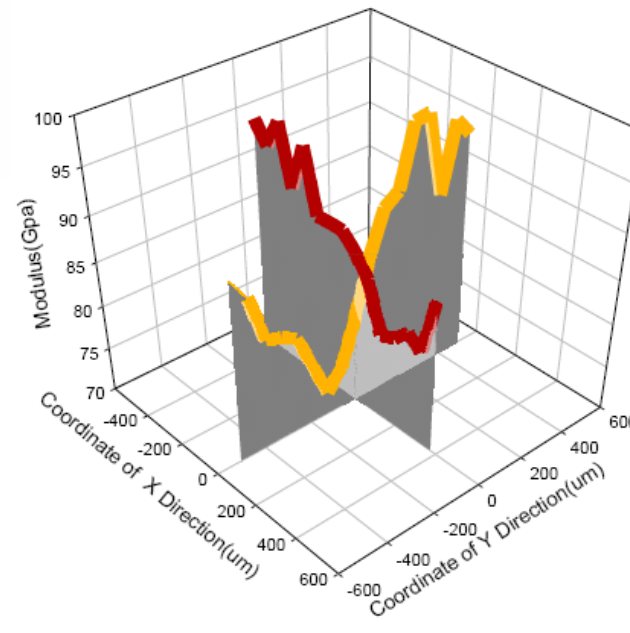
## 2. 牙釉质力学性能的梯度分布

Hardness Gradient of Section C



(a)

Modulus Gradient of Section C



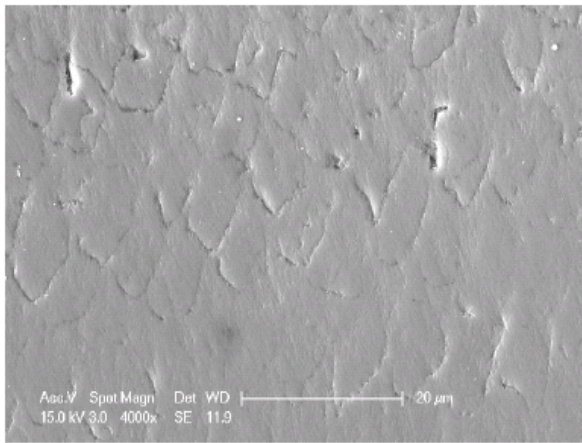
(b)

Fig. 3 Plots showing variations of the modulus and hardness on section C in enamel. The valley-shaped distributions show the gradiently decreasing of modulus and hardness from the outmost surface and the anisotropy in X and Y directions in enamel. In the figure, origin is the cross of X and Y directions. The positive numbers of X and Y directions indicate the left side from the origin to the edge of section C and the negatives indicate the right side from the origin to the edge of section C.

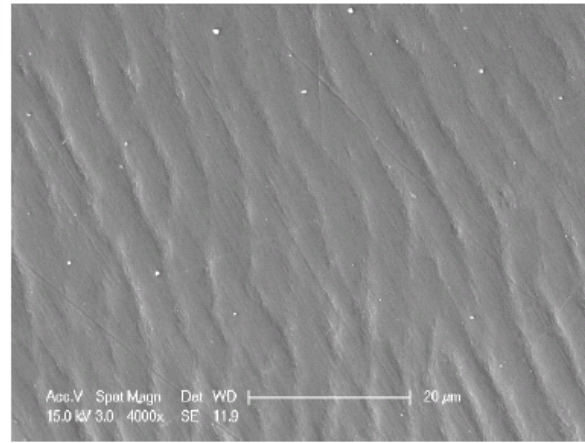


## 结果和讨论

- 牙釉质硬度和模量从外表面向内逐步递减，具有从外向内的梯度分布和非各向同性材料行为。
- 显微观察发现，接近咬合表面的釉柱短而粗，而靠近牙釉质和牙本质交界面的釉柱细而长。



(a)



(b)

Fig. 4 SEM images showing microstructural variations of enamel.

- 釉质力学性质的梯度变化是由其显微结构决定的。

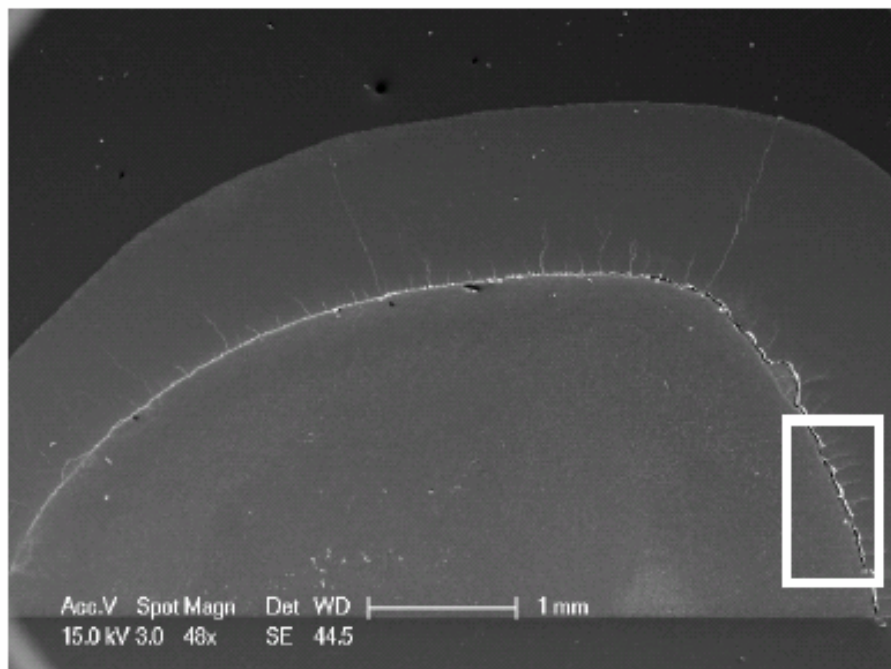




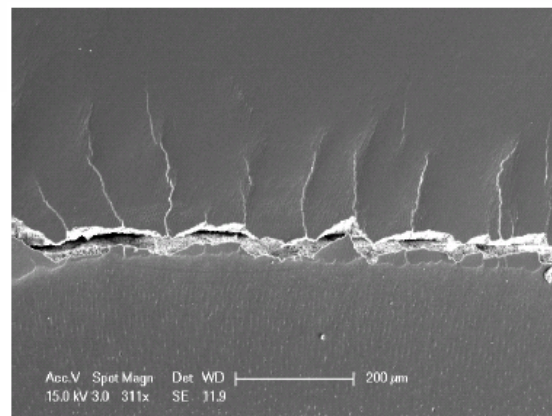
## 结果和讨论

### 3. 牙釉质和牙本质界面特征

- 牙釉质和牙本质的界面存在大量微裂纹，裂纹起始于界面延伸至牙釉质内部。



(a)



(b)

Fig. 5 (a) SEM image showing DEJ in tooth. (b) a part in (a) showing micro-flaws to initiate from DEJ and extend into enamel; and (c) a histogram showing statistics of the length of micro-flaws.



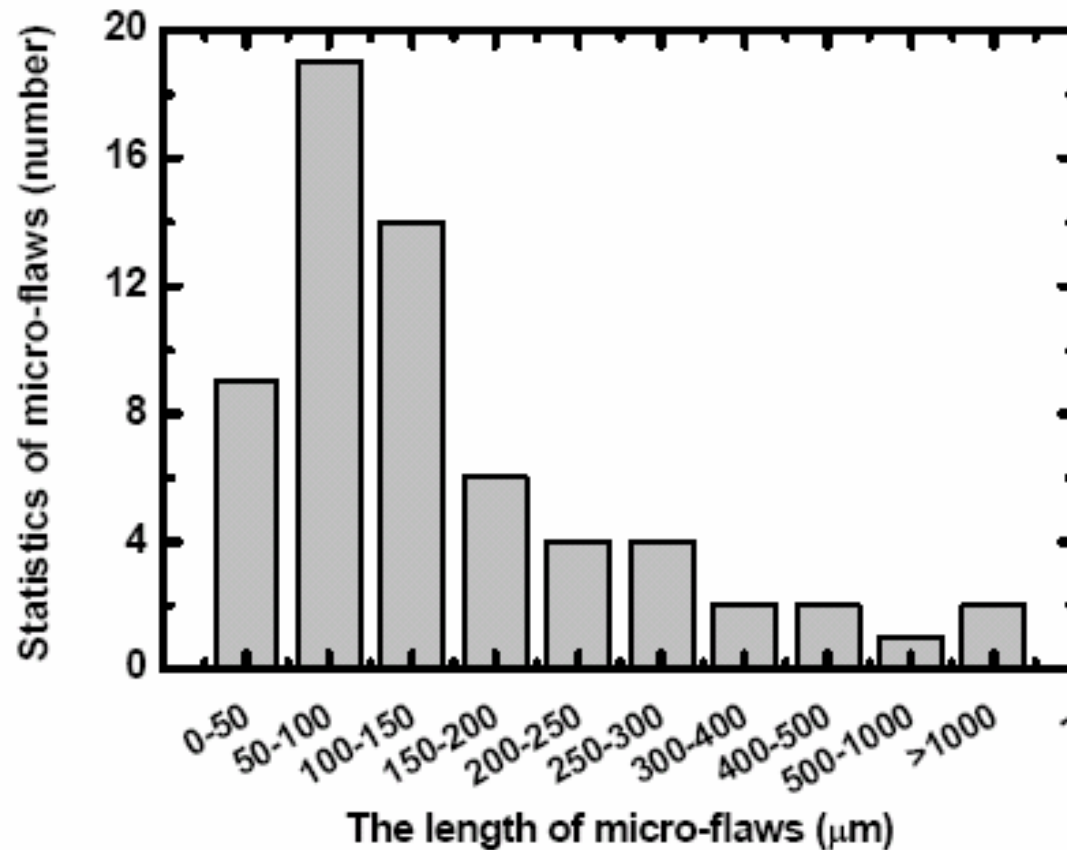
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## 结果和讨论

- 微裂纹平均长度为  $175 \pm 6.5 \mu\text{m}$





## 结果和讨论

- 牙釉质的断裂韧性:  $K_c = (0.52 \square 0.76) \text{MPa} \cdot \text{m}^{1/2}$

(From Marshall, S.J., et al (1) J.Biomed.Mater.Res.,2001,54:87-95; (2) J.Euro.Cera.Soc., 2003,23:2897-2904.)

- 容限压力:  $\sigma_F \square K_C / \sqrt{\pi a}$

$$\sigma_F = (25 \square 33) \text{MPa}$$



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## 结果和讨论

- 用碳膜压力传感器测量咬合力：男性平均咬合力约为 6.6MPa，女性平均咬合力约为 5.2MPa。
- 人的最大咬合力约为 20MPa。  
(From Harrison. A. and Lewis, T.T., J.Biomed.Mater.Res.,1975,9:341-345.)
- 微裂纹不影响牙釉质的正常咀嚼功能。
- 微裂纹的存在可适当的释放由牙釉质和牙本质的模量差异所引起的内应力。
- 微裂纹存在证明了牙釉质的非各项同性特征。





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## 结果和讨论

### 4. 牙齿的材料力学行为象什么？

- 牙釉质是一种生物矿化材料，属天然陶瓷。
- 传统上，人们认为牙釉质的性能与陶瓷性能类似。  
(From (1). Vincent, J.F.V., *Structural Biomaterials*, The Macmillan Press LTD, Landon, 1982; (2). Fawcett D W. *A Textbook of Histology*. 11st ed. Philadelphia: W B Saunders, 1986; )

陶瓷？ 金属？ .....？

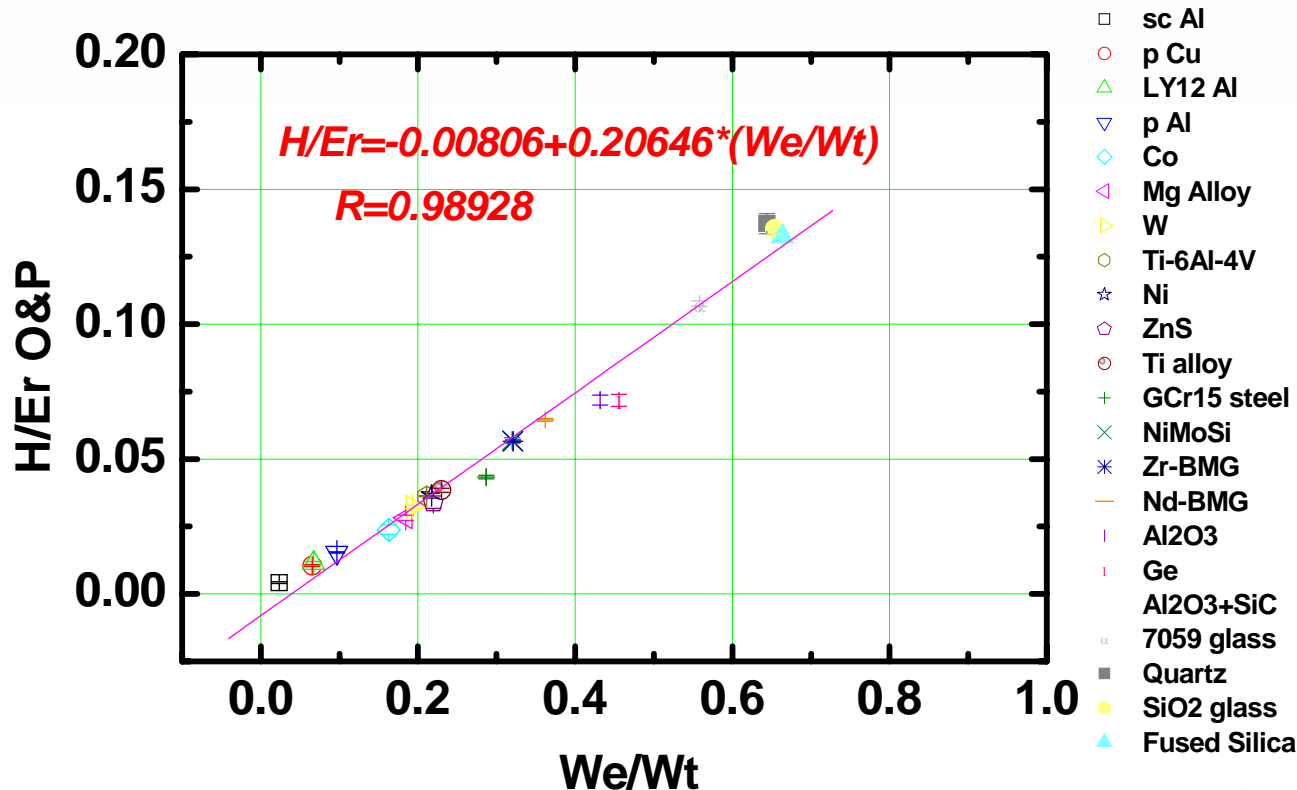






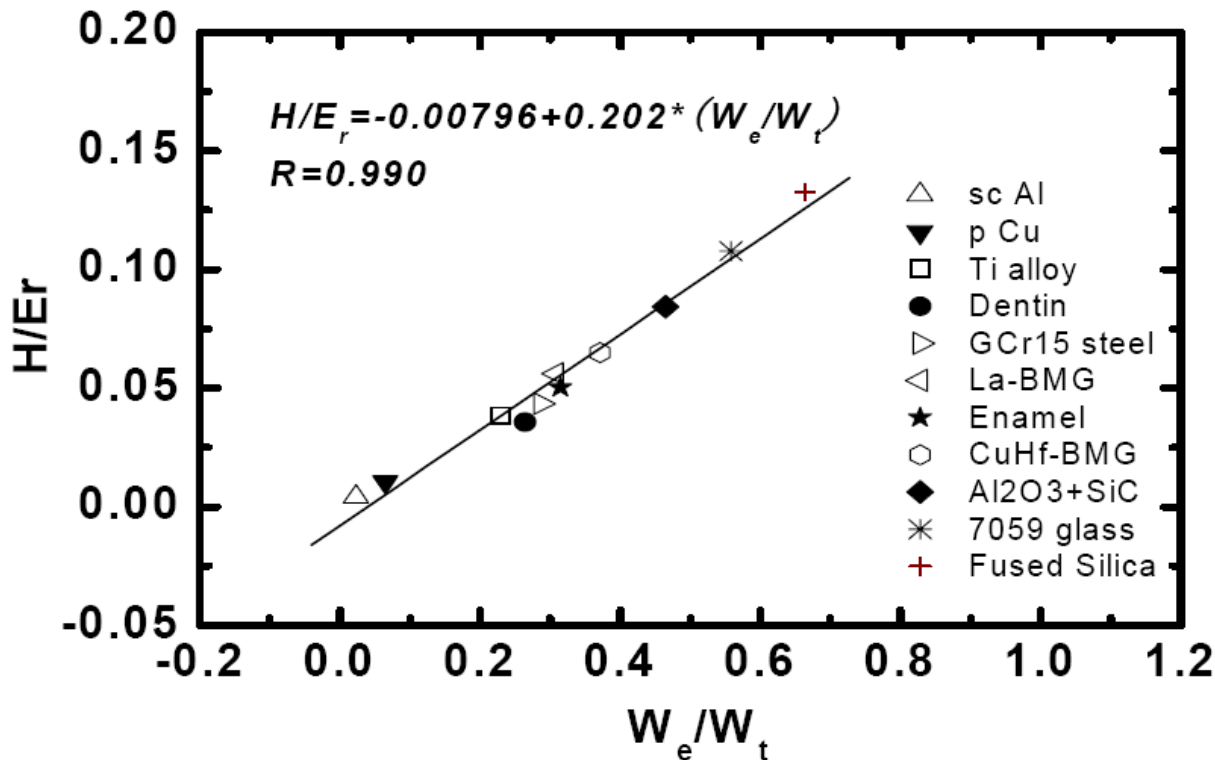
## 结果和讨论

- 硬度和折合模量之比  $H/E_r$  与卸载功和压入总功之比  $W_e/W_t$  之间存在标度关系，这种关系反映了材料属性的分类。(Yang-Tse Cheng, Che-Min Cheng. *Appl. Phys. Lett.*, 1998,73(53):614-616)





## 结果和讨论



- 牙釉质:  $W_e/W_t = 0.33$
- 牙本质:  $W_e/W_t = 0.26$
- 1. 金属玻璃: La基 0.31  
CuHf基 0.36
- 2. GCr15钢: 0.29  
钛合金: 0.23

Fig. 6 Plot showing the relationship between the ratio of hardness to reduced elastic modulus  $H/E_r$  and the ratio of unloading work to total work  $W_e/W_t$ . The value of enamel is located in the range of metallic glasses (La-based BMG and CuHf-based BMG) and the value of dentin is located in the range of Ti alloy and GCr15 steel.



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## 结果和讨论

- 牙釉质力学性能与金属玻璃类似，表明牙釉质在耐磨性与能量耗损方面表现出与金属玻璃相似的性能。
- 牙本质力学性能与合金金属类似，表明牙本质在能量吸收和热传导等方面表现出与合金材料相似的性能。





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## 结 论

- 牙齿的力学行为是非各向同性的：牙釉质力学性能具有从外向内的梯度分布，牙本质力学性能基本上呈各向同性。
- 牙齿的力学性质变化是由其显微结构决定的。
- 牙釉质与牙本质界面存在微裂纹，这些微裂纹不影响牙齿的正常咀嚼功能，并可适当释放界面内应力。
- 牙齿具有类金属力学行为。



# 感谢

1. 国家自然科学基金项目
2. 中国科学院知识创新工程项目



# THANK YOU

